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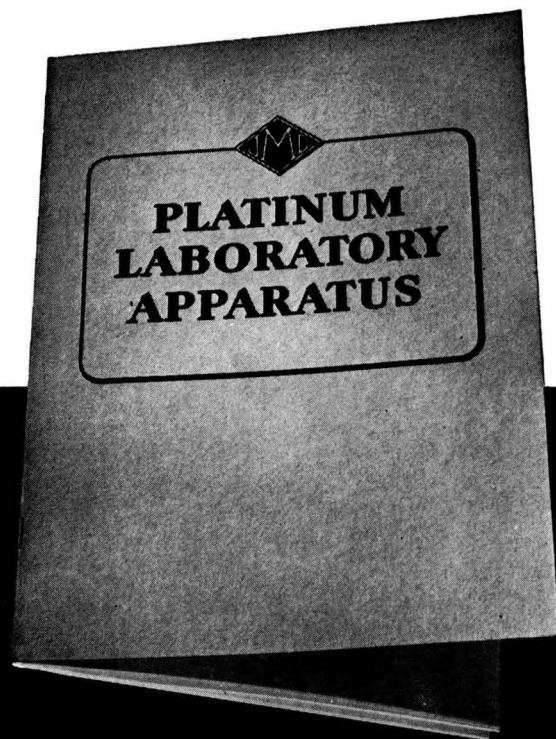
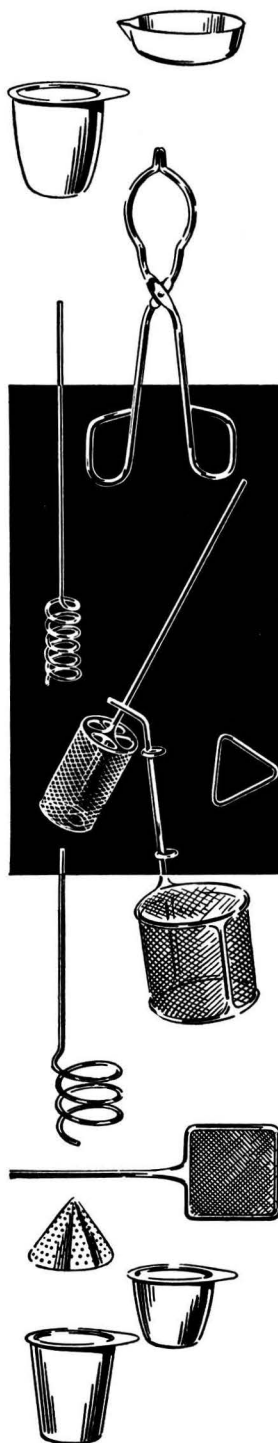
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Atomic-absorption Spectroscopy

Atomic-absorption spectroscopy, originally developed by Dr A. Walsh of the C.S.I.R.O., Melbourne, Australia, has certainly made its mark on the literature. We give here, as a matter of interest, some of the bibliography on the subject. We regret that we are unable to give a complete bibliography in this space or to supply reprints of these papers.

ANALYST:

Atomic-Absorption Spectrophotometry with Special Reference to the Determination of Magnesium. *Allan, J. E.* **83**, 466 (1958)

Determination of Zinc and Other Elements in Plants by Atomic-Absorption Spectroscopy. *David, D. J.* **83**, 655 (1958)

The Quantitative Determination of Some Noble Metals by Atomic-Absorption Spectroscopy. *Lockyer, R., Hames, G. E.* **84**, 385 (1959)

Determination of Calcium in Plant Material by Atomic-Absorption Spectrophotometry. *David, D. J.* **84**, 536 (1959)

Determination of Zinc in Metallurgical Materials by Atomic-Absorption Spectroscopy. *Gidley, J. A. F., Jones, J. T.* **85**, 249 (1960)

SPECTROCHIMICA ACTA:

The Applications of Atomic-Absorption Spectra to Chemical Analysis. *Walsh, A.* **7**, 108 (1955)

An Atomic-Absorption Spectrophotometer and its Applications to the Analysis of Solutions. *Russell, B. J., Shelton, J. P., Walsh, A.* **8**, 317 (1957)

The Determination of Iron and Manganese by Atomic Absorption. *Allan, J. E.* **10**, 800 (1959)

A Simple Atomic-Absorption Spectrophotometer. *Box, G. F., Walsh, A.* **16**, 255 (1960)

The Determination of Metals in Blood Serum by Atomic-Absorption Spectroscopy. I—Calcium. II—Magnesium. *Willis, J. B.* **16**, 259 and 273 (1960)

NATURE:

Determination of Magnesium in Blood Serum by Atomic-Absorption Spectroscopy. *Willis, J. B.* **184**, (4681), **187** (1959)

Some Atomic Reactions by Absorption Spectroscopy. *Broida, H. P., Schiff, H. I., Sugden, T. M.* **185**, 759 (1960)

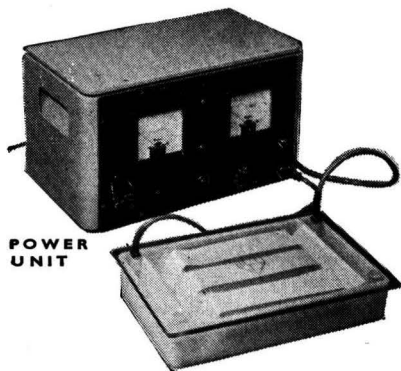
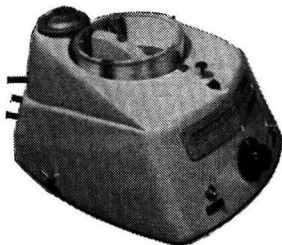
Determination of Calcium in Blood Serum by Atomic-Absorption Spectroscopy. *Willis, J. B.* **186** (4720), 249 (1960)

ANALYTICAL CHEMISTRY:

A Study of Atomic-Absorption Spectroscopy. *Menzies, A. C.* **32**, 898 (1960)

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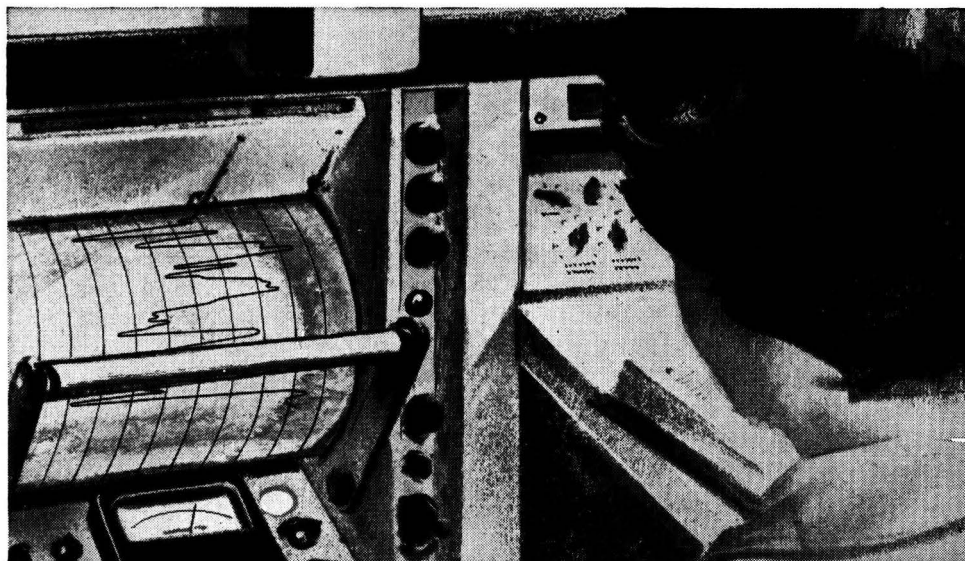
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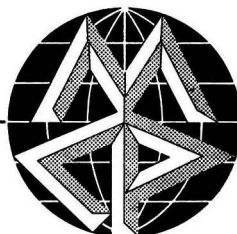
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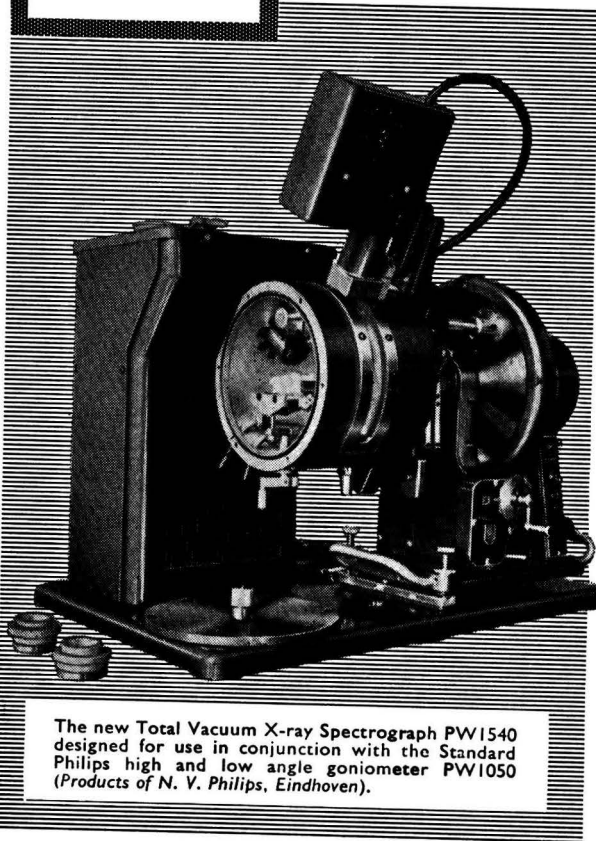
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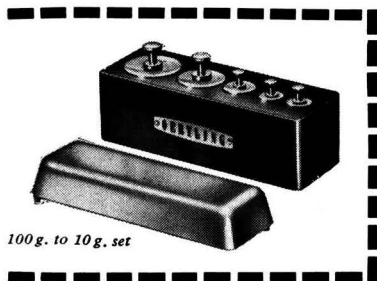
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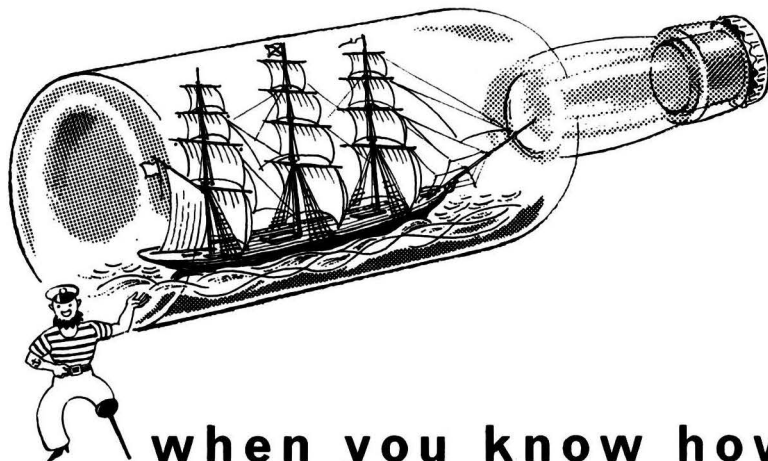
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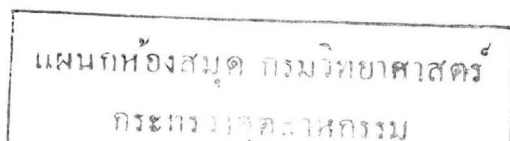
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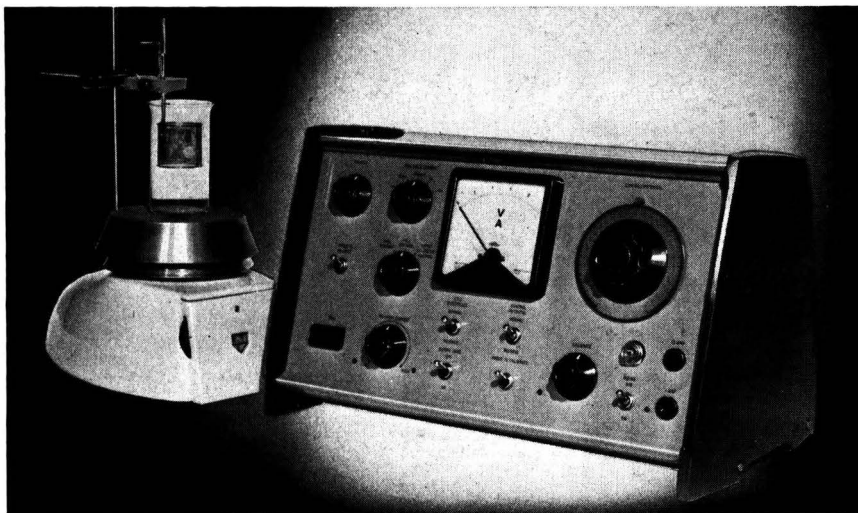
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PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

MIDLANDS SECTION

A SYMPOSIUM on "Analytical Chemistry in the Service of Agriculture" organised by the Section was held on Thursday and Friday, July 14th and 15th, 1960, at Nottingham University. The Symposium was opened by the President, Mr. R. C. Chirnside, F.R.I.C.

The Chair at the first session, on the morning of July 14th, was taken by Dr. D. C. Garratt, F.R.I.C., Vice-President of the Society, and the following papers were presented and discussed: "The Spectrochemical Determination of Metals in Soils and Plants," by R. L. Mitchell, B.Sc., Ph.D., F.R.I.C.; "The Analysis of Herbicides," by L. A. Haddock, M.Sc., F.R.I.C.

At the second session, on the morning of July 15th, the Chair was taken by Professor R. Belcher, Ph.D., D.Sc., F.R.I.C., F.Inst.F., and the following papers were presented and discussed: "The Determination of Insecticide and Fungicide Deposits on Plants," by J. T. Martin, B.Sc., Ph.D., D.Sc., F.R.I.C.; "The Safe Use of Pesticides, with Special Reference to Consumer Protection," by E. J. Miller, B.Sc., Ph.D., A.K.C.; "Analytical Chemistry in the Study of Milk Secretion," by J. A. F. Rook, B.Sc., Ph.D., A.R.I.C.

At the final session, on the afternoon of July 15th, the Chair was taken by the Chairman of the Section, Dr. S. H. Jenkins, F.R.I.C., F.Inst.S.P., and the following papers were presented and discussed: "The Determination of Additives to Animal Feeding Stuffs (with Special Reference to Prophylactics)," by R. F. Phipers, B.Sc., Ph.D.; "The Analysis of Organophosphorus Pesticides," by K. Gardner, B.Sc., F.R.I.C., L.I.M.

There was an attendance of 89 delegates. In the afternoon of July 14th visits were paid to the Horticultural and Veterinary Research Stations of Boots Pure Drug Co. Ltd. at Lenton and Thurgarton, respectively, and in the evening an informal dinner was held at the Portland Building, University of Nottingham. Summaries of the papers appear below.

THE SPECTROCHEMICAL DETERMINATION OF METALS IN SOILS AND PLANTS

DR. R. L. MITCHELL said that spectrochemical methods were particularly suited to the routine determination of several elements simultaneously in a series of related samples. At the Macaulay Institute flame-emission techniques, now generally with direct-reading rather than spectrographic assessment, were widely used for the determination of potassium, sodium and calcium and occasionally other elements such as strontium and manganese. For magnesium in soil or plant extracts the flame source was not particularly reliable, and a porous-cup solution - spark technique was proving satisfactory. Atomic absorption appeared to be equally suitable for magnesium and also for a few other elements such as zinc, but the Institute had had no direct experience of this technique.

For most trace-element determinations a spectrographic method using cathode-layer d.c.-arc excitation was used, either with a semi-quantitative visual assessment for the total content in soils or as a quantitative technique applied to concentrates derived from soil or plant extracts. The concentration technique involved precipitation of the trace metals in an aluminium - iron oxinate carrier with a mixture of 8-hydroxyquinoline,

tannic acid and thionalide at pH 5.2. This gave complete recovery of a number of metals, including many of biological importance, such as Co, Ni, Zn, Mo, Cu, Sn, Pb, V, Ti, Fe, Cr, Ga, Ag and Au, at the microgram level. This permitted determinations to be made at levels below one part in ten million for many elements. For certain elements porous-cup solution - spark excitation with a Hilger Medium Quartz Direct Reader was preferable, and work was in progress at the time of the meeting on the development of other methods for which this Direct Reader could be used in soil and plant analysis.

THE ANALYSIS OF HERBICIDES

MR. L. A. HADDOCK described the analysis of those organic herbicides that were in current use on a commercial scale. The description was restricted in most cases to an indication of suitable methods for measuring the active constituent of the herbicide, particularly when that constituent existed in admixture with inactive isomers. The assumption was made that the herbicide, in varying degrees of purity, could be isolated from formulations for final analysis. The groups of compounds considered were the 4-chloro-2-methyl-, 2:4-dichloro-, and 2:4:5-trichlorophenoxy-substituted lower aliphatic acids, the substituted ureas, the phenyl carbamates, the substituted dinitrophenols, the chlorinated lower aliphatic acids, the ethyl sulphates, triazines and pyridylum compounds. Strictly inorganic compounds such as sodium chlorate were not discussed.

THE DETERMINATION OF INSECTICIDE AND FUNGICIDE DEPOSITS ON PLANTS

DR. J. T. MARTIN said that in recent years considerable interest had been taken in the determination of the amounts of chemicals falling and persisting upon plants in protective crop-spraying practices. Some ten years ago it had been customary to assess dosages in terms of the amounts of chemicals used per acre, but unknown amounts of the active ingredients had been lost by run-off from plants or by the drifting of small droplets. To assess the potencies of the chemicals in pest or disease control and the efficiencies of the spraying machines, analytical methods were required for the determination of deposits on plant surfaces. The use of chemicals toxic to humans and known to persist upon plants also raised the need for analytical methods by which possible consumer hazards could be checked. Analytical methods were now available for many of the spray chemicals in use. This paper dealt with the determination of surface deposits, particularly in relation to the assessment of spraying efficiency.

For effective pest or disease control, adequate coverage of the target was necessary; this was particularly important for fungicides. The amounts of chemical deposited were expressed as μg per sq. cm of plant surface; parts per million of plant tissue had little meaning. In addition to the amount of chemical deposited, its distribution and the coverage of plant surface achieved were important considerations. Methods had been devised by which deposits could be recovered from plant surfaces for examination. For chemical assay, deposits were washed from surfaces with suitable solvents; so far as possible, analyses were made by rapid methods on small areas in assessments of distribution. The methods used for the determination of deposits of materials such as DDT, BHC, dieldrin, endrin, captan, copper, sulphur and mercury and the levels of deposits found in different conditions were described.

THE SAFE USE OF PESTICIDES, WITH SPECIAL REFERENCE TO CONSUMER PROTECTION

DR. E. J. MILLER described the practice in the United Kingdom with regard to the safe use of pesticides. He explained briefly the voluntary Notification Scheme between Industry and the Government, whereby firms informed Departments of their proposals to market new pesticides or to recommend new uses for existing pesticides. Agreement or "clearance" to the proposals in their original or in modified forms was given in published official recommendations, which advised on the precautions to be taken when using the chemicals so as to avoid risks to operators, to consumers and to "third parties" including livestock and wild life. He explained why, at present, tolerances were not proposed, but instead, by means of a code of practice for farmers and growers to follow, it was held that the consumer of a treated crop would be safeguarded against harmful residues. He

concluded with a brief account of the work, both in this country and by international governmental organizations, on analytical methods for pesticide residues in foodstuffs, and mentioned the recently formed Research Study Group on Toxic Chemicals in Agriculture.

ANALYTICAL CHEMISTRY IN THE STUDY OF MILK SECRETION

DR. J. A. F. ROOK briefly described the analytical methods currently in use for the determination of the major milk constituents. He reported the effects on the composition of the milk of a variety of factors, including breed and individuality of the cow, stage of lactation, level and type of feeding, season of the year, udder health and milking technique, and, where knowledge was available, he discussed the fundamental causes of these effects.

The speaker emphasised the need for recognising that a change in milk composition was the result of biochemical or physiological changes within the animal body, and that under controlled experimental conditions it was possible to use milk compositional data as an index of such changes. This concept had given a new dimension to studies on milk composition, and he gave a number of examples of experimental studies incorporating this approach.

THE DETERMINATION OF ADDITIVES TO ANIMAL FEEDING STUFFS (WITH SPECIAL REFERENCE TO PROPHYLACTICS)

DR. R. F. PHIPERS described recent investigations carried out on behalf of the Analytical Methods Committee of the Society. The Society had been approached by the Ministry of Agriculture, Fisheries and Food with a request for information on what methods of analysis were available for the determination of additives to animal feeding stuffs, on whether suitable methods could be provided if none were available, and for comments on whether such methods were within the competency of agricultural analysts. The additives under consideration were divided into certain groups, these being fat-soluble vitamins, water-soluble vitamins, minerals, antibiotics, hormone growth promoters and prophylactics.

Various Panels were set up, and each had its own programme of work in hand. The lecturer dealt, very briefly, with the progress made by the various Panels and went more deeply into the work of the Panel concerned with the analysis of prophylactics.

He had selected the work of the Prophylactics Panel as an example because investigations into this field were not complicated by naturally-occurring sources, such as were encountered by the Vitamin Panels. The problem of obtaining truly representative samples was discussed, and this in turn led to a brief description of the difficulties that were encountered in preparing uniform mixtures of feeding stuffs containing very small quantities of biologically active materials. The prophylactics at present under consideration were the poultry coccidiosis drugs, nitrofurazone and sulphaquinoxaline.

THE ANALYSIS OF ORGANO-PHOSPHORUS PESTICIDES

MR. K. GARDNER said that, during the last decade, increasing use had been made in agriculture of organo-phosphorus pesticides. Although they were not yet used as extensively as some of the chlorinated pesticides such as DDT and BHC, the number and quantity of different organo-phosphorus chemicals used had already become very large.

The two principal aspects of analytical interest were the specific determination of the active constituent and the determination of residues in crops. In this paper he dealt only with the analysis of technical materials and formulations for the biologically active ingredient, and he discussed several of the more important chemicals.

Amongst the first economically important insecticides in this group were the substituted pyrophosphates. Analysis of these compounds was based on differential hydrolysis. Later developments in the field had been the introduction of variety of dialkyl phosphate, phosphorothioate and phosphorodithioate esters. The common dialkyl phosphate grouping was only occasionally encountered in the determinations and, with few exceptions, the analysis of these compounds depended on the specific determination of the toxicity-determining substituent group, often after a preliminary separation from closely related impurities.

MICROCHEMISTRY GROUP

THE twenty-fifth London Discussion Meeting of the Group was held at 6.30 p.m. on Wednesday, June 22nd, 1960, in the restaurant room of "The Feathers," Tudor Street, London, E.C.4. The Chair was taken by the Vice-Chairman of the Group, Mr. C. Whalley, B.Sc., F.R.I.C.

A discussion on "The Direct Determination of Oxygen" was opened by D. W. Wilson, M.Sc., F.R.I.C.

Obituary

PHILIP SCHIDROWITZ

PHILIP SCHIDROWITZ died at his Ealing home on May 17th, 1960. By his death the Society loses one of its oldest members, one who had a distinguished career in two separate fields of applied chemistry. He was born in 1872 in Germany, his parents being naturalised citizens of the United States. He was brought to England when very young and was educated at St. Charles College and University College, London. Subsequently he studied at the Federal Polytechnic, Zurich, and at the University of Berne, where he received his Doctorate with the highest honours for a thesis on xanthates. Thus began the close connection he maintained throughout his life with many chemists on the continent of Europe.

Returning to England, he rapidly gained for himself a reputation as an expert on wines and spirits (particularly whiskey). In the years between 1900 and 1908 Schidrowitz contributed 17 papers on wines and spirits, as well as some on other subjects, such as opium, to *The Analyst* and other journals. Two important papers on the chemistry of whiskey were published in the *Journal of the Society of Chemical Industry* in 1902 and 1905. Papers on brandy (1905) and claret (1907) appeared in the *Journal of the Institute of Brewing*, whilst as early as 1900 Schidrowitz had written in *The Analyst* on The Composition of "Dry" Champagne.

He always kept in his office a series of bound volumes labelled "Whiskey Cases" and, despite his later specialisation in the field of rubber, continued to be retained by leading producers of whiskey for very many years.

His introduction to rubber came via gutta percha in a curious and unexpected manner. He had married, in 1905, Ada Mary Gaine, whose father was a director of the Eastern Telegraph Company. Shortly afterwards, great technical difficulties were experienced with the company's submarine cables, which were insulated with gutta percha. Mr. Gaine asked his son-in-law if he could help. Thus began Philip Schidrowitz's main life's work.

The literature of rubber shows Schidrowitz as the author of something like 500 publications and patents covering almost every aspect of the industry. The flow of these publications on rubber began about 1911, and at the same time those on wines and spirits abruptly ceased. A number of his discoveries deserve the term "epoch-making." For example, his famous British Patent 1111 of 1914 described for the first time the manufacture of a sponge or foam from latex and may be considered as the forerunner of what is now a large and flourishing industry. He also found that rubber latex could be vulcanised without coagulation, and described a number of other technical advances which were responsible in no small degree for the large increase in the consumption of latex in recent years.

In these and many other directions Schidrowitz blazed the trail that was to be followed, with success, by others. The way of the pioneer is seldom easy and rarely profitable. Schidrowitz was no exception—all too often where he sowed, others reaped. Industry was not yet in the frame of mind to seize the opportunities that were offered.

Schidrowitz joined the Society in 1898 and was a Member of Council in 1903–04. He wrote for the *Rubber Journal* a weekly page entitled "Views and Reviews" for a period of almost forty years. He took a leading part in the founding of the Institution of the Rubber Industry in 1921, and served on its Council for many years. In 1940 he was awarded the Colwyn Medal of this Institution (jointly with Dr. H. P. Stevens).

A man of distinguished appearance, Schidrowitz had the power to put forward his views, whether in writing or orally, with great clarity and charm. He had a wonderful sense of humour and many good stories that afterwards went the rounds could be traced back to him.

He is survived by his wife and two sons.

H. J. STERN

Flame-photometric Methods in Metallurgical Analysis

A Review*

By JOHN A. DEAN

(*Department of Chemistry, University of Tennessee, Knoxville, Tennessee, U.S.A.*)

APPLICATIONS of flame photometry to the analysis of metallurgical products are not as widespread as the utility of the technique warrants. The method should be of interest to analysts in production and control laboratories, especially to those in small foundries having no spectrographic facilities. Preliminary preparation of the sample is usually minimal, and multi-element determinations in successive steps are often feasible.

Among the conventional combustible gases, an oxygen-acetylene flame, into which is aspirated an organic solvent, offers the optimum excitation conditions. In such a flame, more than fifty-seven elements are excited, and forty-three of these can be determined with high sensitivity. The emission sensitivities of these elements have been tabulated,¹ and some of the elements pertinent to metallurgical analysis are listed in Table I. If one prefers to speak of detection limits, the compilation by Gilbert² should be consulted. An advantage of flame photometry is that, compared with an arc or spark source, flames excite fewer lines of each element; also, it is less difficult to establish reproducible conditions of excitation and sample introduction into a flame by means of an aerosol. The development of high-temperature flames, such as the oxygen-cyanogen flame,^{3,4} offers promise for the excitation of line spectra of elements whose lines are weak or absent in an oxygen-hydrogen or oxygen-acetylene flame, namely, beryllium, molybdenum, tin and vanadium. Gilbert^{2,3} has tabulated the detection limits of thirty elements in an oxygen-cyanogen flame.

In flame photometry, a solution of the sample to be analysed is sprayed under controlled conditions into an oxygen-fuel-gas flame. To isolate the desired region of the spectrum, the light from the flame passes directly or indirectly, by means of a lens or mirror, into the narrow entrance slit of a monochromator. The intensity of the isolated radiation is measured by a photosensitive detector and some type of meter or electronic amplifier. The advent of the photomultiplier (electron multiplier) tube provided the sensitivity and, consequently, the selectivity needed in direct-reading flame photometry. The increased sensitivity permitted, in turn, a greater degree of spectral selectivity. However, to achieve maximum spectral selectivity, a monochromator equipped with quartz optics and with variable entrance and exit slits must be used. The combination of adjustable slits of good optical quality, adequate gain control in the amplifier of the detecting circuit and a wavelength drum permits selection of the most favourable ratio between background and analytical-line radiation and more effective isolation of the radiation from the test element. Recording attachments are desirable.

Failure to utilise proper equipment imposes needless spectral interferences on the test elements. If wide slits are used, and this is necessary to achieve reasonable emission readings when ordinary photocells or phototubes are used as photo-receptors, the emission lines of cobalt and nickel cannot be resolved from each other or from those of iron, chromium and manganese. Correction graphs offer a partial solution, but their use involves much extra work and detracts from the inherent rapidity of flame photometry. Specificity (interference) factors for many elements have been recently summarised.⁵

Solvent-extraction procedures, after which the organic phase is aspirated into the flame, are being used to an increased extent.^{6,7} The use of organic solvents provides much greater sensitivity and selectivity than was previously believed possible in flame photometry. Increases in emission intensity ranging from ten- to twenty-fold are usual; exceptionally large enhancement has been obtained for aluminum, chromium and the rare-earth metals. Intensification with organic solvent-water mixtures is less—approximately four- to ten-fold. The enhancement achieved by using organic solvents or solvent-water combinations in place of aqueous solutions can be utilised in various ways: (a) more dilute solutions or solutions containing weakly emitting elements can be analysed with ordinary flame-spectrophotometric

* Reprints of this paper will be available shortly. For details, please see p. 696.

equipment and the usual fuel gases and (b) by decreasing the concentration of matrix elements or by selective extraction from these matrix elements, spectral and radiation interferences can often be circumvented.

In flame photometry, by contrast with colorimetry, interfering colour-bodies from similar chemical entities need not be removed, provided that the metal contributing the colour does not enhance or inhibit the light emitted by the test element or emit light of its own at the same discrete wavelength as that of the test element. In particular, many extractive colorimetric methods, formerly dismissed as unsatisfactory, are often directly applicable to flame

TABLE I
WAVELENGTHS AND EMISSION SENSITIVITIES OF LINES AND BANDS USEFUL
IN METALLURGICAL ANALYSIS

Emission-sensitivity values are for a Beckman DU flame spectrophotometer equipped with a 1P28 photomultiplier tube (or a red-sensitive phototube for measurements above 680 $m\mu$), an integral-aspirator burner and a 0- to 10-mV recorder (0 to 100 T-scale units), Slit widths were kept at 0.05 mm, and the photomultiplier tube was operated at 60 volts per dynode and with a 22-megohm load resistor

Element	Wavelength, $m\mu$	Type of emission	Type of flame	Emission sensitivity, p.p.m.*
Aluminium	{ 396.2 484	Atomic line Molecular band	Oxygen - acetylene†	0.4
Boron	{ 518 546			
Cadmium	326.1	Atomic line	{ Air - hydrogen Oxygen - acetylene	0.5
Calcium	422.7			Oxygen - acetylene
Chromium	425.4	Atomic line	Oxygen - acetylene†	0.1
Cobalt	387.3			6.0
Copper	324.7	Atomic line	Oxygen - acetylene	0.6
Gallium	417.2			0.5
Indium	451.1	Atomic line	Oxygen - hydrogen	0.07
Iron	{ 372.0 386.0	Atomic line	{ Oxygen - acetylene Oxygen - acetylene†	2.5
	437	Atomic line		Oxygen - acetylene
Lanthanum	{ 741 405.8	Molecular band	Oxygen - acetylene	2.7
Lead	670.0	Atomic line	Oxygen - acetylene	{ 0.7 5.0
Lithium	{ 285.2 383	Atomic line	Oxygen - acetylene	14
Magnesium	383	Molecular band	Oxygen - acetylene	0.07
Manganese	{ 403.3 352.5	Atomic line	Oxygen - acetylene	1.0
Nickel	404.4			Oxygen - hydrogen
Potassium	{ 766 and 769 328	Atomic line	Oxygen - hydrogen	0.1
Silver	338.3			1.6
Sodium	589.6	Molecular band	Oxygen - acetylene†	1.7
Yttrium	597			0.02
				1.0
				0.6
				0.001
				0.2

* To give one division on the T-scale.

† Metal aspirated in organic solvent rather than in aqueous solution.

photometry when organic solvents are used. I think that here is a fertile field for the development of selective methods for flame photometry. Often the only change required is to substitute an oxygenated solvent, ketone or ester, for the widely used halogen-containing solvents, since the latter release obnoxious hydrogen halides into the burnt flame gases.

Methods for determining constituents in various types of ferrous and non-ferrous alloys and of bulk metals are reviewed in the following discussion. The majority of reported methods applicable to non-ferrous alloys have dealt with aluminium alloys, perhaps because of their paramount position. Flame photometry is equally applicable to the other classes of non-ferrous materials. With tin-based alloys it is generally difficult to prevent extensive hydrolysis of tin salts; consequently, tin, together with any antimony and arsenic, should be removed by volatilisation of the bromide.

ALKALI METALS

The resonance lines of the alkali metals exhibit considerable self-absorption, *i.e.*, the calibration graph bends toward the concentration axis at relatively low concentrations. For potassium, the influence of self-absorption may overlap the ionisation effect, so producing a calibration graph that is upwardly concave initially, but later becomes convex. Self-absorption and ionisation effects are more serious in the hotter oxygen - fuel flames. The handling of alkali samples and standard solutions of alkali metals presents problems if contamination is to be avoided.

For the lithium line at $670.7\text{ m}\mu$, spectral interferences arise from the molecular-band systems of barium, calcium and chromium. Strange⁸ described a method for determining lithium in ternary magnesium - lithium - aluminium alloys containing 1 to 10 per cent. of lithium; Robinson and Ovenston⁹ devised a method for the range 11 to 14 per cent. of lithium. To compensate for the suppression of lithium emission by magnesium and aluminium, Strange recommended addition of these elements to the standard solutions. Robinson and Ovenston used a double-beam instrument and a relatively large concentration of potassium as internal standard. Amounts of acid similar to those used to dissolve the sample were incorporated in the standards. Kuemmel and Karl¹⁰ determined lithium and sodium in ductile cast iron and nodular iron, the flame-photometric measurements being made after preliminary extraction of iron by ether. Solutions prepared from 4-g samples and having a final volume of 50 ml were compared with standards prepared by adding standard solutions of sodium and lithium to a 4-g portion of a cast iron relatively free from these elements. The standard-addition method would be applicable and more rapid for infrequent analyses.

The sodium line at $589.6\text{ m}\mu$ is subject to little spectral interference from other elements, although calcium in large amounts affects the background on the long-wavelength side of it. The general procedure for determining sodium involves aspirating the sample directly and comparing the sodium emission with those of standards prepared from the pure bulk metal and containing different added amounts of a standard solution of sodium. Acid concentration is not particularly critical, but should not exceed certain limits.¹¹ By this method, sodium has been determined in aluminium,^{11,12,13} aluminium alloys,^{13,14} lead^{15,16} and lithium.¹⁷ The sodium content of tungsten¹⁸ has been determined in the residue after tungsten has been sublimed from the sample by heating at 600°C in a stream of carbon tetrachloride. When necessary, the standard-addition method can be used to ascertain the amount of test element present as contaminant in the "pure" metal used in the preparation of the standard solutions. For determining sodium in calcium metal,¹⁹ it was found to be necessary to remove calcium by precipitation with oxalic acid and aqueous ammonia when only an interference filter was used to isolate the sodium light.

