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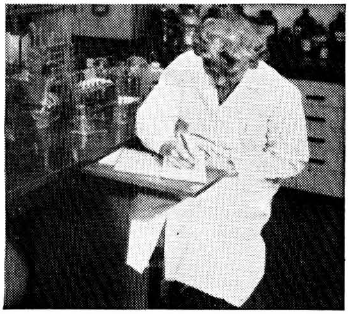

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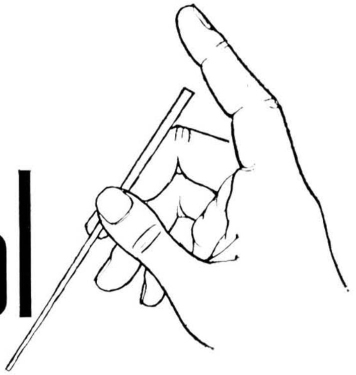

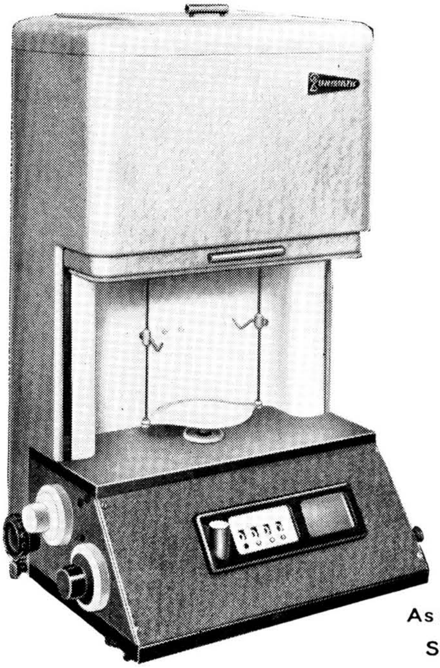

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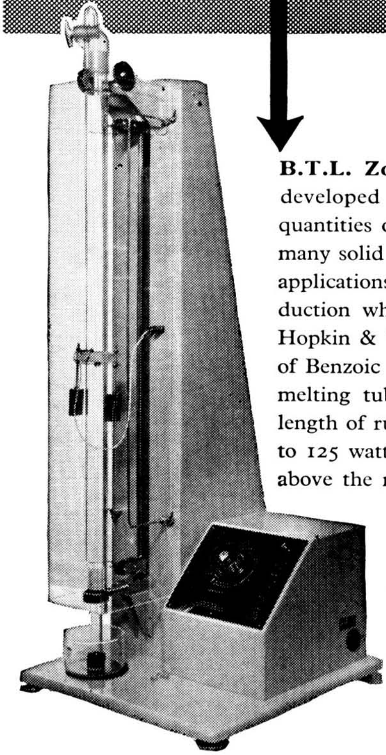

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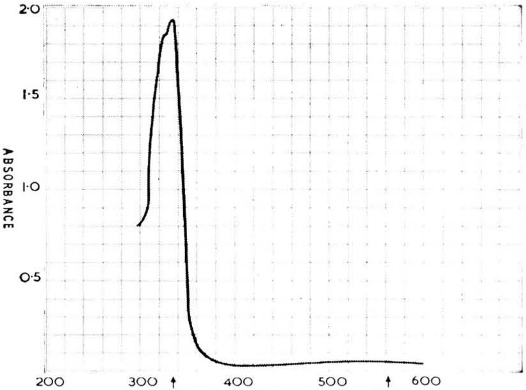


Fig. 1

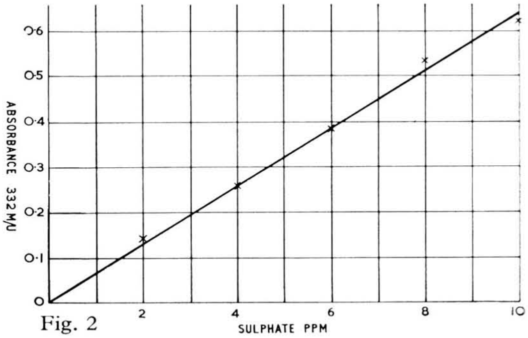
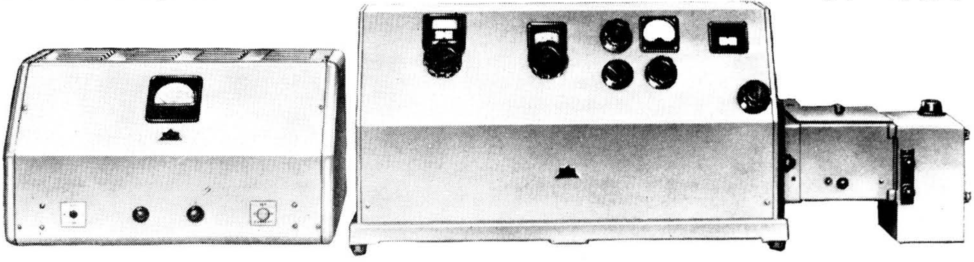


Fig. 2

* *Bertolacini J. R., and Barney J. E., Anal. Chem.* 30, 202 (*1958*)



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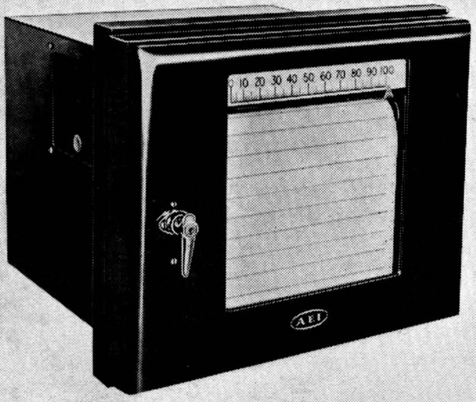

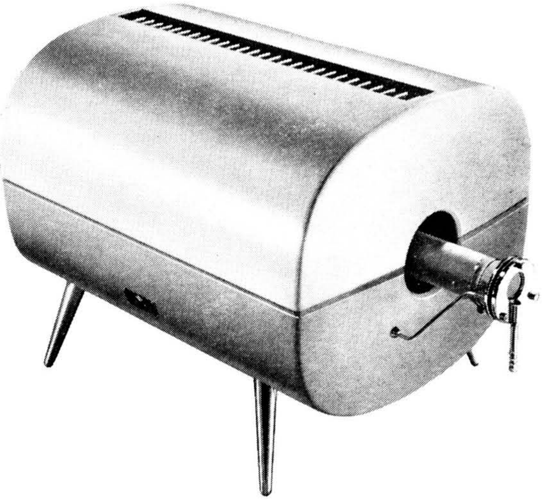

1400°c

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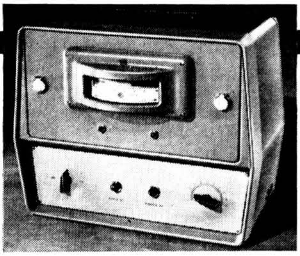

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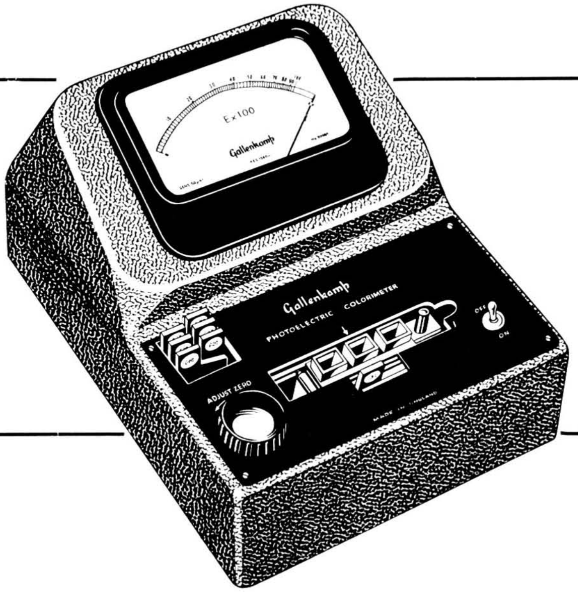
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Philip Roy Ashurst, B.Sc. (Lond.); David Robert Crudgington, D.L.C.; Frederick Nixon.

DEATH

WE record with regret the death of

Charles William Cornwell.

NORTH OF ENGLAND SECTION

THE twenty-fifth Summer Meeting of the Section was held at the Imperial Hotel, Llandudno, from Friday, May 18th, to Monday, May 21st, 1962.

The Chairman of the Section, Mr. J. Markland, B.Sc., F.R.I.C., presided over an Ordinary Meeting at 10.15 a.m. on Saturday, May 19th, at which George B. Manning, B.Sc., M.B., Ch.B., F.R.I.C., gave a lecture entitled "Some Experiences in Forensic Science."

On the Saturday evening the party saw the show at the Grand Theatre, Llandudno, and on the Sunday afternoon made a coach tour, taking tea at Betws y Coed.

MIDLANDS SECTION AND PHYSICAL METHODS GROUP

A JOINT Meeting of the Midlands Section and the Physical Methods Group with the Birmingham and Midlands Section of the Royal Institute of Chemistry was held at 6.15 p.m. on Tuesday, May 1st, 1962, at the Northampton College of Technology, St. George's Avenue, Northampton. The Chair was taken by the Chairman of the Physical Methods Group, Dr. W. Cule Davies, F.R.I.C.

The subject of the meeting was "Recent Developments in Semiconductor Analysis" and the following papers were presented and discussed: "The Spectrographic Determination of Some Impurities in Gallium Arsenide," by J. H. Oldfield, F.R.I.C., and D. L. Mack; "Radioactivation Analysis of Semiconductors," by D. Hazelby, A.R.I.C. (see summary below); "The Determination of Carbon and Silicon in Gallium Arsenide," by A. C. Tyrrell, J. M. Page and D. C. Newton, B.Sc.

The meeting was preceded at 2.15 p.m. by a visit to the Analytical Section of the Caswell Research Laboratories, Plessey Co. Ltd., Towcester.

RADIOACTIVATION ANALYSIS OF SEMICONDUCTORS

MR. D. HAZELBY defined radioactivation analysis as the determination of a trace impurity by measurement of the radioactivity induced when it was bombarded with suitable nuclear particles. Up to the present time irradiation in the thermal neutron flux of an atomic reactor had proved to be the most useful method of activation. Samples were irradiated together with a small amount of the element being determined—the standard—and the concentration of the impurity was calculated by comparing the activity of the standard with that of the impurity, which was chemically separated from the sample.

It was usually necessary to separate the impurity being determined from the sample and the other impurities. The manipulation of the sub-microgram amounts involved was achieved by the addition of milligram amounts of inactive carriers. These mixed with the radioactive impurities and became chemically indistinguishable, so permitting separations to be made by simple chemical procedures such as precipitation or distillation.

By irradiating samples in a reactor such as BEPO at Harwell, in which a neutron flux of 10^{12} neutrons per sq. cm per second was available, it was possible to determine more than 20 elements with a sensitivity of better than 10^{-10} g, and more than 60 elements with a sensitivity of better than 10^{-7} g. Even better sensitivities could be achieved by making irradiations in the core of the DIDO reactor, where the neutron flux was 10^{14} neutrons per sq. cm per second.

A limitation was imposed on activation analysis by the cross-section of the sample material, since the radioactivity of a sample of high cross-section would be too great to be handled in the average radiochemical laboratory. However, in many instances determinations could be made by the use of impurity isotopes with a longer half-life than that of the sample, when the activity of the sample could be allowed to decay before the analysis was begun.

A recent development in activation analysis has been the use of portable neutron generators that produced 14-MeV neutrons. A notable application of this radiation had been to the determination of oxygen. As 14-MeV neutrons could also be moderated to thermal energies, it seemed possible that, although a pile irradiation would still be necessary for the highest sensitivity, such a generator could be used for routine laboratory analyses.

MIDLANDS SECTION AND MICROCHEMISTRY GROUP

A JOINT Meeting of the Midlands Section and the Microchemistry Group was held at 6.30 p.m. on Friday, May 11th, 1962, at the Luton College of Technology, Park Square, Luton. The members of the Microchemistry Group were welcomed to the Midlands Section by the Chairman, Dr. H. C. Smith, M.Sc., F.R.I.C., Dip.Ed., who then introduced Mr. C. Whalley, B.Sc., F.R.I.C., Chairman of the Microchemistry Group, who took the Chair.

The subject of the Meeting was "The Status of Trace Metal Determinations" and the following papers were presented and discussed: "Ferrous Metals," by B. Bagshawe, F.I.M., M.Inst.F.; "Non-ferrous Metals," by W. T. Elwell, F.R.I.C.; "Distribution in Soils," by H. H. Le Riche, Ph.D.

The meeting was preceded at 2 p.m. by a visit to the laboratories, Rothamsted Experimental Station, Harpenden.

A Study of the Determination of Oxygen in Beryllium by Vacuum Fusion*

By M. R. EVERETT and G. E. THOMPSON

(*U.K.A.E.A., Production Group, Springfields Works, Salwick, Preston, Lancs.*)

The relatively high vapour pressure of beryllium metal at the temperature required for the vacuum fusion reduction of its oxide by carbon can lead to severe "gettering" and loss of part of the carbon monoxide evolved in the reaction. Low and variable results for oxygen will be obtained unless the design of the vacuum fusion apparatus and operating technique are carefully controlled.

These design and operating factors have been investigated in part by fitting a recording ionisation gauge to the furnace head of a micro platinum-bath vacuum fusion apparatus, thus monitoring the progress of vacuum fusion reactions and the rate of removal of gas from the furnace head. The gauge has been used under static and dynamic gas conditions to investigate the gettering action of beryllium evaporated during the vacuum fusion of a sample. Other factors investigated include: the pumping speed characteristic of the gas-transfer diffusion pump; the vacuum fusion temperature; the enclosure of samples in capsules; the use of a tin addition with the sample; sample size and the method of sampling.

The importance of these various factors is discussed, and suggestions are made with regard to apparatus design and operating technique. The most important factors are the maintenance of high pumping speeds for high pressures at the crucible and the use of capsules to enclose all samples.

BERYLLIUM is probably the most difficult metal to which the direct application of the vacuum fusion technique for determining oxygen has been seriously applied. Beryllia is stable thermodynamically and requires reaction temperatures of about 1800° C for rapid reduction by carbon. At these temperatures, the vapour pressure of the metal is approximately 13 mm of mercury and evaporated metal can recombine with or "getter" part of the evolved carbon monoxide, thus resulting in low and variable results for oxygen.

The first successful application of the vacuum fusion technique to the determination of oxygen in beryllium was reported in 1955 by Gregory and Mapper,[1] who used a micro-scale (2·5 g) platinum bath operating at 1860° ± 20° C. Sample weights were in the range 2 to 10 mg (approximately), and a minimum ratio of 50 to 1 was specified for the platinum - beryllium content of the bath. Gregory and Mapper's apparatus[2] was designed to provide high pumping speed in the region of the crucible and so minimise gettering losses. Substantially quantitative recovery of oxygen was obtained from the vacuum fusion of known amounts of beryllia, either as such or added to samples of beryllium powder.

In attempting to apply Gregory and Mapper's original technique to the determination of oxygen in samples of beryllium in general, many laboratories have experienced considerable difficulty, usually obtaining variable results that tend to decrease in level in sequence in a series of samples. In 1957, Booth, Bryant and Parker[3] reported that they had not been able to apply the vacuum fusion technique to the determination of oxygen, but, in later papers, Booth and Parker[4,5] reported that satisfactory results were obtained by adding 60 to 70 mg of tin with each sample of beryllium and succeeded in extending the application to samples containing as little as 0·01 per cent. of oxygen. Their apparatus and technique were similar to those used by Gregory and Mapper, but they used a final reaction temperature of 1950° ± 20° C. The precise function of the added tin was not entirely understood, and Parker[6] has suggested that it helped the beryllium to form an alloy with the platinum bath and also reduced gettering by covering the beryllium films evaporated on the walls of the furnace tube.

Still[7] has used a steel bath operating at 1600° to 1650° C for analysing beryllium samples enclosed in steel capsules of low gas content, and has drawn attention to the forms in which oxygen can be present in a sample. He distinguishes between the well crystallised oxide

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* Presented at the meeting of the Society on Thursday and Friday, October 5th and 6th, 1961.

detectable by X-ray methods found in cast metal, and the less stable forms associated with the surface of samples that cannot be detected by X-ray analysis. Recoveries of oxygen from samples of hard-fired beryllia mixed with graphite ranged from 64 (theoretical for BeO) to 35 per cent. w/w, the lower figures being obtained on the larger sample weights.

In contrast to the comparatively low temperatures used by Still,[7] Kallman and Collier,[8] who unsuccessfully tried platinum as a flux for the closely related inert-gas fusion method, finally employed a crucible temperature of 2600° C for the reaction of beryllium samples enclosed in copper-foil capsules, together with a nickel flux.

Wide ranges of reaction temperatures, sample weights, bath materials, apparatus and operating techniques have so far been used for carrying out what is basically a simple process—that of reducing beryllia by carbon and the quantitative collection of the carbon monoxide evolved.

The work described here has been carried out in an attempt to provide a little more information on the various mechanisms associated with the vacuum fusion reaction, and thus reduce some of the emphasis on personal craftsmanship that has tended to be associated with vacuum fusion methods.

APPARATUS

GENERAL—

The design of the Springfields apparatus is based, in general, on that used by Gregory and Mapper,[2] but major changes have been made in the furnace head and the gas-analysis system. The present form of apparatus has been in use since 1956 for the analysis of zirconium, niobium, uranium, thorium, etc., and, for use with beryllium, a second apparatus was built with a Perspex cabinet enclosing the furnace head and the first gas-transfer pump.

The apparatus is shown in Fig. 1.

A two-dimensional layout has been used, and all glassware is rigidly mounted on an asbestos-cement back board 6 feet long by 4 feet high, which is mounted clear of the floor on a framework of slotted aluminium angle. All controls required during analysis are mounted at the front of the apparatus, and gas samples are handled by mercury cut-offs and lines made from 10-mm bore glass tubing. Glass taps are used only in backing lines. A sinter-disc mercury-column manostat controls the level to which all mercury cut-offs are lowered, except the atmospheric cut-off, which allows the furnace head and gas-transfer pumps to be at atmospheric pressure for sample reloading while retaining the remainder of the apparatus under vacuum.

CRUCIBLE ASSEMBLY—

The graphite crucible is $\frac{5}{8}$ inch in diameter and $1\frac{3}{16}$ inches long externally and has an internal cavity $\frac{5}{16}$ inch diameter and $\frac{3}{4}$ inch deep, which is closed by a $\frac{7}{16}$-inch diameter spherical lid seating upon a 45° chamfered edge. The crucible is surrounded by a 0·04-inch thick radiation shield, $\frac{13}{16}$ inch external diameter and 2 inches long, which has 4 vertical slots, $1\frac{7}{8}$ inches long and spaced at 90°, to minimise radio-frequency power absorption. Both crucible and radiation shield are mounted on a $\frac{1}{4}$-inch diameter threaded graphite support peg, shaped to fit a $\frac{1}{4}$-inch bore extension of the silica furnace tube. The graphite components are machined from either Acheson AGT or Morgan EY9166 grades of graphite and all are vacuum de-gassed at 2200° C for several hours in a separate large apparatus before use. This process serves to remove any traces of volatile materials from the graphite and greatly reduces de-gassing time, film formation and apparatus blank value in the micro vacuum fusion apparatus. In the design described above, the object has been to minimise the weight of graphite and so rapidly obtain a low blank rate.

The crucible is designed for use with a 3·5-g platinum bath. This amount of platinum cannot be reduced without risk of the molten platinum failing to cover the bottom of the crucible completely. If this were to happen, some samples might miss the platinum bath, and these would almost certainly react incompletely.

FURNACE HEAD—

The crucible assembly is heated by a 15-kW 450-kc/s medium-output impedance radio-frequency (R.F.) generator, the 3-turn $1\frac{3}{4}$-inch diameter work coil of which is immersed in the Perspex water jacket surrounding the silica furnace tube. This arrangement is designed to ensure a low R.F. voltage across the work coil and so minimise the possibility of gas or metal vapour ionising in the furnace tube. If ionisation were to occur, considerable amounts of gas would be adsorbed on, or desorbed from, the walls of the furnace tube and the determinations would be completely invalid.