Potassium suffers no spectral interference from components of the common metallurgical samples at the wavelengths of the red doublet, 766 and $769\text{ m}\mu$. In the violet, the line at $404.4\text{ m}\mu$ is subject to spectral interference from lead and manganese unless very narrow spectral-band widths are used. Potassium in bulk metals, *e.g.*, aluminium,¹⁶ lead,¹¹ lithium¹⁶ and tungsten,¹⁸ has been determined in a manner similar to that described for sodium.

The flame should be a great help in determining rubidium and caesium. Each of these elements has a pair of intense atomic lines; rubidium at 780 and $795\text{ m}\mu$, and caesium at 852 and $894\text{ m}\mu$. However, to realise the full potentialities of these lines, it is necessary to install a photomultiplier tube having an S-1 response or an infra-red image converter in place of the usual red-sensitive phototube supplied with commercial instruments. Rubidium is subject to spectral interference from the potassium doublet at 766 and $769\text{ m}\mu$ and the lanthanum oxide band system centering around $791\text{ m}\mu$. The molecular-band systems from water tend to increase the background in the vicinity of the caesium line at $894\text{ m}\mu$, and the weak molecular-band systems of calcium, strontium and barium tend to cover the caesium lines when large amounts of the alkaline earths are present. Caesium has been determined in bismuth metal and in bismuth - uranium alloys by Wildy,²⁰ who used the line at $852\text{ m}\mu$ and an image converter. Standards prepared from pure bismuth salts overcame the slight depressive effect of bismuth.

ALUMINIUM

Eshelman and his co-workers²¹ have described a solvent-extraction procedure for determining acid-soluble aluminium. For ferrous alloys, the iron was removed by extraction with *isobutyl methyl ketone* from a solution 5 M in hydrochloric acid; the aluminium was then

extracted, as its cupferrate, into a known volume of *isobutyl methyl ketone* from an acetate solution adjusted to a pH between 2.5 and 4.5. The organic phase was aspirated directly into the flame, and the emission intensity of the atomic line at $396.2\text{ m}\mu$ or the crest of the oxide-band head at $484\text{ m}\mu$ was compared with standards prepared by similar cupferrate extraction of aqueous standards containing aluminium. The atomic line and the oxide-band head have equal emission intensities in an oxygen - acetylene flame, but only the oxide band is suitable when working with the cooler oxygen - hydrogen flame.

For copper- and nickel-based alloys, aluminium is extracted, as cupferrate, after copper and nickel have been removed by separation at a mercury cathode. For magnesium-based alloys, the aluminium cupferrate is extracted directly, without any prior separation. For zinc-based alloys, zinc is removed by extraction of its diethyldithiocarbamate into chloroform. The aluminium is then extracted at pH 5.5 to 5.8 into a known volume of a 0.1 *M* solution of 2-thenoyltrifluoroacetone in *isobutyl methyl ketone*, and the organic phase is aspirated into the flame.

The direct method for aluminium in the ketone solution is far superior to the indirect method based on the depressive effect of aluminium on the flame emission of calcium. All other ions that might depress or enhance the calcium emission must be absent when the indirect method is used.

BERYLLIUM

An indirect method for determining beryllium in beryllium bronze has been reported by Malinowski and Dancewicz.²² After preliminary separation of beryllium by precipitation as hydroxide in the presence of ethylenediaminetetra-acetic acid as masking agent, the beryllium hydroxide is dissolved in nitric acid and then added to a standard solution of strontium. The depression of the strontium line at $460.7\text{ m}\mu$ is fairly linear over the range 40 to 200 p.p.m. of beryllium when the standard contains 750 p.p.m. of strontium.

On the basis of the flame spectrogram of beryllium reported by Gilbert,²³ the direct determination of beryllium may prove feasible. The spectrum contains atomic lines at 234.9 and $265.1\text{ m}\mu$ and an intense band spectrum in the green portion, with prominent heads appearing at 471 and $473\text{ m}\mu$. Non-aqueous solvents might easily provide striking enhancement similar to that observed for aluminium.²¹

BORON

Fornwalt used solutions containing 50 per cent. v/v of methanol in water for determining boron in nickel-plating baths.²⁴ Measurements were made at the $518\text{-m}\mu$ or the $546\text{-m}\mu$ band head, and corrections were applied for flame-background emission by taking readings at the minima on either side of the crests. Interference from aluminium, calcium, chromium, cobalt, copper, iron, manganese and nickel occurs at one or more of the band heads or background minima; the original paper by Dean and Thompson²⁵ should be consulted for details. Dutina²⁶ developed a method for boron-10 "burn-up" in stainless steel, zirconium and Zircaloy; he utilised the lithium-7 formed from boron-10 by neutron irradiation.

CADMIUM

The amount of cadmium metal plated on small cylinders of aluminium, as used in nuclear-energy installations, was determined by Gilbert.²⁷ He used the line at $326.1\text{ m}\mu$, after having increased the amplification of the 1P28 photomultiplier tube to the point at which shot-effect noise became comparable with flame flicker. Cadmium shows up best in an air - hydrogen flame. Spectral interferences arise when copper, calcium or iron are present.

CALCIUM

The resonance line of calcium, located at $422.7\text{ m}\mu$, is preferred to the calcium hydroxide band head at $554\text{ m}\mu$. The former is in a portion of the spectrum free from flame-background emission and from spectral interferences, except for a faint ionic line of strontium. The intense chromium line at $425.4\text{ m}\mu$ should not cause any difficulty with monochromators possessing good resolution. Serious inhibition is encountered from sulphate, phosphate and other elements capable of existing as anions in the flame, e.g., aluminium, chromium, iron and zirconium. Hypotheses about the nature of the depressive effect have been advanced by several workers.^{28,29,30} It is presumably caused by the formation of a compound between

calcium and materials of comparatively low volatility. Inhibition is less when the flame temperature is high. Interference from phosphate and sulphate has been overcome in a novel method described by Yofé and Finkelstein.³¹

The determination of calcium in tungsten¹⁸ and in nickel³² has been reported. In bulk nickel samples, the nickel, together with other minor constituents of the sample, is removed by separation at a mercury cathode, and any aluminium present is extracted, as oxinate, at pH 9. The residual solution is evaporated to dryness, the residue is dissolved in *N* hydrochloric acid, 40 per cent. v/v of methanol is added, and the calcium emission is then measured.

Kuettel and Karl¹⁰ determined calcium and magnesium in ductile cast iron and nodular iron. Phosphorus was the only element causing interference in considerable magnitude. Although phosphorus was partially removed, as phosphine, during solution of the sample, enough was retained to affect the determination of calcium and, to a lesser extent, magnesium. Compensation was achieved by using standards prepared from pure cast iron, the phosphorus contents of the standards being within 0.02 per cent. of those of the samples. Manganese caused a slight decrease in the calcium intensity, but this decrease was constant for between 0.25 and 1.25 per cent. of manganese. The use of standards containing manganese in this range compensated for the suppressing effect on calcium. The flame-photometric measurements were made after preliminary extraction of iron by ether. Solutions prepared from 4-g samples were diluted to 50 ml and were compared with standards prepared by adding standard solutions of sodium, calcium, magnesium and lithium to a 4-g portion of a cast iron relatively free from these elements and having phosphorus, carbon and silicon contents approximately equal to those of the test samples. The standard-addition method would be more convenient and should circumvent the interferences enumerated.

Abresch and Dobner³³ have discussed their experience with flame methods for determining calcium in a steel-plant laboratory.

CHROMIUM

From many types of steel and cast-iron samples and aluminium-based alloys, Bryan and Dean³⁴ selectively extracted chromium^{VI} with *isobutyl methyl ketone* from an aqueous solution *M* in hydrochloric acid and maintained at the temperature of an ice-bath. The organic extract was aspirated directly into the flame, and chromium emission was measured at 425.4 m μ . Although some iron, about 2.5 per cent. of the original concentration, accompanied the chromium in the extract, it did not interfere and, if desired, could be largely removed by washing the organic phase once with fresh *M* hydrochloric acid. The addition of phosphoric acid partly masked the iron.

Less successful are the methods used by Burriel-Martí and his co-workers³⁵ and by Ikeda,³⁶ wherein the chromium emission is measured on the original aqueous solution. Numerous interferences are encountered from other elements and acid anions.

Wever, Koch and Wiethoff³⁷ have determined the ferrite composition of steel. The carbides in chromium - manganese steels were isolated electrolytically, and the chromium, iron and manganese dissolved in the citrate electrolyte were determined. Standards of each of these elements were prepared in a similar citrate solution. Sulphate ion influenced the intensity of the chromium and iron lines, and results were correct only when equivalent amounts, or more, of sulphate to metal ion were present.

COBALT

Of the numerous emission lines of cobalt, only the line at 387.3 m μ is not subject to interference from nickel; it is also well separated from the intense iron line at 386.0 m μ . No satisfactory method has been reported for determining cobalt in steels, although Burriel-Martí and his co-workers studied the problem.³⁵ Unfortunately, these workers used wide slits and were unable to resolve the closely spaced emission lines of cobalt (and nickel) from those of iron, chromium and manganese. It should be possible to devise a suitable solvent-extraction method, as described under "Copper."

Galloway³⁸ determined cobalt, copper and iron in cobalt mattes and concentrates. Iron was removed by double extraction with an ethyl methyl ketone - chloroform mixture, and the combined extracts were washed with fresh 8 *M* hydrochloric acid. After removal of the solvent and destruction of any organic matter, the residual salts were dissolved in water, and the iron emission was measured at 386.0 m μ . The organic phase could have been

aspirated directly, with considerable saving in time. The aqueous layers were combined, heated to remove residual organic solvent and concentrated. Sufficient *isopropyl* alcohol was added to give a concentration of 10 per cent. v/v in the final solution. Cobalt and copper were measured at 387.3 and 324.7 $m\mu$, respectively.

COPPER

Only two intense lines are present in the spectrum of copper, and both exhibit self-absorption. Spectral interference is possible from cadmium, cobalt and nickel.

For all types of non-ferrous alloys, Dean³⁹ atomised the dissolved sample directly into the flame and measured the copper emission at 324.7 $m\mu$. Any of the common acids could be tolerated at concentrations up to 1 *M*. When present in large amounts, tin and antimony were volatilised as their bromides. In cobalt mattes and concentrates, copper has been determined in the aqueous solution after removal of iron³⁸ (see under "Cobalt").

For aluminium-based alloys, Dean and Cain⁴⁰ selectively extracted copper, manganese and nickel (*plus* any cobalt present), as their diethyldithiocarbamates, from a citrate-buffered solution. *iso*Butyl methyl ketone would be a superior solvent to the chloroform used by these workers.

For ferrous alloys, Dean and Lady⁴¹ extracted copper, as salicylaldoximate, into chloroform or *n*-amyl acetate from citrate solutions buffered at pH 3. The iron was masked, and no other interferences were reported.

GALLIUM

Meloche and Beck determined gallium in copper - gallium alloys.⁴² The dissolved sample was atomised directly, and the gallium emission was measured at 417.2 $m\mu$. No emission lines of other elements occur in the immediate vicinity, but zinc, indium, manganese and aluminium slightly affect the emission readings.

INDIUM

Meloche and his co-workers also determined indium in copper - aluminium alloys,⁴³ the sample being dissolved and the solution atomised directly. The indium emission was measured at 451.1 $m\mu$ and compared with compensatory standards. Gilbert has determined amounts of indium corresponding to a film evaporated on supporting surfaces.⁴⁴

IRON

Numerous elements interfere with emission from iron.⁴⁵ As a result, for non-ferrous alloys, Dean and Lady⁴⁶ extracted a sample adjusted to pH 0.5 with six successive portions of acetylacetone. Later work by Dean and unpublished studies by O. Menis and T. C. Rains have shown that a single extraction with *isobutyl* methyl ketone from a solution 5 to 6 *M* in hydrochloric acid is sufficient. With either solvent, the organic phase is aspirated into the flame, and the iron emission is measured at 372.0 or 386.0 $m\mu$.

For cobalt mattes, iron is measured after extraction by ethyl methyl ketone, as described under "Chromium." For carbides, iron is measured, after electrolytic isolation, in the citrate electrolyte; this is also described under "Chromium."

LEAD

Although no methods have been reported for determining lead in alloys, lead has two useful lines at 405.6 and at 368.3 $m\mu$. It can be extracted into several organic reagents, thereby incorporating the enhancement attainable with organic solvents, as has been done in the determination of lead in gasoline.

MAGNESIUM

Situated at 285.2 $m\mu$, the atomic line of magnesium is sensitive, but unfortunately it lies in an OH-band system and requires correction for the flame background; such correction is difficult to achieve. Prominent band systems due to molecules of magnesium hydroxide appear at 371 and 383 $m\mu$. Again, correction for flame-background emission is difficult because of the breadth of the molecular-band systems. The atomic line is not subject to serious spectral interferences from other elements; by contrast, the band crests are susceptible

to severe interference from iron, manganese, potassium and sodium. In a hydrogen - fluorine or a hydrogen - perchlorylfluoride flame, a sharp and intense magnesium fluoride band appears at $359.4\text{ m}\mu$.

For aluminium alloys, the aqueous sample is aspirated without preliminary treatment, and the band head at $383\text{ m}\mu$ is measured. Standards must contain amounts of aluminium and acid equivalent to those in the alloy solution, but other matrix elements exert no effect.⁴⁷

Abresch and Dobner³³ have discussed their experience with flame methods for determining magnesium, and Kuemmel and Karl¹⁰ have determined magnesium in ductile cast iron and nodular iron as described under "Calcium."

MANGANESE

The very intense line at $403.3\text{ m}\mu$ is generally used for the determination of manganese, and serious spectral interference arises when gallium or potassium is present. Proper correction for background radiation and the addition of standards overcome difficulties from aluminium, calcium, iron, magnesium and sodium when these elements are present in amounts equivalent to sample matrices. In this manner, Dippel and Bricker⁴⁸ determined manganese in aluminium alloys, bronze, nickel - copper alloys and steels. Analyses of steels have been reported by Thanheiser and Heyes,⁴⁹ Heyes⁵⁰ and Ikeda.⁵¹ Wever, Koch and Wiethoff³⁷ determined manganese in a citrate electrolyte after the electrolytic isolation of carbides in steels. Dean and Cain⁴⁰ separated manganese from aluminium alloys by selective extraction with diethyldithiocarbamate and aspirated the organic phase directly into the flame.

NICKEL

Like the other elements of the first triad of group VIII, nickel has a spectrum rich in lines. Cobalt interferes with all the major emission lines of nickel except that at $361.9\text{ m}\mu$, and iron interferes with all major nickel lines except those at 341.5 and $345.8\text{ m}\mu$.

No satisfactory method has been reported for determining nickel in ferrous alloys, although Burriel-Martí and his co-workers³⁶ have described a method in which nickel is precipitated with dimethylglyoxime and extracted with chloroform, and the organic phase is stripped with 5 M hydrochloric acid. For aluminium alloys, Dean and Cain⁴⁰ extracted nickel, as diethyldithiocarbamate, into chloroform and aspirated the organic phase into the flame; cobalt, if present, interfered. In nickel-plating baths, Fornwalt²⁴ determined the nickel directly after adding 40 per cent. v/v of methanol to intensify the emission.

PLATINUM METALS

Ruthenium, rhodium and palladium have sensitive and line-rich spectra. Menis and Rains have used flame photometry for determining ruthenium and palladium in certain nuclear-energy applications. They used aqueous solutions containing 50 per cent. v/v of methanol or acetone to enhance emission from ruthenium; palladium was extracted, as the α -furildioxime complex, into *isobutyl* methyl ketone, and the organic phase was aspirated into the flame.

Platinum exhibits two weak lines, neither of which are useful, and osmium and iridium exhibit no lines. Platinum, rhodium and palladium have been determined in the presence of excess amounts of lead and iron⁵² by atomic-absorption spectroscopy.

RARE-EARTH METALS

All the rare-earth elements *plus* lanthanum, scandium and yttrium have intense band spectra. Europium, thulium and ytterbium also exhibit intense line emissions. Rains, House and Menis⁵³ have reported the spectra of these elements and have tabulated the line and band intensities. All the spectra are grouped closely together, and spectral interference is common, particularly with adjacent members. Lanthanum has been studied in methanol - water solutions by Menis, Rains and Dean,⁵⁴ who have also extracted lanthanum with 2-thenoyltrifluoroacetone in *isobutyl* methyl ketone to circumvent certain interferences.⁵⁵ Yttrium has been studied by J. A. Dean and W. J. Carnes, in unpublished work, an extractive method similar to that for lanthanum being used.

SILVER

Of the silver emission lines at 328.0 and $338.3\text{ m}\mu$, the latter is preferable, since it is less subject to self-absorption, and the flame background does not contain the remnants

of the OH-band system that surrounds the former line. In unpublished work, J. A. Dean and C. B. Stubblefield have made a thorough study of the silver lines. Nickel and cobalt have a series of lines in the vicinity of the silver line at $338.3 \text{ m}\mu$, and the presence of calcium and tin increases the flame-background radiation. Narrow spectral-band widths are required to separate the silver line at $328.0 \text{ m}\mu$ from the copper line at $327.3 \text{ m}\mu$.

Galloway⁵⁶ determined silver in blister copper by precipitating silver as chloride, dissolving the precipitate by successive treatments with aqueous ammonia and hot 20 per cent. nitric acid and then measuring the resulting solution; none of the common metals interfered.

ZINC

Ordinary flames containing zinc salts do not provide sufficient sensitivity. However, Russell, Shelton and Walsh⁵⁷ reported a sensitivity of 0.2 p.p.m. for the zinc line at $213.9 \text{ m}\mu$ when atomic absorption was used. Atomic absorption has been applied to the analysis of non-metallurgical materials and should be equally applicable for alloys.

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Analytical Methods Committee

REPORT PREPARED BY THE METALLIC IMPURITIES IN
ORGANIC MATTER SUB-COMMITTEE

The Determination of Small Amounts of Arsenic in Organic Matter

THE Analytical Methods Committee has received the following report from its Metallic Impurities in Organic Matter Sub-Committee. The Report has been approved by the Analytical Methods Committee and its publication has been authorised by the Council.

REPORT

When the Metallic Impurities in Organic Matter Sub-Committee was reconstituted in 1955, with a remit from the Analytical Methods Committee to investigate the determination of small quantities of metals in organic matter, one of its first tasks was to investigate the determination of arsenic by the molybdenum-blue method. The Sub-Committee's Report on this investigation and the recommended procedure for the method (Appendix I, p. 635) appear below.

The Sub-Committee concluded that the molybdenum-blue method, being a spectrophotometric determination, has inherent advantages over the Gutzeit method, which may be regarded as an estimation rather than a determination, since it depends on the evaluation of the intensity of a stain on a test paper, and the judgments of individual analysts may differ slightly. Nevertheless, within this limitation and provided that the details of the method are strictly observed, the Gutzeit method is adequate in many circumstances, particularly when it is necessary to ascertain whether or not an arsenic content exceeds a certain limit. It is also less intricate and time-consuming than the molybdenum-blue method.

For these reasons the Gutzeit method (based on "The Determination of Arsenic in Food Colouring Materials," Report No. 1 of the Sub-Committee on the Determination of Arsenic, Lead and Other Poisonous Metals in Food-Colouring Materials¹ has been revised to bring it up to date and to widen its scope, and the recommended procedure is given in Appendix III (p. 639).

The members of the Sub-Committee were Mr. T. McLachlan (Chairman), Mr. L. Brealey, Miss E. M. Chatt, Messrs. J. C. Gage, T. T. Gorsuch, C. L. Hinton, E. I. Johnson, W. C. Johnson, I. MacIntyre, R. F. Milton, G. Taylor* and G. E. Willis.* In July, 1958, Mr. W. C. Johnson succeeded Mr. McLachlan as Chairman. From 1956 to 1958 Mr. T. T. Gorsuch held a Society for Analytical Chemistry Research Scholarship, and, working at Harwell under the direction of Mr. A. A. Smales, carried out work on radiochemical investigations.²

* Since deceased.

Molybdenum-blue Method

INTRODUCTION

Of the several published variants of the molybdenum-blue method (references to four examples^{3,4,5,6} are given) the procedure recommended in this report follows most closely that of Wyatt.⁵ Organic matter is destroyed by wet oxidation, and the arsenic, after extraction with diethylammonium diethyldithiocarbamate solution, is converted to the arsenomolybdate complex, which is then reduced by means of hydrazine sulphate to a molybdenum-blue compound and determined absorptiometrically.

Towards the end of the Sub-Committee's investigation special efforts were made to establish the lowest quantity of arsenic that could be determined with reasonable accuracy by the final method. This was considered to be a quantity not less than the blank normally encountered in industrial districts, and, therefore, involved work to minimise this blank. Throughout this work the main sources of error in the determination of micro quantities of arsenic by any method—as summarised by Satterlee⁷—were borne in mind.

EXPERIMENTAL WORK

REDUCTION OF ARSENMOLYBDATE TO MOLYBDENUM BLUE—

The first point to be settled by the Sub-Committee was the selection of the most suitable reducing agent for giving the final molybdenum-blue complex, and the choice was narrowed to either stannous chloride or hydrazine sulphate. A solution containing 0.615 per cent. of arsenic was tested with each of the reducing agents. Results by both methods were accurate, but there was a slightly greater variation in the results by the stannous chloride reduction, as shown in Table I.

TABLE I

COMPARISON BY COLLABORATING LABORATORIES OF STANNOUS CHLORIDE AND HYDRAZINE SULPHATE AS REDUCTANTS FOR THE DETERMINATION OF ARSENIC, IN A SOLUTION CONTAINING 0.615 PER CENT. (AS AS)

Reductant	Arsenic (As), %						
	Stannous chloride	0.60	0.61	0.57	0.59	0.64	0.64
Hydrazine sulphate	0.61	0.61	0.62	0.61	0.67	0.67	

Spectrophotometric examination of the coloured complexes showed that the stannous chloride reduction gave an unstable molybdenum-blue complex having no well defined peak absorption, only a broad absorption plateau at approximately 700 m μ . This complex slowly changed into a stable complex (in approximately 24 hours) that appeared to be identical with the complex produced immediately by the hydrazine sulphate reduction, since both had a well defined peak absorption at approximately 840 m μ . The method resulting in the immediate formation of this stable complex was therefore considered to be the more suitable. It was evident that the stannous chloride reduction gave satisfactory results when used in conjunction with a filter absorptiometer if a strict time schedule was followed, but the hydrazine sulphate reduction used in conjunction with a spectrophotometer would prove a more sensitive method independent of any time factor.

The Sub-Committee decided to use hydrazine sulphate on the grounds that (i) it formed a stable complex immediately, (ii) the complex was less affected by variations in acidity of the solutions⁸ and (iii) the reagent was stable and contained no metal ions; material of analytical-reagent grade was satisfactory and readily available. After discussing the accuracy of various instruments available, it was decided that, for maximum accuracy, the use of a spectrophotometer should be specified, and that measurements should be made at a wavelength of 840 m μ for greater sensitivity.

SEPARATION OF ARSENIC—

Three methods for the separation of the arsenic before forming the molybdenum-blue complex were considered: (a) distillation as arsenic trichloride, arsenic tribromide or arsenic pentabromide, (b) volatilisation as arsine and (c) extraction by a thio compound. It was finally decided to use extraction by a thio compound (diethylammonium diethyldithiocarbamate), with preliminary distillation as arsenic trichloride when excessive amounts of heavy metals or insoluble matter were present. The arsine isolation was rejected because

(i) it necessitated an absorption stage, which was likely to be the chief source of error in the procedure and (ii) the absorption solutions used, *viz.*, mercuric chloride - potassium permanganate, iodine - sodium bicarbonate or hypobromous acid, could introduce undesirable complications into the subsequent hydrazine sulphate reduction procedure.

When using sodium ethylxanthate as extractant, one laboratory had obtained low recoveries of arsenic at low arsenic contents, but highly satisfactory results had been recorded over a long period with diethylammonium diethyldithiocarbamate.⁶ The Sub-Committee therefore agreed on the use of diethylammonium diethyldithiocarbamate. Heavy metals that form complexes with this reagent under the conditions of the test can be tolerated in the method up to a limit of about 1000 μg in all. When this amount is exceeded, it is necessary to isolate the arsenic by distillation before carrying out the extraction procedure.

DECOMPOSITION OF THE MATERIAL—

The Sub-Committee agreed that a wet-oxidation procedure must be specified, as no method of dry oxidation could be relied on to give complete recovery of arsenic.

INTERFERENCES—

Silicon, phosphorus and germanium also combine with molybdenum forming heteropolyacids that give the molybdenum-blue colour on reduction. Silica is removed by filtration after wet oxidation, and if traces of silicon compounds persist (from contact with glassware), little or no blue complex is formed from the molybdosilicate in the acid conditions specified in the recommended method; interference by phosphate is completely prevented by the inclusion of an acid washing after isolation of the arsenic diethyldithiocarbamate complex in chloroform; germanium is so rarely encountered that it was not considered by the Sub-Committee. The method is, therefore, specific for arsenic in all normal circumstances.

OUTLINE OF THE METHOD—

Briefly, the proposed method, full details of which are given in Appendix I, consists of the following stages—

- (a) The material is wet oxidised with nitric acid, sulphuric acid and perchloric acid.
- (b) The arsenic is extracted with diethylammonium diethyldithiocarbamate in chloroform.
- (c) The organic matter is destroyed, and the arsenic is combined with molybdic acid to produce the arsenic - molybdate complex. The arsenomolybdate is then reduced with hydrazine sulphate to a molybdenum-blue complex.
- (d) The arsenic is determined by measuring spectrophotometrically the optical density of the molybdenum-blue complex at a wavelength of 840 $\text{m}\mu$ and referring to a calibration graph in the usual manner.
- (e) In special instances when, after wet oxidation, the solution contains appreciable quantities of heavy metals or much insoluble matter, the arsenic is isolated by distillation as the trichloride before extraction as the dithiocarbamate complex.

COLLABORATIVE TESTS OF PROPOSED METHOD—

(a) *Series 1*—The first collaborative tests for the determination of arsenic were made on three samples of organic material by the procedure decided on in the preliminary investigation. The results are shown in Table II.

Agreement was good for Sample 1, in which the arsenic content was high, but difficulty was experienced with Sample 2, which did not wet oxidise easily and, being a medicinal compound, contained only a trace of arsenic. The results for Sample 3 suggested that the method might not be adequately safeguarded against phosphate contamination. This point was examined very thoroughly by two members, who reported the results in Table III, which showed the safeguards to be adequate.

(b) *Series 2*—Further collaborative tests were made with new samples of material representing various levels of arsenic content, *viz.*, a fresh batch of tobacco powder, dried milk and reconstituted blood plasma. A known amount of arsenic was added to the blood plasma. The results obtained in six laboratories, A to F, are shown in Table IV. A seventh laboratory, G, carried out check tests by neutron activation; these results are included in Table IV for comparison.

The results in Table IV were not in as good agreement as was expected. Although, on the whole, the results were consistent in each laboratory, they varied rather widely between laboratories. However, the Sub-Committee agreed that—

- (i) the results for the tobacco powder were satisfactory, the slight variations being caused by the presence of a fair amount of insoluble matter after wet oxidation;
- (ii) the results for the dried milk indicated that this low level of arsenic content was below the lower limit of accuracy of the method and that more work was necessary to determine this limit (see later); and
- (iii) the results for the blood plasma were at variance with the reputed content of added arsenic. This could be due to (1) variable loss of arsenic during the wet-oxidation stage, (2) lack of homogeneity in the reconstituted plasma or (3) adsorption on the surface of the plastic containers.

TABLE II

DETERMINATION OF ARSENIC IN THREE DIFFERENT TYPES OF ORGANIC COMPOUND

Sample 1: procaine hydrochloride with 5 p.p.m. of added As_2O_3 (\equiv 4.05 p.p.m. of As)

Sample 2: Antrycide

Sample 3: tobacco powder

Laboratory	Arsenic (As) found in—		
	Sample 1, p.p.m.	Sample 2, p.p.m.	Sample 3, p.p.m.
A	3.6	0.08	—
B	4.0	0.0	—
	3.8		
C	3.6	0.97	2.3
D	3.6	0.12	1.1
	3.6	0.08	

TABLE III

DETERMINATION OF ARSENIC IN THE PRESENCE OF PHOSPHATE

Arsenic (As) present, μg	Phosphate added (as PO_4^{3-}), mg	Arsenic (As) found, μg	Recovery, %
7.5	Nil	7.4	99
7.5	13.4	7.4	99
7.5	67	7.0	94
7.5	1450	7.4	99
7.5	2900	7.0	94
20	0.03	20.2	101
20	0.3	19.5	97.5
20	60	20.6	106

Further work was then done to clarify the various points arising from the results shown in Table IV.

(c) *Arsenic determination independent of wet oxidation*—The reproducibility of the actual determination of arsenic was checked independently of potential wet-oxidation errors, one laboratory (G) wet oxidising a large sample of the blood plasma and distributing representative samples of the wet-oxidation product to four other laboratories for determination of the arsenic. The results (Table V) showed that good agreement was achieved between the laboratories. It was concluded, therefore, that the method of determination was sound and that the variation in the results for blood plasma must have been due to variation in the samples circulated or to losses caused by faulty wet-oxidation technique.

(d) *Wet-oxidation procedure*—The accuracy of the combined wet oxidation and determination of arsenic was further checked by two laboratories (B and D) wet oxidising identical samples of dried blood plasma to which known amounts of arsenic ($10 \mu\text{g}$ of As) were added before oxidation of the sample. Both achieved 97 to 100 per cent. recoveries.

Replace the body of Table I by—

Sample 1: procaine hydrochloride with 5 p.p.m. of added As_2O_3 (\equiv 3.8 p.p.m. of As)

Sample 2: Antrycide

Sample 3: tobacco powder

Laboratory	Arsenic (As) found in—		
	Sample 1, p.p.m.	Sample 2, p.p.m.	Sample 3, p.p.m.
A	3.4	0.08	—
B	3.7	0.0	—
	3.6		
C	3.4	0.91	2.1
D	3.4	0.11	1.1
	3.4	0.08	

(e) *Lower limit of the method*—The variation in the results for the dried milk (Table IV), particularly when different weights of sample were used, indicated that the arsenic content was below the lower limit of accuracy of the method. In the determination of traces of elements by a colorimetric procedure it is axiomatic that the blank value must not exceed the net experimental value. The optical densities of blank tests reported by the laboratories

TABLE IV
DETERMINATION OF ARSENIC IN ORGANIC COMPOUNDS CONTAINING DIFFERENT LEVELS OF ARSENIC

Sample 4: tobacco powder (second sample)

Sample 5: dried milk

Sample 6: blood plasma with added arsenic equivalent to 3.4 p.p.m. of As

Laboratory	Sample 4		Sample 5		Sample 6	
	Weight of sample, g	Arsenic (As) found, p.p.m.	Weight of sample, g	Arsenic (As) found, p.p.m.	Weight of sample, g	Arsenic (As) found, p.p.m.
A	2.0	3.2	5.0	Nil		
	2.0	3.1	10.0	0.05		
	2.0	3.1	10.0	0.10		
B	5.0	3.1	5.0	0.18	2.8	2.4
	3.5	3.2	10.0	0.20	3.6	2.2
	3.5	3.1	10.0	<0.2	2.0	1.8
C		3.5		0.3	5.0	3.4
					5.0	3.9
					5.0	4.1
D	2.0	3.3	2.0	0.5	2.5	3.1
	2.0	3.0	4.0	0.3	3.3	3.0
	2.0	2.9	10.0	0.04	2.4	3.0
E			10.0	0.03		
			5.0	0.14	2.0	2.15
			5.0	0.10	2.0	2.25
F					2.0	2.45
	2	3.2	5.0	0.06	3.05	3.1
	2	3.1	10.0	0.04	2.1	2.7
	2	3.3	10.0	0.04	2.8	2.8
G*		3.3				
	0.112	3.37	0.149	0.045	0.140	3.06
		3.44		0.047		3.07
	0.145	3.23	0.175	0.038	0.116	2.73
		3.35		0.040		2.74
	0.113	3.48	1.65	0.041	0.066	2.66
		3.65		0.042		2.65
	0.135	3.46	1.34	0.042	0.079	2.88
	3.64		0.043		2.86	
				0.110	2.99	
					3.08	

* These results were obtained by neutron activation, the procedure of Smales and Pate⁸ being used.

TABLE V
DETERMINATION OF ARSENIC IN OXIDISED BLOOD PLASMA SAMPLE

Laboratory	A	B	C	D
Arsenic (As) found, p.p.m.	3.34	3.0	2.95	2.90

varied from 0.04 to 0.10, measured in 2-cm cells, corresponding to a range of 0.6 to 1.5 μg of arsenic. Hence the lower limit of the method was in the range of 0.6 to 1.5 μg of arsenic, depending on the reagents used. However, by using reagents purified by prior extraction with diethylammonium diethyldithiocarbamate as described in Appendix II, the optical-density values of the blank were reduced to 0.01 to 0.03, corresponding to the range 0.15 to

0.45 μg of arsenic. An optical-density value as low as 0.007 was reported from one laboratory when these purified reagents were used, although such a low blank brings in the question of the accuracy of the spectrophotometer in this region. It is considered, however, that use of these purified reagents would extend the range of the method down to 0.5 μg of arsenic should tests at this level be called for. This view is supported by the statistical treatment of the results obtained (see Table VII) in the final collaborative work.

(f) *Final collaborative test: recovery experiments*—To complete the work on the determination of arsenic it was decided that recovery experiments should be performed over the range 0.5 to 10 μg of arsenic, each laboratory adding the requisite amounts of arsenic to samples of sucrose known to be arsenic-free, thereby avoiding possible trouble due to lack of homogeneity in circulated samples. At the lower range of 0.5 to 1.0 μg of arsenic, the reagents used were to be extracted with diethylammonium diethyldithiocarbamate before use. The results of these tests are recorded in Table VI. These results were treated statistically and the standard deviations [$\text{S.D.} = (\sqrt{\Sigma d^2})/(n - 1)$] and coefficients of variation ($100 \times \text{S.D.}/M$) are shown in Table VII.

TABLE VI
RESULTS OF RECOVERY EXPERIMENTS

Arsenic added to 5-g samples of sucrose; purified reagents used for the low range of 0.5 to 1.0 μg of arsenic, but unpurified reagents for the higher levels

Arsenic (As) added, μg	Arsenic (As) found by—			
	Laboratory A, μg	Laboratory E, μg	Laboratory F, μg	Laboratory H, μg
0.5	0.53	0.5	0.6	0.5
	0.45	0.4	0.5	0.6
1.0	1.03	1.0	1.0	0.92
	1.09	0.85	0.9	1.40
2.0	2.2	1.5	1.5	1.8
	2.1	2.2	1.8	1.8
			1.5	
5.0	5.2	5.7	5.1	4.7
	5.1	5.5	4.6	4.7
			4.9	
10.0	10.7	9.7	9.2	9.9
	9.0	9.8	9.8	10.0
			9.6	

TABLE VII
STATISTICAL TREATMENT OF RESULTS IN TABLE VI

Arsenic level, μg	Number of determinations	Mean result (M), μg	Standard deviation	Coefficient of variation, %
10	9	9.7	0.49	5.0
5	9	5.1	0.38	7.4
2	9	1.8	0.29	16.2
1	8	1.02	0.17	16.7
0.5	8	0.51	0.07	13.2

From Table VII it can be seen that the coefficients of variation at the lowest levels, 2.0, 1.0 and 0.5 μg of arsenic, are not significantly different. This unexpected occurrence is held to confirm fully the value of using purified reagents for this low level of arsenic and thereby extending the range of the method below that usually attained with unpurified reagents.

CONCLUSIONS

1. The method recommended in Appendix I is capable of giving consistently accurate results for the arsenic content of organic matter in the range 1.5 to 15 μg of arsenic.
2. The range of the method can be extended to the lower level of 0.5 μg of arsenic by the use of specially purified reagents.
3. Adequate safeguard is provided against interference by silicon and phosphorus; there could be interference by germanium, but this rare element is not likely to be present.

4. In that the molybdenum-blue method is a spectrophotometric determination it has inherent advantages over the Gutzeit method. The latter is an estimation rather than a determination, depending as it does upon visual comparison with standards of colours produced on paper.

Appendix I

RECOMMENDED METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF ARSENIC BY THE MOLYBDENUM-BLUE METHOD

PRINCIPLE OF METHOD—

After destruction of the organic matter by wet oxidation and a preliminary extraction with diethylammonium diethyldithiocarbamate solution, the arsenic is converted to the arsenomolybdate complex, which is then reduced by means of hydrazine sulphate to a molybdenum-blue compound and determined absorptiometrically.

If, after destruction of organic matter, the solution contains more than a total of 1000 μg of heavy metals that form complexes with diethylammonium diethyldithiocarbamate (*i.e.*, copper, bismuth, antimony, mercury, tin and the noble metals) or contains much insoluble matter, the arsenic must be distilled as trichloride before the extraction procedure is begun.

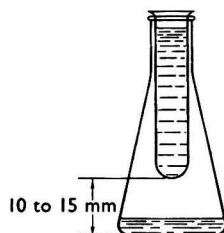


Fig. 1. "Cold finger" condenser

RANGE—

For arsenic contents from 1.5 to 15 μg (as As) in the sample taken. The range can be extended down to 0.5 μg of arsenic by using reagents purified by extraction with diethylammonium diethyldithiocarbamate solution before use (see under "Reagents").

APPLICABILITY—

The method is suitable for the analysis of most types of organic material. It is specific for arsenic in all ordinary circumstances, but the possibility of interference by germanium has not been investigated.

APPARATUS—

NOTE—All glassware should be of borosilicate glass and must be thoroughly cleaned with sulphuric and nitric acids and then thoroughly washed with distilled water immediately before use to ensure that it does not yield traces of arsenic under the conditions of test.

Simple "cold finger" condensers—These consist of small test-tubes with flanged mouths, fitting loosely into 50-ml conical flasks. When the condenser is in position, the bottom should be about 10 to 15 mm from the bottom of the flask (see Fig. 1).

Separating funnels—25-, 50- and 100-ml calibrated separating funnels, with well fitting glass stopcocks and stoppers and with the stems cut short to within about $\frac{1}{4}$ inch of the stopcock barrel.

The following additional apparatus is required if the distillation procedure is used—

Kjeldahl flasks—These should have a capacity of 100 or 200 ml and be made of borosilicate glass or silica, fitted by means of a Quickfit joint (B19 or B24) with a 2-bulb or 3-bulb condenser carrying a tap funnel (see Fig. 2). It is an advantage to have the condenser interchangeable with the condensing extension to the decomposition flask, so that the arsenic can be distilled from the same flask in which the wet decomposition is carried out.

REAGENTS—

All water must be distilled or de-ionised and must be free from arsenic.

The acids supplied "for foodstuffs analysis" can be used for the determination of arsenic without further treatment.

To obtain accurate results at low levels of arsenic (down to $0.5 \mu\text{g}$ of As), certain reagents should be purified by the methods described in Appendix II.

Reagents for the destruction of organic matter are specified in the general methods referred to under "Procedure."

Hydrochloric acid, sp.gr. 1.18—Arsenic-free.

Thioglycollic acid solution—Dilute 12 g of thioglycollic acid (90 per cent. v/v) to 100 ml with water. Store in an amber-coloured glass bottle, and discard after one month.

Potassium iodide - ascorbic acid solution—Dissolve 15 g of potassium iodide and 2.5 g of ascorbic acid in water, and dilute to 100 ml with water. This reagent should be prepared freshly every 2 or 3 days.

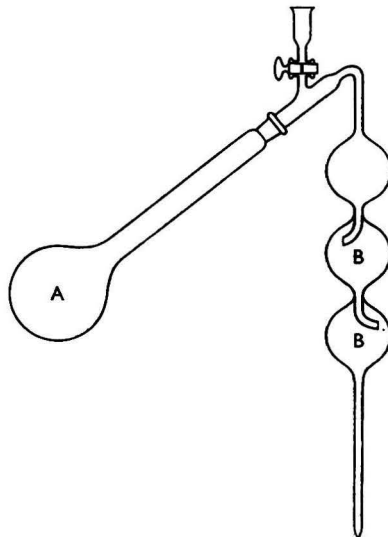


Fig. 2. Kjeldahl flask. Flask A has a capacity of 100 or 200 ml and a neck length of 7 to 8 inches; bulbs B of condenser are of 25 ml capacity, total length of condenser being 18 to 20 inches. The unlettered bulb should be of 25 ml capacity for the three-bulb type of condenser or should be omitted in the two-bulb version.

Chloroform—Redistilled.

Dithiocarbamate reagent—Dissolve 1 g of pure crystalline diethylammonium diethyl-dithiocarbamate (analytical-reagent grade) in 100 ml of redistilled or analytical-reagent grade chloroform. Store in an amber-coloured glass bottle. This solution is not stable and should be discarded after one week.

Sulphuric acid, N—Prepare from arsenic-free sulphuric acid, sp.gr. 1.84. Store in a polythene bottle.

Acid molybdate solution—Mix exactly 250 ml of 10 N sulphuric acid (accurately standardised) with exactly 250 ml of a 7 per cent. w/v solution of ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, in water. Filter into a 1-litre calibrated flask, washing the filter with water, add exactly 250 ml of 4 N perchloric acid (accurately standardised), and dilute to 1 litre at 20°C with water. Store in a polythene bottle.

Hydrazine sulphate solution—A 0.030 per cent. w/v solution in water.

Standard arsenic solution—(a) Dissolve 4.17 g of sodium arsenate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, (analytical-reagent grade) in water, and dilute to 1 litre at 20° C with water.

(b) Dilute 10.0 ml of solution (a) to 1 litre at 20° C with water. Prepare solution (b) freshly as required.

1 ml \equiv 10 μg of arsenic (As).

The following additional reagent is required if the distillation procedure is used—

Chloride - hydrazine - bromide mixture—Grind together intimately a mixture (parts by weight) of sodium chloride, 5, hydrazine sulphate, 0.5, and potassium bromide, 0.02.

PROCEDURE

Reagent blank—Carry out a blank test by the entire procedure, using the precise amounts of reagents used in the test and omitting only the sample.

DESTRUCTION OF ORGANIC MATTER—

General Methods for the Destruction of Organic Matter appear in a separate report⁹ and, of these, Methods of Wet Decomposition (I) A, (I) B, (I) C and (I) D with continuation (I) (b) 1 are suitable for use in the determination of arsenic, the particular method being chosen to suit the type of sample to be analysed. In no circumstances should more than 10 ml of sulphuric acid be used.

When the expected arsenic content is such that the amount of sample taken can be less than 5 g, and if the arsenic is to be extracted directly from this solution, the amount of sulphuric acid can with advantage be reduced *pro rata*, but in no case to less than 5 ml. This reduction of acid will have no deleterious influence on the subsequent extraction of arsenic.

All reagents used in the decomposition must be measured so that the same amounts can be used in the blank.

NOTE—It is commonly accepted that excessive charring at any stage of the wet decomposition will lead to loss of arsenic, especially in the presence of chloride. Gorsuch² has shown that in certain circumstances, at least, such losses do not in fact occur, but, in view of the limited range of the experiments referred to, it is considered that the usual precautions against excessive charring should be continued in practice.

PRELIMINARY TREATMENT OF THE DIGEST (WHEN NECESSARY)—

This procedure is carried out on the test solution and the blank solution after the destruction of organic matter *only if* one or both of the following conditions is encountered—

- (a) the total heavy-metal content of the test solution exceeds 1000 μg or
- (b) there is an excessive amount of insoluble material present in the test solution.

NOTE—In the distillation method it is important to use the relative amounts of reagents as specified, as this ensures a steady evolution of hydrogen chloride gas throughout the distillation, which is essential to the success of the method. Serious divergence from the recommended amounts is liable to lead either to too vigorous a reaction in the early stages of the distillation, whereby arsenious chloride may be swept through the receiver, or to the evolution of water, with consequent failure to obtain quantitative entrainment of the arsenic.

The following directions assume that 8 to 10 ml of sulphuric acid have been used in the wet decomposition. If less acid has been used it should be supplemented at this point.

If the wet decomposition has not been carried out in the Kjeldahl flask of the distillation apparatus (Fig. 2), transfer the solution to it, rinsing in with the minimum amount of water, evaporate to fuming, and allow to cool.

To the cold residue in the flask add 7 ml of water, and cool. Add 5 g of chloride - hydrazine - bromide mixture, avoiding contamination of the ground portion of the neck of the flask, and fit the condenser, moistening the joint with water to prevent leakage. Clamp the apparatus so that the condenser is vertical, with its tip reaching just short of the bottom of a 25-ml measuring cylinder containing 15 ml of water, which is cooled in ice and water. Add 10 ml of hydrochloric acid to the contents of the flask through the tap funnel, and carefully close the tap.

Heat the flask with a microburner at a rate such that the contents are brought to boiling in not less than 30 minutes. After the condenser has become full of steam, continue to heat the flask so that the distillation proceeds smoothly for 3 to 5 minutes. During the whole of this procedure, and particularly at the moment when the steam reaches the cold water

in the receiver, care should be taken to prevent a suck back. The distillation must not be taken too far, *i.e.*, fumes of sulphur trioxide must not appear. When the distillation is complete, open the tap, remove the burner, and disconnect the condenser. Wash down the condenser once with a few millilitres of water, collecting the washings in the cylinder.

SEPARATION OF ARSENIC—

(a) *If the distillation procedure has not been carried out*—Dilute the solution from the destruction of organic matter with 15 ml of water, boil gently for a few minutes, cool to about 70° C, add 10 ml of hydrochloric acid, and allow to cool. Transfer the solution to a 100-ml conical flask, filtering if the solution is not clear and rinsing in with the minimum amount of water.

(b) *If the distillation procedure has been carried out*—Transfer the distillate, without further addition of hydrochloric acid, to a 100-ml conical flask, rinsing in with the minimum amount of water.

Warm the solution from (a) or (b) to about 40° C, add 2 ml of thioglycollic acid solution, mix well, and set aside to cool for 15 minutes. Then cool the solution more rapidly (*e.g.*, in a bath of ice and water) to room temperature, add 1 ml of potassium iodide - ascorbic acid solution, wash down the sides of the flask with a few millilitres of water, and mix carefully. Transfer the solution to a 100-ml calibrated separating funnel containing a few millilitres of chloroform, washing out the flask with several small portions of water. The volume of the solution at this stage should be 45 to 50 ml. Add 5 ml of dithiocarbamate reagent, shake vigorously for 40 seconds, remove the stopper, and wash it with a few drops of chloroform. Allow the layers to separate, and then run the lower layer into a clean 25-ml separating funnel, taking care not to allow any of the aqueous layer to enter the tap of the first funnel. Wash the aqueous layer twice with about 0.5 ml of chloroform, without mixing, and add the washings to the main extract. Extract the aqueous layer with a further 2-ml portion of dithiocarbamate reagent, shaking for 30 seconds, and allow the layers to separate. Run the chloroform layer into the second funnel, washing twice with 0.5 ml of chloroform, as before, and adding the washings to the main extract. Reject the aqueous layer.

Add 10 ml of *N* sulphuric acid to the combined extracts, shake for 5 seconds, and allow the layers to separate.

NOTE—The treatment with *N* sulphuric acid is introduced mainly to prevent any interference from phosphate possibly present in the material being examined. Even a trace of entrained phosphate would form molybdophosphate, which, on reduction, would give a blue colour and so lead to high results for arsenic.

Run the chloroform layer into a 50-ml conical flask, wash the sulphuric acid layer with two small portions of chloroform, without mixing, and add the washings to the chloroform solution in the flask. During this operation care must be taken not to allow any of the aqueous layer to enter the tap of the funnel.

Add 2.0 (± 0.02) ml of acid molybdate solution, measured accurately from a tube pipette, to the chloroform solution, close the mouth of the flask with a glass bulb, and evaporate the chloroform on a boiling-water bath, conducting the evaporation slowly and carefully, so that as little as possible of the acid residue is sprayed up the sides of the flask. When the chloroform has been removed, transfer the flask to a hot-plate, and evaporate until fumes of perchloric acid appear, accompanied by a sudden reaction. Continue to heat for about 1 minute (not longer), allow to cool, and remove the glass bulb, washing it with a few drops of water. Evaporate the contents of the flask just to fuming again, without the glass bulb in position. All traces of organic matter should have disappeared by this stage.

Insert into the flask a "cold finger" condenser (Fig. 1), filled almost to the brim with cold water; the outside of the condenser must be clean and dry. Place the flask on the hot-plate (a hot-plate with a surface temperature of approximately 250° C is suitable for this operation), heat for 10 minutes at a temperature such that a "blanket" of fumes about half fills the flask and the temperature of the water in the condenser rises to about 90° C ($\pm 5^\circ$ C) at the end of the 10-minute heating period. Then allow the solution to cool.

DETERMINATION OF ARSENIC—

Wash down the condenser and the sides of the flask with 7.0 ml of *N* sulphuric acid and then with 2.0 ml of water (use a tube pipette for both additions). Close the flask with a glass bulb, and boil until the total volume is reduced to 6 or 7 ml and free chlorine has been

removed. Cool the solution, which should be clear and colourless at this stage, add 1.0 ml of hydrazine sulphate solution, mix, and drain the flask into a stoppered 10-ml calibrated cylinder or flask, rinsing the conical flask with one or two millilitres of water and using the washings to dilute the solution to the 10-ml mark. Mix thoroughly by shaking, and return the solution to the 50-ml conical flask. Close the mouth of the flask with a glass bulb, and heat the flask on a boiling-water bath for 15 minutes. Remove the flask from the bath, and allow to cool for 30 minutes.*

Measure the optical density of the test solution against the blank solution in 2-cm-cells with a spectrophotometer at 840 $m\mu$.

As a check on the procedure, the optical density of the blank solution measured against a solution consisting of 2 ml of the acid molybdate solution and 8 ml of *N* sulphuric acid should be 0.0 to 0.05 measured on the spectrophotometer, a 2-cm cell being used at a wavelength of 840 $m\mu$. The use of specially purified reagents reduces the blank considerably.

Read the number of micrograms of arsenic equivalent to the observed optical density from the calibration graph established as described below.

PREPARATION OF CALIBRATION GRAPH—

Place 0, 0.2, 0.5, 1.0, 1.5 and 2.0 ml of standard arsenic solution (*b*) in 50-ml conical flasks, and add to each 2.0 ml of acid molybdate solution and 7 ml of *N* sulphuric acid. Mix well, and heat the flasks on a hot-plate until the volume has been reduced to 5 to 6 ml. Cool the solutions, to each add 1.0 ml of hydrazine sulphate solution, mix, and drain the flasks into 10-ml stoppered cylinders, rinsing the flasks with a small amount of water, and use the washings to dilute the main solutions to the 10-ml mark. Mix thoroughly, and return each solution to its original 50-ml conical flask. Close the mouth of each flask with a glass bulb, and heat the flasks on a boiling-water bath for 15 minutes; then allow them to cool for 30 minutes. Measure the optical density of each solution in turn against the first solution (containing no added arsenic) in a spectrophotometer at 840 $m\mu$, a 2-cm cell being used. Construct a graph relating the optical density to the number of micrograms of arsenic.

Appendix II

PURIFICATION OF REAGENTS

Thioglycollic acid solution—Extract 100 ml with 10 ml of dithiocarbamate reagent and then with two 5-ml portions of chloroform. Store in an amber-coloured glass bottle, and discard after one month.

Potassium iodide - ascorbic acid reagent—Extract 100 ml with 10 ml of dithiocarbamate reagent and then with two 5-ml portions of chloroform. Store in a polythene bottle, and prepare freshly every 2 or 3 days.

Sulphuric acid, N—Prepare from sulphuric acid "for foodstuffs analysis." Store in a polythene bottle.

Acid molybdate solution—Extract exactly 250 ml of a 7 per cent. w/v solution of ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, in water with two 10-ml portions of dithiocarbamate reagent and then with three 5-ml portions of chloroform. The final chloroform extract should not be darker than the colour of straw. Some batches of ammonium molybdate give more deeply coloured second extracts; such material will give high blank values and should not be used for the determination of trace quantities of arsenic. Mix the extracted solution with exactly 250 ml of 10 *N* sulphuric acid (prepared from sulphuric acid "for foodstuffs analysis" and accurately standardised), filter into a 1-litre calibrated flask, and wash the filter with water. Add exactly 250 ml of 4 *N* perchloric acid (prepared from perchloric acid, 60 per cent. v/v, and accurately standardised), and dilute to 1 litre at 20° C with water. Store in a polythene bottle.

Appendix III

THE DETERMINATION OF ARSENIC BY THE GUTZEIT METHOD

PRINCIPLE OF METHOD—

After destruction of the organic matter and distillation as chloride, the arsenic is determined by a modification of the Gutzeit method.

* If any fading due to the presence of excess of chlorine is observed, the solution should be re-boiled and the reduction with hydrazine sulphate repeated.

RANGE—

For amounts of arsenic from 0.5 to 5 μg (as As).

APPLICABILITY—

The method is generally applicable.

APPARATUS—

NOTE—All glassware should be of borosilicate glass and must be thoroughly cleaned with sulphuric and nitric acids and then thoroughly washed with distilled water immediately before use to ensure that it does not yield traces of arsenic under the conditions of test.

Kjeldahl flasks—These should have a capacity of 100 or 200 ml and be made of borosilicate glass or silica, fitted by means of a Quickfit joint (B19 or B24) with a 2-bulb or 3-bulb condenser carrying a tap funnel (see Fig. 2). It is an advantage to have the condenser interchangeable with the condensing extension to the decomposition flask, so that the arsenic can be distilled from the same flask in which the wet decomposition was carried out.

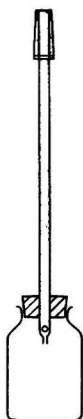


Fig. 3. Arrangement of apparatus used in the Gutzeit test

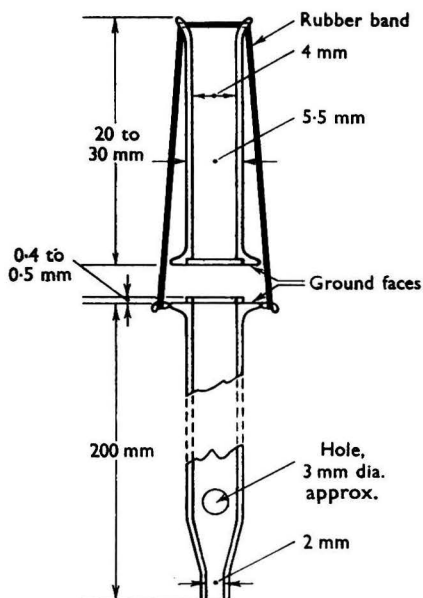


Fig. 4. Details of device for holding Gutzeit test paper

Gutzeit apparatus—This consists of a wide-mouthed bottle of 120-ml capacity, closed by a rubber bung through which passes a glass tube. This tube has a total length of 200 mm and an internal diameter of exactly 4.0 mm (external diameter about 5.5 mm) and is drawn out at the lower end to a diameter of about 2 mm. A hole about 3 mm in diameter is blown in the side near the constricted part. The tube passes through the bung so that, when it is inserted in the bottle containing 70 ml of liquid, the constricted end is above the surface of the liquid and the hole is below the bottom of the bung. The tube has a shallow projection, 0.4 to 0.5 mm thick, at its upper end, which fits into a slight depression in a cap consisting of a short tube of the same internal diameter as the lower tube. The contacting edges of the two tubes are flanged and ground smooth at right angles to the tube so as to fit closely. The short upper tube has a grooved top, and the lower tube two projections, in order that the upper tube may be secured to the lower by means of a rubber band. The complete apparatus is shown in Fig. 3, and the device for holding the test-paper disc is shown in detail in Fig. 4.

REAGENTS—

All water must be distilled or de-ionised and free from arsenic.

Reagents for the destruction of organic matter are specified in the general methods referred to under "Procedure."

Hydrochloric acid, sp.gr. 1.18—Arsenic-free.

Chloride - hydrazine - bromide mixture—Grind together intimately a mixture (parts by weight) of sodium chloride, 5, hydrazine sulphate, 0.5, potassium bromide, 0.02.

Stannous chloride solution—Dissolve 65 g of stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, in 180 ml of water and 200 ml of hydrochloric acid, sp.gr. 1.18. Boil the solution until its volume has been reduced to 200 ml, cool, filter through a fine-grained filter-paper, and keep in a well stoppered bottle.

This solution must comply with the following test—

To 10 ml add 8 ml of distilled water and 8 ml of hydrochloric acid, sp.gr. 1.18, arsenic-free, and distil 16 ml. To the distillate add 50 ml of water and 2 drops of the stannous chloride solution, and apply the general test; the stain produced must not be deeper than a 1-ml standard stain, showing that the proportion of arsenic present does not exceed 0.5 p.p.m.

*Hydrochloric acid - stannous chloride reagent**—Mix 10 ml of stannous chloride solution with 90 ml of hydrochloric acid, sp.gr. 1.18, arsenic-free.

Potassium iodide—Arsenic-free.

Zinc—Zinc pellets containing 0.06 per cent. of copper, or granulated zinc containing 0.01 to 0.02 per cent. of copper.

Lead acetate-treated cotton-wool—Moisten cotton-wool with a 10 per cent. w/v solution of lead acetate in water, and dry it.

Mercuric chloride papers—Soak filter-paper, similar in substance and texture to a Whatman No. 1 filter-paper, in a saturated aqueous solution of mercuric chloride. Dry in a warm atmosphere without exposure to daylight. Reject the edges of the dry papers, which should be stored in the dark until required.

Standard arsenic solution—(a) Dissolve 0.066 g of arsenious oxide, As_2O_3 , in 50 ml of hydrochloric acid, and dilute to 100 ml at 20° C with water.

(b) Dilute 1 ml of solution (a) to 100 ml at 20° C with water. Prepare solution (b) freshly as required.

1 ml \equiv 5 μg of arsenic (As).

PROCEDURE

Reagent blank—Blank tests must be made to ensure that the apparatus and all the reagents used give no visible stain.

DESTRUCTION OF ORGANIC MATTER—

General Methods for the Destruction of Organic Matter appear in a separate report⁹ and, of these, Methods of Wet Decomposition (I) A, (I) B, (I) C and (I) D with continuation (I) (b) 1 are suitable for use in the determination of arsenic, the particular method being chosen to suit the type of sample to be analysed. In no circumstances should more than 10 ml of sulphuric acid be used.

PRELIMINARY TREATMENT OF DIGEST—

NOTE—In the distillation procedure it is important to use the relative amounts of reagents as specified, as this ensures a steady evolution of hydrogen chloride gas throughout the distillation, which is essential to the success of the method. Serious divergence from the recommended amounts is liable to lead either to too vigorous a reaction in the early stages of the distillation, whereby arsenious chloride may be swept through the receiver, or to the evolution of water with consequent failure to obtain quantitative entrainment of the arsenic.

The following directions assume that 8 to 10 ml of sulphuric acid have been used in the wet decomposition. If less acid has been used it should be supplemented at this point.

* **NOTE**—This reagent contains a concentration of stannous chloride ten times greater than that of stannated hydrochloric acid, AsT, of the British Pharmacopoeia.

If the wet decomposition has not been carried out in the Kjeldahl flask of the distillation apparatus (Fig. 2), transfer the solution to it, rinsing in with the minimum amount of water, evaporate to fuming, and then allow to cool.

To the cold residue in the flask add 7 ml of water, and cool. Add 5 g of chloride-hydrazine-bromide mixture, avoiding contamination of the ground portion of the neck of the flask, and fit the condenser, moistening the joint with water to prevent leakage. Clamp the apparatus so that the condenser is vertical, with its tip reaching just short of the bottom of a 25-ml measuring cylinder containing 15 ml of water, which is cooled in ice and water. Add 10 ml of hydrochloric acid to the contents of the flask through the tap funnel, and carefully close the tap.

Heat the flask with a microburner at a rate such that the contents are brought to boiling in not less than 30 minutes. After the condenser has become full of steam, continue to heat the flask so that the distillation proceeds smoothly for 3 to 5 minutes. During the whole of this procedure, and particularly at the moment when the steam reaches the cold water in the receiver, care should be taken to prevent a suck back. The distillation must not be taken too far, *i.e.*, fumes of sulphur trioxide must not appear. When the distillation is complete, open the tap, remove the burner, and disconnect the condenser. Wash down the condenser once with a few millilitres of water, collecting the washings in the cylinder. Transfer the distillate to a 50-ml calibrated flask, dilute to the mark at 20° C with water, and mix well.

DETERMINATION OF ARSENIC—

Pack the glass tube of the apparatus lightly with lead acetate-treated cotton-wool, so that the upper surface of the cotton-wool is 25 to 30 mm below the top of the tube. Place a piece of mercuric chloride paper against the ground end of this tube with the smooth face of the filter-paper downwards to form a diaphragm between it and the upper tube, and fasten the tubes together by means of the rubber band.

Alternatively any other method of attaching the mercuric chloride paper may be used provided that—

- (i) the whole of the evolved gas passes through the paper,
- (ii) that the portion of the paper in contact with the gas is a circle 4.0 mm in diameter and
- (iii) the paper is protected from sunlight during the test.

(a) *If the expected arsenic content of the test solution is more than 5 µg*, mix an aliquot (not more than 25 ml) of the test solution such as would contain from 2 to 5 µg of arsenic with hydrochloric acid in the proportions—

$$x \text{ ml of sample solution;}$$

$$\left(8 - \frac{16x}{50}\right) \text{ ml of hydrochloric acid.}$$

Dilute the solution to 60 ml with water, and add 1 ml of hydrochloric acid-stannous chloride reagent and 1 g of potassium iodide.

(b) *If the expected arsenic content of the test solution is 5 µg or less*, mix the whole of the test solution with 1 ml of hydrochloric acid-stannous chloride reagent and 1 g of potassium iodide, and dilute to 60 ml with water.

(c) *The blank solution* should be treated as in (b).

Transfer the diluted test and blank solutions to separate wide-mouthed bottles, and add 10 g of zinc to each. Immediately place the prepared glass tubes in position, protecting them from sunlight throughout the remainder of the test. Allow the reaction to proceed without the application of external heat for 15 minutes, and then transfer the bottles to a water bath maintained at 35° to 40° C for 30 minutes.

Compare in normal daylight the stain produced on the mercuric chloride paper with a series of freshly made standard stains prepared by adding known amounts of standard arsenic solution (b) to tests carried out under the same conditions as are applied to the sample. A suitable range for the series of standard stains is 0.5 to 5.0 µg of arsenic.

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Analytical Methods Committee

REPORT PREPARED BY THE METALLIC IMPURITIES IN
ORGANIC MATTER SUB-COMMITTEE

Methods for the Destruction of Organic Matter

THE Analytical Methods Committee has received the following report from its Metallic Impurities in Organic Matter Sub-Committee. The Report has been approved by the Analytical Methods Committee and its publication has been authorised by the Council.

REPORT

The members of the Sub-Committee concerned with the preparation of this report were Messrs. T. McLachlan (Chairman), L. Brealey, Miss E. M. Chatt, Messrs. J. C. Gage, T. T. Gorsuch, C. L. Hinton, E. I. Johnson, W. C. Johnson, R. F. Milton and G. E. Willis,* with Miss A. M. Parry as Secretary. In July, 1958, Mr. W. C. Johnson succeeded Mr. McLachlan as Chairman and in January, 1959, Miss E. M. Chatt succeeded Mr. C. L. Hinton. From 1956 to 1958 Mr. T. T. Gorsuch held a Society for Analytical Chemistry Research Scholarship and, working at Harwell under the direction of Mr. A. A. Smales, carried out the work described in "Radiochemical Investigations on the Recovery for Analysis of Trace Elements in Organic and Biological Materials."¹

INTRODUCTION

When organic matter is to be destroyed as a preliminary to the determination of metallic traces, the choice of method will depend (a) on the nature of the organic material and of any inorganic constituent and (b) on the metal that is subsequently to be determined and the method to be used for its determination.

This report sets out a number of recommended methods of combustion, both wet and dry, with a statement of the type or types of organic material to which each may be applied. Any discrimination on account of the metal to be determined is considered here only in rather general terms (except that special methods are necessarily given for mercury).

The influence of the metal and its method of determination on the choice of decomposition procedure will be described more specifically in the report on each metal as it is published,[†] and each method will refer to this report for methods of decomposition.

This approach will provide a wide choice of methods without the necessity of repetition.

WET DECOMPOSITION

The wet decomposition of organic matter by the action of various acids is of almost universal application and the conditions can be adjusted so as to prevent loss of the more volatile elements (e.g., arsenic, antimony and mercury). Some guidance on the choice of

* Since deceased.

† The Sub-Committee's reports on "The Determination of Lead" (*Analyst*, 1959, **84**, 127) and on "The Determination of Small Amounts of Arsenic in Organic Matter" (*Analyst*, 1960, **85**, 629) have already been published.

method is given under "Applicability" and "Disadvantages" at the beginning of the description of each method, but it must be emphasised that unfamiliar materials must always undergo a trial treatment on a small scale before the method to be used is selected. Only in this way can untoward incidents be avoided.

The amounts of acid specified will generally be satisfactory, but workers will learn by experience what are the optimum amounts to use for any particular material.

APPARATUS—

NOTE—All glass or silica apparatus must be thoroughly cleaned with sulphuric and nitric acids and then thoroughly washed with distilled water immediately before use to ensure that it does not yield traces of metals under the conditions of test.

When organic matter is heated with mixtures of concentrated acids in Kjeldahl flasks, experience has shown that decomposition takes place most efficiently when some means for partial reflux of the hot acids is provided, as by an extension to the neck of the flask (Fig. 1). When many oxidations are in progress at the same time, it is advisable to trap the fumes, dilute them with water and dispose of them down the drains rather than into the atmosphere. The following description of suitable apparatus is given for guidance only.

Kjeldahl flasks—These should be made of borosilicate glass or silica (100 to 250 ml nominal capacity) fitted with an extension to the neck by means of a standard ground joint. The extension serves to condense fumes into an acid-fume condenser and carries a tap funnel through which the reagents are introduced (see Fig. 1).

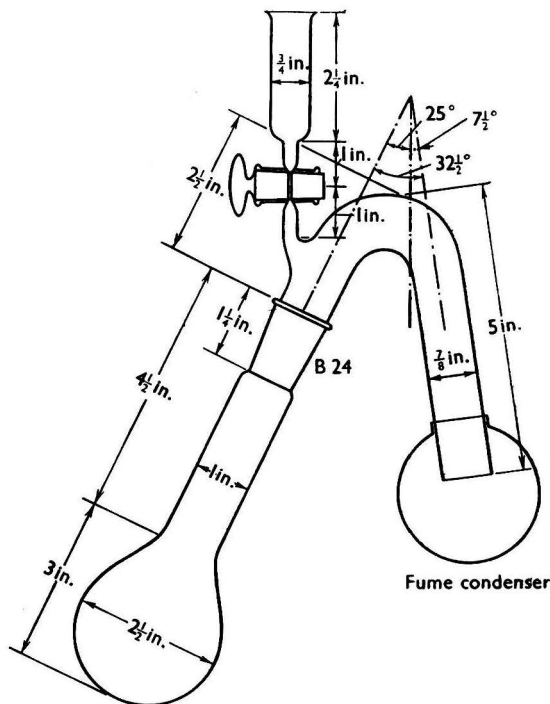


Fig. 1. Modified Kjeldahl flask (open type).
Dimensions are for a flask of 150 ml capacity

Each flask should be supported in a circular hole in an asbestos sheet, and the hole should be of diameter such that the flask receives no direct heat from the burner above the level of the acid.

Kjeldahl digestion rack and acid-fume condenser (Fig. 2)—A current of water is kept flowing through the condenser, and removal of acid fumes can also be assisted by connecting

the upper outlet to a water pump. Gas heating is preferable. The flasks, not being rigidly clamped, are easily handled, when it is necessary to deal with vigorous reactions or excessive frothing, by means of tongs or asbestos finger-guards.

It is a convenience when handling flasks and test-tubes containing hot concentrated acids to have at hand a pair of the nickel tongs made for this purpose. The action of these tongs is improved by binding each of the jaws with asbestos string.

REAGENTS—

It is essential to use reagents and distilled water of suitably low metal content, taking into consideration that the concentrated mineral acids are generally used in amounts several times that of the sample. Some of the more commonly used reagents are now available in grades suitable for food analysis. They should not be transferred from the lead-free-glass bottles in which they are supplied.

Even when these reagents are used, reagent blank determinations will be necessary. No separate instructions are given for reagent blanks, since the procedures follow the lines of the determination proper with obvious modifications, but since the blanks must be prepared with the same quantities of reagents as are used in the tests, the measurement and recording of these quantities must not be overlooked.

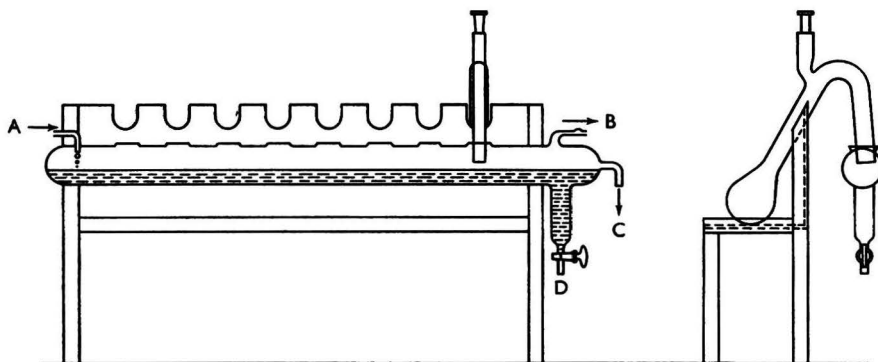


Fig. 2. Acid-fume condenser and modified Kjeldahl flask. A, water inlet; B, connection to pump; C, wide outlet to waste; D, tap with wide outlet to prevent clogging with solid matter

I. Destruction With Nitric and Sulphuric Acids, With or Without the Aid of Perchloric Acid or Hydrogen Peroxide

GENERAL REMARKS

Details are given of four different methods of carrying out the initial stages of the decomposition, depending on the reactivity of the material; the final stages of each are the same, although a choice can be made whether or not to use perchloric acid or hydrogen peroxide to speed the digestion and hence reduce the use of nitric acid and shorten the time taken to complete the removal of all organic matter. Two methods in which nitric, perchloric and sulphuric acids are used *ab initio* are also included.