The spherical lid of the crucible and a silica sample-dropping funnel are raised or lowered by molybdenum and Nichrome-tape suspension wires attached to short pieces of silver-steel rod whose positions are controlled in their respective glass side-arms by annular magnets

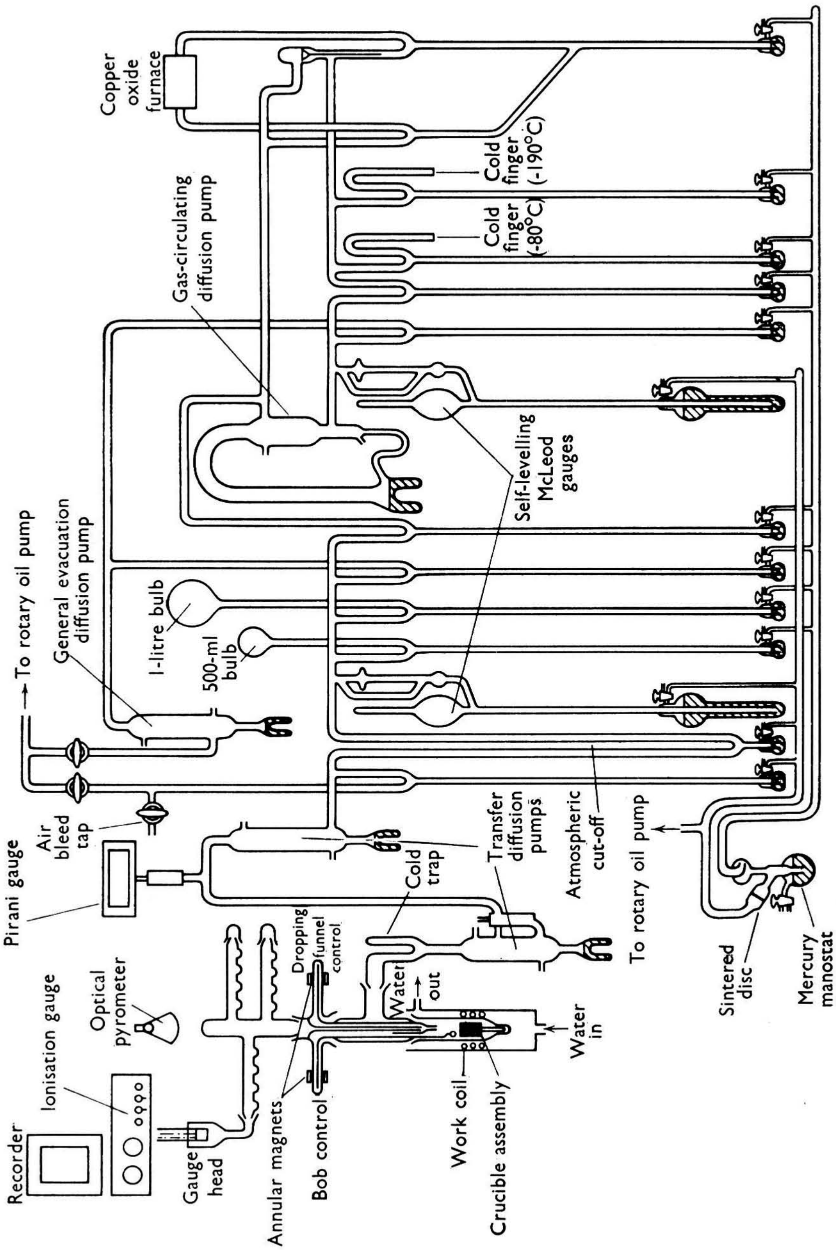

Fig. 1. Vacuum fusion apparatus

exterior to the vacuum system. The spherical lid "centres" on the crucible under the influence of the radio-frequency field.

The 1½-inch diameter silica furnace tube, which has no side-arm, is connected via an Apiezon W40 waxed B34 standard taper joint to a glass furnace head that accommodates up to 12 samples and 3 to 10 g of platinum beads in individual depressions in the side-arms. Samples or platinum are moved in the side-arms by magnetically operated pusher rods so that, when the crucible lid is removed, they fall down the central fixed sample-dropping tube and lowered silica extension funnel into the crucible.

GAS TRANSFER AND MEASUREMENT SYSTEM—

The furnace head is evacuated by an Edwards GM2 2-stage mercury diffusion pump via an in-line cold trap filled with liquid air. The conductance between the crucible and the throat of the diffusion pump is about 3 litres per second and the effective pumping speed at the crucible is 2·6 litres per second for pressures up to at least 30 μ. To provide optimum backing conditions at all times the GM2 pump is backed by a 1-inch 2-stage mercury diffusion pump and volumes of gas are measured in the calibrated backing volume (485 ml) of this second pump by a self-levelling McLeod gauge reading pressures up to 1000 μ. Additional calibrated volumes can be added when necessary by lowering the mercury cut-offs connected to two calibrated bulbs (500 and 1000 ml).

GAS-ANALYSIS SYSTEM—

A low-pressure circulating system is used, in which pressure measurements are made at constant volume by a self-levelling McLeod gauge. The activated hot copper oxide oxidation selective cold-trap system is employed to remove hydrogen and carbon monoxide in sequence from the sample. This sytem has been used in preference to the "oxygen addition" system, which is considered to be slow and cumbersome and the palladium-diffusion Hopcalite-oxidation system, which, although it has been much used, can suffer from side reactions or poisoning of the palladium and possible adsorbtion - desorbtion processes taking place on the Hopcalite.

An aliquot or the whole, but not more than 300 μl, of the gas sample is transferred to the calibrated backing volume (225 ml) of the gas-analysis circulation pump, which is modified according to the recommendations of Naughton and Uhlig[11] to have a backing volume independent of pressure and heater wattage fluctuations.

The gas can be circulated—

(*a*) over activated copper oxide[12] at 350° C,

(*b*) in contact with a cold trap at −80° C,

(*c*) in contact with a cold trap at −190° C or

(*d*) by any combination of (*a*), (*b*) and (*c*)

by operating the requisite mercury cut-offs.

Hydrogen is removed from the system by (*a*) and (*b*) above, and carbon monoxide is removed as carbon dioxide by (*a*) and (*c*) above. The residual gas is nitrogen. After each stage the gas circulation is stopped and the pressure is measured in the calibrated backing volume of the pump.

All operations are carried out according to a predetermined time schedule, which requires a total of 8 minutes for the three-component analysis.

EXPERIMENTAL

PLATINUM CAPSULE TECHNIQUE—

The first vacuum fusion technique used for analysing beryllium followed Gregory and Mapper's[1] general principles and recommendations, except that all samples, whether of massive metal, swarf, powder or flake, were enclosed in platinum capsules. Sample weights were in the range 2 to 10 mg, and the 100-mg platinum capsules were made from short lengths of platinum tubing having a bore of 0·1 inch and a wall thickness of 0·002 inch. A 3·5-g platinum bath was operated at 1900° C and the total addition of beryllium was limited to 1 part in 50 by weight, as recommended. Precision in general was fairly satisfactory; a coefficient of variation of ±10 per cent. was obtained at the 0·4 per cent. oxygen level. The use of capsules was found to be essential for massive samples, otherwise much lower and more variable results were obtained.

TIN ADDITION TECHNIQUE—

Experiments carried out by Booth and Parker's technique,[4] in which 60 to 70 mg of tin of low gas content were added with the beryllium sample to a 3·5-g platinum bath, and the temperature was raised first to 1400° C and finally to 1950° ± 20° C, showed a small increase in level of results for oxygen, but no improvement in precision. It was noted that, at temperatures just above the stipulated range, high results for oxygen and hydrogen were obtained early in a series of samples. This effect was found to be caused by excessive evaporation of tin, which released adsorbed water from the cooler regions of the silica furnace tube; the water then reacted with the hot graphite crucible to form hydrogen and carbon monoxide. It was considered that a positive bias might be operating with the tin addition technique and compensating for gettering losses rather than minimising or eliminating them. From this point of view the platinum capsule technique was preferred, since its main object was to avoid the full evaporation of pure beryllium by enclosing the sample in platinum. The dissolution of the sample in the platinum bath was then more rapid and the period of maximum gettering was reduced both in intensity and time.

TABLE I

EFFECT OF GAS-TRANSFER PUMPING CHARACTERISTIC ON THE VACUUM FUSION DETERMINATION OF OXYGEN IN BERYLLIUM

	Edwards GM2 pump	Suspect pump
Pumping characteristic at crucible	2·6 litre per second for all pressures up to 30 μ	1 litre per second for pressures up to 1 μ (above this pressure the pump stalled)
Oxygen found (results in sequence by platinum capsule technique at 1950° C), % w/w	0·43, 0·40, 0·46, 0·44, 0·38, 0·39, 0·39, 0·45	0·26, 0·06, 0·07, 0·04

PUMPING SPEED—

From the physical properties of beryllium metal and beryllium oxide it is obvious that, at the high temperature required for vacuum fusion reaction, some evaporation of beryllium, and therefore a gettering action, must take place. The gettering action can be regarded as a pump operating in the region of the crucible in competition with the effective pumping speed of the gas-transfer and collection system at that point.

It is obviously advisable to have some information on the characteristics of these two competing pumping systems if the vacuum fusion analysis of beryllium is to be understood. The need for a high pumping speed to remove gases rapidly from the region of the crucible is mentioned in many papers, but is rarely put in quantitative terms.

The effective pumping speed of the gas-transfer diffusion pump at the crucible was measured by fitting a dummy Pyrex-glass furnace tube that has two side-arms level with the mouth of the crucible. To one side-arm was connected a needle valve and source of dry air and to the other a McLeod gauge. The pumping speed at the crucible was measured at pressures up to 30 μ by using the normal gas-collection system of the apparatus to determine the rate at which gas was passing through the system. Measurements were made for two pumps: (*a*) an Edwards GM2 and (*b*) a pump suspected to have a poor performance. The pumping speed characteristics and corresponding vacuum results obtained when in use are shown in Table I.

The results obtained from these two experiments show that the evaporated beryllium, once deposited on the walls of the furnace tube, plays little further part in the gettering process. If the film remained active, progressively lower results in the run would also be obtained with the Edwards GM2 pump. Blank determinations carried out during both runs were normal. Therefore most of the gettering action is largely irreversible and must take place during the evaporation of beryllium; it must take place in the vapour phase or at the moment of deposition, *i.e.*, the gettering is of the "dispersal" rather than the "contact" type.

Chemical determinations have shown that about 15 per cent. of the beryllium added to a platinum bath is evaporated during a run of eight 5-mg samples in platinum capsules allowed to react at 1950° C. This amount of beryllium is far in excess of that required to react with all the gas evolved during a normal run of samples.

Also, it was found that samples having high and low oxygen contents could be analysed alternately in a run without cross effect when a high-performance pumping system was used; this would be impossible if evaporated beryllium films remained appreciably active.

By using the same sample and technique, a further series of results was obtained with the diffusion pump having a poor pumping characteristic. Sample weights of beryllium powder ranging from 3 to 7 mg and also, at intervals in the series of samples, portions of a zirconium sample known to contain 1000 p.p.m. of oxygen were analysed. The results are shown in Table II.

TABLE II

DETERMINATION OF OXYGEN IN BERYLLIUM AND ZIRCONIUM BY VACUUM FUSION WITH THE APPARATUS HAVING POOR GAS-TRANSFER PUMPING CHARACTERISTIC

Sample weight, mg	3·6	35·0	3·2	6·6	24·0	4·4	3·0	33·0
Oxygen found in beryllium, p.p.m. ..	4600	—	3350	900	—	620	2350	—
Oxygen found in zirconium, p.p.m. ..	—	1070	—	—	970	—	—	1040

The results for oxygen (and nitrogen) were correct within the experimental error for the zirconium samples, but, apart from the first sample, the results for oxygen in beryllium were low and variable. These results again indicate that the film of beryllium evaporated from a sample does not significantly influence the results for later samples.

When a pumping system of good performance was used it was found possible to analyse samples of the zirconium containing 1000 p.p.m. of oxygen simultaneously with 5 mg of beryllium of low gas content. The samples were contained in a platinum capsule, the platinum bath was heated to 1950° C and 90 to 100 per cent. of the oxygen content of the zirconium was recovered. This experiment indicated that gettering losses must be small under these conditions.

The factors influencing gettering are therefore the rate, and length of time, of beryllium evaporation and also the instantaneous gas pressures existing in the furnace tube during evaporation of beryllium. The gas pressure in the furnace tube will depend on the rate of sample reaction and, not only the pumping speed at the crucible, but also the maximum rate of gas transfer of the pumping system; *i.e.*, the pumping system must operate at high pressures without loss of speed and the volume of the furnace head must be small. Lower results are obtained when a system that pumps at a rate of 1 litre per second but stalls at 1 μ is used than when a slower system that pumps at a rate of 0·25 litres per second and can operate at pressures up to 30 μ is used.

RECORDING IONISATION GAUGE—

A recording ionisation gauge was used to observe the pressures generated in the vacuum fusion furnace tube during the reaction of beryllium samples. Recorder scans for beryllium powder samples are shown in Fig. 2 and for a sample of massive metal in Fig. 4 (*d*). The samples were enclosed in platinum capsules together with 5 mg of de-gassed tin, and reaction was at 1850° C in a 3·5-g platinum bath.

The samples were transferred to the platinum bath at 800° C, and the time that the radio-frequency power was applied was taken as a datum point. The platinum bath, for example, melted 30 seconds after application of power, and therefore the temperature at this point was about 1700° C; this provided a rough relation between the time scale and temperature.

Three distinct phases of reaction were found for samples of massive metal, and these can be seen in Fig. 4 (*d*). The first occurs when the sample enters the crucible at 800° C, and is caused by release of adsorbed water and decomposition of hydroxide on the surface of the sample. The second occurs about 10 seconds after application of power and probably coincides with the melting of the sample, completion of the decomposition of hydroxide and perhaps some reduction of the less stable surface oxide in contact with graphite or carbides on the surface of the platinum bath. The third takes place much more slowly, after the platinum bath has melted, and is thought to be the reduction of crystalline beryllia present in the massive metal.

For powder samples the first and second phases of reaction are predominant, because practically the whole of the oxygen content of a beryllium powder is associated with the surface as an oxide - hydroxide layer; in fact, the oxygen content of powder milled from ingot appears to be inversely related to the particle size.

Swarf samples are intermediate in character between massive and powder samples, again depending on the increase in surface area produced during the turning or drilling operation.

STATIC GETTERING EXPERIMENTS—

Small samples (3 to 4 mg) of beryllium of low gas content (200 p.p.m. of oxygen; $<$10 p.p.m. of hydrogen) were analysed in a platinum bath at 1900° C in a static system of large volume (3 litres). The recording ionisation gauge was used to monitor pressure changes in the system for 3 kinds of sample.

(*a*) Beryllium sample alone.

(*b*) Beryllium sample in a 100-mg platinum capsule.

(*c*) Beryllium sample with 10 mg of de-gassed tin added.

The curves obtained are shown in Fig. 3.

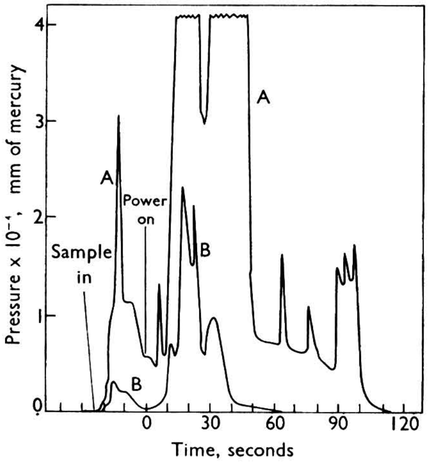

Fig. 2. Pressure generated in furnace head by reaction of samples of beryllium and 5 mg of tin in platinum capsule: curve A, 20 mg of beryllium; curve B, 2·2 mg of beryllium

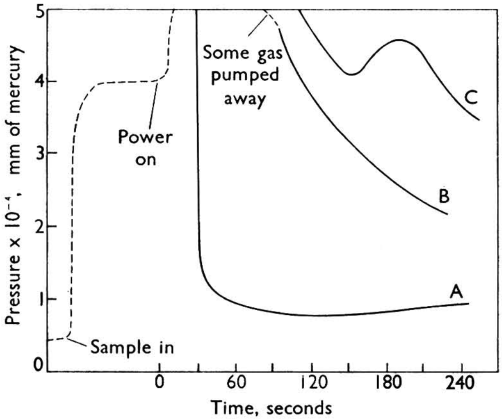

Fig. 3. Curves showing gettering by samples (3 to 4 mg) of beryllium allowed to react in a static system: curve A, beryllium alone; curve B, beryllium in a 100-mg platinum capsule; curve C, beryllium *plus* 30 mg of added tin

It is to be noted that for beryllium sample (*a*) the gas evolved during reaction was rapidly and almost completely gettered 30 seconds after applying power to the crucible; this coincides with the melting of the platinum bath. Sample (*b*) showed no rapid gettering and some gas had to be pumped away to bring the gauge on to the recorder scale. For sample (*c*), with the added tin, it was not necessary to pump gas away, and the pressure fell for about 150 seconds after applying power to the crucible, when either a further period of reaction in the crucible or a period of desorption of gas from the walls of the furnace tube took place. For this sample of beryllium the reaction is usually complete 30 seconds after applying power to the crucible (see Fig. 4) and about 10 μl of gas are evolved. Under the reaction conditions of sample (*a*) this gas was gettered rapidly in not more than 1 second. This gettering action occurring at several microns pressure indicates a fast rate of pumping, probably similar to the normal pumping speed available at the crucible in a vacuum fusion apparatus.

The rapid gettering phase is evidently much reduced in (*b*) and reduced to a lesser extent in (*c*). This can be explained in terms of the more rapid dissolution of the sample in the platinum bath in (*b*) and the reduction in vapour pressure by partial pressure effect. The explanation of (*c*) is proably more complex. Tin is not likely to assist much in the dissolution of the beryllium sample in the platinum bath, because, according to White and Burke,[13] beryllium is not soluble in tin in the liquid phase and, according to Elliot and Kramer,[14] the solubility is only 0·21 per cent. at 1200° C. On the other hand, the tin may initiate a surface reaction with the sample or lower the melting-point of the platinum bath and also, when evaporated from the crucible, desorb physically adsorbed gas from the walls of the silica furnace tube.

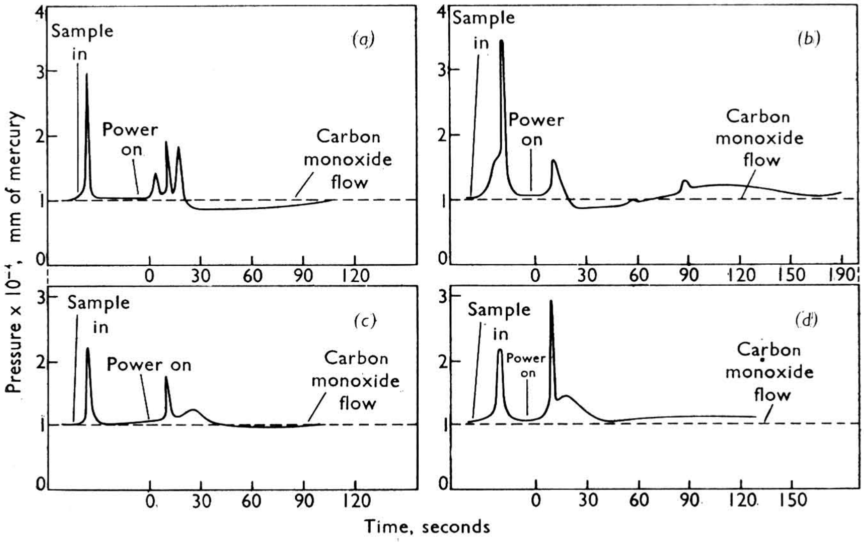

Fig. 4. Curves showing gettering by 5-mg samples of beryllium allowed to react in a constant flow of carbon monoxide: (*a*) beryllium alone; (*b*) beryllium *plus* 10 mg of added tin; (*c*) beryllium in 100-mg platinum capsule; (*d*) beryllium *plus* 10 mg of added tin in 100-mg platinum capsule

DYNAMIC GETTERING EXPERIMENTS—

To investigate the magnitude and duration of the gettering effect under conditions as close to normal as possible, samples (5 mg) of massive beryllium of low gas content (200 p.p.m. of oxygen; <10 p.p.m. of hydrogen) were analysed in the normal manner, except that a constant small bleed of dry carbon monoxide was passed through the furnace and pumping system. Ionisation gauge recorder scans were obtained for—

(*a*) beryllium sample alone,

(*b*) beryllium sample with 10 mg of tin added,

(*c*) beryllium sample in a 100-mg platinum capsule and

(*d*) beryllium sample with 10 mg of added tin in a 100-mg platinum capsule.