A special procedure for mercury in organic compounds is given in Section IV, p. 651.

APPLICABILITY

Given suitable selection, the methods are applicable to the destruction of most organic materials, including such materials as dyestuffs, intermediates, medicinals, rubber chemicals, carbon catalysts, textile assistants, synthetic polymers, biological material, foodstuffs (including beverages and fruit juices), before the determination of most of the common trace metals.

ADVANTAGES

The methods are in most instances speedy and easily controlled, and the temperatures are not high enough to cause losses by formation of silicates.

DISADVANTAGES

The methods are not recommended in the presence of appreciable amounts of alkaline-earth metals, which give insoluble sulphates, since the insoluble sulphates absorb a considerable proportion of trace metals, particularly lead. In such instances decomposition with nitric and perchloric acid should be employed (see Section II, p. 649).

HAZARDS

Hazards are those inseparable from the handling of hot concentrated acids and the possibility, particularly with samples of pure chemicals, that a very vigorous reaction may occur. The latter hazard is small if a preliminary test on the material is carried out as recommended and the appropriate method selected.

METHODS

METHOD (I) A

Weigh 5 g (see Note 1, p. 653) of the well mixed sample into a 100-ml Kjeldahl flask, and add 10 ml of diluted nitric acid (1 + 2). As soon as any initial reaction subsides (see Notes 2 and 3, p. 653) heat gently until further vigorous reaction ceases, and then cool the mixture. Add, gradually, up to 10 ml of sulphuric acid, sp.gr. 1.84, at such a rate as not to cause excessive frothing or heating (5 to 10 minutes are usually required), and then heat until the liquid darkens appreciably in colour.

Continue as given below in "Continuation for Methods I (A) to (I) D."

METHOD (I) B

APPLICABILITY—

For less reactive substances.

PROCEDURE—

Weigh 5 g (see Note 1, p. 653) of the well mixed sample into a 100-ml Kjeldahl flask, and add 5 ml of nitric acid, sp.gr. 1.42. As soon as any vigorous initial reaction subsides, heat gently until further vigorous reaction ceases, and then cool the mixture. Add, gradually, 8 ml of sulphuric acid, sp.gr. 1.84, at such a rate as not to cause excessive frothing or heating (5 to 10 minutes are usually required), and then heat until the liquid darkens appreciably in colour.

Continue as given below in "Continuation for Methods (I) A to (I) D."

METHOD (I) C

APPLICABILITY—

For substances that decompose quietly; more rapid method than A or B.

PROCEDURE—

Weigh 5 g (see Note 1, p. 653) of the well mixed sample into a 100-ml Kjeldahl flask, and add a mixture of 8 ml of sulphuric acid, sp.gr. 1.84, and 10 ml of nitric acid, sp.gr. 1.42 (see Note 4, p. 653). Warm cautiously until the reaction subsides, and then boil rapidly until the solution begins to darken owing to incipient charring.

Continue as given below in "Continuation for Methods (I) A to (I) D."

METHOD (I) D

APPLICABILITY—

Despite the use of dilute acid, some substances (*e.g.*, some basic dyestuffs) subsequently cause trouble owing to their liability to deflagrate violently during charring; appreciable losses of arsenic may be incurred in this way. In such instances the following procedure must be used.

PROCEDURE—

Treat 5 g (see Note 1, p. 653) of the material in a 100-ml Kjeldahl flask with 20 ml of diluted nitric acid (1 + 2), and warm until the initial vigorous reaction is over. At this point a spongy, tarry cake is formed. Cool the mixture, pour off the acid into a beaker, and wash the tarry residue with a small amount of distilled water (three or four 1-ml portions), adding

the washings to the acid liquor in the beaker. Add 8 ml of sulphuric acid, sp.gr. 1.84, to the tarry residue, agitate to disperse the cake, and introduce nitric acid, sp.gr. 1.42, drop by drop, with warming if necessary, until vigorous oxidation ceases. Return the original acid liquor to the flask, and boil until the solution just begins to darken.

Continue as given in "Continuation for Methods (I) A to (I) D."

CONTINUATION FOR METHODS (I) A TO (I) D

(a) WITHOUT ADDITION OF PERCHLORIC ACID OR HYDROGEN PEROXIDE—

Add nitric acid, sp.gr. 1.42, slowly in small portions (1 to 2 ml), heating after each addition, until darkening again takes place. Do not heat so strongly that charring is excessive, or loss of arsenic may occur; a small, but not excessive, amount of free nitric acid must be present throughout. Continue this treatment until the solution fails to darken on prolonged heating to fuming (5 to 10 minutes). The criterion of completion of oxidation is that the final solution is fuming when hot and colourless when colder, but if much iron is present the solution will be pale yellow in colour, frequently with a granular precipitate soluble on dilution. Allow to cool somewhat, dilute the solution with 10 ml of distilled water (this should give a colourless solution, or a faintly yellow one if iron is present), and boil gently to fuming. Allow the solution to cool again, add a further 5 ml of distilled water, and boil gently to fuming. Finally, cool, and dilute the solution with 5 ml of distilled water.

(b) WITH THE ADDITION OF PERCHLORIC ACID OR HYDROGEN PEROXIDE—

Persistent residual colours sometimes obtained in the above procedure may be cleared more easily by use of perchloric acid or hydrogen peroxide, and, in general, the use of perchloric acid can considerably reduce the amount of nitric acid required and complete the oxidation in a shorter time, provided that the presence of chloride is not detrimental in the procedure for determination of the metals.

(b) 1. *With addition of perchloric acid*—Add nitric acid, sp.gr. 1.42, slowly in small portions, heating after each addition, until darkening takes place. Do not heat so strongly that charring is excessive, or loss of arsenic may occur; a small, but not excessive, amount of free nitric acid must be present throughout. Continue this treatment until the solution fails to darken in colour on prolonged heating (5 to 10 minutes) and is only pale yellow in colour. Run into the flask 0.5 ml of perchloric acid, 60 per cent. w/w (see Note 5, p. 653), and a little more nitric acid, and heat for about 15 minutes, then add a further 0.5 ml of perchloric acid, and heat for a few minutes longer. Allow to cool somewhat, and dilute the mixture with 10 ml of distilled water. The solution should be quite colourless, except when much iron is present, when it may be faintly yellow. Boil gently, taking care to avoid bumping, until white fumes appear; allow the solution to cool, add a further 5 ml of distilled water, and again boil gently to fuming. Finally, cool, and dilute the solution with 5 ml of distilled water.

(b) 2. *With addition of hydrogen peroxide*—Proceed as given in section (b) 1, above, to the point of addition of perchloric acid. In place of this add hydrogen peroxide, 100-volume analytical-reagent grade, in small quantities (1 or 2 ml) with a few drops of nitric acid, sp.gr. 1.42. Heat to fuming after each addition of hydrogen peroxide until the residue is colourless or no further reduction of the pale yellow colour can be obtained; cool the solution, dilute it with 10 ml of distilled water, and evaporate to fuming; again dilute the solution with 5 ml of distilled water, and evaporate to fuming. Finally, dilute the solution with 5 ml of distilled water.

METHOD (I) E: DESTRUCTION WITH NITRIC, PERCHLORIC AND SULPHURIC ACIDS

APPLICABILITY—

Suitable for many organic and biological materials.

For dry, finely divided powders and for materials that might react vigorously with nitric acid, preliminary moistening of the sample with a few millilitres of distilled water is advisable.

HAZARDS—

This represents the most vigorous, and therefore potentially the most hazardous, method of wet decomposition, and the necessity for small-scale preliminary trials with any given type

of organic matter is re-emphasised. The operator should wear a face mask when using these procedures.

(i) METHOD

PROCEDURE—

Weigh 2 g of sample into a 500-ml conical flask having a B24 neck, and fit a B24 cone to act as a short air condenser. Add 15 ml of nitric acid, sp.gr. 1.42, and shake to wet the sample completely. Allow any reaction to subside, and then add 10 ml of perchloric acid, 60 per cent. w/w (see Note 5, p. 653), and 5 ml of sulphuric acid, sp.gr. 1.84, swirling the contents of the flask during additions. Place the flask on a cold hot-plate, and switch to medium heat. Starting with a cold hot-plate prevents the too-rapid evaporation of nitric acid before all the readily reactive material has been oxidised. As the temperature rises, the material dissolves with the evolution of brown fumes, which clear to leave a quietly boiling solution with some refluxing taking place in the short air condenser. When most of the nitric acid has been

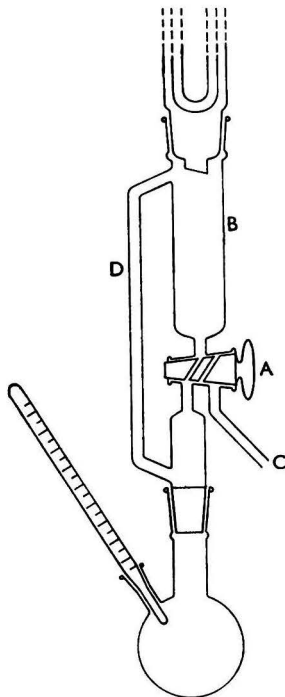


Fig. 3. Apparatus for controlled decomposition of organic material

driven off, with some materials there may be signs of a more vigorous reaction with further evolution of brown fumes. If this occurs, add a few millilitres of nitric acid, and continue heating. Finally, heat the solution until white fumes are evolved; cool, dilute the solution with 5 ml of distilled water, and again heat until white fumes are evolved.

(ii) ALTERNATIVE METHOD

This procedure is particularly flexible, since the increases in temperature and the lengths of the periods of refluxing can be altered to suit the type of sample being decomposed.

Further, except for the periods during which the temperature is being raised, it needs no supervision.

APPARATUS—

As shown in Fig. 3.

PROCEDURE—

Weigh 2 g of sample into the flask, and assemble the apparatus as shown. Add 15 ml of nitric acid, sp.gr. 1.42, allow any reaction to subside, and then add 10 ml of perchloric acid, 60 per cent. w/w (see Note 5, p. 653), and 5 ml of sulphuric acid, sp.gr. 1.84, by way of

the condenser, mixing well during the additions. Set the flask aside for half an hour, then heat gradually to full reflux, and maintain for one hour. Maintaining full heat, turn the tap A through 90° so that liquid distils into the reservoir B. When the temperature has reached 140°C , turn the tap through a further 90° so that the distillate runs out through C into a suitable receptacle; then complete the turn through the full 360° , re-establishing the conditions shown in the figure. Allow to reflux for a further hour, then raise the temperature similarly to 180°C for an hour, then to 200°C for half an hour. Cool, and dilute the residue as required.

II. Destruction With Nitric and Perchloric Acids

GENERAL REMARKS

An important point of this method is that by the omission of sulphuric acid the higher temperature and dehydrating conditions associated with the presence of this acid cannot easily arise and, in the opinion of some operators, this tends to reduce the hazards sometimes connected with perchloric acid combustions. On the other hand, there is considerable risk that, in the absence of sulphuric acid, the digest may boil dry, thus increasing the hazards.

Details of three procedures are given. The first is of fairly wide applicability; the other two, which have been found to be convenient for use with special classes of material, do not differ fundamentally from each other—the differences are mainly in scale of operation.

APPLICABILITY

The method is suitable for the destruction of protein and carbohydrate material. Its use for samples consisting almost entirely of fat is not recommended; the presence of small amounts of fat does not, however, preclude its use. Some chemicals and synthetic materials may be decomposed easily and smoothly, but regard must be had to the possibility of fast reactions sometimes developing; in doubtful cases very small samples should be used.

The procedure is suitable for use before the determination of most of the common trace metals with the exception of mercury.

ADVANTAGES

The method is speedy in most instances and is easily controlled. The attack on the organic matter passes smoothly and automatically from one predominantly by nitric acid to one predominantly by perchloric acid. Perchlorates are generally easily soluble, and this can be an important factor in the subsequent analytical procedure. The temperatures used are lower than in most other wet-combustion procedures, and losses by volatilisation can reasonably be expected to be small.

DISADVANTAGES

The conditions are less severe than in some other procedures, with the result that some types of organic material, notably those containing heterocyclic nitrogen, escape complete destruction. This is a fault that the method shares with some other wet-combustion procedures, and for such materials dry ashing is indicated.

HAZARDS

Hazards are those inseparable from the handling of hot concentrated acids and the possibility, particularly with samples of some pure chemicals, of very vigorous reactions. Reacting mixtures must never be allowed to boil dry. For this reason, when any of these procedures is used, it is desirable not to leave the digestions unattended and to add nitric acid whenever darkening of the digestion mixture occurs.

METHODS

APPARATUS—

See p. 644.

METHOD (II) A

APPLICABILITY—

The following procedure is capable of dealing with a wide variety of materials of biological origin. It may be used for some chemicals and synthetic materials, but initial experience on each kind of such material should be acquired cautiously by qualified persons only, with due regard to possible hazards.

PROCEDURE—

Place in a 200-ml Kjeldahl flask an amount of sample containing not more than 2 g of dry matter. Add 25 ml of nitric acid, sp.gr. 1.42, and boil slowly for 30 minutes. Cool the mixture, and add 15 ml of perchloric acid, 60 per cent. w/w (see Note 5, p. 653). Boil very gently until the solution is colourless or nearly so (see Note 6, p. 654) and dense white fumes appear in the flask. This latter boiling should take nearly one hour. Dangerous conditions may arise if the flask is allowed to boil dry at any time.

METHOD (II) B

APPLICABILITY—

For sugar products when lead is to be determined.

PROCEDURE—

Place in a 100-ml conical borosilicate-glass flask an amount of sample containing not more than 2 g of dry matter. Add 1 ml of distilled water, 3 ml of nitric acid, sp.gr. 1.42, and 2 ml of perchloric acid, 60 per cent. w/w (see Note 5, p. 653), and heat the flask on an electric hot-plate, starting the plate from cold. Use a layer of asbestos paper, if necessary, to moderate the heat. When the liquid turns brown (see Note 7, p. 654), add further nitric acid drop by drop. A colourless solution and white fumes of perchloric acid indicate completion of oxidation.

METHOD (II) C

APPLICABILITY—

For small volumes of liquid samples, *e.g.*, soft drinks.

PROCEDURE—

In a large boiling tube ($1\frac{1}{2}$ inches \times 9 inches) digest a volume of sample containing about 0.25 g of total solids with 2.0 ml of perchloric acid, 60 per cent. w/w (see Note 5, p. 653), and 2 ml of nitric acid, sp.gr. 1.42. It is advisable to use several fragments of acid-washed porcelain to prevent bumping. Add nitric acid, drop by drop, if the solution does not clear quickly after charring (see Note 7, p. 654). Evaporate the solution to fumes of perchloric acid.

III. Destruction With Nitric Acid and Ammonium Nitrate

GENERAL REMARKS

When it is required to determine a number of inorganic components and impurities on the same sample, analysis of residual matter after dry ashing is not permissible if elements such as sodium and potassium, which have volatile compounds, are to be determined; wet oxidation methods are preferable. Methods involving the use of sulphuric acid as an oxidising agent leave unchanged acid in the residue, and this complicates subsequent determinations of mineral matter and precludes the determination of sulphur. The use of perchloric acid leads to incomplete recovery of sulphur. It also tends to the formation of somewhat intractable metaphosphoric acid compounds that inhibit the precipitation of other elements, which may thus escape determination.

APPLICABILITY

The method was originally devised for the determination of calcium, magnesium, sodium, potassium and sulphur, all on one sample (*e.g.*, foodstuffs, as required in serial investigations of individual diets).² It can also be applied when iron, copper and similar elements are to be determined in samples in which the amount of organic matter is small and is easily decomposed.

ADVANTAGES

Oxidation is steady and rapid, the residue can readily be freed from excess of oxidising agent by volatilisation, and the elements are obtained in a form suitable for determination.

DISADVANTAGES AND HAZARDS

Sudden deflagration may result in propulsion of residue from the flask unless heating is carried out with great care.

METHOD (III)

PROCEDURE—

Transfer 1 g of the dried and powdered sample to a 250-ml Kjeldahl flask, and add 10 ml of nitric acid, sp.gr. 1.42. Gently warm the flask until solution is complete, add 10 ml of oxidising reagent (a solution of 50 g of ammonium nitrate and 25 g of nitric acid, sp.gr. 1.42, made up to 100 ml with distilled water), and heat gently to expel water, so that oxidation (indicated by effervescence) proceeds in a melt of ammonium nitrate. From time to time add more reagent, if necessary, and continue until no browning of the solution is observed and a clear melt has been obtained. In the presence of much fat, oxidation is slower and more reagent may be required, and there may be excessive initial frothing if much carbohydrate is present. When oxidation is complete, heat the clear melt more strongly to volatilise the excess of ammonium nitrate (avoid overheating), holding the flask over a free flame to expel salt subliming on the side. Then dissolve the residue in 2 ml of hydrochloric acid, sp.gr. 1.18, evaporate to dryness, fuse the residue in the flask, so as to remove all nitric acid, dissolve it in about 10 ml of *N* hydrochloric acid, and evaporate the solution to a small bulk to ensure conversion of any metaphosphate to orthophosphate. Evaporate to dryness in a stream of warm air, dissolve the residue in a few millilitres of warm water, add a few drops of *N* hydrochloric acid, and dilute to 10 ml with distilled water.

IV. Special Methods of Wet Decomposition for the Determination of Mercury

METHOD (IV) A: DESTRUCTION WITH SULPHURIC, NITRIC AND PERCHLORIC ACIDS

APPLICABILITY—

The method is applicable to samples containing mercury in excess of 5 p.p.m. It is known that slight losses of mercury occur when organic matter is completely oxidised by this method. The loss is of an order usually acceptable when the level in the sample is at 5 p.p.m. or more, and for some purposes the method can be useful at lower levels of mercury content. At a much lower level (0.1 to 0.01 p.p.m.) however, the method fails to give good recoveries. Special methods are available for the preparation of samples for the determination of mercury at these very low levels.

APPARATUS—

In order to minimise losses of mercury by volatilisation, destruction of organic matter is carried out under reflux in the special apparatus shown in Fig. 4.

PROCEDURE—

Weigh accurately about 2.5 g of the well mixed sample, transfer it to the Kjeldahl flask (A) of the special apparatus (Fig. 4) and place the reflux head (B) and the condenser (C) in position.

Maintain a steady flow of water through the condenser. Add, through the side-arm of the Kjeldahl flask, 4 to 5 ml of sulphuric acid, sp.gr. 1.84, and heat the contents of the flask gently until the sample is charred; add nitric acid, sp.gr. 1.42, slowly in small portions (0.25 to 0.5 ml at a time) until the solution darkens between additions. Continue this procedure until the liquid is colourless or pale yellow on prolonged boiling (about 15 minutes) after the last addition of nitric acid. When, during this procedure, the reflux head becomes filled with condensate (which may contain some solidified volatile organic matter), run off the liquid into a 5-ml cylinder, and reserve it. When the wet oxidation is apparently complete, add gradually the contents of the cylinder to the Kjeldahl flask via the side-arm, and boil to fuming, running off the condensate and collecting it as required. If necessary, again pass the condensate through the apparatus until the solution is colourless. Add nitric acid, sp.gr. 1.42, to the Kjeldahl flask until no further darkening occurs. Then add gradually 0.5 ml of perchloric acid, 60 per cent. w/w (see Note 5, p. 653), and heat strongly for 10 minutes. Allow the mixture to cool, wash out the reflux head with the minimum amount of distilled water, and add the washings and separated condensate to the contents of the Kjeldahl flask. Disconnect the apparatus, and boil the contents of the flask for about 15 minutes. The volume at this stage should be about 40 to 50 ml.

Instead of nitric acid, sp.gr. 1.42, hydrogen peroxide, 100-volume analytical-reagent grade, may be used to effect decomposition of the sample. After each small addition of

peroxide, most of the water formed should be driven off so that the digest does not become diluted, and the condensate should be drawn off as it accumulates.

Mercury is then determined on the contents of the Kjeldahl flask by an appropriate method.

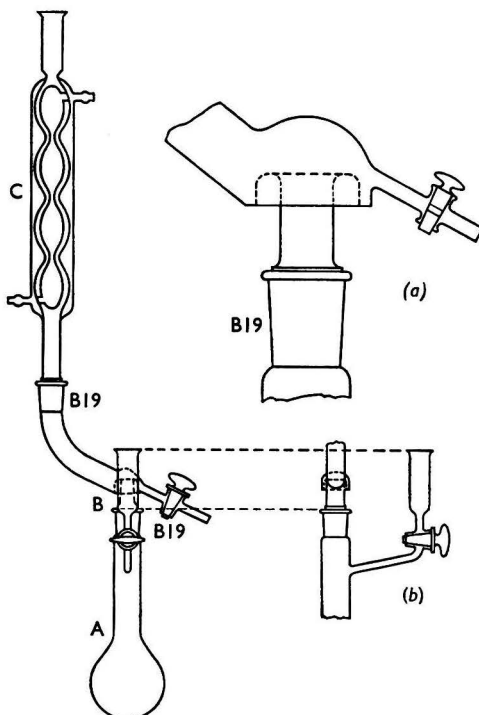


Fig. 4. Arrangement and details of apparatus for the destruction of organic matter in preparation for the determination of mercury. (a) Detail of reflux head. (b) Side view of top part of Kjeldahl flask.

A, Kjeldahl flask fitted with side-arm; B, reflux head; C, double-surface condenser

METHOD (IV) B: DESTRUCTION WITH POTASSIUM PERMANGANATE AND NITRIC AND SULPHURIC ACIDS

APPLICABILITY—

For the partial oxidation of liquids containing relatively small amounts of organic matter.

For mercury in urine and, with modification, for the determination of mercury in animal toxicological specimens, which should be finely minced.

ADVANTAGES—

A mild oxidation that permits quantitative recovery of mercury from samples of urine up to 5 days old.

PRECAUTION—

Overheating must be avoided to prevent volatilisation of mercury.

REAGENTS—

Nitric acid, sp.gr. 1.42.

Sulphuric acid, diluted (1 + 1).

Ammonium hydroxide, sp.gr. 0.88.

Potassium permanganate—Analytical-reagent grade.

Phenol red indicator solution—A 0.02 per cent. solution in 20 per cent. ethanol.

Ammoniacal hydroxylamine solution—A 10 per cent. w/v solution in water. If purification is necessary, dissolve 25 g of hydroxylamine hydrochloride in about 60 ml of distilled water, add 0.2 ml of phenol red indicator solution, and make alkaline with ammonium hydroxide, sp.gr. 0.88, to the full red colour of the indicator. Cool the solution, and extract it with 5-ml portions of a 0.01 per cent. w/v solution of dithizone in chloroform until the last extract remains green; wash the solution free from excess of dithizone by repeated extraction with 10-ml portions of chloroform. Warm the solution until the excess of chloroform has been removed; cool, filter, and dilute the solution with distilled water to 250 ml.

This solution should be freshly prepared on the day of use.

PROCEDURE—

Transfer 100 ml of the liquid sample to a 500-ml round-bottomed flask fitted by means of a standard ground joint to a long water-cooled reflux condenser. Add 40 ml of nitric acid and 3 g of potassium permanganate. Insert the stopper in the condenser, using a thread to prevent an air-tight fit. Boil gently under reflux for 2 hours, and then cool thoroughly. Remove the thread. Shake the flask carefully so that the solution comes into contact with the vapour. Rinse down the condenser.

If necessary, add potassium permanganate until an excess is present after 2 minutes' standing. (A further 1 to 2 g may be added.) Add ammoniacal hydroxylamine solution until the solution is colourless. Add several drops of phenol red indicator and then ammonium hydroxide until the solution attains the full red colour of the indicator, keeping the solution cool during the addition of ammonium hydroxide. Add 18 ml of diluted sulphuric acid and 10 ml of ammoniacal hydroxylamine solution, cool, mix, and allow to stand for at least 3 hours, or preferably overnight.

The solution is now ready for treatment with dithizone.

With material such as liver, 10 to 20 g of the sample may be taken and the procedure described above followed, *but with* the addition of 10 ml of sulphuric acid, sp.gr. 1.84, to complete the digestion under the reflux condenser.

NOTES—

Note 1—The weight of the sample taken will depend (a) on the level of the metal content of the material and (b) on the methods subsequently to be used for the determination of the metal.

For amounts of metal of the order of 10 to 100 parts per million, 5 g is a convenient quantity, but if ultra-sensitive methods are available 2 g is often enough, with consequent saving of time taken to wet oxidise the material and reduction in the amount of acid used.

For biological samples, 10 to 15 g of blood or tissue or 50 ml of urine or plasma are generally sufficient for all determinations; they should be boiled down to small bulk with nitric acid before sulphuric acid is added.

For other liquids, *e.g.*, fruit juices or beverages, take 20 to 50 g of the sample, containing not more than 5 g of solids, and boil down to small bulk with nitric acid before adding sulphuric acid. Continue then as for solid samples.

Note 2—With materials such as tea, or when much carbohydrate is present, the initial reaction may be violent and heating should be delayed, if necessary even overnight. Further nitric acid may then be added as necessary.

With some extremely reactive organic compounds it is necessary to carry out the preliminary treatment with dilute nitric acid in a 500-ml beaker, heating the beaker slowly on a steam-bath until the initial reaction is completed.

Note 3—If excessive frothing is experienced in the earlier stages, a drop or two of secondary octyl alcohol may be added or the preliminary treatment may be carried out in a 500-ml borosilicate-glass beaker with the addition of glass beads to prevent bumping.

Note 4—With some organic materials, *e.g.*, rubbers, coated fabrics and polymers, wet decomposition sometimes takes place more readily if the material is first charred by warming gently with sulphuric acid, sp.gr. 1.84, afterwards adding nitric acid when the initial reaction is completed; but this procedure must not be followed if arsenic is to be determined.

Note 5—USE OF PERCHLORIC ACID. Many oxidations have been carried out safely by the use of perchloric acid, but some explosions have been reported with this reagent. Full precautions should be taken against possible injury in the event of such an explosion, even in well tried procedures. Perchloric acid may be used either at the final stages of Methods (I)A to D, or at the earlier stages described in Methods (I)E and (II)A to C, but it is necessary to allow the vigorous oxidation of organic matter by nitric and sulphuric acids to subside before the temperature is raised sufficiently for the perchloric acid to react. Fuller details of the handling and use of perchloric acid have been published in a Report by the Sub-Committee.⁸

Note 6—Method (II)A does not normally approach conditions where browning occurs (see *Note 7*), but the procedure has the disadvantage of requiring a greater proportion of acids to sample than do methods (II)B or C, and this makes it of less value for some determinations.

Note 7—Hundreds and possibly thousands of determinations have been carried out by methods (II) B and C with no records of explosions having occurred. The ratio of sample to acids is such that darkening or browning may take place at some stage. This should be avoided as far as possible by the addition of further small amounts of nitric acid. The darkening of digestion mixtures containing perchloric acid is regarded by some workers as indicating the onset of dangerous conditions. The real significance of this darkening probably depends upon the nature of the sample, but in any case the condition should not be allowed to persist longer than can be avoided.

DRY DECOMPOSITION

GENERAL REMARKS

Details are given of six methods for dry ashing organic matter. The variations from a simple dry-ashing procedure that have been found necessary are generally occasioned either by the amount or nature of the ash present in the material or by the nature of the metal under investigation.

GENERAL APPLICABILITY

Dry ashing is applicable to the determination of most common metals, usually with the exception of mercury and arsenic, in organic matter. Substances amenable to this method must be charred slowly, and the carbon oxidised quietly and completely; loss of metals by volatilisation or by combination with the material of the container must be avoided by working at the lowest possible temperature. Particular care must be exercised when large amounts of halogens are present in either covalent or ionic form. It has been reported that losses of certain metals (*e.g.*, zinc, tin or antimony) occur when dry ashing is carried out in the presence of halides; such losses can be minimised by ensuring that an alkaline ash remains.

ADVANTAGES

Dry ashing usually requires little attention. Larger amounts of material can be dealt with more conveniently than by wet decomposition by repeated addition of fresh material to already ashed material and re-calcining.

The dry-ashing procedure is of particular advantage when the use of sulphuric acid is objectionable; for instance, for the determination of lead in materials containing appreciable quantities of the alkaline earths, whose sulphates occlude lead sulphate.

The method avoids the use of large quantities of reagents and the high blank values that can result from their use.

DISADVANTAGES

It is sometimes difficult to obtain complete extraction of the metal being determined from certain ignited residues, such as those obtained from some compounded rubbers. Excessive heating also makes certain metallic compounds insoluble (*e.g.*, those of tin). Certain flour products give a dark melt in which carbon particles are trapped and will not burn.

HAZARDS

The slow ignition of some organic materials, *e.g.*, rubber and related materials, can cause the evolution of poisonous fumes, *e.g.*, hydrocyanic acid, and such operations must be carried out in well ventilated fume cupboards.

The method must not be applied to compounds, particularly those of nitrogen, that burn with explosive violence.

METHODS

METHOD A: NO ASHING AID

APPLICABILITY—

For the determination of most common metals, excluding mercury and arsenic, in organic materials that yield a bulky ash, *e.g.*, compounded rubber, proofed fabrics and many solid foodstuffs.

PROCEDURE—

Weigh accurately a suitable quantity of the well mixed sample in a tared silica or platinum basin. Heat first by means of a soft flame, such as that of an Argand burner, to volatilise as much as possible of the organic matter, then transfer the basin to a temperature-controlled muffle furnace, at a temperature preferably not exceeding 420° C (see Notes 8 and 9, p. 656).

If it is suspected that all the carbon has not been removed, cool the ash, add a slight excess of dilute hydrochloric or diluted nitric acid (1 + 2), warm on a steam-bath, and note whether any colour is extracted or whether organic matter is still present. If so, evaporate the mixture to dryness on the steam-bath, and gently char the residue over a small flame until all the organic matter has been destroyed, or better, repeat the ignition at a higher temperature or for a longer period.

METHOD B: ASHING AID: LIGHT MAGNESIUM OXIDE

APPLICABILITY—

For the determination of trace metals, excluding mercury and arsenic, in such natural materials as rubber latex, raw rubber and other substances having a low ash content.

PROCEDURE—

Weigh a suitable amount of the material into a tared silica or platinum basin containing light magnesium oxide (up to 2 per cent. of the weight of the sample) distributed over the base and partly up the sides of the basin. Support the basin in a hole cut in asbestos board so that at least two-thirds of the basin projects below the asbestos. Heat first by means of a soft flame, such as that of an Argand burner, to volatilise as much as possible of the organic matter, then transfer the basin to a temperature-controlled muffle furnace at a temperature preferably not exceeding 420° C, and heat until no carbon remains (see Notes 8 and 9, p. 656).

METHOD C: ASHING AID: MAGNESIUM NITRATE SOLUTION

APPLICABILITY—

For the determination of trace metals, excluding mercury and arsenic, in sugars, sugar syrups and biological materials, but unsuitable when magnesium phosphate may interfere with the subsequent procedure.

REAGENT—

Magnesium nitrate solution—To prepare a solution free from metallic contaminants, adjust the pH of a 50 per cent. w/v solution of magnesium nitrate to 9.5 with ammonium hydroxide, with thymol blue as indicator, and shake with successive portions of dithizone solution in chloroform until the dithizone layer remains green.

PROCEDURE—

Weigh a quantity of the sample, equivalent to not more than 5 g of solids, into a tared silica or platinum basin. Heat first by means of a soft flame, such as that of an Argand burner, to drive off any moisture and to volatilise as much as possible of the organic matter; continue with increasing heating until white fuming ceases and a dry char is obtained (see Note 8, p. 656). Break down the char with a clean glass rod, and moisten it with a little magnesium nitrate solution. Transfer the basin to a temperature-controlled muffle furnace, bring the temperature to about 420° C (see Note 9, p. 656), and maintain the furnace at this temperature until no carbon remains.

METHOD D. ASHING AID: SODIUM CARBONATE

APPLICABILITY—

For the determination of trace metals (excluding mercury), whose salts may be volatile, in dyestuffs, intermediates and medicinals.

PROCEDURE—

Mix intimately a suitable quantity of the well mixed sample with anhydrous sodium carbonate (20 per cent. of the weight of the sample) in a tared silica or platinum basin. Heat first by means of a soft flame, such as that of an Argand burner, until all volatile carbonaceous

matter is driven off. Transfer the basin to a temperature-controlled muffle furnace at a temperature as low as possible, and in any case not exceeding 420° C, and heat until a grey powdery ash is obtained (see Notes 8 and 9). Care must be taken not to fuse the ash, having regard to the fact that its melting-point will possibly be much lower than that of pure sodium carbonate.

METHOD E. ASHING AID: SODIUM CARBONATE SOLUTION

APPLICABILITY—

For the determination of most common metals, excluding mercury and arsenic, in unproofed fabrics, yarns, silk, wool and similar materials.

PROCEDURE—

Weigh a suitable quantity of the sample (cut into strips) into a tared silica or platinum basin. Moisten the material with a 20 per cent. w/v solution of sodium carbonate, evaporate to dryness, and heat with a soft flame, such as that of an Argand burner, until a powdery ash, free from carbonaceous matter, remains (see Note 8). Care must be taken to avoid fusion of the ash. If any difficulty is experienced in removing all organic matter, cool, moisten the ash with a 10 per cent. w/v solution of ammonium nitrate, and continue the ignition at a temperature preferably not exceeding 420° C (see Note 9).

METHOD F. ASHING AID: SULPHURIC ACID

APPLICABILITY—

For the determination of trace metals, excluding mercury and arsenic, in foodstuffs that have a low ash content and materials such as compounded rubbers.

PROCEDURE—

Weigh a suitable quantity of the prepared sample into a tared silica or platinum basin. Heat with a soft flame, such as that of an Argand burner, until all volatile or readily combustible matter has been removed. Then heat rather more strongly until most of the carbon has been removed. If any sooty deposit is formed on the upper half of the basin, remove it by igniting with a flame directed at right-angles to the wall of the basin, but avoiding strong direct heating of the main residue in the bottom of the basin.

Allow the basin to cool, add sulphuric acid, sp.gr. 1.84, from a dropping pipette, round the walls of the basin, in amount just sufficient to moisten the carbonaceous residue. Carefully heat the basin so that copious fumes are evolved until the acid has been driven off and fuming ceases, and then heat more strongly for a few minutes longer. If any organic matter remains, again moisten with sulphuric acid, repeating the procedure until a clean ash is obtained. Finally, moisten with a little sulphuric acid and gently ignite until evolution of fumes almost, but not quite, ceases. Avoid strong ignition in order to retain the ash as far as possible in the form of sulphate.

NOTES—

Note 8—As an alternative to heating with an Argand burner, the sample, weighed in a platinum basin, may be placed in a cool muffle furnace (100° to 150° C) and the temperature raised to about 420° C and left overnight; it is an advantage to draw a slight current of air over the sample during the early stages of the ignition to prevent carbon and tarry matter from being deposited inside the furnace.

Some samples (*e.g.*, rubber) swell considerably during heating; care must be taken to ensure that the basin is large enough to contain the sample under these conditions.

Note 9—Most substances can be ashed in a reasonable time at a temperature as low as 420° C if heated overnight, and such low temperatures are to be preferred.

The time can be reduced by spreading the material in a layer over the basin.