The scans are shown in Figs. 4 (*a*), (*b*), (*c*) and (*d*).

By carrying out the temperature cycle of the furnace with no sample in the tube, no change in carbon monoxide pressure was recorded by the ionisation gauge. Therefore, any pressure changes obtained during reaction of the sample were real and, in particular, any recorded pressures below 10^{-4} mm of mercury can only be caused by gettering effects.

From Fig. 4 it can be seen that marked gettering occurred when a sample of beryllium was analysed; about 10 per cent. of the carbon monoxide was removed over approximately 60 seconds. The effective pumping speed of the GM2 mercury diffusion pump was 2·6 litres per second, therefore the gettering action under these conditions has a pumping rate of about 0·26 litres per second. For samples in platinum capsules (see Fig. 4 (*c*)) no significant gettering was observed, presumably because the formation of a pool of pure beryllium was avoided and dissolution of the sample was more rapid. When the beryllium was analysed in the presence of tin without a capsule (see Fig. 4 (*b*)) the reaction proceeded in a sporadic manner and gettering took place for the first 60 seconds much as it did for a beryllium sample alone (see Fig. 4 (*a*)). Over the next 60 to 100 seconds, however, desorption of gas appeared to take place. Evidently the beryllium had dissolved, been fully converted to beryllium carbide and ceased to evaporate appreciably. The tin, which does not form a carbide, continues to evaporate and, on collision with the walls of the furnace tube, desorbs strongly adsorbed gas from the beryllium film or displaces water from the cooler regions of the tube. When beryllium and tin together in a platinum capsule were analysed no significant gettering or desorption of gas was observed (see Fig. 4 (*d*)).

TEMPERATURE—

Apart from the positive bias in results obtained when operating the tin addition technique at temperatures of the order of 1950° C, no significant temperature effect has been found in any other technique over the temperature range 1800° to 1950° C. No advantage was found in raising the temperature in steps to full operating temperature.

Presumably the increased vapour pressure and evaporation of beryllium that arises from the use of a high reaction temperature is in some measure compensated for by the increased rate of dissolution and reaction of the sample in the bath.

CRUCIBLE LID—

Determinations carried out by the platinum capsule technique and with a normal pumping system, but with the spherical lid removed from the crucible, showed that, for a sample of beryllium powder, results ranging from 1500 to 3000 p.p.m. of oxygen were obtained on a sample known to contain 3000 p.p.m. of oxygen. There was a tendency for the larger samples to give the lower results. Low results were also obtained on samples of massive metal when the crucible lid was removed.

BLANK DETERMINATIONS—

Blank determinations are normally carried out at intervals during a run of samples, and the ranges of gas volumes obtained by the various techniques are listed in Table III.

TABLE III

BLANK VALUES FOR VACUUM FUSION APPARATUS

			Blank values for—		
Details of operating conditions	Time, minutes	Temperature °C	hydrogen, µl at 0° C	carbon dioxide, µl at 0° C	nitrogen, µl at 0° C
Crucible only	5	1960	0·25 to 1·0	0·1 to 0·5	0·1 to 0·2
Crucible + 100-mg platinum capsule	5	1960	1·5 to 2·6	0·6 to 2·4	0·2 to 0·4
Crucible + 100-mg platinum capsule + 5 to 10 mg of tin	3	1850	1·0 to 3·0	2·0 to 4·0	0·1 to 0·3
Crucible + 75 mg of tin	5	1950	3·0 to 8·0	10·0 to 15·0	0·4 to 0·7

The tin was de-gassed by heating several hundred grams at 1200° C in a graphite crucible for 5 hours at a reduced pressure of at least 10^{-5} mm of mercury, and allowing the ingot to cool overnight *in situ* under vacuum. All the pieces of tin used for vacuum fusion were freshly cut from the ingot, which was found to contain 50 p.p.m. of oxygen and 40 p.p.m. of carbon.

The platinum tubing used for the capsules was carefully degreased with trichloroethylene, and dried. A blank determination was always carried out on the particular length of tubing used for the capsules for a series of samples. The ends of the capsules were folded over twice, and this seal rendered them powder tight but not air tight.

FORM OF SAMPLE—

A series of runs on samples of a sintered rod, as detailed in Table IV, ranging from 2 to 10 mg were carried out at 1900° C with the GM2 pumping system. Tin was added as 5 mg of the de-gassed metal and the platinum capsules were as described above.

The results in Table IV indicate that, when a series of samples is analysed, the results (see column A) fall in sequence fairly rapidly in the run. When 5 mg of tin are added with each sample and not enclosed in a platinum capsule, the results (see columns B and E) tend to be higher and rather erratic. When the sample is enclosed in a platinum capsule the results (see column D) tend to decrease slowly in sequence in the run. Optimum precision is obtained when both the sample and the added tin are enclosed in a 100-mg platinum capsule (see column C).

TABLE IV

EFFECT OF THE USE OF PLATINUM CAPSULE AND ADDED TIN ON THE DETERMINATION OF OXYGEN IN A SAMPLE OF BERYLLIUM UNDER STANDARD VACUUM FUSION CONDITIONS

Oxygen found				
A (beryllium sample only), p.p.m.	B (beryllium + tin without capsule), p.p.m.	C (beryllium + tin in capsule), p.p.m.	D (beryllium in capsule), p.p.m.	E (beryllium in capsule + tin not in capsule), p.p.m.
4200,	4450,	4100,	3850,	4550,
3550,	4650,	4300,	3950,	6300,
3400,	4900,	4100,	3750,	4400,
3150	6450,	4200,	3500,	5450
	4800	4500,	3400	
		4250,		
		4250,		
		4300		

The results obtained confirm the necessity of preventing the unrestricted evaporation of both beryllium and tin during dissolution in the vacuum fusion bath by enclosure of both in a capsule.

SAMPLE SIZE—

A series of determinations was carried out on samples of from 2 to 29 mg of beryllium powder to investigate the limitation in size of sample imposed by the method under optimum conditions in the apparatus described. The sample with 5 mg of added tin was enclosed in a 100-mg platinum capsule, and reaction was carried out in a 3·5-g platinum bath at 1850° C; the GM2 pumping system was used. The results are shown in Table V.

TABLE V

DETERMINATION OF OXYGEN IN BERYLLIUM BY VACUUM FUSION ON A RANGE OF SAMPLE WEIGHTS

Sample No.	1	2	3	4	5	6	7
Sample weight, mg	2·2	7·2	11·5	20·0	29·3	29·0	3·0
Oxygen found, p.p.m.	5100	5300	5050	5200	5650	5500	5050

The gas evolution curves recorded by the ionisation gauge for samples 1 and 4 are shown in Fig. 2. The results obtained from this range of sample weights are in agreement within experimental error.

If any significant gettering were taking place it would have been expected that the results from the larger sample weights (with the decreased ratio of platinum to beryllium) would have been appreciably lower than those obtained from the small sample weights. This is only found, however, when a poor pumping system is in use or the maximum gas-transfer capacity of a system is exceeded.

The technique employed in this series of determinations and others has been taken as the basis for the recommended method.

SAMPLING—

For samples of powder of <200 mesh it is possible for heterogeneity of the sample to affect the precision of results obtained on micro vacuum fusion samples. If a single one of the largest particles present were of pure beryllia, its contribution alone to a 2-mg sample would be about 250 p.p.m. of oxygen. Heterogeneity of sample becomes less significant for more finely ground powders and still less if the sample particles are of uniform size. It is essential, therefore, to carry out a series of determinations on a powder sample, and, at all stages, to use careful sampling techniques after homogenising the sample. For a good sample a coefficient of variation of ±5 per cent. can be obtained at the 5000 p.p.m. level on sample weights in the range 2 to 10 mg.

Massive samples of beryllium, whether of cast metal or sintered rod, should be broken or machined, and samples of 2 to 10 mg, or up to 50 mg if of very low oxygen content, should be analysed without delay, otherwise oxide - hydroxide formation on the surface of the sample will increase the oxygen content. It is not permissible to take samples of swarf as representative of a massive sample, as the increase in surface area results in gross contamination by surface oxide and hydroxide (see Table VI).

TABLE VI

EFFECT OF SAMPLE PREPARATION ON DETERMINATION OF OXYGEN IN BERYLLIUM BY VACUUM FUSION

Sample	Oxygen found in freshly prepared massive metal, p.p.m.	Oxygen found in aged massive metal, p.p.m.	Oxygen found in swarf, p.p.m.
Sintered rod	4300	4900	5800
Ingot	300	—	3800

OTHER METHODS—

Coleman, Shaw and Todd,[17] who used a fast-neutron activation technique, have confirmed the results for oxygen obtained by the recommended vacuum fusion method on samples of beryllium powder and sintered rod. They have cross related these results to a zirconium standard sample and to silica as a primary standard. The results are shown in Table VII.

TABLE VII

COMPARISON OF RESULTS FOR OXYGEN BY VACUUM FUSION AND FAST-NEUTRON ACTIVATION

Sample	Mean oxygen found by vacuum fusion, % w/w	Mean oxygen found by fast-neutron activation, % w/w
Sintered beryllium rod sample 3	0·41	0·42
Sintered beryllium rod sample 6	0·43	0·42
Sintered beryllium rod sample 9	0·43	0·42
Sintered beryllium rod sample 12	0·41	0·42
Beryllium powder, 300 to 400 mesh ..	0·50	0·51
Standard zirconium sample	0·100	0·102

DISCUSSION OF THE METHOD

THEORETICAL CONSIDERATION—

The mechanism of the vacuum fusion reaction and the application of thermodynamical calculations has been treated at length by Sloman, Harvey and Kubaschewski.[15] The basic reaction is—

$$BeO_{(solid)} + C \longrightarrow CO_{(gas)} + Be_{(liquid)} \qquad (1)$$

and from the free-energy change in this reaction the equilibrium pressure of carbon monoxide can be calculated for a given temperature. Further favourable free-energy changes are associated with the two other reactions that occur—

$$Be_{(liquid)} + Pt_{(liquid)} \longrightarrow PtBe_{(solution)} \qquad (2)$$

$$Be_{(liquid)} + C \rightleftharpoons Be_2C \qquad (3)$$

The free-energy changes in reactions (2) and (3) are small, and, as Sloman *et al.* indicate, equation (1) is the most important. It should be noted however that equation (3) is reversible; beryllium carbide dissociates appreciably at temperatures of the order of 1800° C, and this dissociation pressure of beryllium vapour is approximately an order lower than the vapour pressure over beryllium metal at the same temperature.

The equilibrium pressure of carbon monoxide for equation (1) and the vapour pressure of beryllium have been calculated from the data tabulated by Kubaschewski and Evans[10] for temperatures of 1600°, 1800° and 2000° C; the results are shown in Table VIII.

Gregory and Mapper,[1] who used data tabulated by Kubaschewski and Evans,[9] obtained a value of $3{\cdot}2 \times 10^{-3}$ mm of mercury for reaction (1) at 1860° C; this value has also been quoted by Kallman and Collier.[8] Parker[6] has quoted a value of 5×10^{-3} mm of mercury for reaction (1) at 1900° C. All these pressures previously quoted appear to be low by a factor of about 1000, and when published created the impression that extremely high temperatures were required for the vacuum fusion analysis of beryllium. From the values shown in Table VIII, it can be seen that temperatures of the order of 1800° C should be practicable for the vacuum fusion reduction of beryllia by carbon. Temperatures lower than 1600° C have an advantage in the lower vapour pressure of beryllium, with the consequent reduced evaporation or gettering, but the reaction will tend to be slow and incomplete because of the small equilibrium pressure of carbon monoxide.

TABLE VIII

EQUILIBRIUM PRESSURES OF CARBON MONOXIDE AND VAPOUR PRESSURES OF BERYLLIUM FOR VACUUM FUSION REACTION AT 1600°, 1800° AND 2000° C.

Temperature, °C	Equilibrium pressure of carbon monoxide, mm of mercury	Vapour pressure of beryllium, mm of mercury
1600	0·068	1·95
1800	1·47	13·5
2000	18·1	66·0

BATH MATERIALS—

Thermodynamics provides a theoretical basis for the practicability of a reaction but no information on the rate of reaction. If, for example, a cube of pure beryllia were placed in a graphite crucible maintained at 1800° C *in vacuo*, then from purely thermodynamic considerations the reaction should reach completion. In practice, however, very little reaction would occur, because the surface of the cube in contact with the crucible would be converted to beryllium carbide and the rate of reaction would be limited primarily by the rates of diffusion of carbon, etc., through the carbide layer.

The essential function of a vacuum fusion bath material is to dissolve the sample and allow any oxides the sample contains to react with dissolved carbon in the bath, thus providing a liquid phase reaction. If the rate of reaction is to be fast, the bath must remain fluid at all stages; any increase in viscosity will result in a reduction in the rate of reaction because of decreased diffusion rates. The viscosity of the bath will be increased if the metal forms a solid carbide or dissolves excessive amounts of carbon, thereby accumulating a layer of carbide or graphite crystals at the surface. For this latter reason a vacuum fusion bath should not be heated above the temperature at which it is to operate. Accumulation of metal carbides from the samples will also affect viscosity and therefore the total number of samples analysed in a bath should be limited. McDonald, Fagel and Balis[16] have examined the classical steel bath with regard to bath viscosity, and published photographs to demonstrate this point. Steel is not an ideal vacuum fusion bath material because, at temperatures above 1600° C, it rapidly becomes viscous owing to carbide formation. This causes incomplete reaction of samples and a progressively rising blank value unless the samples are enclosed in steel capsules or steel having a low gas content is added with the sample to improve temporarily the viscosity of the bath. Alternatively, a volatile metal, such as tin, can be added or the bath can be forcibly stirred, either mechanically or electromagnetically by the use of a low-frequency (10 kc/s) generator. Almost all difficulties reported with a steel bath are connected with incomplete reaction because of bath viscosity. The effect is often mistaken for gettering or lack of reaction temperature.

Platinum has almost ideal properties as a vacuum fusion bath material. It does not form a solid carbide, but conveniently dissolves about 1 per cent. of carbon at temperatures of the order of 1800° C. Also, it will dissolve most metals, is a noble metal and has a low vapour pressure. Its only slight disadvantage is its high melting-point of 1769° C, although it melts in graphite at 1734° C.

GENERAL—

A sample of beryllium is normally transferred to the vacuum fusion crucible at about 800° C or lower. Any water adsorbed on the oxide - hydroxide surface layer of the sample will be released and react with the graphite crucible. It can be seen from Figs. 2 and 4 that this reaction occurs immediately after the sample has entered the crucible. When the radio-frequency power is switched on, the crucible temperature rises and the beryllium sample melts; its vapour pressure and rate of evaporation increase until the vacuum fusion bath melts, probably at about 1700° C for platinum. At this point the evaporation of beryllium will be a maximum. The vapour will come into contact with the hot graphite crucible and lid by collision, and formation of beryllium carbide will reduce the effective vapour pressure to some extent. This evaporated beryllium will getter a proportion of the gas in the furnace head, probably by dispersal gettering, and thus it is suggested that the length of trajectory of the atoms of beryllium vapour before deposition on the walls of the silica furnace tube, and also the area of evaporated film formed, will be of consequence with regard to severity of gettering.

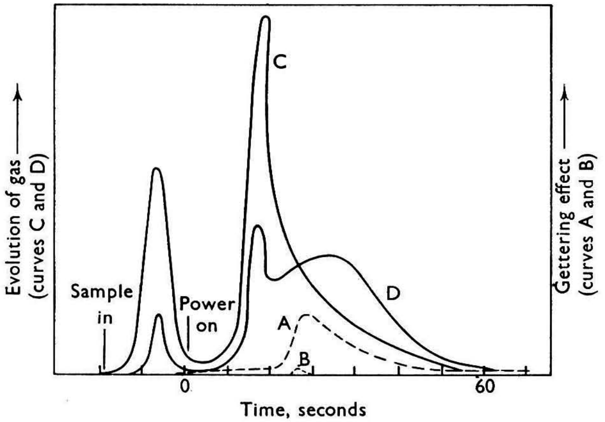

Fig. 5. Diagrammatic representation of evolution of gas and gettering curves: curve A, probable gettering effect of sample of beryllium not enclosed in platinum capsule; curve B, probable gettering effect of sample of beryllium in platinum capsule; curve C, evolution of gas from sample of powdered beryllium; curve D, evolution of gas from sample of beryllium massive-ingot material

A deep crucible of narrow bore will provide the maximum number of collisions with hot graphite for a beryllium atom before it can escape from the crucible. The crucible lid must be a good fit for the same reason. The silica furnace tube should be of as small a bore as practicable to minimise trajectory length and area of film formed.

The evaporating beryllium will getter a proportion of the gas present in the furnace tube, depending upon the pressure of the gas. The gas at this stage probably originates from further decomposition of hydroxide and also contact reaction of oxide on the pool of molten beryllium with the surface of the platinum bath perhaps aided by the presence of tin.

The sample will then dissolve in the bath and the rate of beryllium evaporation will decrease progressively until the beryllium metal is converted to carbide. The beryllia in the sample will be reduced by the dissolved carbon at a rate depending on its particle size, *i.e.*, crystalline beryllia in ingot metal will probably react over a longer period of time than the thin film of beryllia associated with the surface of powder samples. The static gettering experiments indicate that maximum gettering occurs 30 seconds after application of power in the Springfields apparatus and the dynamic experiments that a progressively falling gettering rate operates for up to a further 60 seconds at a pumping speed of about 0·25 litres per second.

The gettering curve therefore appears to consist of a maximum, probably followed by a roughly exponential fall, and the suggested form of this curve is shown in Fig. 5 (curve A).

The intensity of the gettering maximum will be much reduced by the enclosure of the beryllium sample in a capsule, thus avoiding the formation of a pool of pure beryllium on the surface of the bath. The suggested form of this gettering curve is shown in Fig. 5 (curve B).

A pumping system of slow speed or one with a limited maximum throughput carries with it two penalties—

(*a*) increased pressure in the furnace tube and

(*b*) increased time of residence of gas in the furnace tube.

Both these effects will greatly increase the volume of gas gettered. These considerations must be related to the sample size and gas content and the size of sample must be restricted in proportion to the pumping capacity of the gas-transfer system.

The throughput of the gas-transfer pump will increase proportionally with pressure. For a given rate of evaporation of beryllium the efficiency of the getter pump will also increase in proportion to pressure. Therefore, if a larger sample of beryllium is analysed, it would be expected that a lower result would be obtained because the effective size of the getter pump has been increased in relation to the gas-transfer pump. The results in Table V show, within experimental error, no reduction in oxygen level with increasing weight of beryllium sample. From this it is deduced that the gettering error has been substantially overcome by the apparatus and operating technique described. The fast-neutron activation results obtained by Coleman, Shaw and Todd[17] confirm this view (see Table VII).

Some aspects of the action of the added tin are still obscure. The tin may initiate surface reaction of the sample earlier and may, in some way not understood, compete with the evaporating beryllium and reduce the efficiency of the dispersal gettering of the beryllium by decreasing the number of collisions of carbon monoxide and beryllium. It does appear, however, to desorb carbon monoxide, which is physically adsorbed on the evaporated beryllium as shown in Fig. 4 (*b*). Less desirable though, it also desorbs water from the walls of the furnace tube, giving rise sometimes to a positive bias in results, and also, when considerable amounts of beryllium and tin have been evaporated, makes the furnace tube very temperature sensitive. Any change in temperature results in adsorption or desorption of gas. It is considered therefore that any tin added with a sample should be small; about 5 mg is recommended. To provide a constant final reaction temperature the power setting of the radio-frequency generator should not be disturbed during a run. Control should be only by means of the ON - OFF controls.

Ideally, samples should be as small as possible and the temperature of reaction as low as possible. These two factors, together with high pumping performance and the use of capsules, will almost eliminate gettering errors, although a practical compromise has to be made.

With this picture of the mechanism of gettering during a beryllium vacuum fusion analysis in mind, it is possible to indicate the design and operating factors that will result in reasonably accurate and precise results.

RECOMMENDED METHOD

The more important factors in the recommended vacuum fusion technique are summarised below.

DESIGN OF APPARATUS—

(*a*) The crucible assembly should be of previously de-gassed graphite and of small size (see p. 516).

(*b*) The crucible should be deep internally and have a well fitting lid.

(*c*) The work-coil voltage should be low (to avoid ionising the gas or metal vapour).

(*d*) The volume of the furnace tube should be small (200 ml) and provide a short trajectory and small deposition area for evaporated beryllium.

(*e*) The volume of the furnace head sample arms and pumping line should be small (600 ml).

(*f*) Pumping speed at the crucible should be high (2·5 litres per second or more) and maintained at high pressure (up to 30 μ) to provide a high throughput of gas.

OPERATING TECHNIQUE—

(*a*) The platinum charge for the crucible should be of correct size (3·5 g for the crucible described above).

(*b*) Sample weights: 2 to 10 mg for powder, swarf or flake and 5 to 30 mg for massive metal, according to gas content.

(*c*) The sample weight should be restricted, so that the total gas evolved ($<400\ \mu l$) is well within the capacity of the pumping system.

(*d*) Not more than 12 samples or 100 mg of beryllium should be analysed in a 3·5-g platinum bath.

(*e*) All samples should be enclosed, together with 5 mg of de-gassed tin, in 100-mg platinum capsules.

(*f*) The crucible should be at about 800° C when the sample is inserted, and the final operating temperature should be 1800° to 1850° C.

(*g*) The time for gas collection should be 3 minutes.

(*h*) The blank value should be determined on a platinum capsule made from the centre portion of the length of tubing used for the samples and containing 5 mg of de-gassed tin; the test should be carried out mid-way through the series of samples.

(*i*) The power setting of the radio-frequency generator should not be altered during a run.

The method outlined above has been used without difficulty for beryllium samples having oxygen contents ranging from 0·1 to 3·0 per cent. w/w and it is considered that the lower limit of usefulness could be extended to 0·01 per cent. w/w. For a single determination at the 0·4 per cent. w/w oxygen level, a coefficient of variation of ±3 per cent. can be obtained on a homogeneous sample.

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REFERENCES

1. Gregory, J. N., and Mapper, D., *Analyst*, 1955, **80**, 230.
2. ——, ——, *Ibid.*, 1955, **80**, 225.
3. Booth, E., Bryant, F. J., and Parker, A., *Ibid.*, 1957, **82**, 52.
4. Booth, E., and Parker, A., *Ibid.*, 1958, **83**, 241.
5. ——, ——, *Ibid.*, 1959, **84**, 546.
6. Parker, A., Proceedings of Symposium on Analytical Chemistry of Beryllium, Blackpool, 1960, *P.G. Report* 171(S), H.M. Stationery Office, London, 1961.
7. Still, J. E., *in* "Determination of Gases in Metals," *Special Report No.* **68**, The Iron and Steel Institute, London, 1960.
8. Kallmann, S., and Collier, F., *Anal. Chem.*, 1960, **32**, 1616.
9. Kubaschewski, O., and Evans, E., "Metallurgical Thermochemistry," Butterworth-Springer Ltd., London, 1951, p. 305.
10. ——, ——, "Metallurgical Thermochemistry," Second Edition, Pergamon Press Ltd., London, 1956, pp. 331 and 322.
11. Naughton, J. J., and Uhlig, H. H., *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 750.
12. Walter, D. I., *Anal. Chem.*, 1950, **22**, 297.
13. White, D. W., and Burke, J. E., "The Metal Beryllium," American Society for Testing Materials Washington, D.C., 1955, p. 563.
14. Elliot, R. O., and Kramer, E. M., U.S. Atomic Energy Commission Report AECU-3022, New York, 1952.
15. Sloman, H. A., Harvey, C. A., and Kubaschewski, O., *J. Inst. Met.*, 1952, **80**, 391.
16. McDonald, R. S., Fagel, J. E., jun., and Balis, E. W., *Anal. Chem.*, 1955, **27**, 1632.
17. Coleman, R. F., Shaw, R. S., and Todd, R., personal communication.

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The Determination of Carbon in the Less Common Metals and in Highly Alloyed Stainless Steels*

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The combustion process in the determination of carbon has been considered with respect to the satisfactory evolution of carbon dioxide into the gas stream. The conclusion has been reached that the most satisfactory combustion conditions for general application are those in which a fluid melt is produced and maintained by the addition of a suitable flux. The need for a sufficiently high temperature to maintain such a fluid melt has led to the use of high-frequency induction heating as an alternative to the normal resistance furnace.

DEVELOPMENTS in modern engineering technology, and in particular that of the production of nuclear energy, have stimulated considerable interest in the long-standing problem of determining carbon in metals. Several metals previously rarely encountered have become important; so also has a new range of highly alloyed stainless steels and alloys for use at high temperature. The use in nuclear reactors of carbon dioxide as a coolant gas and of graphite as a moderator are also important factors; both can give rise to "pick-up" of carbon by metals with which they come into contact.

Carbon may be present in a metal in several forms; in solid solution, as free carbon, as a carbide, as carbonate or adsorbed carbon dioxide on the metal surface. In certain circumstances the determination of the amount of carbon present in each of these forms is required, but in most metallurgical problems a knowledge of the total carbon content is sufficient.

The determination of total carbon, by the usual method of combustion in oxygen, comprises two separate processes—

(*i*) The metal must be made to burn in such a way that all the carbon, in whatever form it is present, is set free as gaseous carbon dioxide.

(*ii*) The whole of this carbon dioxide (and none from any other source) must be separated from the excess of oxygen and measured.

The processes of separation and measurement have received much attention in the literature, and several satisfactory procedures are available. Some discussion of these was given in an earlier paper,[1] with a description of the conductimetric method used in the work described here.

This paper presents a discussion of the combustion stage of the determination of carbon in metals based on the authors' experience in examining a wide range of materials. Notes on the combustion procedures found to give satisfactory results are presented, with relevant details of the equipment used.

THE COMBUSTION PROCESS—

Most metals and alloys will burn in oxygen if heated to a sufficiently high temperature. If this is higher than any practicable furnace temperature, a metal can often be made to burn more easily with the help of a flux to dissolve an oxide skin or of an igniter that sets fire to the sample by burning rapidly and causing a local temperature rise.

Unfortunately, mere combustion, even if complete, does not necessarily set free all of the carbon into the gas stream as carbon dioxide. The readiness with which carbon dioxide is released depends on the conditions prevailing in the sample both during and after combustion. These conditions are usually determined by the relationship between the melting-point of the metal oxide and the temperatures involved in the combustion process. If the

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oxide is volatile at the furnace temperature, release of carbon dioxide will be certain and rapid; few oxides, however, behave in this way. With most metals one of the possibilities described below applies—

(*a*) The oxide may melt at a temperature between that of the furnace and that attained during combustion. Transient fusion then takes place, and some carbon can be "locked up" in a relatively large semi-fused mass of oxide. This represents the least favourable possibility; experience shows that in these conditions evolution of carbon dioxide may take up to several hours to complete. Unfortunately, most of the so-called newer metals fall into this category, as do the stainless steels. Combustion temperatures can be extremely high; the surface temperature of iron burning in oxygen at one atmosphere pressure is said to reach 2300° C and that of titanium and zirconium 3000° C or more.[2]

(*b*) The oxide may melt and remain fluid at the furnace temperature. Convection stirring will then ensure a rapid transfer of carbon dioxide to the gas phase. Lead and copper are two good examples; iron, with its oxide melting above 1500° C, is a borderline case.

(*c*) The oxide may not melt at all. Oxide formed in this way would be of a powdery nature and diffusion of carbon dioxide into the gas stream would be reasonably rapid. The heat of combustion of most metals is too high for this often to occur. Tungsten behaves in this way if the furnace temperature is not too high.

From a consideration of these possibilities it is clear that release of carbon dioxide will be made much easier if, in a combustion, some fluxing material can be added to make the whole mass thoroughly fluid at the furnace temperature. It is our experience that such conditions are much the most satisfactory, and efforts are always made to apply this principle of a completely fluid melt.

In any particular instance the choice of flux and the amount required are determined by a number of factors, several of which are closely inter-related—

(*i*) *Nature of the sample*—The flux must be capable of producing a wholly fluid melt with the oxide of the sample metal.

(*ii*) *Carbon content of the sample*—The sample weight used must contain sufficient carbon for reasonable precision of measurement.

(*iii*) *Sensitivity of the measurement*—The more sensitive the measurement, the smaller the sample weight needed; smaller sample weights lead to the possibility of greater flux-to-sample ratios, and hence to more effective fusion.

(*iv*) *Carbon content of the flux*—This contributes a proportion of the total carbon being measured; if this proportion is too high it naturally imposes a limit on the precision attainable.

(*v*) *Furnace temperature attainable*—Generally, the higher the temperature the better the fluxing action.

(*vi*) *The boat or crucible*—The nature and amount of the flux must be compatible with the resistance to attack of the refractory.

(*vii*) *Method of heating*—Two forms of furnace are commonly employed for the determination of carbon, *viz.*, the normal resistance type and the high-frequency induction furnace. In a resistance furnace the sample is heated by transmission of heat through the furnace tube from a heating element outside it; any sample material placed in the furnace tube in due course assumes the furnace temperature. In an induction furnace the sample is heated by resistance heating in the sample itself, arising from induced electric currents. This transfer of power to the material in the furnace is usually spoken of as "coupling" with the electric field. The amount of power that can be transferred, and thus the temperature reached and maintained, is determined by the nature and amount of the material in the furnace. Provided that conditions are suitable, the temperatures reached in this type of furnace are higher than those readily obtainable in a normal resistance furnace. Most metals couple well, but most oxides do not, so that in an induction furnace, as combustion proceeds and the metal changes to oxide, there is a distinct danger that once the heat of combustion has been dissipated the melt will cool and solidify. For the oxide mass to remain fluid in such a furnace, the flux used must be such that coupling can be maintained throughout. It may also happen that a sample does not in itself provide sufficient coupling for heating to the ignition-point to take place. In these circumstances the flux used must also supply the coupling necessary to initiate the combustion.

FLUXES AVAILABLE—

Having discussed what is required of the flux, it is appropriate to consider the characteristics of the flux materials available and what can be achieved by their use.

We normally use metals rather than oxides as fluxes; their heat of combustion makes them useful as "igniters" and their coupling properties in the induction furnace make possible the burning of samples that alone would not heat up to the ignition-point. In our experience, tin, lead, copper and iron have proved most useful. Tin is an igniter rather than a flux. It is available in a state of high purity and has the merit of a low carbon content (about 5 p.p.m.). It burns readily with the production of considerable heat, but the oxide contributes little or nothing to fluidity or to coupling and the use of tin is therefore mainly confined to the tube furnace. Lead burns to an oxide melting below 900° C and is a good flux for use in the tube furnace; the oxide, like that of tin, shows little or no coupling and this limits its usefulness in the induction furnace. If the lead is heated to bright redness immediately before use, its carbon content can be reduced to about 1 p.p.m. Copper, if treated in the same way as lead, gives an equally low blank value. Copper oxide is fluid at temperatures within the range of the tube furnace, and, as both the metal and its oxide are capable of coupling, it is also eminently suitable in the induction furnace. Iron is superior to copper in coupling and as an igniter, but it has the disadvantage of a high carbon content of at least 20 to 30 p.p.m. The higher melting-point of its oxide makes it less effective than copper as a flux in the tube furnace.

The acidic glass-forming oxides, vanadium pentoxide (V_2O_5) and "boron phosphate" ($B_2O_3.P_2O_5$), are sometimes useful as fluxing additives. Reaction between the metal oxide produced by the burning of the sample and one of these fluxing oxides can lead to the formation of a fusible glass. In our experience these glasses have poor coupling properties and they are of less value in an induction furnace than in a tube furnace. It has been found possible to reduce the carbon content of specimens of both vanadium pentoxide and boron phosphate to less than 10 p.p.m. by pre-heating them in oxygen.

STANDARDISATION—

Calibration of the method of measurement used in the determination of carbon is relatively straightforward, but the problem of deciding whether a combustion procedure has freed all the carbon present in a sample is more difficult. It is not possible to make up true synthetic standards such as are used in wet methods of analysis; added carbon would not necessarily behave in the same way as that already present in a sample.

Over a wide range of ferrous alloys the British Chemical Standards provide reference materials, the carbon contents of which have been determined independently by several analysts. With some of the more highly alloyed stainless steels and with most non-ferrous metals no such convenient standards are readily available. Collaboration with other laboratories interested in similar problems is, however, a useful substitute when it can be arranged. When no means of comparison with other workers' results exists a useful approach has been to try to obtain consistent results with more than one type of flux or more than one combustion procedure. If the results so obtained agree, they are likely to be near the truth. When the results disagree, more confidence is usually placed in the higher figures until another procedure is found that may resolve the difficulty.

The difficulties encountered in the determination of carbon in a particular metal depend not only on the nature of the metal but also on the level of the carbon content. Very high carbon contents are relatively easy to determine. Only small samples are required so that high flux-to-sample ratios can be used, thus minimising combustion problems. The level of the blank value is not significant, but other factors can become important. Great care is sometimes necessary to secure a truly representative sample—weighing must be very accurate—and the calibration of the method of measurement must be carried out with the utmost precision.

Low carbon contents accentuate the difficulties of determination, particularly as the use of large samples is necessary. The central problem then becomes that of reducing the blank value to a sufficiently low and constant figure. This is helped by thorough pre-ignition of the crucible or boat and by suitable choice and treatment of flux.

THE SAMPLE—

There is much accumulated experience, for example in the steel industry, on the methods of preparing metal samples for determinations involving combustions. Much of this experience relates to combustions carried out in refractory boats heated in a tube furnace. In such a procedure it is generally considered that the most satisfactory conditions are those in which the sample, together with any flux used, should be well distributed along the boat. The sample is best present as small chips, and too coarse a particle size or too uneven a distribution of the sample in the boat can lead to incomplete recovery of carbon.

Some of these difficulties become less important when the sample, with a suitable fluxing addition, is burned in a crucible in a high-frequency induction furnace. This difference in behaviour is in part due to the higher temperatures attained in the induction furnace, but a further important factor operates. For a fluxing addition to function satisfactorily adequate contact between the flux and the sample must take place. In a crucible heated in an induction furnace a more complete mixing and stirring together of sample and flux takes place than occurs in a combustion boat heated in a tube furnace. Provided that suitable fluxing is used, the induction furnace permits single pieces of metal to be burned as easily as finely divided material.

For certain of the more reactive metals, in particular beryllium, a different and important limitation has been found to exist. These metals have a high heat of combustion, and, if large samples or large pieces of metal are used, eruptive burning can sometimes occur leading to material being scattered from the boat or crucible. With such metals therefore, we are normally limited to the examination of relatively small weights of well sub-divided metal.

There are some additional considerations that led us to the use of small sample weights for many of our determinations. The limited capacity of a boat or crucible means that, when a large flux-to-sample ratio must be maintained, the sample cannot exceed a certain size.

Perhaps a more compelling reason has been that most of our determinations are in connection with research projects in which the amount of material available for examination is usually small. Arising from the trend towards the use of smaller amounts of sample is an increased chance of revealing inhomogeneity in the material under examination. For purely practical purposes when an average figure is called for this may be a disadvantage; the "good agreement" that can be obtained with samples of from 1 to 5 g is not always found with samples of about 0·1 g. The disclosure of any inhomogeneity should not, however, be without scientific value, and, when it can be demonstrated, the research metallurgist may well have been provided with valuable additional information.

DETERMINATION OF CARBON IN SPECIFIC MATERIALS—

The general problems encountered in the combustion stage of the determination of carbon have been discussed, and it is now appropriate to consider some specific examples. In Table I are shown some of the materials that have been examined with the ranges of

TABLE I

RANGE OF CARBON CONTENTS FOR VARIOUS MATERIALS

Material	Range of carbon content, p.p.m.	Flux used	Furnace used
Molybdenum	0 to 100	Pb	Resistance
Tungsten	0 to 250	—	
Silicon	10 to 50	Pb	
Stainless steels (up to 20/25 and 25/20)	100 to 800	Cu	Induction
Nickel and most alloys (Inconel, Alnico)	10 to 400	Cu	
Nimonic alloys	800 to 1500	Fe	
Zirconium	500 to 1500	Fe	
Uranium	500 to 4000	Fe	
Titanium	200 to 1500	Pb - Cu	
Beryllium	100 to 800	Cu - Fe	

carbon content encountered, the flux used and the type of furnace preferred for each. Some further notes on these materials are given below.

Molybdenum—This gives satisfactory results in the tube furnace without a flux, as the oxide formed is volatile. The volatility of the oxide can, however, be troublesome in that the cooler parts of the combustion tube can become blocked by masses of sublimed oxide. Use of a lead flux permits much of the oxide to be kept in the boat, thus delaying the ultimate choking of the tube.

Tungsten—This also burns well without a flux; the solid oxide formed does not appear to retain carbon.

Silicon—The formation of a tenacious surface film of silica makes combustion difficult, even when the silicon is molten. Use of metallic lead as a flux avoids this difficulty, however, and silicon can then be burned in a tube furnace.

Stainless steels—The more highly alloyed varieties do not burn easily in a normal tube furnace. At the higher temperatures attainable in an induction furnace no difficulty is encountered, and either iron or copper may be used as a flux. Copper is favoured because the low blank value for this material is useful when examining steels of low carbon content.

Nickel—This metal and many of its alloys can be burned under conditions similar to those used for stainless steel. Again, when the carbon content of the metal is low, a copper flux is favoured.

Nimonic alloys—These particular nickel alloys are specially formulated to be resistant to heat and oxidation. They can, however, be burned in the same way as other nickel alloys, although the carbon contents encountered are not usually low enough for the iron blank value to be troublesome.

Zirconium and uranium—Both these metals have been burned successfully with an iron flux in an induction furnace.

Titanium—This metal, if present in a well sub-divided form, can be slowly oxidised without ignition.[1] A more satisfactory method has been described by Imperial Chemical Industries Ltd.[3]; in this a lead flux is used and the metal is burned in a tube furnace. The metals are preheated in argon and the argon is gradually displaced with oxygen. By the use of an induction furnace and a mixed copper - lead flux, we have found it possible to avoid the need for preheating the sample in argon.

Beryllium—This metal combines several of the least desirable features for the determination of carbon. Burning is difficult to induce and when it does take place the reaction is so vigorous that the sample is sometimes scattered explosively. For a fluid melt to be obtained and kept hot, high flux-to-sample ratios are necessary. For a reasonable precision of measurement a low blank value and a relatively high sample weight are desirable, as the carbon content may be as low as 100 p.p.m. Some compromise must be arrived at between these conflicting factors and requirements. The procedure currently favoured is to use a combined iron - copper flux and to get rid of the blank value from the iron before burning the sample. About 1½ g of iron is first put into a crucible and burnt as if it were a sample. The crucible is removed from the furnace after it has partly cooled, a 2-g coil of copper wire and the beryllium sample are added, and the crucible is then returned to the furnace and the determination is carried out. Through the coupling effect of the copper the beryllium is heated to its ignition-point, the copper also burns and the heat produced re-melts the iron oxide; this then assists in the fluxing and coupling of the slag, so that the whole mass can be kept molten for several minutes. Even by this method only about 0·3 g of beryllium can usually be burned satisfactorily, larger sample weights often being scattered by the violence of their own combustion.

Other materials analysed successfully by one or other of the methods described include chromium, cobalt, manganese, tantalum, tantalum carbide and boron carbide.