The temperature required will vary according to the material being ashed. In general the ash must not be sintered or fused, but with substances containing much ash, higher temperatures are required.

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The Determination of α -(4-Chloro-2-methylphenoxy)propionic Acid in Chloromethylphenoxypropionic Acids by Gas-Liquid Chromatography with an Internal Standard

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A method is described for determining α -(4-chloro-2-methylphenoxy)-propionic acid in samples of chloromethylphenoxypropionic acids containing 85 to 100 per cent. of the active acid. The method involves conversion of the extracted acids to their butyl esters, addition of an internal standard (dimethyl phthalate) to the sample and analysis by gas-liquid chromatography, with use of the simple, sensitive and inexpensive apparatus described. The precision of a single determination is better than ± 1 per cent., expressed as 95 per cent. confidence limits.

A SELECTIVE herbicide formulation is based on CMPP, which is a mixture of chloromethylphenoxypropionic acids containing α -(4-chloro-2-methylphenoxy)propionic acid as the active principle together with various proportions of 6-chloro-2-methyl-, 4:6-dichloro-2-methyl- and 2-methylphenoxypropionic acids. Haddock and Phillips¹ recently used a conventional chromatographic method for determining the active acid and mentioned a gas-chromatographic method. The method described here is superior to both these methods and can be used as an accurate measure of the total α -(4-chloro-2-methylphenoxy)propionic acid content. The gas chromatograph described has been in continuous use for more than 3 months at 230° C with consistent excellent performance.

CONVERSION OF ACIDS TO A FORM SUITABLE FOR ANALYSIS

With the intention of using a gas-chromatographic method to separate the active acid from impurities, an esterification step was deemed necessary. Since the acids can be almost entirely converted to the butyl esters, this ester was chosen for the analysis. In the preparative procedure described below, which takes from 3 to 4 hours, an acidified sample of the formulation is extracted with chloroform to obtain the total acid. The chloroform extract is then evaporated under fractionation conditions to small volume, *n*-butyl alcohol containing dry hydrogen chloride is added, and the butyl esters of the total acids are obtained as a 30 to 40 per cent. w/w solution in *n*-butyl alcohol.

PROCEDURE—

Weigh 10 to 20 g of formulated CMPP solution, transfer to a 250-ml separating funnel with 90 to 100 ml of distilled water, add 100 ml of chloroform, and acidify to Congo red by adding 10 per cent. w/w aqueous hydrochloric acid. Shake vigorously to extract the precipitated acid, set aside for 10 minutes, and run the lower chloroform layer into a clean dry 250-ml dropping funnel, the exit tube from which is fitted with a B14 cone joint. Wash the aqueous layer with 30 ml of chloroform, set aside for 5 to 10 minutes, and run the chloroform layer into the dropping funnel containing the original extract. Repeat this washing with two more 30-ml portions of chloroform. (Care must be taken to ensure that none of the interfacial matter is allowed to run into the extracted chloroform solution, which should be bright and clear.)

Weigh a 100-ml round-bottomed flask having a B24 neck and containing a few porcelain chips, and attach it to a 12-inch \times 1-inch Vigreux column fitted at its upper end with a multiple adapter. To the adapter attach the dropping funnel containing the chloroform solution and a water separator fitted with a tap and a reflux condenser. Evaporate the chloroform solution to about 25 ml, operating the water separator as a reflux head at a reflux ratio of about 1 to 1 and taking about 20 to 30 minutes. Rinse the dropping funnel with 50 ml of *n*-butyl alcohol redistilled from 0.1 per cent. w/w of metallic sodium, and collect the rinsings

in the 100-ml flask. Remove a further 50 ml of distillate, add 50 ml of a 2 per cent. w/w solution of dry hydrogen chloride in *n*-butyl alcohol, and allow the mixture to reflux for 30 minutes.

Remove 50 ml of distillate, add 50 ml of the alcoholic solution of hydrogen chloride, reflux for 30 minutes, and again remove a further 50 ml of distillate. Remove excess of the hydrogen chloride catalyst by adding and distilling off two successive 50-ml portions of

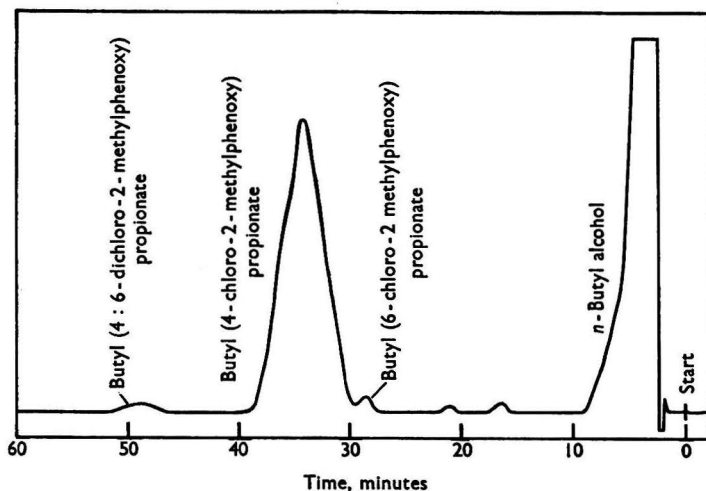


Fig. 1. Chromatogram of mixture containing butyl esters of chloromethylphenoxypropionic acids in *n*-butyl alcohol (not to scale)

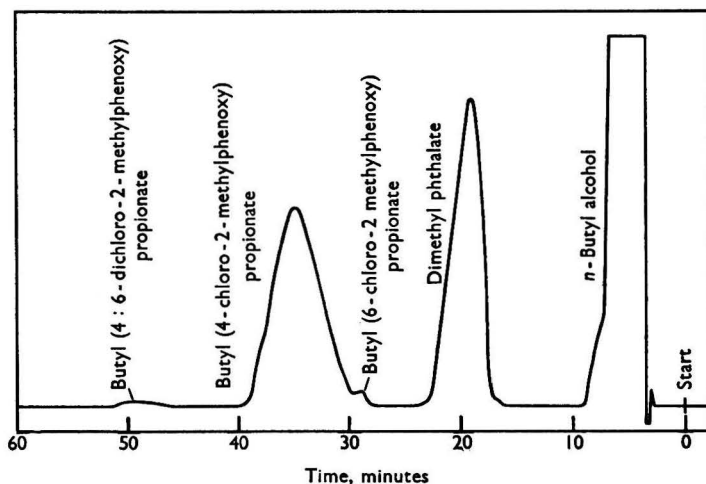


Fig. 2. Chromatogram of mixture containing dimethyl phthalate and butyl esters of chloromethylphenoxypropionic acids in *n*-butyl alcohol (not to scale)

redistilled *n*-butyl alcohol at a reflux ratio of 1 to 1. Complete the distillation by carefully removing distillate at near total reflux until, after cooling and draining from the column, the contents of the flask weigh 10 to 15 g. From a previous determination of the total acid content of the formulation, calculate the equivalent acid content of the alcoholic solution obtained (*T*).

Determination of the acid value of the final sample and correction of this for residual free hydrogen chloride shows that conversion is at least 99 per cent., so that any discrepancies caused by preferential esterification can be ignored.

A solid sample of CMPP can be esterified in a similar manner by weighing 3 to 5 g of sample into a weighed flask having a B24 neck, adding 75 ml of the alcoholic solution of hydrogen chloride and then continuing as described above.

GAS-CHROMATOGRAPHIC ANALYSIS

SELECTION OF INTERNAL STANDARD—

Various compounds were examined, but all except dimethyl phthalate were unsuitable. Dimethyl phthalate is eluted from the chromatographic column between two small impurity peaks (see Figs 1 and 2) and has a sharper peak than was desired, but it was selected in the absence of a better compound.

DESCRIPTION OF APPARATUS—

A commercial instrument reputedly usable up to 250° C gave excessive break-down troubles when operated above 200° C. This difficulty was overcome by constructing a gas chromatograph consisting of a heating unit, a four-filament thermal-conductivity cell, a column of copper tubing 10 feet in length, a carrier-gas source, an electronic recorder and conventional ancillary equipment.

The heating unit consisted of two concentric Pyrex-glass pipes, each 3½ feet long. The inner pipe (internal diameter 3½ inches; ⅜ inch thick) was wound with resistance wire on the outside for its entire length (total resistance 120 ohms); the leads terminated in a plug connected to a Variac transformer. The inner pipe had a winding of asbestos yarn and a 1-inch roll of heat-insulating fibre over the resistance wire. The whole assembly fitted tightly inside the outer pipe (internal diameter 6 inches; ½ inch thick). This heating unit rested horizontally on two wooden blocks at a convenient height from the bench top.

The four-filament thermal-conductivity cell (obtainable from the Gow - Mac Instrument Company, Madison, New Jersey, U.S.A.) consisted of a square stainless-steel block incorporating two pairs of matched filaments with 12-inch long leads from the block.

The chromatographic column was a 10-foot length of ¼-inch external diameter copper tube (20 gauge) packed with 25 per cent. w/w of polypropylene sebacate on Celite 545, and the carrier gas, a mixture of 75 per cent. of nitrogen and 25 per cent. of hydrogen, was supplied from the usual arrangement of cylinders and gas regulator.

The carrier-gas pre-heater tubing, gas-chromatographic column and exit tubes were arranged so that the thermal-conductivity cell was centrally located in the heating unit. The temperature was maintained at 230° C by means of the Variac transformer, which was set so that the continuous current flowing through the heating unit was sufficient to balance heat losses at the working temperature.

The electronic recorder was a 10-mV Sunvic high-speed recorder (type RSP2), and the remaining equipment was that normally used for connections, except for the sample-injection system and the detector bridge circuit.

SAMPLE-INJECTION SYSTEM—

Initial experiments with glass - metal seals and similar connections at temperatures above 200° C were not entirely satisfactory, and an all-metal system was devised utilising silicone-rubber discs as the self-sealing leak-tight diaphragm. An Agla micrometer syringe was used to measure the amount of sample injected into the system. The all-metal system consisted of a piece of ¼-inch external diameter tubing welded perpendicularly to the middle of an ordinary metal coupling. One side of the latter was attached to the chromatographic column and the other side had a flat silicone-rubber disc screwed down tight on its face. The carrier gas entered through the perpendicular tubing.

DETECTOR BRIDGE CIRCUIT—

A schematic diagram of the four-filament circuit is shown in Fig. 3.

INTERNAL-STANDARD METHOD

The use of an internal standard necessitates preparation of standards containing pure butyl α -(4-chloro-2-methylphenoxy)propionate and dimethyl phthalate. Prepare such

standards by weighing 3.0 to 3.5 g of dimethyl phthalate into a suitable container and adding 2.8 to 3.0 g of pure butyl α -(4-chloro-2-methylphenoxy)propionate and about 3.5 g of *n*-butyl alcohol. Standards should be prepared at least in duplicate.

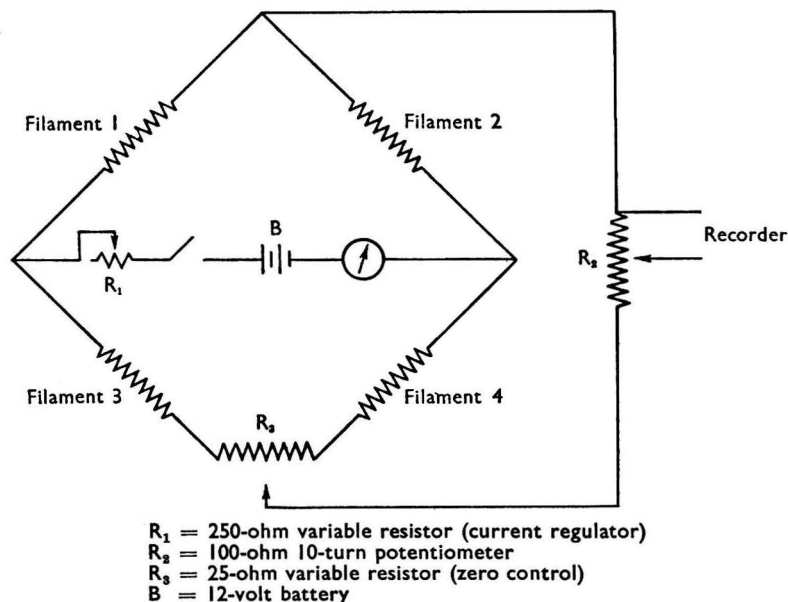


Fig. 3. Schematic diagram of four-filament detector bridge circuit

DETERMINATION OF FACTOR F FROM STANDARD SOLUTION—

Inject 2 drops of well mixed standard solution into the instrument at 230° C, with the recorder chart switched on, and record a chromatogram under the following conditions—

Column length—10 feet.

Column packing—25 per cent. w/w of polypropylene sebacate on Celite 545.

Column temperature—230° C.

Bridge current—190 mA.

Carrier gas—Nitrogen - hydrogen mixture (75 + 25).

Outlet pressure—385 mm of mercury.

Inlet pressure—Slightly below atmospheric (about 750 mm of mercury).

Flow rate—1.2 litres per hour.

Katharometer—Four-filament thermal-conductivity cell.

Chart speed—15 inches per hour.

After elution, calculate the areas under the dimethyl phthalate and butyl α -(4-chloro-2-methylphenoxy)propionate peaks by multiplying the peak heights by the peak widths at half the peak heights. Calculate factor F from the expression—

$$F = \frac{\text{Area under dimethyl phthalate peak}}{\text{Area under CMPP peak}} \times \frac{\text{Weight of CMPP in standard, g}}{\text{Weight of dimethyl phthalate in standard, g}}$$

in which CMPP refers to butyl α -(4-chloro-2-methylphenoxy)propionate.

PROCEDURE—

Weigh 1.8 to 2.0 g of the sample of butyl esters in *n*-butyl alcohol (prepared as described on p. 657) into a tube containing 0.4 to 0.6 g of dimethyl phthalate. Mix well, inject 2 drops into the chromatograph, and record a chromatogram under the conditions described above

(see Note). After elution, calculate the areas under the dimethyl phthalate and butyl α -(4-chloro-2-methylphenoxy)propionate peaks as before. Calculate the percentage of butyl α -(4-chloro-2-methylphenoxy)propionate in the sample from the expression—

$$\frac{\text{Area under CMPP peak}}{\text{Area under dimethyl phthalate peak}} \times \frac{\text{Weight of dimethyl phthalate present, g}}{\text{Weight of sample, g}} \times \frac{214.5}{270.5} \times \frac{F}{T} \times 10,000,$$

where T is the percentage of total acids in the sample of butyl esters.

NOTE—Satisfactory results have also been obtained with a column length of 6 feet, a column temperature of 250° C, a bridge current of 160 mA, an outlet pressure of 430 mm of mercury, an inlet pressure of 5 mm of mercury and a chart speed of 30 inches per hour.

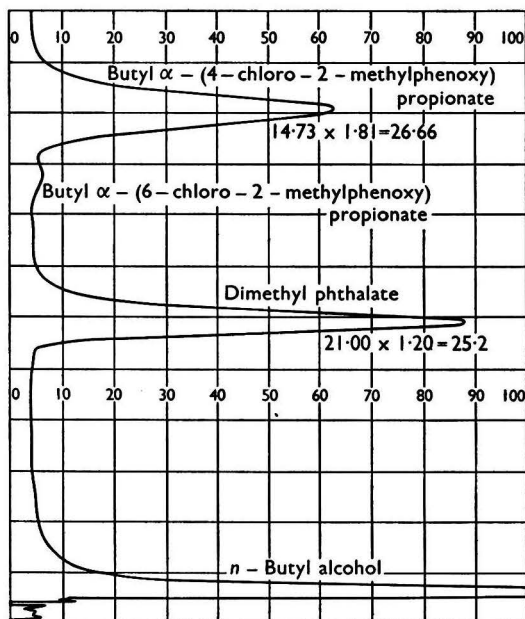


Fig. 4. Typical chromatogram

EXAMPLE OF CALCULATION—

A chromatogram obtained as described above from a sample of chloromethylphenoxypropionic acids is shown in Fig. 4. The percentage of α -(4-chloro-2-methylphenoxy)propionic acid in this sample was calculated from the results shown below—

	Standard	Sample
Weight of dimethyl phthalate present, g	3.0836	0.5867
Weight of pure butyl α -(4-chloro)-ester present, g	2.8563	—
Weight of test solution containing 30.47 per cent. w/w of total acids (as butyl esters), g	—	1.8011
Dimethyl phthalate peak on chromatogram—		
Height, mm	20.13	21.00
Width at half the peak height, mm	1.15	1.20
Butyl α -(4-chloro)-ester peak on chromatogram—		
Height, mm	12.61	14.73
Width at half the peak height, mm	1.70	1.81

Factor F was therefore given by—

$$\frac{20.13 \times 1.15}{12.61 \times 1.70} \times \frac{2.8563}{3.0836} = 0.9997,$$

and the percentage of α -(4-chloro-2-methylphenoxy)propionic acid in the sample was calculated from the expression—

$$\frac{14.73 \times 1.81}{21.00 \times 1.20} \times \frac{0.5867}{1.8011} \times \frac{214.5}{270.5} \times \frac{0.9997}{30.47} \times 10,000 = 89.7.$$

ALTERNATIVE (TOTAL-AREA) METHOD

In this method, the prepared solution of butyl esters is used without the addition of an internal standard. A chromatogram is recorded under the conditions used in the internal-standard method, but the chart speed is decreased to 6 inches per hour. The areas under all the peaks except those eluted in the first 5 minutes are calculated from the peak heights and the widths at half the peak heights; six peaks, including that of the α -(4-chloro)-ester, are usually measured, and the percentage of butyl α -(4-chloro-2-methylphenoxy)propionate is calculated from the expression—

$$\frac{\text{Area under peak for } \alpha\text{-(4-chloro)-ester, sq. mm} \times 100}{\text{Total area under peaks, sq. mm}}$$

The result found by this method is the percentage of free acid, assuming that butylation of all the acids initially present is quantitative.

TABLE I
REPRODUCIBILITY OF THE INTERNAL-STANDARD METHOD

Sample	Test solution No.	α -(4-Chloro)-acid found, %	Average, %
A	1	90.8, 91.9	91.2
	2	91.0, 89.9	
B	1	91.8, 91.2	
	2	91.6, 91.7	
C	1	90.8, 91.8	
	2	91.4, 91.0	
D	1	90.4, 91.3	
	2	91.9, 91.9	

TABLE II
COMPARISON OF RESULTS BY DIFFERENT METHODS

Sample No.	α -(4-Chloro-2-methylphenoxy)propionic acid found by—		
	internal-standard method, %	Haddock and Phillips's method, ¹ %	total-area method, %
1	90.0	90.1	96.1
2	95.7	93.7	95.6
3	95.0	96.0	—
4	93.8	94.8	95.0
5	86.1	—	91.6
6	91.1	—	94.1
7	91.2	94.0	—
8	91.8	93.4	93.5
9	89.5	90.6	93.4
10	92.2	94.5	92.6
11	93.0	96.6	94.7
12	93.2	96.1	93.0
13	93.0	91.5	—
14*	100.0	—	99.6

* Sample of pure α -(4-chloro-2-methylphenoxy)propionic acid.

DISCUSSION OF RESULTS

A series of values for factor F was obtained from duplicate determinations carried out over 3 days; the results were 1.002, 0.9956, 0.9917, 0.9965, 0.9993, 1.006, 0.9979 and 1.009 (average 0.9998).

Four separate esterifications were carried out in duplicate, and duplicate chromatograms were recorded by the proposed internal-standard method for each test solution. The results are shown in Table I, and similar reproducibility was attained in duplicate determinations on over fifty different samples.

Table II shows the results of a series of determinations by the internal-standard method, the total-area method and Haddock and Phillips's method.¹

The proposed method has also been used to determine α -(4-chloro-2-methylphenoxy)-butyric acid (as its butyl ester); for this determination, a 4-foot column packed with 30 per cent. of Silicone E301 on Celite 545 and a column temperature of 250° C were used, with diethyl phthalate as internal standard.

CONCLUSIONS

The proposed internal-standard method provides a reasonably precise, reproducible and accurate procedure for the routine determination of α -(4-chloro-2-methylphenoxy)-propionic acid in chloromethylphenoxypropionic acid formulations, the extracted acid from which contains more than 85 per cent. of the α -(4-chloro)-compound. A complete analysis takes 4 to 5 hours, but several determinations can be completed in a normal working day.

We thank Mr. E. A. Taylor for carrying out the determinations by Haddock and Phillips's method and the Directors of Lankro Chemicals Ltd. for permission to publish this paper.

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The Effect of Substituent Groupings on the Chromatographic Behaviour of Phenoxyacetic Acids

Part I. Methyl-substituted Phenoxyacetic Acids

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Paper chromatograms for thirteen methyl-substituted phenoxyacetic acids were run in two solvent mixtures, the conditions being rigorously standardised. The results show that the R_M values for these acids depend on (a) the phenoxyacetic acid group, (b) the number of methyl groups present, (c) the relative positions of the phenoxyacetic acid group and the methyl group or groups and (d) the relative positions of the methyl groups.

IN one of the earliest papers dealing with the theory of chromatographic behaviour, Martin¹ predicted a relationship between the adsorption coefficient of a substance and its chemical potential and chemical structure. The chemical potential of the molecule was considered to be the sum of the chemical potentials of the groups comprising the molecule; the chemical potential of any group was considered to be independent of the rest of the molecule. To a first approximation, therefore, the addition of a group to a molecule should have a particular effect on its chemical potential and hence on the adsorption and partition coefficients, independent of the composition or structure of the rest of the molecule.

Martin's equation relating the R_F value of a substance and its partition coefficient (α) between an aqueous and an organic substance was—

$$\frac{1-R_F}{R_F} = \frac{\alpha}{K}$$

in which K is a constant depending on the paper and the solutes. From this equation, Bate-Smith and Westall² defined the R_M value, *i.e.*, $\log_{10}(\alpha/K)$, and showed that, for a series of glucosides and complex hydroxy compounds, such as tannins, to a first approximation the relationship between the R_M value and the number of glucoside or other repetitive units in the molecule was linear. These and other workers found similar relationships for many other series of compounds, including carbohydrates,^{2,3,4} amino acids^{5,6} and carboxylic acids.^{7,8,9}

Isherwood and Hanes,¹⁰ for carboxylic acids chromatographed in *n*-propyl alcohol and ammonia solution, found that the relationship between the R_M value and the number of carbon atoms in the alkyl chain was not truly linear. Kalbe,¹¹ for dicarboxylic acids, showed that the linear relationship between the R_M value and the number of carbon atoms in the chain was valid over only a limited range. Rappe and Hellström¹² obtained R_M values for a series of halogenated carboxylic acids chromatographed in an aqueous mixture of *cyclohexane*, benzene and acetic acid and found that the relationship between the R_M value and the number of carbon atoms in the chain was not linear for α -bromo acids. However, they established that the difference produced in the R_M values by the addition of a methylene group was the same for the chloro-, bromo- and iodo-derivatives of a mono-halogenated acetic acid and the corresponding α -halogenated propionic acid. They also reported reasonably constant differences between the R_M values for chloro- and bromo-derivatives and bromo- and iodo-derivatives of corresponding acids and suggested that these differences might be produced by differences in atomic volume, dipole moment of the functional group and polarisability of the halogen atom.

Reichl⁹ and Schauer and Burlisch¹³ attempted to correlate the R_M values found in several solvent systems with the structures of chemical compounds. To this end, two constants were determined for each solvent system, a fundamental constant, $R_M^1(f)$, and a group constant, $R_M(g)$, the R_M value for a compound having n substituent groups being given by $R_M(f)$ plus $nR_M(g)$. This relationship was stated to be universal, and work on amino acids, carboxylic acids, sugars¹⁴ and alkaloids¹⁵ showed this statement to be apparently correct. Franc and Jokl¹⁶ studied homologous series obtained by adding methylene groups to a parent compound and stated that, although Bate-Smith and Westall's equation was valid for the first three members of any series, the increments of R_M value for further members decreased with the length of the chain. They made the supposition that the relationship between the number of carbon atoms in the side chain of a molecule and the R_M value was logarithmic instead of linear, but stated that the linear relationship was valid when a methyl group was introduced into an aromatic nucleus.

We have investigated the series of methyl-substituted phenoxyacetic acids and suggest that the phenoxyacetate grouping plays a dominant part in the adsorption of the acids or their ammonium salts on materials with which the carboxy group can form hydrogen bonds and is therefore the fundamental group. Since the degree of adsorption is determined mainly by this group, the R_M value of any particular acid should also be so determined.

The R_F value of a substance is determined not only by its chemical structure, but also by other factors, *e.g.*, the composition of the development phases, the nature of the support paper, the direction of the paper fibres relative to that of the flow of the development phases, the manner of development (radial, ascending or descending), the length of the run, the distance of the starting line from the surface of the solvent, the concentration of the solute in the dried spot, the presence of other ionic substances and the temperature at which the chromatogram is developed. To ensure that variation in the R_F values of the series were produced by changes in chemical structure and not any other main factor, the experimental conditions were rigorously standardised throughout.

We had previously¹⁷ found that, for a small series of chloro- and methyl-substituted phenoxyacetic acids chromatographed under standard conditions in *n*-butyl alcohol - water or *n*-butyl alcohol - ammonium hydroxide solvents, although the relationship between the R_M value and the number of substituent groups was approximately linear, there was a small yet appreciable difference between the R_F values for isomers.

During preliminary investigations, chromatograms were run at various temperatures between 18° and 25° C, and it was noted that the R_F values increased with temperature. However, above 23° \pm 0.5° C, variations of 1° C in temperature during a run caused partial separation of the components of the solvent system, which in turn caused water-logging of the paper, streaky spots and an uneven solvent front. In order to maintain the standard conditions, including the shape of the spots, a temperature of 23° \pm 0.5° C was used throughout, and maximum reproducibility of results was obtained.

EXPERIMENTAL

Conditions affecting the R_F value were standardised as described below. Immediately before use, the *n*-butyl alcohol was fractionally distilled, and the fraction boiling between 118° and 118.5° C was used. The water was de-ionised by the usual methods, and the

aqueous solution of ammonium hydroxide was taken from one batch, which was used throughout the series. The solvents were mixed and were allowed to attain equilibrium at $23^{\circ} \pm 0.5^{\circ} \text{C}$ over 3 days, during which time they were frequently shaken. When ready for use, the alcoholic layer was placed in the bottom of an all-glass tank, the temperature of which was thermostatically controlled at the chosen value.

The paper used was taken from one batch of Whatman No. 1 filter-paper and was used in the machine direction; it was pre-treated with ammonia vapour for 3 hours before use to ensure neutralisation of any carboxylic acid groups produced by oxidation of the aldehyde groups of the paper.

The amount of solute used was standardised by applying a 0.0025-ml portion of a 1 per cent. w/v solution of each acid in *n*-butyl alcohol and by air-drying the spots during application to reduce dispersion.

The paper was carefully adjusted so that the applied spots were a standard distance above the surface of the solvent, and solvent was allowed to run in an upward direction for $13\frac{1}{2}$ hours at the controlled temperature.

Several spots of the various acids were placed on each paper, together with a standard spot of phenoxyacetic acid. If the R_F value of the standard varied by more than 0.02 unit of R_F from a pre-determined mean (the average of twenty-five to thirty runs), the paper was discarded.^{2,18} All the acids used were chromatographically pure, only one spot, fairly uniform in shape, being obtained for each acid on development.

The chromatograms were developed with a 0.04 per cent. w/v solution of bromocresol purple in a (1 + 5) mixture of formaldehyde and absolute ethanol that had been brought¹⁹ to pH 5; they were then exposed to ammonia vapour. The acids appeared as yellow spots on a purple background, which rapidly faded, but was periodically regenerated by exposure to ammonia vapour.

DISCUSSION OF RESULTS

The R_F values found and the R_M values calculated are shown in Table I. The R_F value for each acid is the mean value found from at least four acceptable chromatograms, the individual variation for each acid being not more than 0.02 unit of R_F from the quoted mean.

TABLE I
VALUES OF R_F AND R_M FOR PHENOXYACETIC ACIDS IN SYSTEMS CONTAINING
n-BUTYL ALCOHOL

Acid	Solvent A*		Solvent B†	
	R_F	R_M	R_F	R_M
Phenoxyacetic	0.200	0.600	0.300	0.360
2-Methylphenoxyacetic	0.330	0.300	0.395	0.190
3-Methylphenoxyacetic	0.260	0.455	0.380	0.215
4-Methylphenoxyacetic	0.245	0.475	0.380	0.215
2:3-Dimethylphenoxyacetic	0.350	0.265	0.420	0.145
2:4-Dimethylphenoxyacetic	0.350	0.265	0.490	0.020
2:5-Dimethylphenoxyacetic	0.360	0.255	0.445	0.095
2:6-Dimethylphenoxyacetic	0.385	0.205	0.465	0.060
3:4-Dimethylphenoxyacetic	0.300	0.370	0.380	0.215
3:5-Dimethylphenoxyacetic	0.320	0.320	0.410	0.160
2:3:6-Trimethylphenoxyacetic	0.420	0.130	0.510	-0.020
2:4:5-Trimethylphenoxyacetic	0.410	0.160	0.480	0.040
2:3:5-Trimethylphenoxyacetic	0.415	0.145	0.480	0.040
2:4:6-Trimethylphenoxyacetic	0.440	0.095	0.515	-0.025

* *n*-Butyl alcohol saturated with water.

† *n*-Butyl alcohol saturated with 1.5 *N* ammonium hydroxide.

Although for mono-, di- and trimethyl-substituted phenoxyacetic acids there is a linear relationship between the number of substituent groups and the average R_M value, and the increment for these average values is approximately the same for the two solvents, it is apparent from a more detailed study that the expression suggested by Reichl⁹ and Schauer and Burlisch¹³ does not adequately account for the factors influencing the R_M value. We suggest that, in addition to the fundamental and group factors, there are, for these nuclear-substituted compounds, at least two steric factors dependent on (a) the position of the substituent group relative to the fundamental group and (b) the position of the substituent groups relative to each other.

Since the R_M values for the substituted acids are in the order shown below—

Mono-substituted acids	..	2-methyl < 3-methyl < 4-methyl
Di-substituted acids	..	2:3-dimethyl < 2:4-dimethyl < 2:5-dimethyl < 3:5-dimethyl < 3:4-dimethyl
Tri-substituted acids	..	2:3:5-trimethyl < 2:4:5-trimethyl

we suggest that the greater the distance between the fundamental group and the substituent group, the smaller is the effect on the R_M value of the molecule and that the nearer the substituent groups are to one another, the smaller is the effect on the R_M value.

Although these effects are regarded as complementary, the major factor is considered to be the relative positions of the fundamental and substituent groups. When two or more substituent groups are present, the "average" position should be considered.

The apparent anomaly of acids substituted in both 2- and 6-positions is regarded as being caused by steric inhibition of adsorption of the fundamental group on the paper; the physical bulk of the hydrophobic part of the molecule concentrated about the fundamental group produces this effect.

We thank Mr. J. Hall for preparing some of the acids used.

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The Determination of Magnesium in Plant Material with Titan Yellow

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A reliable method is described for determining magnesium in plant material; interference from phosphorus, calcium, aluminium, manganese, iron, copper and zinc is overcome. Although more time-consuming than most procedures involving use of Titan yellow, its accuracy is similar to that of Metson's volumetric procedure.

IN connection with work on leaf analysis in relation to fruit nutrition, the reaction between magnesium and Titan yellow has been investigated in some detail, and a method for determining magnesium in plant material has been developed. This method has now been in routine use for 2 years, during which time no difficulties have been experienced in obtaining accurate and reproducible results.

From the numerous papers published about this reaction, it is clear that the intensity of the coloured adsorption compound is affected by (a) the amount of Titan yellow used, (b) the nature and amount of protective colloid used, (c) the concentration of sodium hydroxide in the final solution, (d) the temperature at which the reaction occurs, (e) the time for which the magnesium hydroxide - dye adsorption compound is set aside and (f) the presence of other ions. These factors have been investigated, and the optimum conditions for carrying out the reaction have been determined.

EXPERIMENTAL

TITAN YELLOW—

Mikkelsen and Toth¹ first drew attention to the variation between different batches of dye in the sensitivity of their reaction with magnesium. This has also been noted by other workers, but no investigations appear to have been carried out on the nature of different batches of Titan yellow.

Four samples of dye (A, B, C and D) were examined by chemical analysis, paper chromatography and spectrophotometry. Samples A, B and C were from the same source, but different batches, and sample D was from a different source.

Chemical analysis showed the presence of sodium chloride in different amounts; samples A and C contained about 7 per cent., sample B about 55 per cent. and sample D about 3 per cent. This is presumably introduced during a salting-out process in the manufacture of the dye.

Examination of the samples by paper chromatography, a phenol - ethanol - water mixture (40:25:40) being used as solvent, produced a yellow spot (R_f 0.28 to 0.35) and, under ultra-violet light, a spot showing intense violet fluorescence (R_f 0.55 to 0.65). By visual comparison, the relative concentrations of the yellow spots were $A = C > D > B$ and of the fluorescent spots $D > A = B = C$.

The ultra-violet and visible absorption curves were plotted for the four samples in 0.002 per cent. aqueous solution. For each sample two peaks were observed, one at 330 $m\mu$ and one at 405 $m\mu$. The ratios of the heights of these peaks were—

Sample	A	B	C	D
Ratio peak height at 405 $m\mu$ to peak height at 330 $m\mu$	2.2	2.0	2.2	0.46

Each sample of Titan yellow tested therefore consisted of sodium chloride, the yellow compound having R_f 0.28 to 0.35 and absorption peak at 405 $m\mu$ and a fluorescent compound having R_f 0.55 to 0.65 and absorption peak at 330 $m\mu$. The relative amounts of the components varied from batch to batch and, in particular, from source to source. The effective component in the reaction with magnesium is that having its absorption peak at 405 $m\mu$, and measurement at this wavelength of a 0.002 per cent. aqueous solution gives the relative sensitivities of different batches of dye. There is therefore little point in specifying a particular concentration of Titan yellow, since this will vary from batch to batch. Each batch must be standardised as described under "Method."

PROTECTIVE COLLOID—

Until 1948, starch or mixtures of starch and glycerol were the reagents most commonly used to prevent precipitation of magnesium hydroxide. In 1948, Heagy² introduced polyvinyl alcohol as colloid protector and pointed out the increased sensitivity achieved by its use. Mitchell³ has criticised its use because polyvinyl alcohol gives a red colour with Titan yellow, and, although it also increases the red colour produced with magnesium hydroxide, the resultant effect is a marked reduction in the range of optical-density measurements. His results are based on a concentration of 0.2 per cent. w/v of polyvinyl alcohol in the final solution, and at this level it is true that the sensitivity is less than that attainable at lower concentrations of the alcohol. This is because polyvinyl alcohol reacts with Titan yellow in alkaline solution to form an adsorption compound and competes with magnesium hydroxide for the dye. For maximum sensitivity, therefore, its concentration must be controlled at the minimum necessary to prevent precipitation of magnesium hydroxide. The optimum concentration in the final solution was found to be 0.02 per cent. w/v for the determination of 100 μg of magnesium in 20 ml of solution.

CONCENTRATION OF SODIUM HYDROXIDE—

At the optimum concentration of polyvinyl alcohol, the sensitivity of the reaction was at a maximum when the concentration of sodium hydroxide in the final solution was between 0.4 and 0.8 *N*. A final concentration of 0.4 *N* was therefore chosen, since at this value the optical density of the blank was decreased.

EFFECT OF TEMPERATURE—

A slight increase in the optical density of the adsorption complex was observed with increasing temperature up to 30° C; above this temperature the optical density decreased rapidly, particularly at the higher concentrations of magnesium. A temperature of 25° C was selected as optimum for colour development.

STABILITY OF ADSORPTION COMPOUND—

No significant change in the optical densities of solutions was observed over 2 hours, but measurements were usually made from 30 minutes to 1 hour after colour development.

EFFECTS OF OTHER IONS—

Elements normally present in plant materials and that might be expected to cause interference are phosphorus, calcium, aluminium, manganese, iron, copper and zinc.

Phosphorus—The effect of phosphorus, as phosphate, was examined at different concentrations of magnesium in the final solution. At 1 p.p.m. of magnesium, phosphate equivalent to 10 p.p.m. of phosphorus had no effect. At 2.5 p.p.m. of magnesium, phosphate decreased the optical density of the solution when present in concentrations above 1 p.p.m. of phosphorus. At 4 p.p.m. of magnesium, the optical density was decreased by 10 per cent. in presence of 1 p.p.m. of phosphorus, 18 per cent. in presence of 5 p.p.m. and 22 per cent. in presence of 10 p.p.m.

In addition to this direct effect on the adsorption of Titan yellow by magnesium hydroxide, phosphate produced turbidity or precipitation in solutions containing about 25 p.p.m. of calcium, owing to formation of calcium phosphate.

No control over interference by phosphate could be achieved by using a compensating solution, as recommended by some workers,^{4,5} unless calcium was first removed; even then, control was not effective in presence of more than 2.5 p.p.m. of magnesium. The most effective treatment was found to be the removal of phosphate from the solution by passage through an anion-exchange resin in the chloride form.

Steyn⁶ used De-Acidite E to remove phosphate from plant-digest solutions before the determination of magnesium by titration with ethylenediaminetetra-acetic acid. The use of this resin in our work gave complete removal of phosphate in the pH range 1.5 to 7.0.

Calcium—As observed by many workers, the presence of calcium increases the optical density of the magnesium hydroxide - dye adsorption compound. Its effect, however, was found to be dependent on the concentration of magnesium. At 1 p.p.m. of magnesium, up to 50 p.p.m. of calcium had no effect. At 2.5 p.p.m. of magnesium, an increase of 10 per cent. in the optical density was observed in presence of 5 p.p.m. of calcium, and the optical density then remained constant in presence of up to 50 p.p.m. of calcium. At 4 p.p.m. of magnesium, an increase of 20 per cent. was caused by the presence of 5 p.p.m. of calcium, and the optical density then remained constant in presence of up to 50 p.p.m. of calcium.

Interference from calcium is normally overcome by using a compensating solution. Since enhancement of the colour by calcium reaches a constant value, the use of a compensating solution is permissible provided that phosphate has previously been removed.

Manganese, copper, iron, zinc and aluminium—Interference from these elements was prevented by using a solution containing triethanolamine, hydroxylamine hydrochloride and aluminium chloride, as recommended by Mehlich.⁷ When this solution is used, manganese to magnesium ratios up to 1 to 1, copper to magnesium ratios up to 0.4 to 1, iron to magnesium ratios up to 2 to 1, zinc to magnesium ratios up to 0.2 to 1 and aluminium to magnesium ratios up to 2 to 1 can be tolerated without interference. It is most unlikely that ratios greater than these will be encountered in plant material.

METHOD

REAGENTS—

Ion-exchange resin—Shake 150 g of De-Acidite E (obtainable from the Permutit Co. Ltd.) with three 200-ml portions of a 5 per cent. solution of sodium carbonate, three 200-ml portions of distilled water, three 200-ml portions of 0.5 *N* hydrochloric acid and again with three 200-ml portions of distilled water. The resin is then in the chloride form and ready for use.

Titan yellow solution, 0.1 per cent.—Dissolve 0.2 g of Titan yellow in 200 ml of distilled water; use the reagent obtainable from the British Drug Houses Ltd. for spot tests or from Hopkin and Williams Ltd. (code No. 8686).

Titan yellow - polyvinyl alcohol reagent solution—Dissolve 0.2 g of polyvinyl alcohol (obtainable from the British Drug Houses Ltd.) in 100 ml of boiling water. When cool add x ml of the 0.1 per cent. solution of Titan yellow, and dilute to 200 ml. (Determine the value of x for each batch of dye as described under "Standardisation of Titan Yellow Solution.") Prepare this solution freshly each day.

Compensating solution—Dissolve 3 g of analytical-reagent grade calcium chloride hexahydrate, 1 g of analytical-reagent grade hydroxylamine hydrochloride, 0.5 g of aluminium chloride hexahydrate and 100 ml of triethanolamine in water, and dilute to 1 litre.

Sodium hydroxide solution—Dissolve 16 g of analytical-reagent grade sodium hydroxide in water, and dilute to 200 ml.

Standard magnesium solution—Dissolve 5.068 g of analytical-reagent grade magnesium sulphate heptahydrate in water, and dilute to 500 ml.

1 ml \equiv 1 mg of magnesium.

PREPARATION OF ION-EXCHANGE COLUMN—

Prepare an ion-exchange column from a 50-cm length of glass tubing, 1.2 cm in diameter, tapered at its lower end and connected to a swan-neck capillary tube, the outlet from which is about 20 cm above the base of the column. Place a small plug of glass-wool in the bottom of the tube, and pour in water until drops issue from the capillary. Pour a slurry of the resin into the tube, a portion at a time, until a column about 20 cm long is obtained and the level of the top of the column is about 1 cm below the outlet of the capillary. Wash the resin with water until the effluent is colourless.

STANDARDISATION OF TITAN YELLOW SOLUTION—

Prepare solutions containing 0.005, 0.01, 0.015, 0.02, 0.025 and 0.03 per cent. of Titan yellow in 0.1 per cent. polyvinyl alcohol. To pairs of tubes containing 0 and 100 μ g of magnesium and 2 ml of compensating solution in a volume of 12 ml add 4 ml each of dye solution and sodium hydroxide solution. After 30 minutes measure the optical densities of the solutions in 1-cm cells at 550 $m\mu$ with a Unicam SP600 spectrophotometer. Plot a graph of the difference in optical density between the solutions containing 100 and 0 μ g of magnesium (ΔA) against the concentration of Titan yellow present. The value of ΔA will reach a maximum, and the concentration of Titan yellow at which this occurs is selected for use. The amount of the 0.1 per cent. solution of Titan yellow (x ml) needed to prepare a solution having this concentration can then be calculated.

PROCEDURE FOR DETERMINING MAGNESIUM—

Weigh 1 g of plant material, previously ground in a Wiley mill to pass through a 40-mesh sieve and then dried at 105° C for 1 hour, into a borosilicate-glass tall 250-ml beaker. Add 25 ml of concentrated nitric acid, cover the beaker with a watch-glass, and digest at low temperature until no solid material remains. Add 2.5 ml of 60 per cent. perchloric acid, continue digestion until fumes of perchloric acid are evolved, slightly unc over the beaker, and continue to heat until nearly all the perchloric acid has been removed. Cool, add 25 ml of water, boil, and filter the solution through a Whatman No. 540 filter-paper into a borosilicate-glass 100-ml calibrated flask. Dilute to the mark, and mix.

By pipette, place a 20- or 40-ml portion of the solution (depending on the amount of magnesium present) in a squat 100-ml beaker, and add dilute ammonia solution until the pH is between 3 and 4 (use a pH meter). Pour the solution on to the prepared ion-exchange column, wash through with water until 100 ml of effluent have been collected in a graduated borosilicate-glass flask, mix the solution, and, by pipette, place a 10-ml portion in an Exelo stoppered and graduated 25-ml tube.

Prepare a series of standard solutions covering the range 0 to 100 μg of magnesium by placing the necessary amounts of a standard magnesium solution in stoppered tubes and diluting each solution to 10 ml. To the sample and standard solutions add 2 ml of compensating solution, and place the tubes in a stainless-steel rack in a water bath at 25° C. To the contents of each tube add 4 ml of Titan yellow - polyvinyl alcohol reagent solution, and then immediately add 4 ml of sodium hydroxide solution. After 30 minutes, measure the optical densities of the solutions in 1-cm cells at 550 $m\mu$ with a Unicam SP600 spectrophotometer, and calculate the magnesium content of the sample from the calibration graph.

REGENERATION OF RESIN—

Dilute a 5-ml portion of the effluent from the column to approximately 40 ml. Add 2 ml of a 2.5 per cent. acid solution of ammonium molybdate (prepared by dissolving 2.5 g of analytical-reagent grade ammonium molybdate in 100 ml of 10 N sulphuric acid) and 0.4 ml of a 1 per cent. solution of stannous chloride (prepared by dissolving 0.626 g of powdered tin in 10 ml of concentrated hydrochloric acid and diluting to 100 ml). Compare any blue colour developed with that of a similarly treated standard solution containing 5 μg of phosphorus. When the blue colour is equal to that of the standard, regenerate the resin by the procedure described previously. Regeneration is normally required after eight to ten samples have passed through the resin.

RESULTS

PRECISION—

Ten determinations on a sample of apple leaves gave a mean content of 0.155 per cent. of magnesium, with a standard deviation of 0.004 and a coefficient of variation of 2.5 per cent. For blackcurrant leaves, the mean content of magnesium was 0.272 per cent., with a standard deviation of 0.002 and a coefficient of variation of 1 per cent.

ACCURACY—

Magnesium was determined in various plant materials, and the values were compared with those found by a volumetric procedure⁸ involving use of 8-hydroxyquinoline; the results are shown in Table I.

TABLE I
MAGNESIUM CONTENTS OF PLANT MATERIALS BY 8-HYDROXYQUINOLINE AND PROPOSED METHODS

Sample	Magnesium content found by—	
	8-hydroxyquinoline method, %	proposed method, %
Lucerne	0.146, 0.143, 0.140 (mean 0.143)	0.135, 0.140, 0.135 (mean 0.138)
Oat grain	0.109, 0.113 (mean 0.111)	0.120, 0.115, 0.120 (mean 0.118)
Tomato leaf	0.566, 0.550, 0.550 (mean 0.555)	0.550, 0.555, 0.555 (mean 0.553)
Pasture herbage	0.205, 0.205, 0.202 (mean 0.204)	0.205, 0.205, (mean 0.205)
Kale leaf	0.100, 0.100 (mean 0.100)	0.105, 0.105, 0.105 (mean 0.105)
Cabbage leaf	0.097, 0.111, 0.090 (mean 0.100)	0.120, 0.120, 0.120 (mean 0.120)
Apple leaf	0.146, 0.147, 0.147 (mean 0.147)	0.145, 0.145, 0.145 (mean 0.145)
Blackcurrant leaf	0.273, 0.274, 0.276 (mean 0.274)	0.270, 0.275, 0.275 (mean 0.273)
Strawberry leaf	0.260, 0.267, 0.268 (mean 0.265)	0.265, 0.270, 0.270 (mean 0.268)

Although the proposed method is more time-consuming than are most of those involving use of Titan yellow, its accuracy is similar to that of the volumetric method.

I thank Dr. C. Bould for his interest and advice during this work.

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The Separation of Palladium from Niobium and Zirconium

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The separation of palladium from either niobium or zirconium by extraction from an acid iodide solution into *isobutyl methyl ketone* has been successfully carried out. Although palladium is virtually completely extracted, no significant traces of niobium or zirconium could be detected in the organic phase.

THIS work was initiated to assist the analysis of a series of binary palladium - niobium and palladium - zirconium alloys for one or the other of their major constituents. An effective separation scheme was sought that would be free from the hazards of occlusion and coprecipitation and be more rapid than an ion-exchange procedure. Solvent extraction was thought to be the best field for investigation.

A survey of the literature on solvent extraction revealed no reliable methods for the separation of large amounts of palladium from either zirconium or niobium. Mixed butyl phosphoric acids¹ are effective in extracting niobium and zirconium from aqueous solutions, but also extract up to 5 per cent. of palladium. Zirconium thiocyanate can be extracted into various organic solvents, but again a small amount of palladium is extracted.² Few of the chelate complexes that form between metal ions and such reagents as acetylacetone and 8-quinolinol are suitably specific. Those that are specific, for instance, the formation of the dimethylglyoxime derivative of palladium and its subsequent extraction into chloroform,³ will only accommodate trace amounts of the element. The extraction of niobium^{4,5,6,7} and zirconium⁴ from hydrofluoric acid solutions into several organic solvents has been reported, but it was thought desirable to avoid the use of such solutions if at all possible, owing to practical handling difficulties. In addition, all traces of fluoride ion would probably have to be removed before the final determination. A report that zirconium was not extracted from 6.9 *M* hydriodic acid by diethyl ether⁸ was, however, taken as a significant starting point for further study, especially as palladium is known to form complex halides.

Since niobium, and to a lesser extent zirconium, is not easy to get into and maintain in solution, the choice of composition of the aqueous phase is narrowed considerably, particularly if the use of hydrofluoric acid is to be avoided. However, it has been shown⁹ that iodide extractions can be equally well performed in the presence of sulphuric acid and potassium iodide as in the presence of hydriodic acid alone, and, as solutions of the alloys in sulphuric acid could be obtained with little difficulty, this approach was attempted.

EXPERIMENTAL

Palladium - zirconium alloys were dissolved in aqua regia, and the resulting solution was heated to the appearance of fumes with sulphuric acid to give a sulphate solution. Palladium - niobium alloys had to be fused with potassium hydrogen sulphate and the residue dissolved in 10 per cent. oxalic acid solution. Sulphuric acid and *M* aqueous potassium iodide were added, whereupon a dense precipitate of palladium iodide was formed, together with hydriodic acid and a little free iodine. Addition of excess of potassium iodide resulted in a partial redissolution of the precipitate to yield a dark red-brown solution.

Initial attempts to extract the palladium iodide from this heterogeneous mixture with either diethyl ether or *diisopropyl ether* proved disappointing, since the precipitate appeared only slightly soluble in the organic phase and collected between the two phases. It was found, however, that *isobutyl methyl ketone* was a highly effective solvent for palladium iodide, and by adjustment of the conditions it was possible to obtain virtually 100 per cent. efficiency of extraction from the aqueous phase into the organic phase.

It was noted that the presence of excess of potassium iodide enhanced the extraction of palladium; in fact, at least 4 moles of potassium iodide were required for every mole of palladium for extraction to be complete. In the finalised procedure a 10 per cent. excess of potassium iodide was satisfactory. The concentration of sulphuric acid did not appear

critical, although a value of approximately 20 per cent. v/v was ultimately chosen, since this was found to prevent emulsification and aid the formation of a sharp boundary between the two phases. The use of equal volumes of aqueous and organic phases allowed palladium to be extracted with ease at concentrations of up to 1 mg per ml; thus 100 ml of *isobutyl* methyl ketone would accommodate 100 mg of palladium. It was not considered important to equilibrate the solvents before use.

The extractions were carried out in a 500-ml separating funnel with intermittent shaking by hand over a period of a few minutes. The completion of the extraction was readily discernible by the total discharge of colour from the aqueous layer. The layers were separated, and the organic phase was back-washed with a few millilitres of 20 per cent. sulphuric acid. After this treatment there was no significant trace of palladium in the aqueous phase; likewise there was no significant extraction of either niobium or zirconium into the organic phase.

Palladium was determined, after removal of the *isobutyl* methyl ketone by evaporation and destruction of any organic residue by oxidation in the presence of nitric acid, by the standard gravimetric procedure with dimethylglyoxime. Both zirconium and niobium were determined by precipitation with cupferron and subsequent ignition to the oxides.

The success of the procedure stems from the aptitude of palladium to form a complex iodide, PdI_4^{2-} , whereas neither niobium nor zirconium forms a stable iodide in aqueous solution. No attempt has been made to study the system exhaustively, particularly with regard to interferences, although the presence of chloride ions was found to have a deleterious effect, allowing partial extraction of both niobium and zirconium. During the investigation it was discovered that palladium sulphate was extracted to the extent of 80 per cent. from 20 per cent. v/v sulphuric acid by equal volumes of *isobutyl* methyl ketone. Thus a suitable separation from niobium or zirconium could be effected by this means alone with the use of a continuous-extraction apparatus or by multiple batch extractions.

RESULTS

Some synthetic samples were prepared, put through the separation procedure, and the recoveries determined. Typical results are shown in Table I and indicate that within the limit of experimental error the recoveries were complete.

TABLE I
RECOVERIES OF NIOBIUM, ZIRCONIUM AND PALLADIUM

	Amount added, g	Amount recovered, g
Niobium	0.0496	0.0496
	0.0212	0.0212
	0.0020	0.0020*
Zirconium	0.0272	0.0274
	0.0272	0.0274*
Palladium	0.0438	0.0437
	0.0438	0.0439†

* In presence of 0.1125 g of palladium.

† In presence of 0.10 g of niobium.

The work described has been carried out as part of the general research programme of the National Physical Laboratory, and this paper is published by permission of the Director of the Laboratory.

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A Constant Cathode Potential Electro-deposition Apparatus

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An automatic constant cathode potential electro-deposition apparatus is described. The apparatus keeps the potential between a reference electrode and the cathode within ± 5 mV of any pre-set value in the range +3 to -3 volts. Currents of up to 8 amps are available.

Transistors are used throughout, and the whole apparatus, including power supplies and potentiometer, is self-contained.

CONSTANT cathode potential electro-deposition is a well known analytical technique that has found considerable application, particularly in metallurgical analysis. If the technique is to be used frequently, the apparatus must be automatic, and several designs for potentiostats have been published.^{1 to 10}

These designs fall into two groups. The first and largest group consists of a d.c. supply for the cell, with some motor-driven arrangement to adjust the current. Any error in the potential between the cathode and the control electrode is made to operate the motor and adjust the current; sometimes adjustment is possible in both directions, sometimes only in one. This system is inherently slow in operation and is usually bulky. Since correction

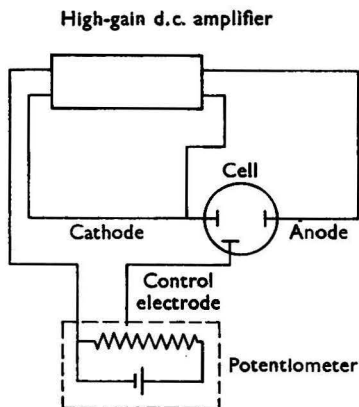


Fig. 1. Basic design of apparatus

cannot take place at the frequency of the ripple in rectified a.c. supplies, it is desirable to use accumulators to supply the cell current, as otherwise there may be a considerable ripple in the voltage across the cell. (It is practically impossible to produce currents of a few amps with a ripple of only a few millivolts by using conventional smoothing techniques.) Accumulators of the necessary voltage and capacity add considerably to the bulk of the apparatus and the difficulty of maintenance.

The second type of design, *e.g.*, that described by Bewick and his co-workers,⁹ consists of a valve amplifier that drives the cell directly. This type gives very rapid response (up to 160 kilocycles per second is possible⁹) and virtually no ripple, at the expense of being limited to a small maximum current.

The apparatus described here combines the high current capacity of the former type with the absence of accumulators and ripple of the latter. The rate of response is between those of the two types and is entirely adequate for analytical work. The whole apparatus, including all power supplies, controls and the potentiometer for setting the cathode potential, is contained in a box of just over 1 cubic foot in volume. The cathode current can vary from 8 amps to zero. The potential between the cathode and the control electrode can be set

anywhere in the range $+3.0$ to -3.0 volts and will be held constant to better than ± 5 mV. The ripple voltage across the whole cell is less than 10 mV. Transistors are used throughout, and there is no "warming-up" delay or drift in voltage. Modifications are possible to increase the output current, to allow an output current in both directions or to decrease the size.

BASIC DESIGN—

Basically, the apparatus consists of a high-gain d.c. amplifier connected as shown in Fig. 1. The potentiometer is set to the required cathode-to-control-electrode potential, and the difference between this and the actual potential, the error voltage, is amplified; the resultant current is passed through the cell. An error voltage of 5 to 10 mV is sufficient to pass 8 amps through the cell.

The high current required by the cell suggested the use of transistors in the output stage of the amplifier, so they are used throughout. Since the maximum power that the output stage can dissipate limits the maximum voltage available across the cell, it was decided to cool the chassis with water in order to increase the permissible dissipation. This has the additional advantage of increasing the stability of the input stage. Since the apparatus is used in a chemical laboratory, water is readily available. For ease of operation, the facilities listed below are provided.

- (i) A meter that can be switched to measure either the current flowing through the cell or the voltage across it and that can also be used for setting up the apparatus.
- (ii) A switch to reverse the anode and cathode connections to the cell so that an unsuitable deposit on the cathode can be removed by reversing the current, and the cathode can be replated.
- (iii) A dummy load that can be connected in place of the cell to allow adjustments to be made before the cell is connected.
- (iv) A standard cell and arrangements to use the amplifier and dummy load as a galvanometer to set up the potentiometer.
- (v) A switch to reverse the potentiometer connections to allow the control electrode to be positive or negative with respect to the cathode.
- (vi) A means of limiting the maximum current that can flow through the cell to a pre-determined value to prevent deposition from being too rapid.

DESCRIPTION OF APPARATUS

The basic circuit is shown in Fig. 2 and the complete circuit in Fig. 3.

OUTPUT STAGE AND CELL SUPPLY—

The output stage is the heart of the apparatus and needs careful design. The main requirement is for a high current with a reasonable voltage available to drive it through the cell. When the apparatus was built, the available transistors having the highest current rating were the Newmarket "Goltop" power series, which can pass 3 amps each. Three of these are used in parallel, as shown in Fig. 2. Ignoring for the moment R_{26} and its associated supply, it can be seen that the cell current is that flowing through the transistors and that the voltage across the transistors is the cell-supply voltage *minus* the voltage across the cell. In the worst instance, therefore, the whole supply voltage can be across the transistors, producing considerable power dissipation at full current. In fact, this dissipation limits the supply voltage and hence the voltage available across the cell. The maximum junction temperature allowed is 75° C. With the transistors screwed directly to the aluminium chassis, without insulation between, and a copper water pipe soldered to the chassis round them, a total thermal resistance from junction to water of 3.3° C per watt can be achieved. This permits 15 watts per transistor, allowing a supply of 5 volts at 9 amps. The supply used rises to 10 volts at lower currents in case a higher voltage is needed. It is possible that the thermal resistance could be decreased still further by using, for example, a thick copper chassis (or sub-chassis), so allowing a higher voltage supply. In each instance, the thermal resistance outside the transistor should be checked by using a thermocouple on the transistor stud, and the internal resistance (quoted by the manufacturer) should be added.

Resistor R_{26} and its associated supply provide a small current (about 0.5 amp) to ensure that the current through the cell can be decreased to zero while some current still flows

through the transistors. The transistors must be able to withstand the full voltage of this supply.

It is necessary to ensure that the maximum permitted current is not exceeded in any transistor. Resistor RV_2 controls the total base-current available to the output stage, and RV_3 and RV_4 , together with R_{17} , control its distribution. It is arranged that the emitter current of each output transistor can be separately measured, and adjustment of RV_2 , RV_3 and RV_4 allows each to be set to about 3.25 amps (maximum). If insufficient control of total current is available on RV_2 , owing, for instance, to the current gain being low, then R_{14} should be altered.

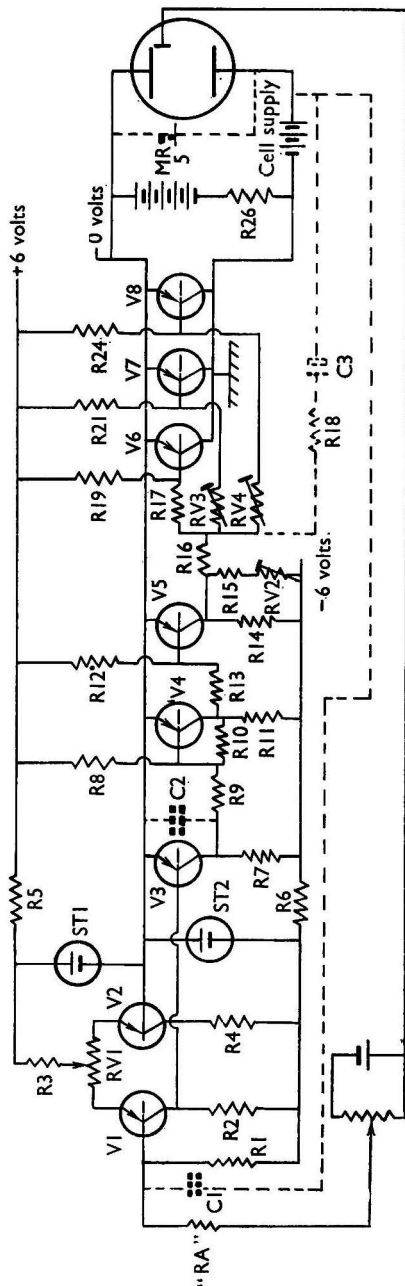


Fig. 2. Basic amplifier circuit (for values of components, see Appendix, p. 679)

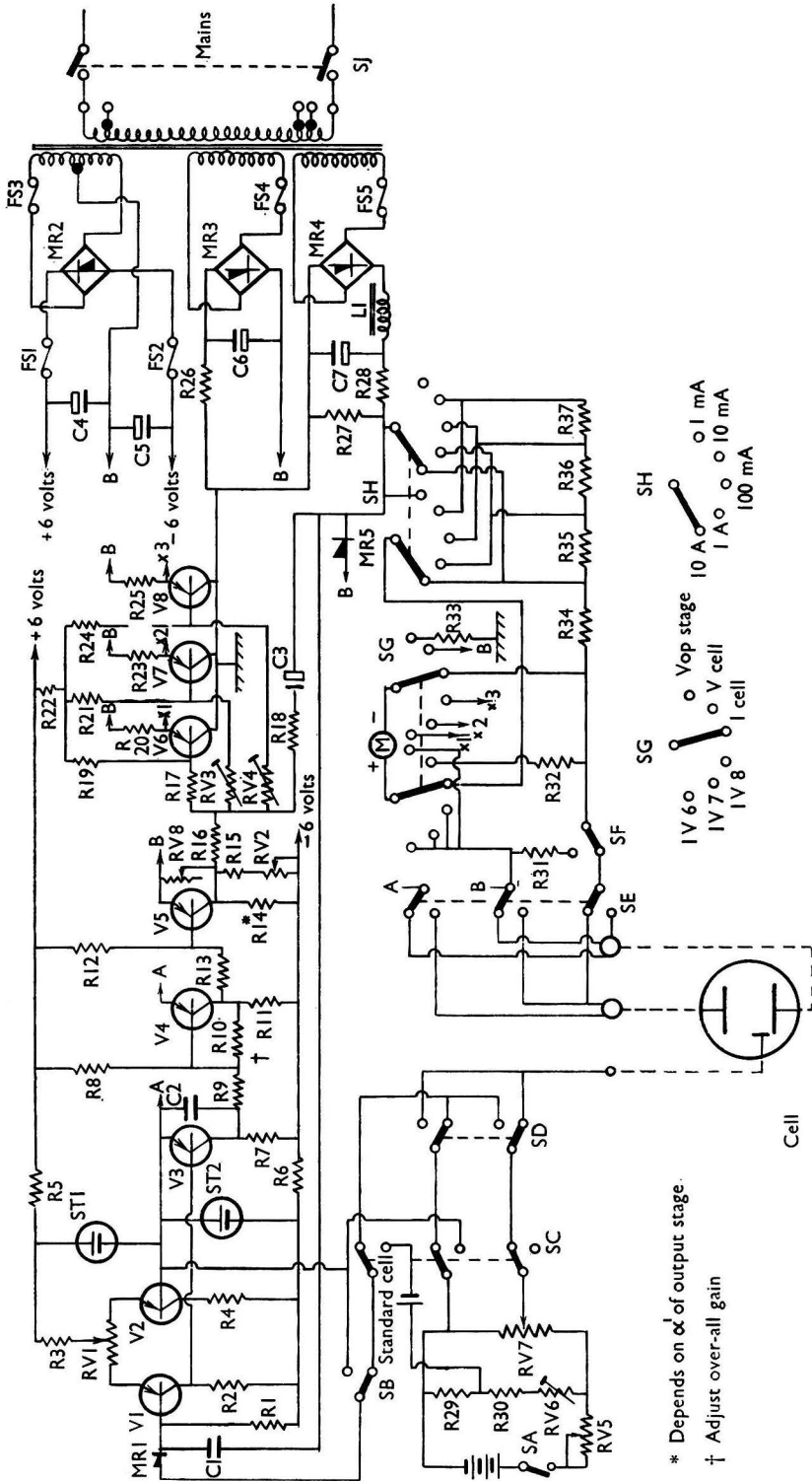


Fig. 3. Complete circuit (for values of components, see Appendix, p. 679)

* Depends on α of output stage.

† Adjust over-all gain

INPUT CIRCUIT AND AMPLIFIER—

Since the constancy of the controlled potential depends on the stability of the input circuit, a pair of transistors, V_1 and V_2 , is used, connected differentially (as a "long-tailed pair"). The two transistors are mounted in adjacent holes in a metal block screwed to the water-cooled chassis, thereby ensuring that they are at the same temperature. The positive and negative supplies to this stage are stabilised by cadmium - nickel electrolytic stabilisers to reduce the effect of variations in supply voltage.

The potential of the control electrode is backed off and applied to the base of V_1 , the base of V_2 being connected to the cathode. A variation in the potential of the control electrode alters the base current of V_1 and hence the collector current, and this signal is amplified by the following stages. The base current of V_1 varies with temperature from about $2 \mu\text{A}$ at 25°C to about $4 \mu\text{A}$ at 15°C . A steady current of $3 \mu\text{A}$ is provided by R_1 , so that the current through the control electrode is limited to $\pm 1 \mu\text{A}$. This is satisfactory when a calomel electrode is used, provided that bubbles are excluded from the path of the current; the current does not appear to polarise the electrode appreciably. Resistor RV_1 allows the circuit to be balanced initially.

The remainder of the amplifier, V_3 to V_6 , is fed from lines at $+6$ volts and -6 volts, the circuit being conventional. To reduce drift and the effect of changes in the high-tension lines, each stage is designed so that the desired current swing is almost equal to the maximum current that the stage can pass. Also, each stage is designed so that it is impossible to exceed the transistor ratings by overloading the input. Transistor V_3 is mounted in a third hole in the same block as V_1 and V_2 , and V_4 is clipped to the chassis by means of a standard clip. Transistor V_6 , which dissipates nearly 1 watt, is screwed to the chassis, with a thin mica washer between to insulate it.

STABILITY—

The whole system of amplifier plus cell forms a closed-loop feedback system having a loop gain of up to 90 dB, and it is necessary that it be stable under all conditions. To ensure stability, the high-frequency gain must be sacrificed, but it is undesirable to decrease this further than is necessary for any particular cell. Also, the ripple across the cell must be kept down to a few millivolts.

A very large capacitance connected directly across the cell would satisfy these conditions, but the value required (about $50,000 \mu\text{F}$) is inconveniently large. However, the Miller effect can be used to increase the apparent value of a given capacitor and so to bring the required capacitance down to a reasonable value. The components used are shown dotted in Fig. 2. C_3 is the Miller capacitor, and R_{18} controls the response at high frequencies, when it would otherwise depend on the non-linear input resistance of the output stage. C_2 decreases the gain at frequencies above that at which R_{18} becomes effective. C_1 and "RA" ensure that feedback at high frequencies occurs from the anode of the cell, so that any difference in phase between anode and control electrode has no effect. At low frequencies and for direct current, feedback is, of course, from the control electrode. The amplifier should be stable with the values given, unless the over-all gain is too high, and this can be adjusted by altering R_{10} .

Metal rectifier MR_5 prevents reversed voltage from appearing across the cell and hence across C_3 , which is an electrolytic capacitor.

If the base of V_1 is made progressively more negative, the current flowing through V_3 will at first decrease, as it should. However, under overload conditions, when the base of V_1 is very negative, its collector current will decrease, and the current in V_3 will increase again. This reverses the sign of the feedback and causes the output current to lock off. This undesirable state of affairs is prevented by using a diode, MR_1 , in place of "RA" in Fig. 2. This has low impedance at currents of $1 \mu\text{A}$ or so, but will not pass the $150 \mu\text{A}$ that must flow if the collector current is to be decreased.

METER—

A meter is fitted and is normally used to measure the current flowing to the anode of the cell, but it can also be used to measure the emitter current in each of the output transistors individually to measure the voltage across the cell or across the transistors. This last voltage is the difference between the cell voltage and the cell-supply voltage, and measuring it shows if there is any voltage to spare or if the current is limited by the available voltage. The meter switching is shown on the complete circuit in Fig. 3. SG is the function switch, and SH

alters the range when measuring the cell current. The shunts, R_{24} , R_{25} , R_{26} and R_{27} , are so arranged that the ones not in use are shorted out, and the circuit is arranged so that the resistance of the switch contacts does not appear in series with the shunts in use. It is essential that SH should be a "shorting" or "make-before-break" type and that SG should not be. The shunts used for measuring the emitter currents of V_6 , V_7 and V_8 (R_{20} , R_{23} and R_{25} , respectively) are left in circuit permanently to avoid altering the current distribution during measurement.

POTENTIOMETER—

The potentiometer used to back off the calomel electrode - cathode potential is built into the apparatus and is included in Fig. 3. Potentials up to 3 volts may be needed and must be set to an accuracy of 10 mV or better, *i.e.*, a resolution of better than 1 in 300 is required. This resolution can be obtained in one turn of one dial if a large diameter "precision wire-wound potentiometer," RV_7 , is used. A reversing switch, SD, is provided to allow the voltage to be applied to the calomel electrode in either polarity. Three mercury cells are used to operate the potentiometer. A standard cell is provided to allow compensation for variations in battery voltage. When SC is pressed, a portion of the voltage across the potentiometer is backed off by the standard cell and applied to the amplifier. The voltage is adjusted by RV_5 , and the current flowing in the dummy cell indicates when the resulting voltage is zero. (RV_1 has already been adjusted to give a suitable current, with the input shorted out by pressing SB.) The pre-set resistor RV_6 determines the exact voltage across the potentiometer when this happens.

CURRENT LIMITER—

It is sometimes desirable to limit the maximum current that can flow through the cell to a value considerably smaller than 8 amps in order to get a more adherent deposit. This facility is provided by RV_8 , which shunts V_5 and so limits the current available to the output stage. Arrangements should be made for the resistor to become open circuited at the high-resistance end of its travel, so as to remove its effect completely.

With the limiter in use, the maximum current through the cell will depend to some extent on the total voltage across the cell, since this voltage affects the current through R_{26} . A slight re-adjustment of RV_8 may therefore be necessary when the cell is connected.

POWER SUPPLIES—

The power supplies are also shown in Fig. 3. The two 6-volt lines from MR_2 are smoothed by a conventional capacitor-smoothed filter, the capacitor being chosen to reduce the ripple voltage to about 10 per cent. of the mean; this smoothing is sufficient. The 15-volt supply from MR_3 is similar. The current supply for the cell is taken from a bridge rectifier, MR_4 , feeding a choke-input filter. This is necessary to smooth the high currents taken. The bleed resistor, R_{27} , prevents the voltage from rising too high on no load, and the series resistor, R_{28} , together with the resistance of the rectifier and associated circuit, reduces the output voltage from 10 volts at no current to 5 volts at the maximum. This keeps the output transistors within their temperature rating.