A low-carbon ferro-silicon-chrome is believed to be one of the most difficult materials to burn by the normal combustion procedures. As a further check on the merits of the procedure we have evolved, two attempts were made to determine the carbon on a sample of this material. The fluxing conditions used were similar to those for the combustion of beryllium, and the weight of the sample taken was 0·5 g. A satisfactory melt was obtained and the two results, indicating a level of carbon of about 200 p.p.m., differed from each other by less than 10 p.p.m.

A study has also been made of the pick-up of carbon by metals exposed to atmospheres of carbon dioxide. By machining off and separately examining successive thin layers from test specimens, the degree of penetration of carbon can be determined, as well as the total amount of carbon taken up. Mild steels, stainless steel, Inconel and zirconium have been examined in this way and the carbon has been determined in layers as thin as 0·002 inch and weighing only a few milligrams.

It is interesting to note that the carbon content of aluminium should for so long have been difficult to determine by a combustion procedure. Wet methods are, in fact, still advocated in the **1961** edition of a standard text-book.[4] By following the principles set out in this paper we attempted the determination of carbon in aluminium by combustion. The method used for examining beryllium was thought the most appropriate, as this metal is similar in many respects to aluminium. Sample weights of from 0·2 to 0·3 g were tried, and a reasonably smooth combustion was obtained, the melt showing adequate fluidity. Several determinations were carried out on AnalaR aluminium, and the few samples examined were shown to have carbon contents of from 50 to 80 p.p.m.

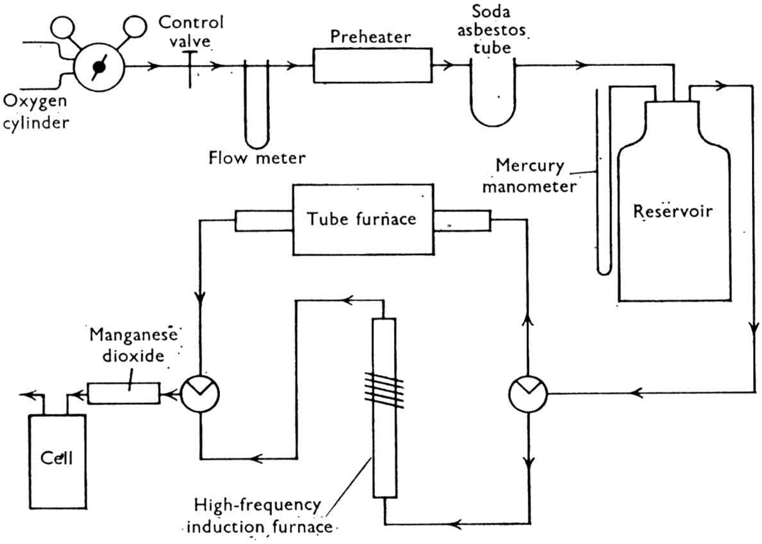

Fig. 1. General arrangement of apparatus and oxygen-flow diagram

EXPERIMENTAL

APPARATUS—

Fig. 1 shows the general arrangement of the apparatus. Both tube and induction furnaces are available and two-way taps permit the use of the same oxygen supply and conductimetric measuring system with either furnace. This arrangement is advantageous in that, while either furnace is opened for loading, the oxygen flow in the conductimetric cell can be maintained through the other.

Much of this equipment has been described previously,[1] but those details that differ significantly from the earlier account are considered below.

Induction furnace—This is a high frequency (10 Mc/s) furnace of American manufacture (Lindberg Engineering Company). The sample is burnt in a small crucible standing on a refractory pedestal inside a vertical silica tube. The furnace is provided with an external variable auto-transformer connected in the input to the main power transformer; the addition of such a control is essential if a wide variety of samples is to be handled.

Among the advantages of the induction furnace are the higher temperature attainable and the fact that this high temperature is developed in the sample itself without having to be transmitted through a furnace tube and combustion tube. A minor advantage is the smaller volume of the combustion tube, which takes less time to sweep; there is, of course, no need to move the sample into a hot zone after sweeping.

Resistance furnace—This is a platinum-wound furnace capable of operating at tube temperatures of up to 1500° C.

CRUCIBLES—

Both Lindberg (fireclay) and LECO, Laboratory Equipment Corporation (zircon refractory) crucibles have been used. We find the LECO variety preferable for the more difficult combustions. Experience has shown that it is essential to heat both types to at least 1100° C before use, and not to allow them to cool for more than 5 or 6 minutes before putting in the sample and transferring to the furnace. The tube furnace is used for pre-ignition of both crucibles and boats, and a check of the completeness of the process can be made.

FLUXES—

Pure tin is purchased in ingot form from Associated Lead Manufacturers Ltd. It is milled with a clean cutter into suitably sized chips, which are washed with acetone in a Soxhlet extractor and dried before use.

AnalaR quality lead foil or lead chips are heated to bright redness in a refractory boat over a Meker burner and poured from this directly into the crucible or boat used for analysis.

High-conductivity copper wire (from Pirelli-General Cable Works Ltd., Southampton) is wound into a suitably shaped coil and heated with a Meker burner to bright redness immediately before use. In the induction furnace it is necessary to use fairly thin wire (about 30 s.w.g.) because thick wire has insufficient electrical resistance to heat up satisfactorily. An alternative method of cleaning copper-wire coils is to etch them in dilute nitric acid, rinse in demineralised water, and dry in a desiccator over soda-lime. It has been found that drying an acid-cleaned coil in the oven can result in its picking-up as much as 20 to 30 p.p.m. of carbon.

The most satisfactory iron at present commercially available is the B.C.S. Pure Iron Granules No. 149/1.

CONDUCTIMETRIC CELL—

The thin bands of platinum foil that formed the electrodes of the original cell[1] have been replaced by thick silver rings, platinum plated and blacked on the outer surfaces, and with silver connecting wire welded to them. The electrode stem is thus much more robust and the contacts more secure. In re-blacking the electrodes it is necessary to connect the cell electrodes together as a combined cathode and to use an auxiliary platinum anode; if the method of periodic reversal of current is employed, a white encrustation of silver chloride may be formed at any pinholes in the plating. The seven fine holes in the gas distributor plate are now drilled to a diameter of 0·006 inch.

PROCEDURE—

Use of the induction furnace—The heating and combustion of a sample in this furnace can be so rapid that it is necessary to take precautions against a reduction of oxygen pressure below that of the atmosphere. After the sample crucible has been put in place the two-way taps are turned to allow the oxygen to flow through the furnace and sweep out any carbon dioxide present. When a steady conductance reading is obtained the oxygen flow is increased and the pressure in the system is made to rise by partially closing the furnace exit tap. Care is taken to manipulate this tap so that the normal flow of gas through the cell is not exceeded. When the reservoir pressure is 4 or 5 inches of mercury, the power is switched on to burn the sample, and the control valve and furnace exit tap are so manipulated that by the time combustion is complete the normal reservoir pressure and flow rate are restored. It may also be necessary, especially if a rather large amount of flux is being used, to reduce the furnace power, by means of the variable auto-transformer mentioned earlier, to prevent overloading of the power circuit. The furnace should remain switched on for several minutes after oxygen has ceased to be absorbed; it is usually left on until nearly all the carbon dioxide has passed into the cell.

Measurement—The sensitivity switch is always kept closed during the whole period of the analysis; this avoids small changes in the cell temperature that can be caused by the operation of the switch and the consequent alteration of the electric current flowing in the cell.

Calibration—The calibration of the conductimetric cell with accurately known amounts of carbon dioxide is carried out as described below. A small amount (5 to 8 mg) of pure calcium carbonate is weighed in a small platinum boat, which is then placed on the refractory pedestal of the induction furnace. The furnace tube is swept with oxygen at the correct flow rate and, when a steady conductance reading is established, the power is switched on at a reduced voltage so that the boat becomes red hot and the calcium carbonate decomposes slowly over a period of 4 or 5 minutes. This method has several advantages. Only the platinum boat itself is heated, there is no disturbance of the oxygen flow such as is caused by opening the tube of the resistance furnace to move the boat, and the heating can be slow enough to avoid any danger of the calcium oxide being thrown out of the boat. A series of six or seven such measurements, spread over the available conductance range, is sufficient to establish the calibration graph; in our experience this remains constant for several months. With the present design of cell the change in the factor with changing conductance of the sodium hydroxide is no longer negligible, as it was in our earlier work; the factor rises by about 2 per cent. as the conductance falls from 11,000 to 7000 micromhos.

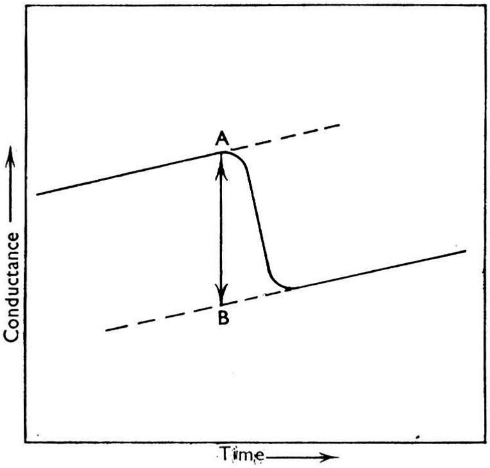

Fig. 2. Conductance - time graph

Calculation—In the measurement of extremely small amounts of carbon some improvement in accuracy can be obtained by plotting conductance readings against time as in Fig. 2. The conductance drop AB caused by the absorption of carbon dioxide from the combustion of the sample is then determined from this graph. The normal slow rise in conductance of the cell due to evaporation should produce a rising straight line graph of the same slope both before and after the combustion. The straightness and parallelism of these lines provides a check on the constancy of the conditions and also on the completeness of evolution of carbon dioxide from the combustion.

Another graphical device that can be most valuable is to analyse several portions, of different weights, from the same sample, and to plot amount of carbon found against sample weight. The results should lie on a straight line, whose intercept on the line of zero sample weight indicates the blank value and whose slope gives the carbon content of the sample. The length of the straight part of the graph is an indication of the range of sample sizes that will give satisfactory results, and the blank value determined in this way is likely to be more accurate than the result of an analysis carried out without a sample. The determination of carbon is one of the many instances for which a true blank determination cannot be performed. With no sample present, the temperature rise due to its combustion does not take place, and the contribution made to the blank value by the boat or crucible and its surroundings may thereby be altered.

RESULTS

The precision of the method of measurement was discussed in an earlier paper,[1] and results obtained with the resistance furnace on British Chemical Standard cast iron and steel samples were reported.

In Table II are shown some results obtained in the induction furnace on a range of B.C.S. materials. With the exception of those on the high-carbon ferro-chrome, these determinations were carried out over the past 3 years in the course of checking combustion procedures. The precision indicated is thus rather less than would be expected from a series of consecutive checks with the same procedure being used for each. The results obtained do show, however, that the use of the induction furnace need not be limited to the more difficult metals. In particular, the results obtained on the cast iron indicate that complete oxidation of carbon to carbon dioxide occurs despite the absence of a red-hot combustion tube.

TABLE II

RESULTS ON SOME B.C.S. MATERIALS

B.C.S. No.	260/1	206	235/1	203/1	204/1
Material	Pure iron	Cast iron	18/8/Ti stainless steel	Low-carbon ferro-chrome	High-carbon ferro-chrome
B.C.S. Average	0·014	2·59	0·042	0·045	4·56
B.C.S. Range	0·013 to 0·015	2·54 to 2·63	0·040 to 0·046	0·038 to 0·049	4·51 to 4·64
Results	0·0136,	2·52,	0·040,	0·047,	4·64,
(Induction	0·0141,	2·59,	0·043,	0·046,	4·57,
furnace	0·0142,	2·63,	0·046,	0·051	4·63,
used for	0·0149,	2·56	0·037,	—	4·54,
all	0·0138,	—	0·040,	—	4·59
determinations)	0·0144	—	0·041	—	—

Examination of the high-carbon ferro-chrome was recently suggested to us as providing a useful check on some of the views put forward in this paper. This material is difficult to burn; further, because of the high carbon content a sensitive assessment of the completeness of the recovery of carbon can be made. Five determinations have been carried out on this material with the results shown in Table II. The samples were burnt in the high-frequency furnace; 2 g of copper were used as a flux and 10 to 20 mg of sample were taken for each determination.

REFERENCES

1. Still, J. E., Dauncey, L. A., and Chirnside, R. C., *Analyst*, 1954, **79**, 4.
2. Harrison, P. L., and Yoffe, A. D., *Proc. Roy. Soc. A.*, 1961, **261**, 357.
3. Imperial Chemical Industries Ltd., "The Analysis of Titanium and its Alloys," Third Edition, I.C.I. Ltd., London, 1959.
4. The British Aluminium Co. Ltd., "Analysis of Aluminium and its Alloys," London, 1961.

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The Identification and Determination of Foreign Phases and Constituents in Metals, with Special Reference to Beryllium*

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The wide scope of analysis required to permit a correlation to be established between the constitution and properties of a metal is discussed. The view is expressed that the state of combination and the manner of distribution of impurities, as well as the amounts present, must be determined. This is shown by reference to analytical work on beryllium; results on several different commercial varieties are reported.

Attention is directed to the presence of several impurity phases, including oxide, carbide, nitride and elemental silicon and aluminium. Two intermetallic compounds have been denoted, but are as yet only incompletely identified.

The value of selective solution methods for isolating some non-metallic constituents is stressed.

ONE of the difficult problems in metallurgy is to discover what influence impurities may have on the properties of a metal. The contribution that analysis can make to the study of this problem has often been confined to the provision of a list of the impurity elements present, with figures denoting the accurately determined concentrations of each. Information of this type is always valuable, and in some circumstances is sufficient in itself to explain all the effects observed.

The interactions between individual impurities and between these impurities and the metal matrix, can lead to the formation of several separate phases. Consequently, the state of combination and the manner of distribution of the impurities present are usually further important factors to be considered. In general therefore, to establish an adequate correlation between the properties of the metal and the impurities it contains, the scope of analysis should be broadened to provide considerably more information than is obtained in the conventional elemental analysis.

In this paper a general analytical study of a series of specimens of beryllium metal is described. Although beryllium is in many respects unusual, the approach adopted in this study could provide a useful pattern for guiding analytical work on other metals.

INVESTIGATION METHODS

There are many techniques of investigation that could be adopted to extend the scope of analysis. Those that promise to provide the most useful information, complementary to that obtained by the well established quantitative methods, are—

(*a*) Optical microscopy.
(*b*) Electron microscopy.
(*c*) Electron diffraction.
(*d*) X-ray diffraction.
(*e*) Selective solution or evaporation.
(*f*) X-ray fluorescence, electron micro-probe analyser.
(*g*) Microradiography.
(*h*) Radioactivation and autoradiography.
(*i*) Micro spectroscopy.
(*j*) Chemical prints and electrography.

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* Presented at the meeting of the Society on Thursday and Friday, October 5th and 6th, 1961.

Of these methods, the first five have been used in the work described in this paper. Notes on the use made of these are given below. Brief details of the methods used for quantitative determinations are also included.

Optical microscopy—

Examinations of broken or suitably polished and etched surfaces have revealed that many inclusions do occur in beryllium. It has also been possible to discover something about the spatial distribution of these inclusions in and around the metal crystals.

Electron microscopy and electron diffraction—

In this work these two techniques have been used in close conjunction, as specimens viewed in the microscope (a Siemens Elmiskop 1) can also be examined by transmission electron diffraction.

The low penetrating power of electrons limits the application of both techniques to the investigation of thin films, surfaces or small particles.

So far attention has been concentrated on the examinations of particles found in separated residues (see under "Residues from Selective Solution or Evaporation"). The electron diffraction facilities in the microscope include "selected-area" diffraction, whereby diffraction patterns can be observed corresponding to small selected areas in the field of view of the instrument. By this means it is possible in certain circumstances to examine and identify single extracted particles.

Preliminary trials only have been carried out on examinations of surface replicas and of thin sections of the metal. Many small particles have been seen with sizes ranging down to less than 100 A, *i.e.*, far below the limit of resolution of optical microscopy.

X-ray diffraction—

Beryllium is a favourable metal for direct X-ray diffraction analysis of any impurity constituents that may be present. The low atomic number of beryllium allows unusually low concentrations of such impurity phases to be detected and identified by direct examination. In many instances the crystal size of each phase found can also be estimated.

The majority of the X-ray diffraction patterns were taken in an 11·46-cm diameter powder camera with CuK α radiation.

The metal specimens were examined by mounting a solid fragment in the camera in place of the usual small-diameter cylinder of powder. A flat surface was chosen or specially prepared on the fragment, and this surface was then arranged so that it intercepted the collimated X-ray beam at nearly glancing angle. Oscillation or rotation of the specimen was deliberately omitted. With this arrangement, the comparatively large crystal size of the beryllium and of some of the impurity phases gives rise to a "spotty" or "peppered" character of the Debye - Scherrer lines. This condition is commonly regarded as undesirable, but in these examinations advantage was taken of the effects to estimate the average crystal size of each constituent detected.

The examination of the residues obtained by selective solution (see below) was carried out by the usual powder technique. However, rotation of the powder specimen was often deliberately omitted to permit estimates of crystal size to be made from the peppered character of the diffraction patterns.

Residues from selective solution or evaporation—

The use of selective solution or evaporation permits certain impurity phases to be separated from the bulk of the metal so that they may be concentrated and examined in detail.

Considerable use has been made of this "residue" approach in the study described here.

Solution rather than volatilisation has been favoured, as it takes place at room temperature and thus offers less risk of changing the nature or form of the material being separated. As the solvent, we have used principally a solution of bromine in methanol. Other solvents, such as dilute acids or strong alkali, have proved useful on occasions, as they permit different selections of foreign phases to be separated from the metal.

These residues have been collected on small detachable discs mounted at the bottom of specially made centrifuge tubes. By this means sub-milligram amounts of residue can be made readily accessible for detailed examination.

QUANTITATIVE DETERMINATIONS—

Some of the quantitative determinations of impurities in beryllium have presented considerable difficulties. These difficulties have been accentuated by the small amounts of sample normally available for examination.

Spectrographic methods based on examination of beryllium oxide[1] have been used for the determinations of most of the metallic impurities.

The major metal impurity, iron, has been determined chemically by spectrophotometric procedures based on either thioglycollic acid or bathophenanthroline.

Oxygen has been determined by a semi-micro vacuum fusion procedure employing an iron bath.[2]

The total-carbon content has been determined by a combustion procedure with a combined copper - iron flux in an induction furnace; the carbon dioxide was measured conductimetrically.[3]

Silicon has been determined by a molybdenum-blue method on a solution obtained by dissolving the beryllium in an excess of a concentrated solution of sodium hydroxide.

Determinations of nitrogen have been carried out by a semi-micro Kjeldahl procedure on a solution of the metal prepared by boiling under reflux with dilute sulphuric acid. The final measurement has been by the sodium phenate - hypochlorite method.[4]

In any analytical investigation, correlation of results is an important feature of the work. It is particularly useful in considering the relation between the quantitative results obtained in the normal chemical determinations and the more qualitative information presented by most of the other techniques described.

The results of analytical investigations of a metal must also be related to the metallurgy of the particular metal. An understanding of the pattern of the impurity content found is often greatly assisted by a knowledge of the method by which the metal is manufactured.

METALLURGY OF BERYLLIUM

The principal ore of beryllium is beryl, a complex aluminium beryllium silicate. This is converted to beryllium oxide and then via the chloride or fluoride to the metal. The chloride is used in an electrolytic process and the fluoride is reduced with magnesium metal.

The products from both these processes are commonly fabricated by powder metallurgy, as cast beryllium is, for many applications, a rather unsatisfactory constructional material. Vacuum casting is used however as an intermediate purifying stage. The castings are then broken down to a powder ready for sintering, by heat and pressure, to the solid metal.

RESULTS AND DISCUSSION

The various separate free phases that have been identified in different samples of beryllium are listed below.

Beryllium oxide	(BeO).
Beryllium carbide	(Be_2C).
Beryllium nitride	(Be_3N_2).
Silicon	(Si).
Aluminium	(Al).
Carbon (graphite)	(C).
Magnesium fluoride	(MgF_2).
Intermetallic compound	(type Be_5Y).
Intermetallic compound	(type $Be_{13}X$).