POSSIBLE MODIFICATIONS—

The apparatus as described works satisfactorily for electro-deposition analysis. Various modifications are possible to increase the range of application. The output current can be increased by using more or higher-powered transistors in the output stage and re-designing the driver stage if necessary. Current flow in both directions through the controlled electrode can be obtained by increasing the backing-off current through R_{26} and removing MR_5 . Some other means of protecting C_3 must then be used, for example, a battery in series. The dry battery operating the potentiometer could be replaced by a mains-operated supply, Zener diodes being used for stabilisation. The over-all size can be considerably decreased by replacing the selenium rectifiers with germanium-junction rectifiers.

PERFORMANCE—

The ripple across the cell is less than 10 mV in operation, and, when unselected transistors are used in the input stage, the controlled potential drifts by about 1 mV during "warming up"

and by less than 1 mV per day after that. A 10 per cent. change in mains voltage produced a change of 0.9 mV in the potential, and a 5° C change in the temperature of the water produced at 2.5 mV change.

CONCLUSIONS

The components required are listed in the Appendix. It is estimated that the total cost (excluding labour) is about £50. If it is desired to heat and stir the contents of the cell, the power supply for the heater and stirrer can conveniently be included in the box with the amplifier.

The apparatus has been used for some time and is convenient in operation. As a check on its performance, separations of silver, copper, cadmium and zinc and of copper, lead, tin and antimony from solutions containing all four metals have been performed, the methods described by Alfonsi^{11,12} being used. In the first instance, once the technique had been mastered, recoveries of each metal were almost always within 0.4 mg of the amounts present, the total weight of metal present being about 1 g; in the second, the yields were slightly less consistent, but were still within the range of those reported by Alfonsi.¹²

A commercial version of this apparatus is being developed.

APPENDIX

LIST OF COMPONENTS USED IN THE CONSTRUCTION OF THE APPARATUS (Figs. 2 and 3)

R ₁	= 470,000-ohm resistor.
R ₂	= 4700-ohm wire-wound resistor.
R ₃	= 2700-ohm wire-wound resistor.
R ₄	= 2700-ohm resistor.
R ₅ , R ₆	= 560-ohm resistor.
R ₇	= 4700-ohm resistor.
R ₈	= 22,000-ohm resistor.
R ₉	= 1000-ohm resistor.
R ₁₀	= 2200-ohm resistor.
R ₁₁	= 100-ohm resistor.
R ₁₂	= 680-ohm resistor.
R ₁₃	= 40-ohm resistor.
R ₁₄	= 20-ohm resistor.
R ₁₅	= 10-ohm resistor.
R ₁₆	= 2-ohm wire-wound resistor.
R ₁₇	= 1-ohm wire-wound resistor.
R ₁₈	= 0.3-ohm wire-wound resistor.
R ₁₉ , R ₂₁ , R ₂₄	= 68-ohm resistor.
R ₂₀ , R ₂₃ , R ₂₅	= 24-milli-ohm wire-wound resistor.
R ₂₂	= 120-ohm resistor.
R ₂₆	= 25-ohm resistor.
R ₂₇	= 10-ohm 10-watt wire-wound resistor.
R ₂₈	= 0.35-ohm 35-watt wire-wound resistor.
R ₂₉	= 300-ohm wire-wound resistor.
R ₃₀	= 500-ohm wire-wound resistor.
R ₃₁	= 0.2-ohm 20-watt wire-wound resistor.
R ₃₂ , R ₃₃	= 10,000-ohm high-stability resistor, 5 per cent. tolerance.
R ₃₄	= 8-milli-ohm wire-wound resistor.
R ₃₅	= 72-milli-ohm wire-wound resistor.
R ₃₆	= 0.73-ohm wire-wound resistor.
R ₃₇	= 8.1-ohm wire-wound resistor.
RV ₁	= 250-ohm variable resistor.
RV ₂ , RV ₈	= 5-ohm 2-watt variable resistor.
RV ₃ , RV ₄	= 2-ohm variable resistor.
RV ₅	= 250-ohm variable resistor.
RV ₆	= 300-ohm variable resistor.
RV ₇	= 1000-ohm variable resistor.
C ₁ , C ₂	= 2-μF condenser.
C ₃	= 3000-μF condenser, 12-volt working.
C ₄	= 1000-μF condenser, 6-volt working.
C ₅	= 5000-μF condenser, 6-volt working.
C ₆	= 1000-μF condenser, 24-volt working.
C ₇	= 10,000-μF condenser, 12-volt working.
L ₁	= 2.5-millihenry 10-amp choke.
V ₁ , V ₂ , V ₃	= OC71 transistor.
V ₄	= OC72 transistor.

V_5, V_6, V_7, V_8	=	VI5/30P transistor.
ST_1, ST_2	=	15BC20 stabiliser (obtained from Mercia Enterprises Ltd.).
MR_1	=	G5M metal rectifier.
MR_2	=	12-volt 2-amp metal bridge rectifier.
MR_3	=	12-volt 0.7-amp metal bridge rectifier.
MR_4	=	12-volt 10-amp metal bridge rectifier.
MR_5	=	12-volt 0.5-amp metal rectifier.
FS_1	=	0.5-amp fuse.
FS_2, FS_3	=	2-amp fuse.
FS_4	=	1-amp fuse.
FS_5	=	10-amp fuse.
SA	=	Single-pole on - off switch.
SB	=	Single-pole change-over switch (spring-loaded).
SC	=	3-pole change-over switch (spring-loaded).
SD	=	2-pole change-over switch.
SE	=	3-pole 10-amp change-over switch.
SF	=	Single-pole 10-amp change-over switch.
SG	=	6-way 2-pole break-before-make switch.
SH	=	6-way 2-pole make-before-break switch.
SJ	=	2-pole on - off switch.
Miscellaneous	}	10—0—200—220—240 volts transformer. Rating: 5.5—0—5.5 volts, 2 amps; 10 volts, 10 amps; 12 volts, 0.5 amp.
		1-mA 80-ohm meter.
		Standard cell.
		Three RM1R mercury cells, 1.3 volts each.

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Notes

THE DETERMINATION OF 2:6-DICHLORO-4-NITROANILINE IN DITRANIL AND SOME FUNGICIDAL FORMULATIONS BY INFRA-RED SPECTROSCOPY

A RECENT development in the control of Botrytis disease in lettuce, tulips and various other crops is the introduction of fungicidal preparations based on 2:6-dichloro-4-nitroaniline. Commercial samples of the raw material (ditranyl) should not contain more than 5 per cent. of 2-chloro-4-nitroaniline and 2 per cent. of chloranil, and the first problem in analysing ditranil is to determine the amounts of the two impurities and the active material, 2:6-dichloro-4-nitroaniline, present. Chemical methods were neither satisfactory nor sufficiently specific, and column chromatography, although attempted with several solvent systems and supporting media, was eventually rejected as being time-consuming and erratic in performance. It was found that an infra-red absorption method would provide the required information rapidly and reliably.

The second problem is to determine the amount of active material in dusts, *e.g.*, Allisan, and in dispersible-powder formulations. Investigation showed that similar infra-red measurements could also be used for both these determinations.

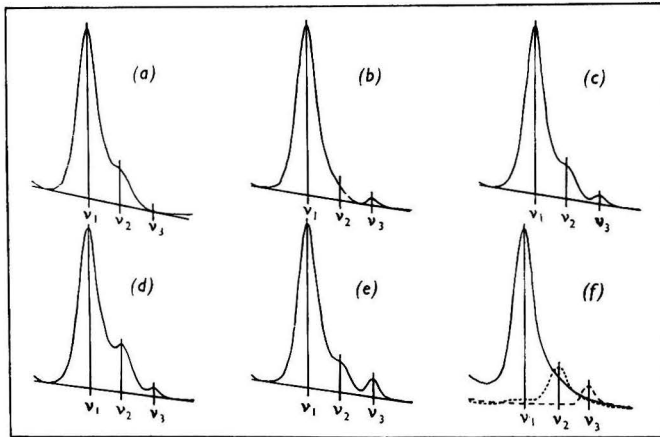


Fig. 1. Infra-red spectra of standard solutions. Each spectrum recorded from 1175 to 1095 cm^{-1} in 1-mm cells: $\nu_1 = 1145 \text{ cm}^{-1}$; $\nu_2 = 1128 \text{ cm}^{-1}$; $\nu_3 = 1113 \text{ cm}^{-1}$

Spectrum	2:6-Dichloro-4-nitroaniline—		2-Chloro-4-nitroaniline—		Chloranil—	
	in chloroform, %	in solid, %	in chloroform, %	in solid, %	in chloroform, %	in solid, %
(a)	0.380	95	0.02	5	0	0
(b)	0.396	99	0	0	0.004	1
(c)	0.376	94	0.02	5	0.004	1
(d)	0.356	89	0.04	10	0.004	1
(e)	0.372	93	0.02	5	0.008	2
(f) ———	0.400	100	0	0	0	0
(f) — — —	0	0	0	0	0.008	2
(f)	0	0	0.04	10	0	0

EXPERIMENTAL

Although 2:6-dichloro-4-nitroaniline and related compounds are not particularly soluble in organic solvents, their solubility in chloroform is such as to permit measurement of their infra-red spectra over restricted ranges. Between 1175 and 1095 cm^{-1} , 2:6-dichloro-4-nitroaniline, 2-chloro-4-nitroaniline and chloranil have absorption bands at 1145, 1128 and 1113 cm^{-1} , respectively, as shown at (f) in Fig. 1, and it is this absorption upon which the simultaneous determination of the three components in ditranil is based. The spectra of standard solutions are recorded between 1175 and 1095 cm^{-1} , as shown at (a), (b), (c), (d) and (e) in Fig. 1, and a calibration graph relating

base-line absorption to concentration is plotted for each component. The spectrum of a solution of the sample in chloroform is similarly recorded and the amount of each of the three components present is evaluated from the calibration graphs. The infra-red measurements were made with a Perkin - Elmer double-beam spectrometer (model 21) fitted with a sodium chloride prism and set to record at 20 cm^{-1} per minute with a mechanical slit width of 0.16 mm .

The 2:6-dichloro-4-nitroaniline present in Allisan is extracted by shaking with diethyl ether. After filtration, the ether is removed by heating on a steam-bath, and the residue is dissolved in a suitable amount of chloroform. The spectrum of this solution is compared with that of a standard solution of 2:6-dichloro-4-nitroaniline recorded under the same conditions. The 50 per cent. dispersible powder is shaken with chloroform and then allowed to settle; the supernatant solution is used directly for infra-red measurements.

METHOD

PROCEDURE FOR DITRANIL—

Prepare mixed standards in chloroform containing 0.356 to 0.396 per cent. of 2:6-dichloro-4-nitroaniline, 0 to 0.04 per cent. of 2-chloro-4-nitroaniline and 0 to 0.008 per cent. of chloranil. Weigh 40.0 mg of sample into a 10-ml calibrated flask, dissolve in chloroform, and dilute to the mark with chloroform. Record the infra-red spectra of the standard and sample solutions over the range 1175 to 1095 cm^{-1} . Use cells of 1 mm thickness, and set the instrument to record under suitable quantitative operating conditions. Measure the base-line absorption at 1145 , 1128 and 1113 cm^{-1} , and, from measurements on the spectra of the standard solutions, plot a calibration graph for each component. Hence calculate the amount of each component present in the sample.

PROCEDURE FOR ALLISAN—

Prepare a standard solution by weighing 40 mg of 2:6-dichloro-4-nitroaniline into a weighing bottle and dissolving it in 20 ml of chloroform. Weigh 1 g of sample into a dry 100-ml stoppered cylinder, add about 60 ml of ether, and shake for 30 minutes. Filter into a flask, wash the cylinder and filter-paper with ether, and evaporate the contents of the flask to dryness by heating on a steam-bath in a current of air. Dissolve the residue in 20 ml of chloroform. Record the infra-red spectra of this solution and the standard solution as described for ditranil, and measure the base-line absorption at 1145 cm^{-1} . Calculate the amount of active ingredient present in the sample from the expression—

$$2:6\text{-Dichloro-4-nitroaniline present, \%} = \frac{\text{Absorption of sample solution}}{\text{Absorption of standard solution}} \times 4.$$

PROCEDURE FOR 50 PER CENT. DISPERSIBLE POWDER—

Weigh 0.4 g of sample into a dry 200-ml stoppered cylinder, add 100 ml of chloroform, by pipette, and shake for 30 minutes. Allow to settle, and use the clear supernatant solution for the infra-red measurement. Use the standard solution described for Allisan, and record the spectra of standard and sample solutions as described for Allisan. Calculate the amount of active ingredient present in the sample from the expression—

$$2:6\text{-Dichloro-4-nitroaniline present, \%} = \frac{\text{Absorption of sample solution}}{\text{Absorption of standard solution}} \times 50.$$

DISCUSSION OF RESULTS

The results of two separate determinations on a prepared mixture containing 2:6-dichloro-4-nitroaniline (92.4 per cent.), 2-chloro-4-nitroaniline (7.2 per cent.) and chloranil (0.4 per cent.) were 93.0 and 92.5 per cent., 6 and 7 per cent. and 0.5 and 0.5 per cent., respectively, for the three components. Results for ten batches of ditranil examined ranged from 92.1 to 97.6 per cent. for 2:6-dichloro-4-nitroaniline, from 2 to 4 per cent. for 2-chloro-4-nitroaniline and from 0 to 0.5 per cent. for chloranil. The 2:6-dichloro-4-nitroaniline contents of ten formulated batches of Allisan ranged from 3.92 to 4.15 per cent., and from 47.8 to 52.3 per cent. was found in four batches of dispersible powder.

The precision of the determination of 2:6-dichloro-4-nitroaniline in ditranil by the proposed method is good (within ± 1 per cent.), and the impurities, 2-chloro-4-nitroaniline and chloranil, can be determined with adequate precision (within ± 10 per cent.). The accuracy with which impurities can be determined depends on the absence of similar compounds that absorb between

1175 and 1095 cm^{-1} . Chemical experiments and infra-red measurements in other spectral regions showed that 2-chloro-4-nitroaniline and chloranil were the major impurities in the materials examined. The precision of the determination of ditranil in dust and dispersible-powder formulations is of the order of ± 1 per cent.

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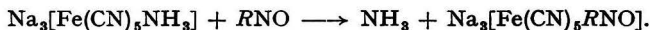
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A QUALITATIVE TEST FOR MONONITROTOLUENES WITH TRISODIUM PENTACYANOAMMINOFERRATE

THE analyst in the explosives laboratory frequently has to identify materials suspected to be explosives or explosives intermediates. When rapid identification is desirable, the use of colour reactions can result in large economies in time. For aromatic nitro compounds, Janowski's reaction provides a simple and rapid test for classifying the di- and trinitrotoluenes according to the colours developed in alkaline acetone.^{1,2} Unfortunately, the mononitrotoluenes do not develop colours under the conditions of Janowski's reaction, and there has long been a need for a simple and rapid test for their detection. Some experimental work carried out in developing a suitable test is described in this Note.

The reagent chosen for the test was trisodium pentacyanoamminoferrate, first introduced by Baudisch as a reagent for the detection of nitrosobenzene, with which it formed a violet complex in neutral solution.³ The ferrate is a yellow-green solid prepared by the action of concentrated ammonia on sodium nitroprusside.⁴ It is readily soluble in water and sparingly soluble in ethanol and diethyl ether; it is normally used as an aqueous solution, which deteriorates on standing and should therefore be freshly prepared.

The test consists in the reduction of the nitro compound to a nitroso compound by Okhuma's method for reducing chloromycetin.⁵ The nitroso compound is then treated with a solution of trisodium pentacyanoamminoferrate; a coloured complex is formed in accordance with the equation⁶—



The reaction is photo-sensitive and will not occur in the absence of light. In some instances, it is slow even in the presence of light.

EXPERIMENTAL

The test was applied to the three mononitrotoluenes in turn. A small amount of sample was dissolved in hot ethanol in a test-tube in a hot-water bath. Reduction was then effected by bringing the solution to the boil in presence of zinc dust and an aqueous solution of calcium chloride. The solution was then filtered, cooled to room temperature, and colour was developed by the dropwise addition of an aqueous 1 per cent. solution of trisodium pentacyanoamminoferrate.⁶

Under these conditions colours were not always developed, and when they did appear it was difficult to distinguish between the three isomers. Attempts to develop colour in various organic solvents by using different proportions of reduced filtrate and of trisodium pentacyanoamminoferrate solution were not successful. Colours developed more rapidly and were better defined in water than in organic solvents. Colour was therefore developed in aqueous instead of ethanolic solution, and optimum conditions for detecting mononitrotoluenes were established by trial.

METHOD

REAGENTS—

Ethanol, 66 O.P.

Calcium chloride solution, 10 per cent., aqueous.

Trisodium pentacyanoamminoferrate solution, 1 per cent., aqueous—Freshly prepare this solution before use.

Zinc dust—Analytical-reagent grade.

PROCEDURE—

Dissolve 1 drop or 10 mg of sample in 3 ml of hot ethanol in a clean dry test-tube. Add 7 drops of calcium chloride solution and then 50 mg of zinc dust. Heat the contents of the test-tube to boiling-point in a water bath, boil for 1 minute, filter, and cool the filtrate to room temperature.

Place 4 drops of cool filtrate in a clean dry test-tube, dilute to 2 ml with distilled water, add 1 drop of trisodium pentacyanoamminoferrate solution, and note any colour change that occurs when the mixture is set aside.

o-Nitrotoluene forms a pink or red colour, *m*-nitrotoluene forms a reddish violet colour and *p*-nitrotoluene forms a violet-blue colour. Nitrobenzene (forming a reddish violet colour), 2:4-dinitrotoluene (forming a violet-red colour) and 2:4:6-trinitrotoluene (forming a violet-red colour) interfere with the test.

DISCUSSION OF RESULTS

The difference between the shades of the colours produced by the mononitrotoluenes is distinct. When any doubt exists, however, it can easily be resolved by carrying out the test with pure samples of the three mononitrotoluenes.

After completion of this work, our attention was directed to a paper in which Ohkuma described the colour reactions of some aromatic nitro compounds with trisodium pentacyanoamminoferrate.⁷ When Ohkuma's milder reduction conditions were used and colour was developed in ethanolic solution, the ferrate was often precipitated; colours were frequently ill defined and changed with concentration of sample and with time. Table I shows the results obtained when the two versions of the test were applied to nitro compounds commonly encountered in an explosives laboratory.

TABLE I
REACTIONS OF AROMATIC NITRO COMPOUNDS WITH TRISODIUM PENTACYANOAMMINOFERRATE

Compound	Ohkuma's method ⁷		Proposed method	
	Colour developed	Limit of detection, μg	Colour developed	Limit of detection, μg
<i>o</i> -Nitrotoluene	Red	10	Pink or red	10
<i>m</i> -Nitrotoluene	Red	10	Reddish violet	10
<i>p</i> -Nitrotoluene	Violet	15	Violet-blue	10
Nitrobenzene	Pink	15	Reddish violet	15
2:4-Dinitrotoluene	Violet-red	15	Violet-red	15
2:4:6-Trinitrotoluene (TNT)	Brown	75	Violet-red	50
Mononitroresorcinol (MNR)	Yellow*	—	Yellow*	—
2:4-Dinitroresorcinol				
4:6-Dinitroresorcinol				
2:4:6-Trinitroresorcinol (styphnic acid)				
2:4:6-Trinitrophenylmethylnitramine (tetryl)	Green-brown	100	Green	50
2:4:6-Trinitrophenol (picric acid)	Green-brown	100	Olive green	100

* No change with ferrate.

With the proposed test, three nitro compounds form colours similar to those formed by the mononitrotoluenes, namely, 2:4-di- and 2:4:6-trinitrotoluene, and nitrobenzene. Application of Janowski's reaction would distinguish between the mononitrotoluenes, which form no colour, and 2:4-di- and 2:4:6-trinitrotoluene, which form blue and blood-red colours, respectively, in this reaction.⁸ Nitrobenzene could not be distinguished in this way, but it is not normally encountered in commercial explosives. Its interference is not therefore likely to cause confusion, but it should be borne in mind as an additional possibility when the usual confirmatory physical tests are carried out.

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MODIFICATIONS TO A COLORIMETRIC METHOD FOR DETERMINING
DICHLOROPHEN

THE method described by Gottlieb and Marsh¹ for determining phenolic fungicides involves use of 4-aminoantipyrine, with a solution of potassium ferricyanide as oxidising agent. Potassium ferricyanide solution is also used in the method for determining phenols described in Hopkin and Williams's monograph.²

Work done in this Inspectorate on the colorimetric determination of dichlorophen (5:5'-dichloro-2:2'-dihydroxydiphenylmethane) on textiles showed that different amounts of potassium ferricyanide led to different calibration graphs and that reagent blank solutions were highly coloured and somewhat unstable. These facts led to an investigation into the use of alternative oxidising agents in conjunction with the 4-aminoantipyrine reagent solution. It was found that potassium periodate gave satisfactory results, reagent blank solutions being more stable and less highly coloured.

The use of this oxidising agent was investigated over the pH range 9.25 to 10.4; for this purpose, solutions were buffered by means of sodium tetraborate and sodium hydroxide. Optical densities covering the range 40 to 300 μg of dichlorophen per 50 ml of solution were measured at 510 $\text{m}\mu$ with a Unicam SP600 spectrophotometer. The measurements were made with the reagent blank solution as zero, and the temperature of the solution was controlled within the limits 15° to 20° C; optical densities were found to be constant for 5 to 30 minutes. Calibration graphs were linear over the range 40 to 200 μg of dichlorophen at all pH values and were almost identical for pH values from 9.25 to 10.0, but above pH 10.0 optical-density values were slightly lower. Outside the range 15° to 20° C, it was found that optical densities varied with temperature, but, above certain minimum amounts, variation in the concentration of the reagent was not critical, provided that the corresponding reagent blank solution was used.

METHOD

REAGENTS—

Buffer solution, pH 9.7—Dissolve 13.75 g of sodium tetraborate and 1.125 g of sodium hydroxide in a 1 litre of distilled water.

4-Aminoantipyrine solution—Prepare a 1 per cent. w/v solution of the reagent in distilled water, and filter if necessary.

Potassium periodate solution, 0.25 per cent. w/v, aqueous.

Standard dichlorophen solution—Dissolve 0.200 g of pure 5:5'-dichloro-2:2'-dihydroxydiphenylmethane in acetone, and make up to 100 ml in a calibrated flask with acetone. Dilute 10.0 ml of this solution to 1 litre with the buffer solution to give a solution containing 20 μg of dichlorophen per ml.

PROCEDURE—

Extract a 1.0 or 2.0-g sample of textile (cut into small pieces) four times for 5 minutes each time with 25-ml portions of boiling buffer solution. Combine the extracts, cool, and make up to 200 ml in a calibrated flask with buffer solution. Filter a portion of this extract through a dry filter-paper, and place 2.0 ml of the clear filtrate, by pipette, in a 50-ml calibrated flask. Dilute to about 30 ml with buffer solution, and add 1.5 ml of 4-aminoantipyrine solution. Mix well, add 10.0 ml of potassium periodate solution, and dilute to the mark with buffer solution. Similarly prepare a reagent blank solution, and measure the optical density of the sample solution in 1- or 2-cm cells at 510 $\text{m}\mu$, with the reagent blank as zero, within 5 to 30 minutes after preparation. Calculate the dichlorophen content of the sample from a previously prepared calibration graph.

PREPARATION OF CALIBRATION GRAPH—

Place 0, 2.0, 4.0, 6.0, 8.0, 10.0 and 15.0-ml portions of standard dichlorophen solution in separate 50-ml calibrated flasks, and dilute each portion to about 30 ml with buffer solution. Add to the contents of each flask 1.5 ml of 4-aminoantipyrine solution, and then 10.0 ml of potassium periodate solution, and make up to 50 ml with buffer solution. Measure the optical densities as described above with the solution containing no dichlorophen as zero. Plot a graph of optical density against dichlorophen content.

RESULTS

The results for the calibration graph at pH 9.7, which was linear up to a dichlorophen content of 300 μg , were—

Dichlorophen present, μg	40	80	120	160	200	300
Optical density (1-cm cell)	0.066	0.130	0.194	0.257	0.320	0.476
Optical density (2-cm cell)	0.128	0.255	0.388	0.510	0.635	0.950

Determinations of the dichlorophen content of a textile gave values of 1.26, 1.26, 1.23 and 1.24 per cent. at pH values of 9.25, 9.7, 10.0 and 10.4, respectively. These results agreed with those found by the original method involving use of potassium ferricyanide solution.

Since this Note was submitted for publication, Ochynski has described a method for determining phenol,³ in which he used a solution of ammonium persulphate as oxidant in the 4-aminoantipyrine reaction.

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EVALUATION OF CRUDE GLYCERINE

THE quality of crude glycerine derived from fats, whether in the course of soap manufacture, hydrolysis or other means, has in the past been assessed by analysis involving such determinations as those of glycerol, ash, organic residue and sometimes moisture. Methods for these tests were laid down as International Standard Methods in 1911, supplemented by the recommendation of the British Expert Committee in 1914. The method of determining glycerol was improved¹ by using sodium periodate (NaIO_4); this was included in the text published as British Standard 2621-5: 1955. The organic residue, which is the "total residue at 160° C less the ash," serves to give a measure of the extent to which the glycerine has been purified, contaminated or altered in processing; it is a tedious analytical method, with its repeated weighings, requiring careful attention to a standard procedure, and the figures are not always reproducible. It gives a measure of the sum of the soap, polyglycerol and other organic matter non-volatile at 160° C, but does not give a measure of other impurities that are volatile at 160° C. In the evaluation of crude glycerines for subsequent purification, such as by distillation, it is important to have warning of the presence of such volatile materials.

From time to time it has been suggested that there were ways of evaluating crude glycerines from tests now normally undertaken without having to determine organic residue. Some time ago it was decided, with the help of those who were interested in the evaluation of crude glycerine, to examine the value of the so-called "matter-(organic)-non-glycerol" (MONG) for a great variety of crude glycerines, MONG being "100 less the sum of the glycerol (by the periodate method), ash and water (by the Karl Fischer method)." During the period 418 sets of figures have been collected so as to compare MONG and organic residue on both soap lye and saponification crude glycerines. Mostly, the figures were similar and did not differ by more than the reasonable cumulative experimental errors of the individual determinations. In about 25 per cent of the tests, MONG was higher than the organic residue by amounts larger than the cumulative experimental errors of the individual determinations, and this indicated the presence of organic matter, other than glycerol, that was volatile at 160° C. In several of these instances (see Table I, samples A, B, C and D) the trimethylene glycol content was determined and was found to make up nearly all the difference between MONG and the organic residue. For samples E and F, which had been made by the alcoholysis of fats, the difference was apparently accounted for by residual methanol in the crude glycerine. The detailed figures are shown in Table I.

In about 8 per cent. of the 418 tests the organic residue was higher than MONG to a greater extent than would be expected from what were considered to be reasonable cumulative experimental errors in the glycerol and moisture determinations, and when, in addition, an allowance of 0.2 per cent. was made for polymerisation of glycerol, shown to be liable to occur during the

organic-residue determination. It is thought that the cumulative experimental error to cover glycerol and moisture determinations might be 0.35 per cent., so that the total error in this direction might, if the polymerisation in the organic-residue determination is included, be as much as 0.55 per cent. The tests in which organic residue exceeded MONG by more than 0.55 per cent. were mainly those up to 1 per cent. and there were in the whole series of 418 sets of figures only 4 crude glycerines in which the difference figures were greater than 1 per cent., three being only just above this figure and one being 1.34 per cent. This last-mentioned crude glycerine was one of particularly poor quality, having an organic residue of 3.18 per cent. It is known that the presence of caustic and carbonate alkali in crude glycerine will affect the Karl Fischer moisture result, making MONG too low.² When in this series the appropriate correction was made for the high alkalinity of the crude glycerine, the amount by which the organic residue exceeded MONG was reduced, but not completely eliminated. It seems likely that the allowance for cumulative experimental errors has not been high enough and that the differences in the direction of the organic residue being higher than MONG are nothing more than the errors already referred to, coupled with the errors known to occur sometimes in the determination of organic residues.

TABLE I
ANALYSIS OF CRUDE GLYCERINES

Crude glycerine sample	Glycerol, %	Ash, %	Water, %	Organic residue (a), %	Mong (b), %	(b - a), %	Trimethylene glycol,* %
A	81.51	7.62	8.27	0.88	2.60	1.72	1.5
B	81.26	7.79	8.41	1.21	2.54	1.33	1.4
C	80.71	7.38	8.62	0.91	3.29	2.38	2.0
D	81.73	8.26	8.29	0.97	1.72	0.75	1.2
E	91.26	0.68	4.13	0.38	3.93	3.55	—
F	85.88	0.80	8.80	0.50	4.52	4.02	—

* Determined by gas - liquid chromatography.

It is concluded from the survey so far made that in normal crude glycerines, whether from soap lyes or from hydrolysers (so-called saponification crude), MONG is a figure of the same order as the organic residue, while in abnormal crude glycerines, MONG includes organic impurities (volatile at 160° C) that would not be included in the organic residue figure. It is proposed, therefore, that MONG should be considered as an improved alternative to organic residue.

It is appreciated that others may wish to ventilate opinions on this, but it does seem that the way is open to substitute MONG for organic residue and thereby save the analyst tedious and unnecessary work, and at the same time ensure that a crude glycerine is not over-evaluated.

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HEXACHLOROTELLUROUS ACID AS A PRECIPITANT FOR CAESIUM

In the determination of radioactive caesium it is customary to weigh and count as the perchlorate or chloroplatinate after separation from potassium and other elements. The preparation of the perchlorate is rather inconvenient, and chloroplatinic acid is expensive, besides requiring rather prolonged precipitation at high dilution if contamination by traces of potassium is to be avoided.¹ It has long been known that the caesium and potassium salts of hexachlorotellurous acid possess widely different solubilities in hydrochloric acid,^{2,3} and use has been made of this fact in developing a rapid and convenient method for precipitating caesium with relatively slight co-precipitation of potassium. The reaction is carried out by adding hexachlorotellurous acid reagent to a solution of the caesium in 11 to 12 N hydrochloric acid. This reagent is prepared by dissolving 10 g of tellurium dioxide in concentrated hydrochloric acid, evaporating to small bulk, and diluting the cooled residue to 100 ml with 11 to 12 N hydrochloric acid.

The results shown in Table I were obtained by adding 2-ml portions of the reagent to solutions of 25.2 mg of caesium chloride in 6.1 ml of 11.1 *N* hydrochloric acid, in the presence of caesium-137 tracer and various amounts of potassium chloride. After having been set aside for 30 minutes at room temperature, the suspensions were spun in a centrifuge and the amount of caesium precipitated in each test was determined by comparing the activity of the supernatant liquid with that of the solution before addition of the reagent. The precipitates were afterwards collected in sintered-glass crucibles (porosity 4), washed well with 11.3 *N* hydrochloric acid and acetone, dried under an infra-red lamp, and weighed.

TABLE I
PRECIPITATION OF CAESIUM HEXACHLOROTELLURITE IN THE PRESENCE OF
POTASSIUM CHLORIDE

Weight of caesium chloride taken, 25.2 mg		
Weight of potassium chloride, mg	Proportion of caesium precipitated, %	Weight of washed precipitate, mg
0	99.4	44.8
0	99.4	44.2
5.5	99.0	45.2
19.5	98.7	45.0
39.2	98.4	45.5
62.2	98.6	48.3

As caesium hexachlorotellurite has an appreciable solubility in approximately 12 *N* hydrochloric acid (Wheeler² quotes a value of 0.05 per cent.), washing should be kept to a minimum. On analysis the precipitate was found in duplicate determinations to contain 34.3 and 36.1 per cent. of chlorine: Cs₂TeCl₆ requires 35.1 per cent. of chlorine. It may be reprecipitated, if desired, by dissolving in a small volume of *N* hydrochloric acid and then diluting with 11 to 12 *N* hydrochloric acid.

This technique may be applied after caesium has been precipitated as bismuthinitrite⁴ or as bismuthi-iodide.⁵ For the former, the bismuthinitrite is dissolved directly in concentrated hydrochloric acid. For the latter, a suspension of the bismuthi-iodide in hydrochloric acid is treated cautiously with a drop of saturated sodium nitrite solution; the hexachlorotellurous acid reagent is added after the removal by centrifugation of the sodium chloride and iodine formed. Any residual iodine is dissolved out when the hexachlorotellurite precipitate is washed with acetone.

Caesium hexachlorotellurite decomposes slowly in the presence of moisture, especially when in contact with a metallic surface, but samples on aluminium counting planchets, for example, may be protected for storage by moistening them with a 5 per cent. solution of polystyrene in benzene and evaporating the solvent to give an impervious film.

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THE FLAME-PHOTOMETRIC DETERMINATION OF BARIUM AND SULPHATE: AN IMPROVED TECHNIQUE

We have recently modified our method for determining barium and sulphate with an E.E.L. flame photometer (Evans Electro Selenium Ltd.)¹ In the original method, the sulphate was precipitated as barium sulphate, and this was separated by centrifugation and suspended in a 1 per cent. solution of starch for analysis by flame photometry. In the modified version, the barium sulphate is dissolved in a solution of ammonium ethylenediaminetetra-acetate. The advantage in this procedure is that the precipitate cannot settle during aspiration in the flame photometer; perfect homogeneity and therefore a steady reading are thereby ensured.

The principal application of the method in this laboratory has been in the analysis of synthetic detergents, both raw materials and finished products. However, the method is applicable to many other types of product, and a general description is therefore given.

METHOD

APPARATUS—

An E.E.L. flame photometer, model A, and Wratten No. 65A or 77 (mercury monochromat) filters were used. (The No. 65A filter has now been deleted from the Kodak catalogue, but is still available in the form of gelatine sheet.)

REAGENTS—

Hydrochloric acid, concentrated.

Barium chloride solution, 1 per cent.

Ammonium ethylenediaminetetra-acetate solution—Dissolve 5 g of ethylenediaminetetra-acetic acid in 100 ml of water, add 50 ml of ammonia solution, sp.gr. 0.880, and dilute to 500 ml with water.

Standard sulphate solution—Prepare a 0.2042 per cent. w/v solution of sulphuric acid or a 0.2958 per cent. w/v solution of sodium sulphate. Both solutions contain 2000 p.p.m. of sulphate, as SO_4^{2-} .

PROCEDURE—

Accurately weigh a sample containing 0.1 to 0.2 g of sulphate, as SO_4^{2-} , dissolve it in water, and transfer quantitatively to a 100-ml calibrated flask. Add 10 ml of concentrated hydrochloric acid, dilute to the mark, and mix thoroughly. The solution must be free from surface-active matter and from anions (other than sulphate) having insoluble barium salts.