It should be noted that individual specimens do not, in general, contain all these phases.

Tables I, II and III show some of the results obtained from examination of specimens representing beryllium in five different forms. Much of the information that has been gathered however, does not lend itself to tabular presentation, and this further information is considered below in relation to the other results in the discussion of individual impurity phases.

Oxide—

Two forms of the oxide have been recognised—

(*i*) A crystalline oxide of crystallite size $>$ about 0·2 μ.
(*ii*) A near-amorphous oxide of crystallite size $<$ about 50 A.

The crystalline oxide has been found in all specimens of fabricated metal examined. It is detected by X-ray diffraction directly in the metal and also in residues from bromine - methanol, acid or alkali solutions of the metal.

TABLE I

CHEMICAL EXAMINATION

Material*	Oxygen found, p.p.m.	Carbon found, p.p.m.	Silicon found, p.p.m.	Iron found, p.p.m.	Aluminium found, p.p.m.	Magnesium found, p.p.m.
Ingot (E)	500	800	$<$20	600	500	50
Powder (E)	5000	500	50	900	1200	100
Tube (E)	7000	400	200	800	600	50
Rod (Mg)	8000	600	400	1300	500	500
Sheet (Mg)	5000	500	400	1200	1400	100

* E denotes metal manufactured by electrolysis; Mg denotes metal manufactured by magnesium reduction.

Specimens of powder all contain several thousand parts per million of oxygen, as determined by vacuum fusion analysis, but direct X-ray diffraction examination does not always reveal any crystalline oxide. Bromine - methanol residues, however, give an extremely diffuse X-ray diffraction pattern of beryllium oxide. This indicates that the oxide is present, but in a poorly crystalline state.

It was surmised that this form of the oxide originated as a surface film on the particles of metal powder. To test this hypothesis, some fine drillings were prepared from a vacuum cast specimen. Examination of a residue derived from these drillings revealed large amounts of a poorly crystalline oxide similar to that obtained from powder specimens. The residue from a solid piece of the ingot contained some of the crystalline oxide, but only traces of the near-amorphous form.

TABLE II

DIRECT X-RAY EXAMINATION

Material*	Beryllium oxide found, %	Beryllium carbide found, %	Silicon found, %	Aluminium found, %	Intermetallic compound (type Be_5Y) found, %	Intermetallic compound (type $Be_{13}X$) found, %
Ingot (E)	n.d.	about 0·1	n.d.	about 0·1	n.d.	n.d.
Powder (E)	n.d.	n.d.	n.d.	about 0·1	n.d.	n.d.
Tube (E)	about 1	about 0·1	n.d.	n.d.	about 0·1	$<$0·1
Rod (Mg)	about 1	about 0·1	$<$0·1	n.d.	about 0·2	$<$0·1
Sheet (Mg)	about 1	about 0·1	$<$0·1	$<$0·1	about 0·2	$<$0·1

* E denotes metal manufactured by electrolysis; Mg denotes metal manufactured by magnesium reduction; n.d. denotes not detected.

When bromine - methanol residues from powder samples are examined in the electron microscope, the form taken by this near-amorphous oxide can clearly be seen.

In Fig. 1, the wispy semi-transparent flakes are those of the oxide, and it is not hard to imagine these as originating as a thin skin on metal particles.

The surface film on beryllium probably consists of a hydrous oxide, such as normally occurs on aluminium. Support for this suggestion lies in the fact that in vacuum fusion determinations it is found that the hydrogen content of powders is invariably considerably higher than that of solid samples.

When beryllium powder is sintered, the surface oxide appears to be retained, but is crystallised by the heat treatment involved in the sintering process. The bulk of the

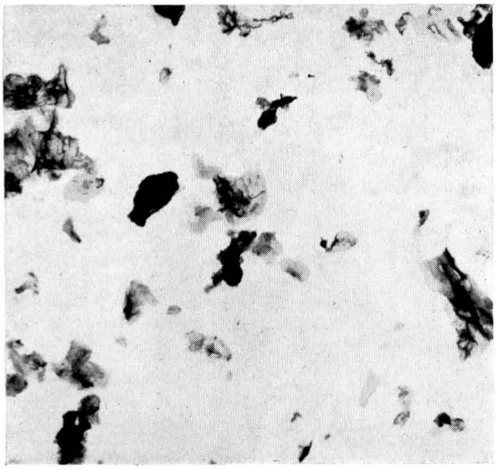

Fig. 1. Electron micrograph (× 4000) of particles extracted from a beryllium powder

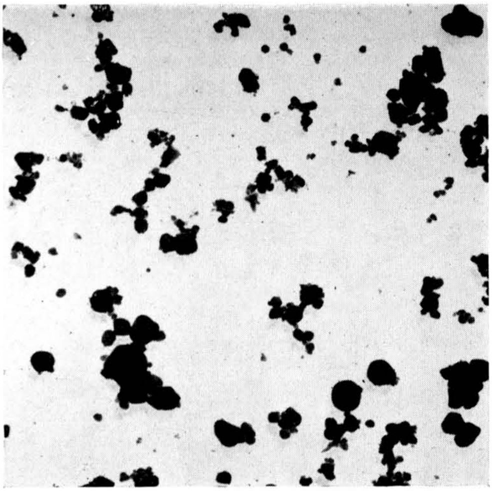

Fig. 2. Electron micrograph (× 4000) of particles extracted from a specimen of sintered beryllium

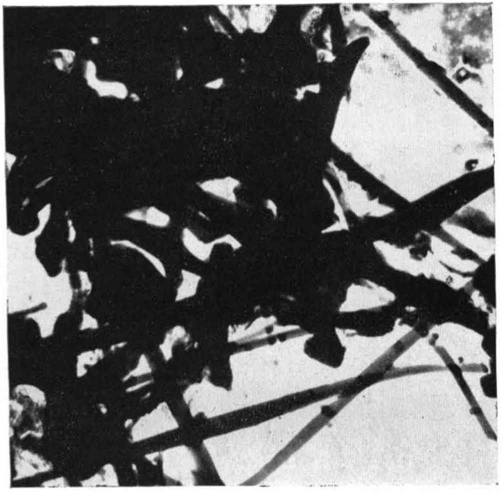

Fig. 3. Electron micrograph (× 4000) of particles extracted from a specimen of ingot beryllium

crystalline oxide found in sintered metal is probably formed in this way. An electron micrograph of a residue from some sintered metal is shown in Fig. 2. Most of the particles are those of crystalline oxide, and the distinction between these and the oxide particles from powder, shown in Fig. 1, is marked.

Determinations of oxygen in chemically reactive metals like beryllium must take into account the contribution made by oxide present on the surface of the metal specimen. Care must be taken to minimise the surface area of samples of metal being examined, and solid pieces rather than turnings or drillings should be used.

CARBON—

Unlike oxygen, carbon does not react with beryllium in the cold, and thus it is possible to have free carbon in specimens of the metal. However, if the metal has been heated to a high temperature, *e.g.*, melted and cast, carbide (Be_2C) formation will have taken place.

A sample of "electrolytic flake" beryllium that had not been through any fabrication process was examined by the residue technique. Some graphite was detected; this originated presumably in the graphite electrodes used in the manufacture.

In all the specimens of fabricated metal examined, the carbide has been the only carbon-containing phase detected. The crystallites of the carbide phase are generally about 5 μ in size, but are occasionally considerably larger. Some particularly well formed and large carbide crystals have been found in an ingot specimen and an electron micrograph of a bromine - methanol residue from this ingot shows these crystals clearly (see Fig. 3).

An interesting analytical point arises, in that carbide has been found in residues from solution of the metal in boiling dilute acids. Some laboratories use a similar boiling-acid extraction procedure to isolate and determine the free-carbon content of beryllium. This separation, although probably satisfactory for the examination of electrolytic flake beryllium, would seem to be invalid for fabricated specimens.

TABLE III

X-RAY EXAMINATION OF BROMINE - METHANOL RESIDUES

Material*	Beryllium oxide found, % of residue	Beryllium carbide found, % of residue	Beryllium nitride found, % of residue	Silicon found, % of residue	Magnesium fluoride found, % of residue	Total amount of residue, % of metal
Ingot (E)	20	60	n.d.	20	n.d.	0·03
Powder (E).. ..	†	n.d.	n.d.	n.d.	n.d.	1·3
Tube (E)	90	10	trace	3	n.d.	0·8
Rod (Mg)	80	10	2	5	1	1·6
Sheet (Mg)	70	20	<1	7	n.d.	0·6

* E denotes metal manufactured by electrolysis; Mg denotes metal manufactured by magnesium reduction; n.d. denotes not detected.

† Residue consists of amorphous oxide and undissolved metal.

NITRIDE—

Nitrogen can be readily detected and determined in specimens of beryllium by chemical analysis, but no phase containing nitrogen has been detected by direct X-ray diffraction studies on the metal. However, careful application of the bromine - methanol residue technique has shown that nitrogen is present as extremely finely divided (sub-micron size) beryllium nitride.

SILICON—

Elemental silicon of crystallite size similar to that of beryllium carbide, *i.e.*, about 5 μ, is detected in most specimens both directly and in residues.

The free silicon is probably formed in the conditions that lead to the disappearance of free carbon. Silica or silicates are readily reduced by hot beryllium, but as no beryllium silicide appears to exist, free silicon is formed.

The procedure used for chemical determination of silicon in beryllium must take into account the elemental state of this impurity, as the normal acid solvent does not dissolve free silicon.

In a few specimens, silicon has been detected and determined by chemical analysis, but has not been found by X-ray examinations, either of the metal or of residues. This suggests that in these specimens silicon may be present in some other form.

MAGNESIUM FLUORIDE—

Small amounts of this compound have been detected in bromine - methanol residues from a few specimens of metal made by the magnesium-reduction method. The compound, which is present as relatively large crystallites (about 10 μ), probably results from incomplete removal of slag in the manufacturing process.

METALLIC IMPURITIES—

Up to now, apart from the elemental analysis, information on metallic-impurity phases has been obtained only by means of direct X-ray diffraction examination of the metal. No selective solvent has been found that allows these phases to be separated for examination in greater detail. The use of other techniques, such as electron microscopy combined with electron diffraction is now being explored.

One metallic impurity, which is revealed in X-ray diffraction patterns as a face-centred cubic phase of lattice parameter 4·04 A, is clearly free aluminium or an aluminium-rich alloy. This is only present in a few specimens of high aluminium content. In one specimen the average size of the crystals of this phase appeared to be as large as 20 or 30 μ.

Most samples of sintered metal contain phases that have been ascribed to intermetallic compounds of beryllium. At least two such compounds have been observed, and details of these are shown in Table IV.

TABLE IV

STRUCTURE DATA ON INTERMETALLIC PHASES IN BERYLLIUM

		Symmetry	Unit-cell dimensions, A
Phases found	Be_5Y	Cubic	6·1
	$Be_{13}X$	Cubic	10·4
Analagous compounds ..	Be_5Fe	Cubic (Fd3m)	5·89
	$Be_{13}Ca$	Cubic (Fm3c)	10·31

The formulae Be_5Y and $Be_{13}X$ have been chosen on the basis of the particular types of crystal structure the X-ray diffraction patterns indicate for the two compounds. Other workers[5,6] have reported the presence in specimens of beryllium of phases similar to one or both of these compounds.

The phase denoted as Be_5Y occurs in many more specimens than does $Be_{13}X$, and, when both phases are present, Be_5Y is almost always in the higher concentration.

Iron is usually the major impurity metal in beryllium and it is known to form a compound Be_5Fe. The possibility thus arises that Y might be identified with iron. The lattice parameter determined for Be_5Y is, however, larger than that reported in the literature[7] for the iron compound. Experimental preparations in the laboratory of a beryllium alloy of the Be_5Fe type have confirmed the structure data recorded in the literature. The simple identification of Y with iron must therefore be ruled out. There are several elements that will form beryllium compounds with this type of structure, and so it is most probable that Y is not a single element and that the phase is a "mixed" compound.

Similar considerations apply to the identity of X in the $Be_{13}X$ phase. The cubic crystal lattice identified here appears to be isostructural with such compounds as $Be_{13}Ca$ and $Be_{13}Mg$[8] and is quite distinct from that of Be_5Y.

With these intermetallic compounds, it is of interest to note that changes in the concentration and constitution are likely to take place at elevated temperatures. This particular aspect of beryllium metallurgy is a subject of much importance at the moment.

Only a limited amount of experimental work has been carried out by us on this problem so far. A difference between the two intermetallic phases has, however, been observed. The Be_5Y phase dissolves in the beryllium matrix on heating above about 850° C, but the $Be_{13}X$ phase remains unchanged up to 1000° C.

CONCLUSIONS

Considerable progress has been made in the general analytical investigation of impurities in beryllium, but it is clear that the results are as yet incomplete.

Non-metallic impurities have been examined in some detail, but the metallic impurities have proved more difficult to study, and the role of the minor impurities in particular remains obscure. With impurities in general, much remains to be discovered about the dispositions relative to the metal matrix.

A feature of this study has been the continual need to relate experience gained on one specimen to that gained on others. The consideration of one sample or one method of investigation in isolation can lead to unsound conclusions. The broader the scope of the techniques available in this type of investigation and the wider the range of specimens examined, the more reliable and useful is the information obtained.

We thank members of the Research and Development Department at the Erith Laboratories of the United Power Company Ltd. for their help and advice. We also thank several of our colleagues in the Chemistry and Technical Services Division for carrying out much of the experimental work.

REFERENCES

1. Smith, A. L., and Fassel, V. A., *Anal. Chem.*, 1949, **21**, 1095.
2. Still, J. E., *in* "The Determination of Gases in Metals," *Special Report No.* 68, The Iron and Steel Institute, London, 1960, p. 43.
3. Still, J. E., Dauncey, L. A., and Chirnside, R. C., *Analyst*, 1954, **79**, 4.
4. Crowther, A. B., and Large, R. S., *Ibid.*, 1956, **81**, 64.
5. Pointu, P., Espagno, L., Azou, P., and Bastien, P., *Compt. Rend.*, 1960, **250**, 2365.
6. Moore, A., *J. Nuclear Materials*, 1961, **3**, 113.
7. Teitel, R., and Cohen, M., *Trans. A.I.M.E.*, 1949, **185**, 285.
8. Baker, T. W., and Williams, J. W., *Acta Cryst.*, 1955, **8**, 519.

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DISCUSSION ON THE FOREGOING THREE PAPERS

DR. T. R. PHILLIPS asked Mr. Everett whether any attempts had been made to analyse the gases evolved during the different experiments performed.

MR. EVERETT in reply stated that the evolved gases had been analysed for hydrogen, carbon monoxide and nitrogen in all except the dynamic experiments. Checks had been made for the presence of water and carbon dioxide, but no significant amounts had been found.

MR. W. MOSER asked Mr. Everett whether, in presence of tin, the delayed peak on the vapour-pressure curve and the displacement of sorbates from the upper regions of the fusion tube might be connected with possible formation of volatile SnO, which was a stable gaseous species above about 1100° C.

MR. EVERETT replied that SnO might possibly be involved in the delayed pressure rise found when a beryllium sample with added tin was analysed. The mechanism could be fairly complicated, but, whether SnO or H_2O were released, the effect on the vacuum fusion method would be the same, *i.e.*, decomposition of an oxygen containing volatile material on the hot graphite crucible to form spurious amounts of carbon monoxide with a consequent high bias in results. Booth and Parker (*Analyst*, 1959, **84**, 547) mention SnO as a possible surface contamination of tin, which is thermally decomposed on pre-heating to 1400° C.

An explanation of the delayed pressure rise was that it was caused by desorption of gas from surfaces under bombardment by evaporated tin and that this process only became apparent after the beryllium sample had fully dissolved in the platinum bath and been converted to carbide, thus bringing to an end the gettering action of evaporating beryllium, which would mask the desorption of gas by evaporating tin. Tin does not form a carbide and would continue to evaporate after the beryllium had been converted to carbide.

MR. E. J. MILLETT asked Mr. Everett why the header volume should be small for optimum performance when increased header volume should have given a lower peak pressure for a given pulse of gas, and gave a lower rate of "clean up" by evaporated metal. He went on to ask if commercially available pumps with an effective speed of at least 30 litres per second would not have given a more significant improvement than the Edwards GM2, which had an effective speed of only 4 litres per second, and also whether there was any specific reason why complex mercury cut-offs were used rather than standard vacuum taps.

MR. EVERETT emphasised in his reply that the most important factor was the *throughput* of the gas-transfer system. The system must remove the maximum *amount* of gas from the region of the crucible in the shortest possible time, and this was obtained when the pumping speed at the crucible was large, the head volume small, to avoid the unnecessary expansion of gas, and the pump was capable of operating at relatively high pressures. The smaller head volume gave a faster rate of pump-down and a shorter residence time for gas; this more than compensated for the initial higher peak pressure with regard to gettering.

A diffusion pump of lower speed able to operate at relatively high pressures might have a better gas throughput characteristic for a particular application than a pump of higher speed that could only operate efficiently at much lower pressures. For example it was found, as mentioned in the paper, that lower results for oxygen were obtained when a pumping system having an effective rate of 1 litre per second but stalling above 1 μ was used, than when a system having a pumping rate of 0·25 litres per second capable of operating at pressures of up to 30 μ without loss of speed was used. This effect was found with samples that evolved a sufficiently large volume of gas to stall the former pumping system but not the latter.

The pumping speeds generally quoted in the paper were for the region of the crucible. The GM2 pump had a speed of 10 to 15 litres per second at the throat, and although a 30-litre per second pump would be an improvement provided it had a greater gas throughput, the conductance of the line between pump and crucible would have to be increased also if any marked advantage were to be obtained.

Mercury cut-offs of the type used have been found to be much more reliable than glass taps and to require much less maintenance, so that the serviceability of the apparatus described had been 98 per cent. over a period of years.

MR. L. J. HOLT asked Mr. Everett if any evidence had been found to corroborate the work of Pearce and Masson, who determined oxygen in steels and obtained much higher results at low levels than were obtained by conventional vacuum fusion.

MR. EVERETT stated that the paper by Pearce and Masson certainly had caused a major controversy at the recent Symposium on Gases in Metals (Iron and Steel Inst. Special Report No. 68, 1960). On reading their paper, one was convinced that there was a basic fallacy somewhere and that it was not a valid application of the isotope-dilution technique because (*a*) true equilibrium might not have been reached with all the oxygen in a sample and (*b*) dilution of ^{18}O might have taken place because of the liberation of ^{16}O, as water, etc., adsorbed on the walls of the furnace tube.

MR. R. F. COLEMAN, in answer to the previous question about Pearce and Masson's method of determining oxygen by isotope dilution, said he would like to mention some of his own work that threw some light on that method. He had now extended the fast-neutron activation method to the determination of oxygen in almost all elements and generally had obtained good agreement with vacuum fusion for about ten different metals. In particular, he would like to quote results obtained by the three methods on two B.I.S.R.A. standard metals.

Sample	B.I.S.R.A. vacuum-fusion method	Isotope-dilution method	Fast-neutron activation method
BNL 11	145 p.p.m.	254 p.p.m.	160 p.p.m.
BPL 15	32 p.p.m.	63 p.p.m.	37 p.p.m.

Mr. Coleman added that, as could be seen, the results agreed well with those by the vacuum-fusion method, but were significantly different from those by Pearce and Masson's method.

MR. D. G. HIGGS said that it was gratifying to learn that Mr. Coleman had obtained good agreement between results for oxygen in steel by vacuum fusion and isotope dilution. It might interest members present to learn that they had recently received a communication from Mr. Masson in which he claimed good agreement for nitrogen between the three techniques employed. The initial discrepancies were apparently due to a two-fold cause; first, the isotope-dilution values were incorrect owing to an arithmetical error, and secondly, the nitrogen values by vacuum fusion were low. It had been found that, by using a higher temperature for fusion (2000° to 2200° C), much closer agreement between all three methods was obtained. It would be interesting to learn whether the difference between values for oxygen by vacuum fusion and isotope dilution was due to similar causes.

MR. H. J. C. CHALLIS said that the paper by Mr. Everett and Mr. Thompson had been extremely useful in that it provided answers to problems that had been outstanding for several years. He asked if Mr. Everett would care to comment on (*a*) the higher results of 6000 p.p.m. of oxygen compared with the average of about 4000 p.p.m. on the rod (Table IV), (*b*) preparation of the small sample to prevent oxidation and (*c*) whether the presence of oxygen in the volatilised beryllium on the walls of the furnace tube had been confirmed.

MR. EVERETT said in reply to (*a*) that the results of 6000 p.p.m. of oxygen on the sintered rod sample (columns B and E, Table IV) were obtained when added tin was used and was not enclosed in a platinum capsule. This led to the unrestricted evaporation of tin, which, on contact with the inner walls of the silica furnace tube, released adsorbed water. This mechanism was confirmed by analysis of successive portions of tin, as such, not in a capsule, at 1950° C. In general, it was found that very high results for oxygen were obtained on the first few samples and the level decreased progressively to 30 p.p.m. of oxygen. The spurious amounts of oxygen when expressed in terms of effect on a 5-mg sample of beryllium gave rise to a positive bias of up to 4000 p.p.m. of oxygen.

With regard to question (*b*) it was essential that samples of massive metal were freshly prepared and that none of the original surfaces should be included in the sample. The effect was shown in Table VI. These conditions were most easily met by fracturing or crushing a portion of the sample and then selecting a suitably sized fragment.

In answer to (*c*) he said that it would not be at all easy to prove directly the presence of gettered carbon monoxide in the evaporated beryllium film. The film could not be handled in air without contamination with oxygen or moisture from the air.

MR. C. WHALLEY asked if Mr. Still could give more information about the blank values obtained with the various fluxes. Particularly, he wanted to know the treatment given to metallic lead to free it from carbon and what proportion of the total carbon determined was due to the flux when pure iron was used, since this must have had an appreciable carbon content.

MR. STILL said that by heating either lead or copper to a bright red heat immediately before use, the carbon content of each could be reduced to 1 or 2 p.p.m. This type of pre-treatment had not been successful with iron, as too much oxidation of the metal took place before useful lowering of the carbon content had occurred. No commercial supply of iron had been discovered in which the carbon content was less than 20 to 30 p.p.m.

The proportional contribution of a given blank obviously varied inversely as the amount of carbon being determined. When this amount was small, and a particularly low blank was therefore required, either he did not use iron, or, if its use was essential, he pre-burned the iron and made a further addition of copper to assist the combustion of the sample.

MR. R. SCHOLEY asked Mr. Still what proportion of carbon was recovered from highly alloyed steels and zirconium alloys in a conventional platinum-wound tube furnace relative to that in the R.F. furnace.

MR. GREEN replied, and said that no straightforward answer could be given to this question. Clearly, variations in furnace temperatures and in fluxing conditions could lead to varying recoveries of carbon. In a recent examination of a batch of a highly alloyed stainless steel the opportunity arose of comparing results with those obtained in another laboratory. He had used a high-frequency furnace, but the other laboratory had used a conventional tube furnace at 1350° C. The results with the tube furnace were variable and the level found was between 50 and 80 per cent. of that indicated by the induction-furnace results.

MR. G. A. DAVIDSON asked whether Mr. Still found it necessary when using an induction furnace for the combustion of high-carbon irons to use a catalyst to ensure complete conversion of the carbon to carbon dioxide.

MR. STILL stated that under the conditions used, experience on standard steels and cast irons had shown no evidence that such a catalyst was necessary.

MR. E. J. MILLETT, commenting on Mr. Everett's reply to part of his previous question that greased taps were unreliable, pointed out that they had used a greased-tap system without difficulty of any sort for three years and had handled much smaller amounts of gas in the vacuum fusion analysis of silicon and germanium. He then referred to the comments on surface oxide and sample preparation and said that they had obtained reproducible surfaces on aluminium samples only by turning at high speed to a mirror finish with the exclusion of air and with carbon tetrachloride as a lubricant; he asked if this might be applicable to beryllium.

MR. EVERETT said, on the question of taps *versus* cut-offs, that, in addition to grease films already mentioned, glass taps had other disadvantages, such as a possible cause of virtual leaks and the need for periodic regreasing if the laboratory temperature varied appreciably; also, there was a consequent risk of breakage when the grease was cold. He maintained that for cleanliness and reliability, and when a large volume of work had to be handled, mercury cut-offs of the type described were superior to glass taps.

With regard to the mirror polishing of samples under carbon tetrachloride, such a refined technique was not justifiable for most beryllium samples of higher oxygen content. The technique might, however, have application for super pure material.

MR. T. D. REES stated that, on certain refractory alloys, he had obtained low results for carbon in the tube furnace, even at 1400° C, compared with results by the induction furnace. He asked Mr. Still if he had tried the classical "dodge" of a preliminary extraction with a solvent such as ammonium cupric chloride to facilitate the ignition of these alloys in the tube furnace. Mr. Rees added that he was interested in any comparative results the authors might have.

MR. CHIRNSIDE said that because of his longer experience he might more appropriately attempt an answer to this question. His own experience indeed went back to the time when there was no method available for the determination of carbon in some metallic materials, for example a 50/50 nickel - iron alloy, other than that depending on preliminary dissolution in copper ammonium or copper potassium chloride. The progress in other technologies, notably in improved refractories and in high-temperature electric furnaces, had made the "solution" approach obsolescent. It was at best a makeshift procedure to which there were some doubts attached as to the possible loss of carbon.

The Determination of Some Trace Impurities in Gallium Arsenide by Square-wave Polarography*

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The use of 1 M hydrochloric acid as a base electrolyte in square-wave polarography has been investigated, and methods are described for determining bismuth, copper, indium and cadmium in gallium arsenide at concentrations of 1 p.p.m. or less. In an appendix, the diffusion coefficients in 1 M hydrochloric acid for some reversibly reduced ions are calculated.

GALLIUM arsenide is an important member of the group III–V semi-conductor compounds and is required in a high degree of chemical purity. However, it is difficult to develop reliable and direct methods for determining trace elements present at concentrations of 1 p.p.m. or less in gallium arsenide. In this work square-wave polarography has been used for several such determinations.

EXPERIMENTAL

The procedure adopted was similar to that described previously.[1] The sample of gallium arsenide was dissolved in a mixture of nitric and hydrochloric acids, the solution was evaporated to dryness, the residue was dissolved in 1 M hydrochloric acid, and a square-wave polarogram was recorded for the solution; 1 M hydrochloric acid was used as base electrolyte because several ions that were of interest were probably polarographically active in it.[2] However, although the ions of elements such as bismuth^{III},[3] copper^{II},[3] lead^{II},[3] thallium^{I},[3] cadmium^{III},[3] tin^{II},[4] uranium^{VI} [5] and neptunium^{IV} [6] give reduction waves in this medium, a description of the acid as a base electrolyte in square-wave polarography has not been reported.

In the method for analysing gallium arsenide, it was initially assumed that the arsenic would be completely oxidised to arsenic^{V} during solution of the sample. However, it was found that variable trace amounts of arsenic up to 50 μg remained in the tervalent state. This posed a difficult interference problem, as arsenic^{III}, but not arsenic^{V}, was found to be polarographically active in 1 M hydrochloric acid. This problem was overcome by using potassium bromate to oxidise the arsenic^{III} to arsenic^{V}.

APPARATUS—

Continuous polarograms were recorded with a Mervyn - Harwell square-wave polarograph. The normal drop-time of the drop from the mercury capillary electrode in open circuit was 3·5 seconds, the rate of flow of mercury from the capillary being $1{\cdot}43 \times 10^{-3}$ g per second. Twice-distilled mercury was used in the reservoir supplying the capillary electrode and for the mercury-pool anode in the polarographic cell. The latter was maintained at 25° C in a thermostatically controlled bath. Before polarography, solutions were de-oxygenated by passage of oxygen-free nitrogen for 5 minutes. The calibrated glassware used was of grade A specification.

REAGENTS—

The concentrated nitric and hydrochloric acids used were of transistory grade, obtained from the British Drug Houses Ltd. The grade of concentrated sulphuric acid used was Judactan W.A.B.A. All other chemicals were of AnalaR grade.

The pure water required was prepared by distillation from a Manesty still fitted with a tin condenser and was stored in a polythene aspirator. The purity of this distilled water was determined by polarographic analysis of the residue after evaporation; it was shown to contain less than one part per thousand million each of bismuth, copper, lead, indium and cadmium.

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Standard solutions were prepared according to conventional procedures and were stored in polythene bottles fitted with polythene screw-on lids. No change in any solution was observed after storage for 1 month.

INVESTIGATIONS WITH HYDROCHLORIC ACID AS BASE ELECTROLYTE—

The ions found to give reduction waves in 1 M hydrochloric acid are listed in Table I. The effect of each ion was examined by adding it, in the form of a standard solution from a 1-ml calibrated pipette, to 4 ml of 1 M hydrochloric acid contained in a polarographic cell and then recording a square-wave polarogram for the solution. A calibration graph was plotted of the peak height of the reduction wave against the concentration of the ion.

TABLE I

IONS GIVING REDUCTION WAVES IN 1 M HYDROCHLORIC ACID

Ion	Potential of peak of wave, volts against mercury-pool anode	Remarks
Selenium^{IV}	0·07 and 0·45	Peak height for given concentration decreased with successive polarograms. Wave at 0·07 volt has distinctive shape and sharply defined peak
Bismuth^{III}	0·08	Calibration graph not completely linear below 0·15 µg per ml
Molybdenum^{VI}	0·09	Calibration graph not plotted. Peak height altered appreciably with small changes in concentration of hydrochloric acid
Antimony^{III}	0·14	Calibration graph not completely linear below 0·1 µg per ml
Uranium^{VI}	0·19 and 0·90	Both calibration graphs not completely linear below 1 µg per ml. Wave having peak at 0·19 volt interfered with following wave for copper at 0·22 volt
Copper^{II}	0·22	Calibration graph showed slight curvature below 0·1 µg per ml
Lead^{II}	0·43	Below 0·1 µg per ml, "hump" in polarogram for base electrolyte interfered with measurement of peak height
Tin^{II}	0·45	Impossible to separate waves for lead and tin. Total peak height for a mixture of lead and tin is three-quarters of the calculated value
Thallium^{I}	0·47	In presence of 0·25 µg of lead per ml, a similar concentration of thallium is just detectable
Arsenic^{III}	0·42, 0·63 and 0·85	Wave having peak at 0·42 volt has very distinctive shape. Calibration graph for this wave linear to below 0·25 µg per ml; that for wave having peak at 0·63 volt linear down to 2·5 µg per ml and wave disappears at 0·25 µg per ml
Indium^{III}	0·59	Calibration graph linear from 1 to 0·02 µg per ml
Cadmium^{II}	0·64	Possible to determine indium in presence of cadmium or *vice versa* in range 0·025 to 0·25 µg of each per ml. Waves overlap, but peaks distinguishable
Tellurium^{IV}	0·77	Peak height for given concentration decreased with successive polarograms

The calibration graphs were linear over at least a ten-fold range of concentrations for bismuth^{III}, antimony^{III}, copper^{II}, lead^{II}, tin^{II}, thallium^{I}, indium^{III} and cadmium^{II}. However, the presence of a "hump" at 0·45 volt (see "Determination of Reagent Blank Values") in the polarogram for the 1 M hydrochloric acid alone interfered with measurement of the heights of the small peaks for lead, tin and thallium ions when these were added to the acid.

With tin, it was found that, if 0·5 ml of 0·005 N potassium bromate was added in order completely to oxidise any tin^{II} to tin^{IV}, a reduction wave having a peak at 0·48 volt was obtained on the resulting polarogram. The peak height of this wave was about 50 per cent. less than that of the wave for tin^{II} recorded in the absence of bromate. It is considered that the wave having a peak at 0·48 volt was produced by reduction of tin^{II} and that the latter was formed by reduction of tin^{IV} at a less negative potential. However, the absence of a wave corresponding to the reduction of tin^{IV} to tin^{II} is surprising, as such a wave is obtained by the d.c. polarography of tin^{IV} in hydrochloric acid.[7,8] The change in potential of the peak of the wave for tin^{II} from 0·45 to 0·48 volt is unusual. Some experiments were carried out on the recovery of less than 1 µg of tin after evaporation to dryness of tin^{II} with a mixture of nitric and hydrochloric acids, during which any tin^{II} would be oxidised to tin^{IV}. However, the polarogram of a solution of the residue in 1 M hydrochloric acid showed a wave having a peak at 0·45 volt. When an excess of potassium bromate solution was added, the peak potential was increased to 0·48 volt and the peak height decreased by about 50 per cent. It seems possible that the change in peak potential is due to the increased redox potential of the solution caused by the excess of bromate solution added.

The calibration graphs for bismuth^{III}, antimony^{III} and copper^{II} were not completely linear at low concentrations (see Table I). This lack of linearity is due to the fact that the peak heights for these ions, when measured at a high sensitivity setting of the polarograph, are taken against curved and sharply falling base lines and not, as is usual, against an approximately flat horizontal base line. The calibration graph for copper showed slight but distinct curvature at concentrations of about 0·1 μg per ml.

The effect on bismuth^{III} and antimony^{III} of adding 0·01 per cent. of gelatin was studied. The polarograms obtained were similar in appearance to those recorded in absence of gelatin, but the peak heights of the reduction waves were increased by 60 per cent. for bismuth^{III} and 40 per cent. for antimony^{III}.

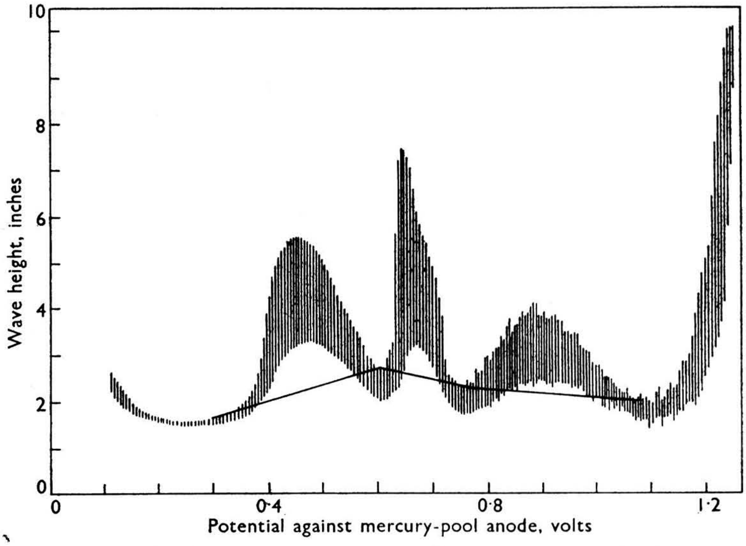

Fig. 1. Continuous square-wave polarogram at one-thirtysecond maximum sensitivity for arsenic^{III} at a concentration of 12·5 μg per ml in 1 M hydrochloric acid

Molybdenum^{VI} gave a reduction wave having a peak at 0·09 volt. The height of this peak varied considerably with slight changes in concentration of hydrochloric acid, and it is not therefore considered that molybdenum can be determined in 1 M hydrochloric acid. A possible explanation of the variation in peak height is that, depending on the concentration of hydrochloric acid, a certain proportion of the added molybdenum^{VI} is present as colloidal molybdic acid, which is not reducible polarographically.

Although uranium^{VI} gave a satisfactory wave having a peak at 0·19 volt, Milner and Nunn[5] have shown that the peak height decreases with increasing concentration of hydrochloric acid. The wave having a peak at 0·19 volt is presumably produced by the reduction of uranium^{VI} to uranium^{V}, and the stability of uranium^{V} decreases with increasing concentration of acid. The wave having a peak at 0·90 volt is formed by the reduction of uranium^{V} (or uranium^{IV}, if uranium^{V} is unstable) to uranium^{III}.

Arsenic^{III} at a concentration of 4 μg per ml gave two reduction waves having peaks at 0·42 and 0·63 volt. However, as shown in Fig. 1, at higher concentrations (about 12 μg per ml), an ill-defined third wave was observed, with a peak at about 0·85 volt. By analogy with results found by d.c. polarography of arsenic^{III},[8] it seems probable that the first two waves are produced by the reduction of arsenic^{III} to elemental arsenic and that the third wave represents the reduction of arsenic to arsine. Polarograms showing the reduction waves of arsenic^{III} in 1 M hydrochloric acid containing 0·01 per cent. of gelatin were similar in appearance to those recorded in the absence of gelatin, but the peak heights of the waves at 0·42 and 0·63 volt were decreased by about 60 and 30 per cent., respectively.

Selenium^{IV} and tellurium^{IV} both gave reduction waves, the heights of which steadily decreased when successive polarograms were recorded for the same solution. The lack of reproducibility of these reduction waves makes them unsatisfactory for quantitative use; however, it was possible to detect tellurium in tellurium-doped samples of gallium arsenide by means of the reduction wave for tellurium.

DETERMINATION OF REAGENT BLANK VALUES—

The main reagent blank values to be considered were, first, that of the 1 M hydrochloric acid used as base electrolyte and, secondly, that of the mixture of nitric and hydrochloric acids used to dissolve the sample.

Fig. 2 shows a polarogram of the 1 M hydrochloric acid, and it can be seen that no reduction waves are present, except for a slight "hump" having maximum height at about 0·45 volt. This "hump" is thought to be caused originally by variation in the capacity of the mercury drop with its d.c. potential, as it was found that measurements of the capacity* showed a similar variation with a maximum at 0·45 volt. This variation in capacity is considered to be due to the known variation in the surface tension of the mercury drop with its d.c. potential. The blank value for 1 M hydrochloric acid is therefore considered to be negligible.

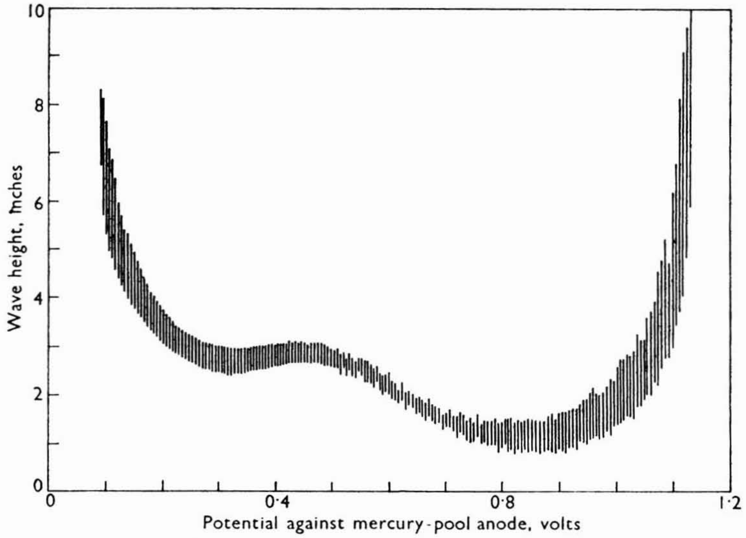

Fig. 2. Continuous square-wave polarogram at one-quarter maximum sensitivity for 1 M hydrochloric acid base electrolyte

The blank value for the mixture of nitric and hydrochloric acids was determined by evaporating to dryness five times the volume of mixture required to dissolve samples (evaporation of the usual volume of mixture gave extremely small blank values). Thus, 25 ml of 3 M nitric acid, 5 ml of hydrochloric acid, sp.gr. 1·18, and 1 ml of a solution containing 10 mg of sodium carbonate per ml (added in order to facilitate subsequent solution of the residue in 1 M hydrochloric acid) contained in a polytetrafluoroethylene beaker were evaporated to dryness under an infrared lamp. The residue was dissolved in 4 ml of 1 M hydrochloric acid, the solution was transferred to a polarographic cell, and a square-wave polarogram was recorded. Two reduction waves were observed on the polarogram; one (for copper) had a peak at 0·22 volt and the other (for lead) a peak at 0·43 volt. The average weight of copper found by using calibration graphs in ten experiments was 0·15 μg, the maximum and minimum weights being 0·20 and 0·13 μg; the average weight of lead found was 0·3 μg.