By pipette, place a 5-ml portion in a 10-ml centrifuge tube, add 5 ml of 1 per cent. barium chloride solution, mix, and spin in a centrifuge for 3 minutes at 4000 r.p.m. and 6 inches radius. Reject the supernatant liquid. Add 10 ml of water, suspend the precipitate by stirring thoroughly with a glass rod, and spin in the centrifuge as before, again rejecting the supernatant liquid. Add ammonium ethylenediaminetetra-acetate solution exactly to the 10-ml calibration mark, and stir until the precipitate has completely dissolved, warming gently if necessary.

Subject a 5-ml portion of standard sulphate solution to identical treatment; this yields a final solution containing 1000 p.p.m. of sulphate, as SO_4^{2-} .

Use ammonium ethylenediaminetetra-acetate solution to set the zero of the E.E.L. flame photometer, and adjust the instrument to give full-scale deflection with the solution containing 1000 p.p.m. of sulphate. Maintain these adjustments, and analyse the sample solution.

Calculate the percentage of sulphate, as SO_4^{2-} , in the sample from the expression—

$$\frac{\text{Scale reading}}{\text{Weight of sample, g} \times 5}$$

RESULTS

The modified version was not considered sufficiently different from the original method to require additional testing, but calibration graphs were plotted for concentrations of sulphate from 0 to 1000 p.p.m., each filter being used in turn. These graphs confirmed that the modification to the method did not affect the linear relationship between concentration of sulphate and scale reading.

A detergent powder was analysed by the procedure described above, after removal of surface-active matter. The sodium sulphate content found was 20.6 per cent., and the conventional gravimetric method gave a result of 20.5 per cent.

In a recovery experiment, 600 p.p.m. of sodium sulphate were added to a sample of sulphate-free sodium dodecylbenzene sulphonate, which was then analysed. The sodium sulphate content found was 600 p.p.m.

We thank Colgate - Palmolive Ltd. for permission to publish this Note and Dr. A. C. Blaskett, of C.S.I.R.O., for suggesting the modification described.

REFERENCE

1. Cullum, D. C., and Thomas, D. B., *Analyst*, 1959, **84**, 113.

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D. C. CULLUM
D. B. THOMAS
Received March 31st, 1960

Book Reviews

SEMIMICRO EXPERIMENTS IN GENERAL CHEMISTRY AND QUALITATIVE ANALYSIS. By NICHOLAS D. CHERONIS and HERMAN STEIN. Pp. x + 310. New York: John de Graff, Inc. 1959. Price \$4.00.

This is essentially a manual of practical work in general elementary chemistry, the semi-micro technique being used throughout, and is the result of eight years' experience of teaching a one-year course in an American college. Divided into two parts, it contains in all 38 chapters, each of which is prefaced by a background discussion of the theory underlying the experiments described in it.

The first part is divided into 30 chapters, with a total of 115 exercises ranging from the usual gas preparations to a refreshingly large number of experiments in physical chemistry. This section also includes chapters on organic chemistry. The second part, 8 chapters, is devoted to inorganic qualitative analysis along more or less traditional lines, with an introduction to paper chromatography and ion exchange.

Chemistry teachers in the grammar schools of this country have generally accepted the use of small-scale methods for practical work in qualitative analysis and organic preparations, but, with few exceptions, they have not extended the technique to the whole field of practical work in general chemistry; this manual shows well the possibilities of extension. The apparatus used is that familiarly associated with the technique as practised in this country, but some of the experiments described and reagents used would be thought outside the range circumscribed by the usual school syllabuses. There is a dearth of preparations of typical inorganic compounds. In the chapters dealing with organic chemistry, few of the traditional preparations are described, but a broader, more realistic approach is preferred, including an elementary study of fats, proteins, polymers, etc. This approach will not be acceptable to the traditionalist, but may well be the shape of things to come in future "O-level" work.

The second part, dealing with qualitative analysis, has little to commend it for use in this country, as most of the teaching here is tied to the requirements of the "A-level" examinations. The treatment of a few of the less familiar elements in the scheme is poor and would be better omitted.

The book is well printed, but the format, with its perforated pages, would soon present an untidy appearance under normal school conditions. The use of chapter and section references instead of pages is most irritating as well as time-consuming.

This manual should find a place on the shelves of the more progressive teachers in grammar schools, for there are many ideas in it for making the practical work more versatile and less time-consuming than at present.

H. HOLNESS

LES RÉACTIONS ÉLECTROCHIMIQUES. By G. CHARLOT, Mme. J. BADOZ-LAMBLING and B. TRÉMIL-LON. Pp. viii + 398. Paris: Masson et Cie. 1959. Price (paper) 6000 fr.; (cloth boards) 6800 fr.

Any work on this subject from this school will be received with interest by all analytical chemists concerned with electrode processes and electrochemical methods of analysis. The series of papers on the interpretation and application of polarisation curves that has appeared during the past few years has undoubtedly whetted appetites for the comprehensive exposition that comprises the first part of this book. A praiseworthy attempt is made to devise a unified approach to electrochemical problems from a novel angle, a provocative and stimulating angle, which will repay the study required for its understanding by bringing new ideas and a fresh appreciation of many different aspects of the subject. The concise, almost terse, style renders digestion a little difficult, but is complementary to the lucidity of the treatment. Perhaps we may hope for a translation following that of Professor Charlot's "Quantitative Inorganic Analysis," which would be of much assistance to English-speaking peoples. The treatment is essentially experimental; no attempt is made to cover the thermodynamics or reaction mechanisms dealt with in theoretical electrochemical texts, nor is any attention directed to industrial electrochemistry and its special problems. This in itself is a welcome feature to practising analytical chemists, who seek to understand the systems with which they are particularly concerned. The method of determining

current - voltage curves is described, their qualitative significance and application to fast and slow reactions are discussed, the influence of physical factors is considered, and then a survey of electrochemical methods of analysis is given. This covers potentiometry, amperometry, coulometry, and recent developments in chrono-electrometry and polarography and finishes with a review of work in fused salts and non-aqueous media. One is left rather breathless after all this, but the treatment is compendious rather than superficial, and the references are full. There are omissions, some of which may be repaired in future editions, but this is to be expected in a work of this nature; and there are matters that could be hotly debated, but this is to the good. It is understood that this work has been well received on the Continent, and it certainly merits close attention from all working or teaching in this field. The printing leaves a little to be desired, especially in the smallest type-faces, but the indexes and general production are good. The price is unfortunate, but perhaps inevitable, yet it may cause many to wait for a translation, possibly with some revision or expansion, for this is a living subject and still young.

E. BISHOP

AUTOMATIC TITRATORS. By J. P. PHILLIPS. Pp. viii + 225. New York and London: Academic Press Inc. 1959. Price \$6.00; 48s.

There is no doubt that during the past few years there has been a distinct tendency to introduce automatic titration equipment into analytical laboratories.

In some instances, this apparatus has permitted analysts to take samples and to titrate them with appropriate reagents to pre-set end-points, often making use of anticipatory devices that slow down the titration just before the end-point. In others, it has been possible to carry out full-scale titrations on batch samples. Moreover, under suitable conditions, it is possible to withdraw a liquid sample from a plant stream, to titrate this sample to a pre-set end-point and to repeat this cycle of operations at appropriate intervals of time.

With all these changes taking place, the appearance of this book on "Automatic Titrators" is indeed timely.

It should be emphasised at once that the book is a very good one and very well written. It contains a surprisingly large amount of up-to-date information on automatic titrations. After a preliminary introduction, the author outlines some general considerations of titrator design. He then discusses successively the various forms of automatic titration, *i.e.*, potentiometric, amperometric, dead-stop, conductimetric, photometric, thermometric and coulometric, and the appropriate equipment for these tests. Titration curves in their original forms and the first, second and even third derivatives of such curves are dealt with.

Fully automatic and continuous titrations are discussed, and there are final chapters on commercially available titrators and on the applications of automatic-titration methods. There are excellent sets of up-to-date references at the end of each chapter.

Although Phillips is obviously an enthusiast, he approaches his subject with a "down-to-earth" attitude that enables him to make some very shrewd observations on the extravagant claims sometimes put forward by makers of automatic-titration equipment.

Analytical chemists who are already using automatic titrators will be well advised to read this book carefully, because it is brim-full of ideas, some of which they are bound to incorporate in subsequent work.

Even those who still cling to manual forms of titration with colorimetric end-point indicators might usefully try to avoid being too embarrassed by such terms as "thyatronons" and "resistance capacitance networks" and spare some time for studying the wider implications of this rather revolutionary approach to titration work. They, as experienced analysts, will be able to ask the right questions about these new procedures, *i.e.*, questions about the accuracy, reproducibility and standardisation of such tests. They will want to know, for example, whether the coulomb will be a satisfactory standard in many coulometric tests or whether, after all, performance against a known chemical will be the real arbiter.

J. HASLAM

ION EXCHANGE RESINS. Fourth Edition. Pp. iv + 68. Poole, Dorset: The British Drug Houses Ltd.

The fourth edition of this booklet provides very useful information about the Permutit and Amberlite series of ion-exchange resins now available. Some of the resins can be purchased as general grades, and others are available as "Analytical grades" and "Chromatographic grades."

Detailed information is given about each resin, *i.e.*, about its chemical nature, particle size, density and capacity as an anion or cation exchanger. The precautions that must be taken in the regeneration of the spent resin are described, as well as the effects of temperature, oxidising and reducing agents and strong acids and alkalis on the resins.

A special chapter is included on the newer ion-exchange membranes, and there is an excellent description of the use of the various ion-exchange resins in analytical work and in other miscellaneous applications.

In a future edition, it might be useful to give more information about the chemical structures of these ion-exchange resins, whether cross-linked or not. Further, the chapter on recommended applications for specific resins could be expanded considerably; it is not particularly satisfactory to know that information about, *e.g.*, the treatment of sugar solutions by a particular ion-exchange resin, may be found in manufacturer's literature. Incidentally, there has been some jumbling of the figures in Fig. 3, p. 38.

The references to books, reviews and original papers are comprehensive, and the booklet can be heartily recommended to analytical chemists.

J. HASLAM

RADIOACTIVE TRACERS IN CHEMISTRY AND INDUSTRY. By PASCALINE DAUDEL. With a foreword by IRÈNE JOLIOT-CURIE. Translated by ULLI EISNER, Ph.D., D.I.C. Pp. xii + 210. London: Charles Griffin & Co. Ltd. 1960. Price 36s.

This little book by a distinguished French author is a translation, with some additions and revision, of a French text published in 1955, at 800 francs. Its main purpose is to classify the many ways of using radioactive tracers, and this it does well by choosing examples of each type from published work. There are five chapters and two appendices—

- (1) Radioactive tracers—general principles.
- (2) Application of tracer techniques to the study of reaction mechanisms.
- (3) Exchange reactions.
- (4) The use of tracer techniques in chemical analysis.
- (5) Radioactive tracers in industry.

Appendix 1. Table of the principal radioactive isotopes (4 pages).

Appendix 2. Experimental procedures (11 pages).

The chapter on tracer techniques in chemical analysis is the longest (50 pages) and provides a useful introduction for readers who are not familiar with the subject.

But, apart from the classification of the different uses of tracers, little of the "expertise" of the author is apparent, and the book is one to be read by the non-specialist as an introductory text, but it is not likely to find a permanent place on his bookshelves.

A. A. SMALES

A STATISTICAL MANUAL FOR CHEMISTS. By EDWARD L. BAUER. Pp. x + 156. New York and London: Academic Press Inc. 1960. Price \$4.75; 38s.

Statistics made its first incursion into analytical chemistry with "Student" some fifty years ago, but it is only within the last decade or so that it has become a general tool for the analyst using chemical methods, although it has been an essential element in biological analytical methods for more than twenty years.

The present volume is written by a chemist and does not purport to be more than the title signifies—a manual that states what the chemist needs to know about his results and how to get that information without considerations of the ratiocination leading thereto. In this respect it is a lucid exposition based on numerical illustration and capable of being followed by any assistant of G.C.E. level.

The volume differs from most elementary books on statistics in that the variance and standard deviation are derived throughout from the range of replicate results, apart from one illustration of the method of squares of deviations from the mean. This has the advantage of eliminating those tedious sums of squares, but calls for special tables, which are provided in the appendixes.

The subjects dealt with include experimental design, analysis of variance (introducing a new portmanteau word, ANOVA, which at first sight suggests either nutritional or endocrine associations, at least to a biochemist), comparisons of means, correlation and regression with reference to colorimetric analysis, sampling and routine control. The whole of the ordinary work of the analyst in a chemical laboratory is therefore covered.

The book is well produced, but contains a number of misprints, which, while offering no difficulty to one familiar with statistics, may prove great puzzles to the person for whom the book is primarily designed. Thus, on p. 18, the 95 and 99 per cent. confidence limits are worked out to be the same, but the resultant variation in individuals is correctly expressed. Again, on p. 24, Table 2, the comparison column gives a measure of the mean effects P, T and C, not C, P and T.

The book begins, as every book on statistics should in the absence of an international convention of symbols, with a glossary of symbols used, but some confusion occurs in the treatment of analyses of variance from the use of the same symbol to denote at times the true mean (*i.e.*, the mean divested of errors) and at others the grand mean, *i.e.*, the observed mean of all experiments.

In such complicated typesetting as treatises on statistics demand, such errors as have been mentioned are easily missed in first printings and can readily be remedied later. Within its limitations as a manual primarily for the man at the bench, the book is clearly written and serves a useful purpose, but the price of 38s. for such a slender volume of 156 pages is not likely to encourage sales.

J. I. M. JONES

AN INTRODUCTION TO CHEMICAL NOMENCLATURE. By R. S. CAHN, M.A., Phil. nat., F.R.I.C.
Pp. viii + 96. London: Butterworths Scientific Publications. 1959. Price 10s. 6d.

In the relatively short period since the publication of Dr. Mitchell's book, there have been many changes in British chemical nomenclature. To mention but a few, there are the alphabetical order for substituents, etc., the Anglo-American agreed naming of compounds containing one phosphorus atom and the rules for the nomenclature of steroids; these are surely if slowly gaining ground, the last despite the Fiesers. Evidently there is more to come, for the Editor to the Chemical Society observes that the time is not yet ripe for a complete text-book of nomenclature.

On the inorganic side, the IUPAC Nomenclature of 1957 has been adopted extensively, though not quite in its entirety. Here are a few points: the symbol Ar represents argon; there is a lengthy but limited list of trivial names for acids; the prefix "peroxo" is used for acids formerly denoted as "peroxy" or simply "per"; the endings -ous and -ic for salts, though not recommended, may be retained when no more than two valencies are involved, with the hope that they will ultimately vie with old soldiers; $\text{Li}(\text{AlH}_4)$ is lithium tetrahydridoaluminate. Among the divergencies are the retention of tungstate for wolframate and nickelate for niccolate; sodium hydrogen-carbonate is written as three words; HIO_4 remains as periodic acid, with H_6IO_5 distinguished as orthoperiodic acid, whereas IUPAC names the former as tetroxiodic (VII) acid and the latter periodic or orthoperiodic acid. It should be added that many simple familiar names are retained.

Most organic compounds can be, and often are, named in different ways, quite apart from any trivial names that may exist. The first recipe now is relatively straightforward; first catch your principal functional group, set it in position in the parent compound, give it the lowest available number and finally add the other substituents as prefixes in alphabetical order. From the above, it follows that the parent compound is not necessarily the largest recognisable unit; numbering may be predetermined by other factors, *e.g.*, that peculiar to the parent compound. The concept of "functional groups" is one that has crept unheralded into British usage; without going into detail here, for practical purposes they are those that can be designated by suffixes. There is an order of seniority for such groups that permits the principal one to be selected. However, as in the culinary field, the recipe is not always as simple as it seems. For example, there are occasions when a compound contains principal groups attached both to a chain and to a ring system, and the selection may then become a matter of personal opinion.

For polycyclic hydrocarbons and heterocyclic compounds the IUPAC 1957 Rules, themselves following the Ring Index system, are adopted with one small difference. The recently introduced use of commas instead of colons to separate numerals is extended by example to bicyclo-hydrocarbons, whereas the other authorities employ full stops.

Attention is drawn to the distinction between substitutive nomenclature, *e.g.*, 2-naphthylacetic acid, and conjunctive nomenclature, *e.g.*, naphthalene-2-acetic acid. The former is generally preferred here, while the latter, adopted mainly for indexing purposes, is widely used in America, and it must be admitted that it has advantages for naming compounds of the EDTA series.

The author states that organic chemical nomenclature is an infuriating subject. The present book will not meet every case—after all, it is only intended as an "Introduction"—but it should serve to moderate the fury without involving undue labour; the occasional light touch helps.

A few rather obvious errors are concentrated on p. 81.

B. A. ELLIS

THE PHARMACEUTICAL POCKET BOOK. Seventeenth Edition. Pp. xii + 576. London: The Pharmaceutical Press. 1960. Price 30s.

The first edition of this book was published in 1906 and was intended as a guide for students of pharmacy. In later editions the scope was widened and information of value to the practising pharmacist included. The present edition contains about 150 more pages than the preceding one, published in 1953, and embodies information of value to those analysts who may be concerned with the examination of pharmaceutical products.

A particularly good feature, new to this edition, is the Table of Solubilities extending over 31 closely printed pages and giving values for six solvents. The summary of the legislation connected with pharmacy and the sale and handling of drugs is comprehensive, up-to-date and of real value to all who are associated with pharmaceutical business. The article on Isotonic Solutions has been extended to nearly twice the length of its counterpart in the sixteenth edition, and there is a substantial table of values. Also revised is the section on Biochemical Analysis, which, however, is not intended as more than a summary for the assistance of students.

The 32 pages listing proprietary names of drugs, with their corresponding approved names, will help to clarify some of the confusion promoted by the multiplicity of names so often given to modern remedies.

The above are only a few of the many valuable features contained in this well bound and modestly priced volume published under the auspices of the Council of the Pharmaceutical Society of Great Britain and revised by the Staff of the Department of Pharmaceutical Sciences.

NOEL L. ALLPORT

L'ANALYSE CHIMIQUE ET PHYSICO-CHIMIQUE DE L'EAU: EAUX NATURELLES; EAUX USÉES. By J. RODIER. Second Edition. Pp. xiv + 358. Paris: Dunod. 1960. Price NF 48.

This useful and up-to-date volume is a complete revision of a practical handbook first published in 1950. The emphasis is chiefly on the analysis of natural waters, but considerable space is devoted to polluted waters. Short bibliographies are included in each chapter. Practical details are given for the more important physico-chemical determinations: density, pH, rH, electrical conductivity, temperature, turbidity, colour and suspended matter. The topical character of the book is well illustrated by the inclusion of methods for determining radium, radon, and α -, β - and γ -radioactivity in waters. Chemical tests include those for acidity, alkalinity, hardness and gaseous constituents; the various forms of nitrogen and sulphur; the commoner cations (Ba, Ca, Sr, Li, Mg, K, Na, Sb, Cd, Cr, Co, Hg, Pb, Cu, Al, Fe, Mn, Zn and U); anions (F, Cl, Br, I, borate, silicate, cyanide, phosphate and polyphosphates); also As, Se, V and phenols. Short notes are included on the interpretation of the analytical results.

For polluted waters, details are given for the determination of B.O.D., permanganate value and synthetic detergents, and two putrescibility tests are described. Methods for controlling the sterilisation of water are also included.

There is little to criticise in this valuable book. English readers may find the expression "mg %₀₀" a little puzzling without some explanation. In the account of the B.O.D. test, no mention is made of the use of a mineralised water for dilution purposes. Other notable omissions are tests for nickel and tin (found in plating wastes), titanium (paper-mill wastes), silver (plating and photographic wastes) and ferrous iron (mine waters and pickle liquors).

Dr. Rodier's book is well printed and bound and can be warmly recommended to all workers in the field indicated by the title.

L. KLEIN

Publications Received

- CHEMICAL INSTRUMENTATION: A SYSTEMATIC APPROACH TO INSTRUMENTAL ANALYSIS. By HOWARD A. STROBEL. Pp. xviii + 653. Reading, Mass., U.S.A., and London: Addison-Wesley Publishing Company Inc. 1960. Price \$9.75; 74s.
- ADVANCES IN APPLIED MICROBIOLOGY. Volume 2. Edited by WAYNE W. UMBREIT. Pp. xii + 384. New York and London: Academic Press Inc. 1960. Price \$12.00; 86s.
- FLUIDIZATION AND FLUID-PARTICLE SYSTEMS. By FREDERICK A. ZENZ and DONALD F. OTHMER. Pp. x + 513. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1960. Price \$15.00; 120s.
- THE INTERNATIONAL ENCYCLOPEDIA OF PHYSICAL CHEMISTRY AND CHEMICAL PHYSICS. Editors-in-Chief: E. A. GUGGENHEIM, J. E. MAYER and F. C. TOMPKINS. Topic 6: The Kinetic Theory of Gases. Volume 1, Elements of the Kinetic Theory of Gases. By E. A. GUGGENHEIM, M.A., Sc.D., F.R.S. Pp. xii + 92. Oxford, London, New York and Paris: Pergamon Press Ltd. 1960. Price 17s. 6d.
- DIE QUANTITATIVE BESTIMMUNG DER ALKALOIDE IN DROGEN UND DROGENZUBEREITUNGEN. By Prof.Dr.rer.nat. OTTO-ERICH SCHULTZ and Prof.Dr.rer.nat. FELIX ZYMALKOWSKI. Pp. x + 295. Stuttgart: Ferdinand Enke Verlag. 1960. Price (paper) DM 73; (cloth boards) DM 77.
- CHEMICAL PLANT INSTRUMENTATION: SOME NOTES ON THE USE OF MEASURING INSTRUMENTS. Pp. viii + 55. London: The Association of British Chemical Manufacturers. Price (members) 6s.; (non-members) 7s. 6d.
- THE CHEMISTRY OF YTTRIUM AND SCANDIUM. By R. C. VICKERY, D.Sc., Ph.D. Pp. viii + 123. Oxford, London, New York and Paris: Pergamon Press Ltd. 1960. Price 40s.
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- GAS CHROMATOGRAPHY ABSTRACTS 1959. Edited by C. E. H. KNAPMAN; Assistant Editor: C. G. SCOTT. Pp. x + 164. Sponsored by The Gas Chromatography Discussion Group (Associated with the Hydrocarbon Research Group of the Institute of Petroleum). London: Butterworths Scientific Publications. 1960. Price 42s.
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- TEXTBOOK OF PHARMACOGNOSY. By T. E. WALLIS, D.Sc., F.R.I.C., F.P.S., M.I.Biol., F.L.S. Fourth Edition. Pp. xii + 640. London: J. & A. Churchill Ltd. 1960. Price 50s.
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Nuclear Science Series: NAS-NS-3010.
- THE PERIODIC TABLE. By D. G. COOPER, B.Sc., F.R.I.C. Second Edition. Pp. x + 93. London: Butterworths Scientific Publications. 1960. Price 7s. 6d.
- ANALYTICAL STANDARDS FOR LABORATORY CHEMICALS AND REAGENTS 1960. Sixth Edition. Pp. 302. Dagenham: May & Baker Ltd. 1960. Gratis.
- PRINCIPLES OF CHEMICAL THERMODYNAMICS. By CHARLES E. REID. Pp. xii + 306. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1960. Price \$7.80; 63s.
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- HOMOLYTIC AROMATIC SUBSTITUTION. By G. H. WILLIAMS. Pp. viii + 133. Oxford, London, New York and Paris: Pergamon Press Ltd. 1960. Price 45s.
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HANDBUCH DER PAPIERCHROMATOGRAPHIE. Edited by I. M. HAIS and K. MACEK. Band II
BIBLIOGRAPHIE UND ANWENDUNGEN. Pp. xxiv + 726. Jena, Germany: Veb Gustav
Fischer Verlag. 1960. Price DM 44.

Reprints of Review Papers

REPRINTS of the following Review Papers published in *The Analyst* are available from the Assistant Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1 (not through Trade Agents). Orders MUST be accompanied by a remittance for the correct amount made out to The Society for Analytical Chemistry.

- "The Analysis of Synthetic Detergents," by W. B. Smith (February, 1959). Price 2s. 6d.
- "The Infra-red Analysis of Solid Substances," by G. Duyckaerts (April, 1959). Price 2s. 6d.
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- "Zone Melting, with Some Comments on its Analytical Potentialities," by E. F. G. Herington (December, 1959). Price 5s.
- "The Analytical Chemistry of Zirconium," by G. W. C. Milner and J. W. Edwards (February, 1960). Price 5s.
- "Light-scattering Methods for the Chemical Characterisation of Polymers," by F. W. Peaker (April, 1960). Price 5s.
- "The Determination of Vitamin B₁₂," by W. H. C. Shaw and Christine J. Bessell (June, 1960). Price 5s.
- "Analysis of Organo-silicon Compounds, with Special Reference to Silanes and Siloxanes," by J. C. B. Smith (July, 1960). Price 5s.
- "Flame-photometric Methods in Metallurgical Analysis," by John A. Dean (this issue; available shortly). Price 5s.

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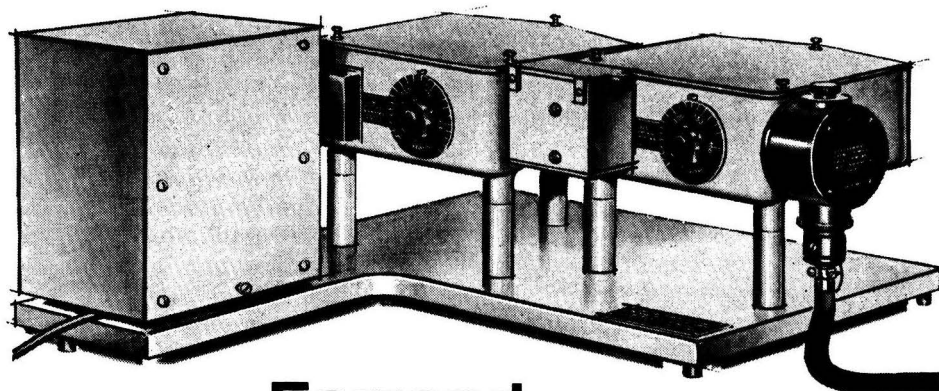
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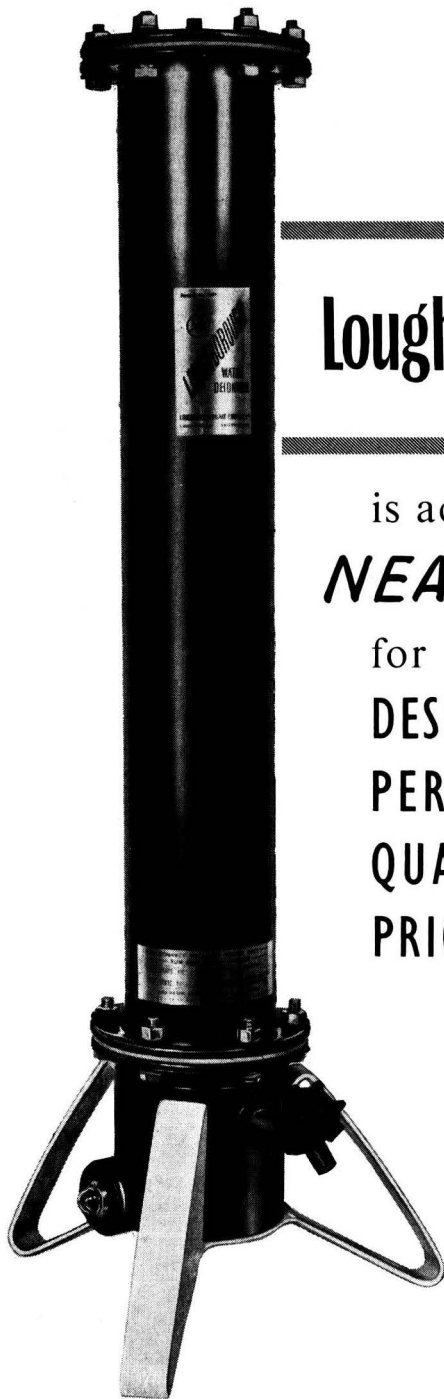
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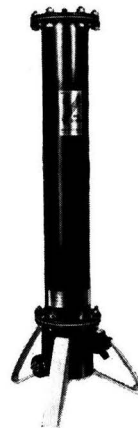
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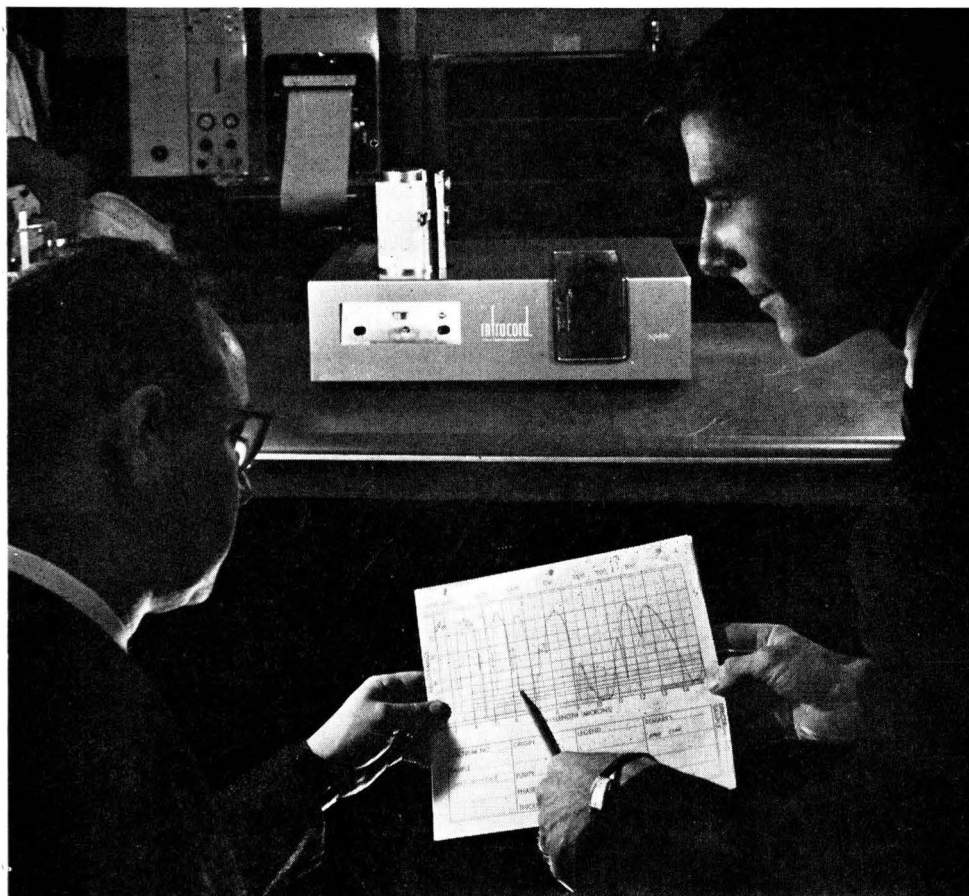


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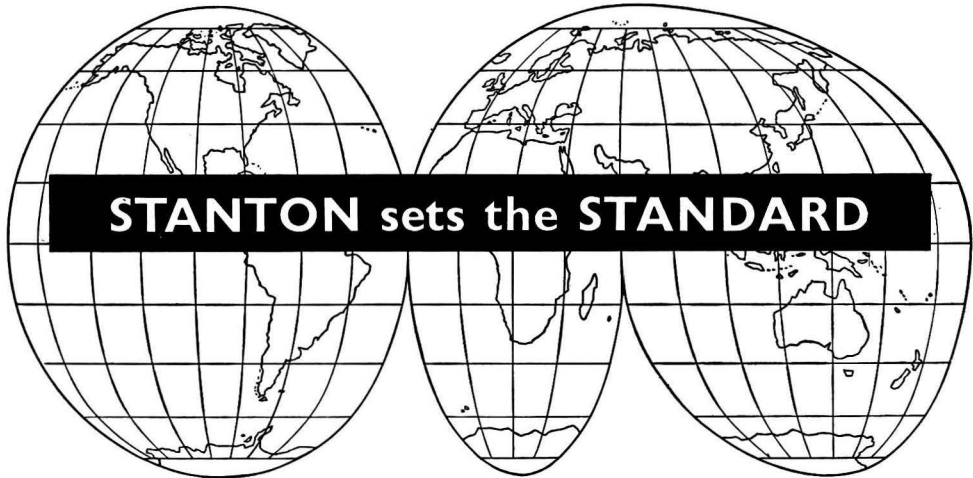
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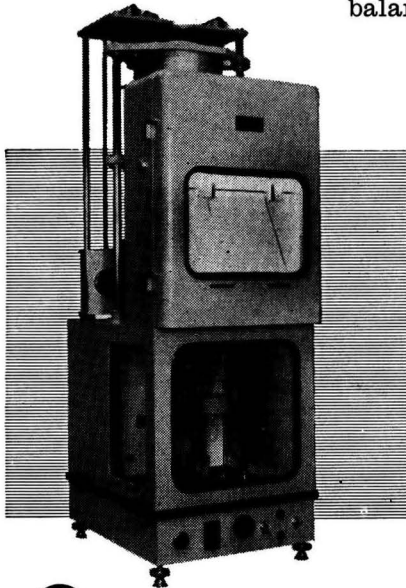
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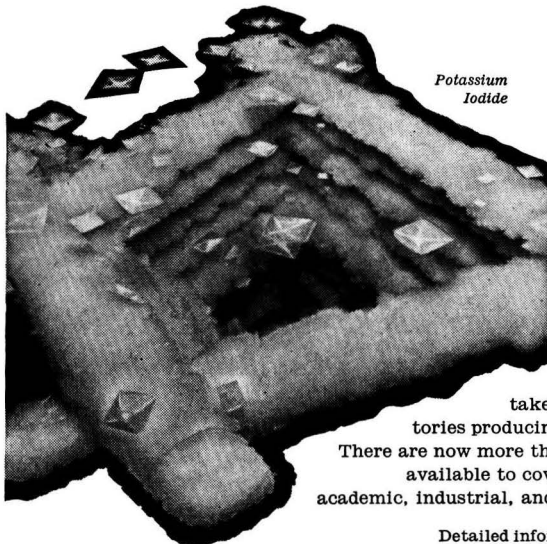
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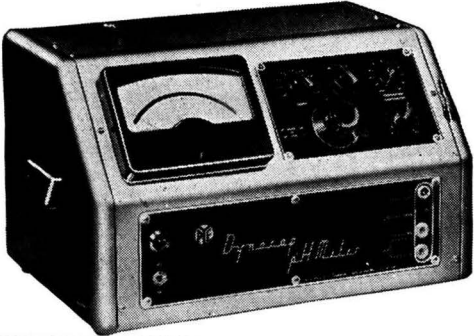
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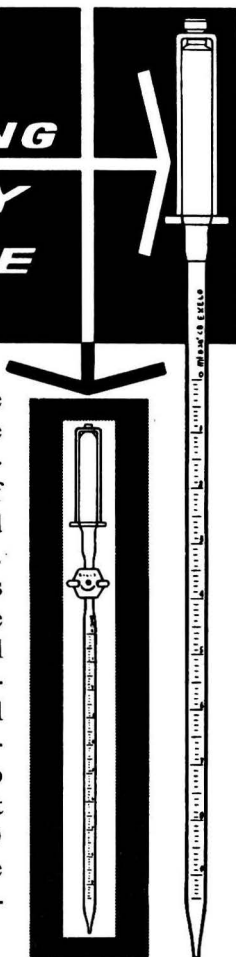
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