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* The Mervyn - Harwell square-wave polarograph can be used to record a "double-layer capacitogram" for a particular base electrolyte; this shows the variation in capacity of the mercury drop with its d.c. potential.

Since the volumes of acids used were five times those used in dissolving samples, in later experiments blank values for copper and lead were taken as 0·03 and 0·06 µg, respectively.

METHOD

The method described below was used for analysing samples of gallium arsenide.

PROCEDURE—

A sample was cut from an ingot of gallium arsenide on a cutting wheel, boiled in methylated spirit and etched to a mirror surface in a hot mixture of sulphuric acid, 30 per cent. w/v hydrogen peroxide and water (60:20:20); about one-tenth of the original weight of sample was removed by etching. The sample then was washed in water, dried under dust-free conditions and placed in a polytetrafluoroethylene beaker, to which were transferred, by pipette, 5 ml of 3 M nitric acid and 1 ml of hydrochloric acid, sp.gr. 1·18. The beaker was covered with a polytetrafluoroethylene lid and heated on a warming-plate until the sample had dissolved, and the solution so obtained was evaporated to dryness under an infrared lamp. The residue was dissolved in a mixture of 4 ml of 1 M hydrochloric acid and 0·4 ml of 0·005 N potassium bromate (this volume of bromate solution was always sufficient to oxidise any remaining arsenic^{III} to arsenic^{V}); the residue took about 1 hour to dissolve. The resulting solution was transferred completely to a polarographic cell, and a continuous square-wave polarogram was recorded at a suitable sensitivity setting of the polarograph. The peak heights of the reduction waves on the polarogram were measured, and the concentrations of impurities necessary to cause such waves were ascertained from calibration graphs.

DISCUSSION OF THE METHOD AND RESULTS

It was found necessary to add the bromate solution at the same time as the hydrochloric acid, since the oxidation of arsenic^{III} by bromate was slow and the time needed for complete oxidation was about an hour. This reaction is probably slow because of the large concentration of arsenic^{V} already present (about 0·8 M); oxidation of low concentrations of arsenic^{III} alone in hydrochloric acid was found to be more rapid. The latter oxidation was studied by adding 30 or 50 µg of arsenic^{III} to 4 ml of 3 M hydrochloric acid and titrating this solution with potassium bromate solution; after each addition of bromate solution, a square-wave polarogram was recorded, and the peak height of the reduction wave for arsenic^{III} at 0·42 volt was measured. A graph was plotted showing the decrease in concentration of arsenic^{III} with the volume of potassium bromate solution added. The graph was linear, and the end-point of the titration could be obtained by extrapolation to zero concentration of arsenic^{III}. Typical titration results are shown in Table II, from which it can be concluded that 1 micro-equivalent of arsenious oxide can be determined with an error of less than ±10 per cent.

TABLE II

RESULTS FOR TITRATION OF ARSENIOUS ION IN HYDROCHLORIC ACID WITH POTASSIUM BROMATE SOLUTION

The solutions used were 0·002669 N arsenious oxide and 0·005159 N potassium bromate

Arsenious solution added to 4 ml of 1 M hydrochloric acid, ml	Arsenic added, µg	Arsenious oxide present, micro-equivalents	Titre of bromate solution, ml	Arsenious oxide found, micro-equivalents	Arsenic found, µg
0·50	50	1·335	0·27	1·393	53·4
0·50	50	1·335	0·27	1·393	53·4
0·30	30	0·867	0·16	0·825	28·6

To investigate the probable error in determining bismuth, copper, indium and cadmium, several samples were cut from the same portion of an ingot of gallium arsenide. Two of the samples were analysed as described above, and both were found to contain negligible amounts of these elements. To each of the other samples were added, before solution, known weights of bismuth^{III}, copper^{II}, indium^{III} and cadmium^{II} in the form of standard solutions. The treated samples were then analysed as before, the weights found of the four added ions being calculated with use of the calibration graphs plotted with 1 M hydrochloric acid alone as base electrolyte. Experiments showed that the results found by using the calibration graphs agreed with those obtained when a standard-addition method was applied to the solution of the sample. The results are shown in Table III, and typical polarograms in Figs. **3** and **4**. It can be seen from Fig. **3** that the peaks of the waves for indium and cadmium were just resolved. Since the wave for bismuth could not be kept on the scale of the recorder chart

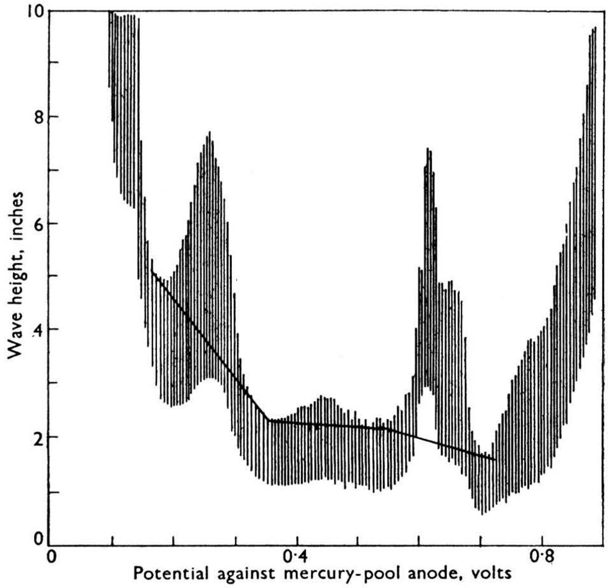

Fig. 3. Continuous square-wave polarogram at one-quarter maximum sensitivity for a 0·2241-g sample of gallium arsenide to which had been added 0·5 μg each of copper, indium and cadmium (see Table III)

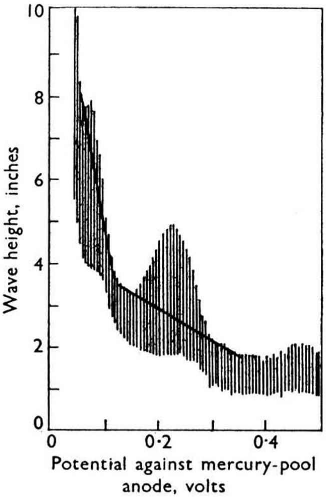

Fig. 4. Part of continuous square-wave polarogram at one-quarter maximum sensitivity for a 0·2241-g sample of gallium arsenide to which had been added 0·5 μg each of bismuth and copper (see Table III)

at one-quarter maximum sensitivity, it was necessary to decrease the sensitivity to one-eighth maximum, as indicated in Fig. 4.

Some results for the determination of indium in an ingot of gallium arsenide are shown below; if it is assumed that the indium is uniformly distributed in the portion of ingot examined, the agreement between the results is reasonably good.

Weight of sample, g	0·4398	0·4018	0·3608	0·3871	0·3555	0·3983
Indium found, μg	0·07	0·10	0·10	0·06	0·05	0·11
Indium content, p.p.m. w/w ..	0·15	0·25	0·28	0·13	0·14	0·28

The proposed method was used to study the variation with temperature of the solubility of copper in gallium arsenide; the results are shown in Table IV and agree with those previously found by using a radioactive isotope of copper.[9]

TABLE III

RECOVERIES OF TRACE ELEMENTS ADDED TO GALLIUM ARSENIDE

Weight of sample, g	Weight of bismuth—		Weight of copper—		Weight of indium—		Weight of cadmium—	
	added, μg	found, μg	added, μg	found, μg	added, μg	found, μg	added, μg	found, μg
0·2241*	0·50	0·39	0·50	0·49	0·50	0·43	0·50	0·41
0·2645	0·50	0·35	0·50	0·46	0·50	0·45	0·50	0·41
0·3745	0·50	0·37	0·20	0·24	—	—	0·20	0·18
0·3268	0·50	0·40	0·20	0·24	0·20	0·16	—	—

* Polarograms for this sample are shown in Figs. 3 and 4.

TABLE IV

RESULTS FOR SOLUBILITY OF COPPER IN GALLIUM ARSENIDE AT VARIOUS TEMPERATURES

Temperature of heat treatment, °C	Weight of sample, g	Weight of copper found, μg	Concentration of copper, p.p.m. w/w	Concentration of copper, atoms per c.c.
1150	0·1862	32·4	174	9×10^{18}
1000	0·2118	23·8	112	6×10^{18}
850	0·1630	2·6	16	8×10^{17}

CONCLUSIONS

The probable error of the method for determining bismuth, copper, indium and cadmium in gallium arsenide can be deduced by considering the recoveries of added known weights of these ions. It is considered that 0·5-μg amounts of bismuth, copper, indium and cadmium can be determined with an error of 20 per cent., but this error will increase when amounts less than 0·5 μg are determined because errors in measuring the heights of small peaks will have a proportionately greater effect.

It is considered that the limit of detection is 0·05 μg for copper, indium and cadmium, which, with the maximum usable weight of sample (0·5 g), is equivalent to a concentration of 0·1 p.p.m. w/w. The limit of quantitative determination for bismuth is 0·5 μg, or 1 p.p.m. on a 0·5-g sample of gallium arsenide; less than 0·5 μg of bismuth can be detected, but the calibration graph is then non-linear.

I thank Miss A. Newman and Mr. N. Capeling for their assistance in the experimental work and Mr. N. Rain for his development of the sulphuric acid and hydrogen peroxide etch for gallium arsenide.

Appendix

The height of a wave produced by a reducible ion in continuous square-wave polarography is usually given in units of inches on the recorder chart at a known sensitivity setting of the instrument. However, if the surface area, A, of the mercury drop at its fall is known, the height may be converted into a quantity termed the apparent interfacial conductance, G.

This is defined as the resistive conductance through which will flow an alternating current, ΔI, of the same magnitude as is produced by the electrode reaction when a square-wave voltage of peak-to-peak amplitude ΔV appears across it, *i.e.*—

$$G = \frac{\Delta I}{\Delta V \times A} \quad \ldots \quad (1)$$

In the work described above ΔV was 0·016 volt, ΔI could be found by using the calibration resistances of the square-wave polarograph, and A (calculated from the rate of flow of mercury, m, and the drop time, assuming the mercury drop to be spherical) was $2{\cdot}43 \times 10^{-2}$ sq. cm.

It has been shown[10,11] theoretically by consideration of diffusion theory that, for a simple reversible reduction reaction at the dropping-mercury electrode, when the reductant dissolves in the solution or the mercury phase, that the average value of G (in mhos per sq. cm) for the Mervyn - Harwell square-wave polarograph is given by the expression—

$$G = 5{\cdot}61 \times 10^{4}.n^{2}\left[\frac{P}{(1+P)^{2}}\right] \times \sqrt{D} \times C \quad \ldots \quad (2)$$

where n is the number of electrons involved in the reduction of each ion, D is the diffusion coefficient of the reducible ion expressed in square centimetres per second, C is the concentration of reducible ions (in gram moles per litre) and P is given by—

$$\exp\left[\frac{\mathrm{E} - \mathrm{E}_{\frac{1}{2}}}{RT}\right]n\mathrm{F}.$$

In this expression E is the d.c. potential of the dropping-mercury electrode and $\mathrm{E}_{\frac{1}{2}}$ is the half-wave potential of the reducible ion.

When ΔV is large (0·016 volt or more) a more correct expression for G is—

$$G = 5{\cdot}76 \times 10^{3}n\left[\frac{\lambda}{\Delta V(2+\lambda)}\right] \times \frac{P}{(1+P)^{2}} \times \sqrt{D} \times C \quad \ldots \quad (3)$$

where λ is given by—

$$\exp\left[\frac{\Delta V.n\mathrm{F}}{2RT}\right] - 1.$$

When ΔV is 0·016 volt and the temperature is 25° C it can be shown that $\frac{\lambda}{2+\lambda}$ is equal to 0·153, 0·301 and 0·436 for reactions having electron transfers of 1, 2 and 3, respectively. Thus, as in equation (2), G is proportional to D, C, n^2—approximately for equation (3)—and the expression—

$$\frac{P}{(1+P)^{2}}$$

It can be seen from equation (3) that G is at a maximum when P is equal to 1, *i.e.*, when E equals $\mathrm{E}_{\frac{1}{2}}$. Thus—

$$G_{\mathrm{max.}} = 1{\cdot}44 \times 10^{3}n\left[\frac{\lambda}{\Delta V(2+\lambda)}\right] \times \sqrt{D} \times C \quad \ldots \quad (4)$$

It can be deduced from equation (1) that the peak height for a reducible ion is proportional to $G_{\mathrm{max.}}$. Therefore the numerical values for the expression $\frac{\Delta I}{\Delta V.C}$, calculated in Table V, give an indication of the relative sensitivity of the square-wave polarograph for each ion reducible in 1 M hydrochloric acid. The larger the value of $\frac{\Delta I}{\Delta V.C}$ for a particular ion, the lower will be the concentration of that ion detected by the polarograph; the results in Table V show that antimony$^{\mathrm{III}}$ is the ion with the lowest detection limit in 1 M hydrochloric acid.

Equation (4) shows that, if $G_{\mathrm{max.}}$, C and n are known for a particular ion, then $\sqrt{D}$, the square root of the diffusion coefficient of the ion, may be determined. In Table V, $\sqrt{D}$ has

TABLE V

RELATIVE SENSITIVITIES AND DIFFUSION COEFFICIENTS OF IONS REDUCIBLE IN 1 M HYDROCHLORIC ACID

Ion	Potential at peak of wave, volts	Change in valency	Number of electrons involved	Concentration of solution		Instrumental sensitivity (fraction of maximum)	Peak height, inches	Value* of $\frac{\Delta I}{\Delta V} \times 10^{-6}$	Value† of $\frac{\Delta I}{\Delta V \times C}$	Value‡ of $\sqrt{D} \times 10^{-3}$ calculated from—	
				µg per ml	gram moles per litre × 10^{-6} (C)					equation (4)	value of I
Bismuth^{III} ..	0·08	III → O	3	0·25	1·20	$\frac{1}{8}$	3·0	7·50	6·25	2·19	2·89
Antimony^{III}	0·14	III → O	3	0·25	2·05	$\frac{1}{16}$	4·0	20·00	9·80	3·41	3·06
Uranium^{VI} ..	0·19	VI → V (?)	–	2·50	10·50	$\frac{1}{8}$	3·2	8·00	0·76	—	—
	0·90	V → III (?)	–	2·50	10·50	$\frac{1}{8}$	2·4	6·00	0·59	—	—
Copper^{II} ..	0·22	I → O	1	0·10	1·57	$\frac{1}{4}$	2·5	3·13	1·99	—	—
Lead^{II} ..	0·43	II → O	2	0·10	0·48	$\frac{1}{4}$	1·7	2·13	4·43	3·37	3·17
Tin^{II} ..	0·45	II → O	2	0·10	0·84	$\frac{1}{4}$	2·4	3·00	3·57	2·71	3·35
Thallium^{I} ..	0·47	I → O	1	1·0	4·89	$\frac{1}{4}$	5·5	6·81	1·24	7·08	9·44
Arsenic^{III} ..	0·42	III → O (?)	–	4·0	53·4	$\frac{1}{4}$	8·5	10·62	0·20	—	—
	0·63	O → III (?)	–	4·0	53·4	$\frac{1}{4}$	10·0	12·50	0·23	—	—
Indium^{III} ..	0·59	III → O	3	0·1	0·87	$\frac{1}{4}$	4·3	5·38	6·21	2·16	—
Cadmium^{II} ..	0·64	II → O	2	0·1	0·89	$\frac{1}{4}$	2·7	3·38	3·78	2·88	2·94

* The peak height in inches for concentration C was converted into a height expressed as mhos. The calibration resistances for the instrument showed that a peak height of 1 inch at $\frac{1}{4}$, $\frac{1}{8}$ and $\frac{1}{16}$ maximum sensitivity was equivalent (within 5 per cent.) to 2, 4 or 8 × 10^{-8} amp, respectively. ΔV was 16 × 10^{-3} volt.

† These values show the relative sensitivities of the ions.

‡ See text.

been calculated from equation (4) for the ions bismuth^{III}, antimony^{III}, lead^{II}, tin^{II}, thallium^{I}, indium^{III} and cadmium^{II}. These ions are all reversibly reduced at the dropping-mercury electrode and are all soluble[12] to some extent in mercury; the use of equation (4) should therefore be valid for these ions. For comparison, $\sqrt{D}$ for each ion has also been calculated from a known value of the diffusion-current constant, I,[2,8] assuming that I equals $607n\sqrt{D}$. In general, there is agreement between the two values of $\sqrt{D}$ obtained for each ion.

REFERENCES

1. Jennings, V. J., *Analyst*, 1960, **85**, 62.
2. Meites, L., "Polarographic Techniques," Interscience Publishers Inc., New York, 1955.
3. Ferrett, D. J., Milner, G. W. C., Shalgosky, H. I., and Slee, L. J., *Analyst*, 1956, **81**, 506.
4. Ferrett, D. J., and Milner, G. W. C., *Ibid.*, 1956, **81**, 193.
5. Milner, G. W. C., and Nunn, J. H., *Anal. Chim. Acta*, 1959, **21**, 266.
6. Slee, L. J., Phillips, G., and Jenkins, E. N., *Analyst*, 1959, **84**, 596.
7. Milner, G. W. C., "The Principles and Applications of Polarography and other Electroanalytical Processes," Longmans, Green & Co. Ltd., London, 1957.
8. Kolthoff, I. M., and Lingane, J. J., "Polarography," Second Edition, Interscience Publishers Inc., New York, 1952.
9. Fuller, C. S., and Whelan, J. M., *J. Phys. Chem. Solids*, 1958, **6**, 173.
10. Barker, G. C., *Anal. Chim. Acta*, 1958, **18**, 118.
11. Barker, G. C., Faircloth, R. L., and Gardner, A. W., U.K. Atomic Energy Research Establishment Report C/R 1786, Harwell, 1956.
12. Sidgwick, N. V., "The Chemical Elements and their Compounds," The Clarendon Press, Oxford, 1950.

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Luminescence of some Piazselenols

A New Fluorimetric Reagent for Selenium*

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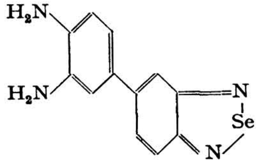
The reaction of selenous acid with three aromatic *ortho*-diamines has been investigated. Selenous acid reacts with 2,3-diaminonaphthalene in acid solution to form the strongly fluorescent 4,5-benzopiazselenol. This compound can be extracted from the acid aqueous phase by organic solvents and used for determining down to 0·002 μg of selenium. As a reagent for the fluorimetric determination of selenium, 2,3-diaminonaphthalene is considerably more sensitive and convenient than the 3,3′-diaminobenzidine previously recommended.

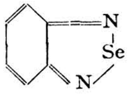
The 3,4-benzopiazselenol formed by reaction with 1,2-diaminonaphthalene is only weakly fluorescent, but, in carefully de-aerated solutions, also emits a phosphorescence band. A similar phosphorescence band is emitted by de-aerated solutions of the unsubstituted piazselenol.

SELENOUS acid reacts with aromatic *ortho*-diamines to produce compounds containing the selenodiazol five-membered ring system. The reaction with an excess of 3,3′-diaminobenzidine to form 3′,4′-diaminophenylpiazselenol (I) has been adapted for the absorptiometric[1,2,3] and fluorimetric[4,5] determination of small amounts of selenium. For fluorimetric work of high sensitivity, this reagent suffers from several disadvantages. First, the fluorescence sensitivity of the compound is comparatively low. It has a fluorescence efficiency of only 5·5 per cent. in aerated solution, and the extinction coefficient at the exciting wavelength is also comparatively low, so that the fluorescence sensitivity index is only 0·003 at 2·29 μ^{-1} (436 mμ). As noted previously,[5] the search for an alternative fluorimetric reagent for selenium giving a higher fluorescence efficiency and extinction coefficient could be well worth-while if exceedingly low concentrations of selenium have to be determined. The second disadvantage of 3,3′-diaminobenzidine as a reagent is that it contains two pairs of *ortho*-diamine groups, only one of which reacts with selenium under the conditions of test, so that the resulting piazselenol is still comparatively strongly basic and can only be extracted from aqueous solution into organic solvents by increasing the pH value of the solution. This complicates the analytical procedure in presence of metals whose hydroxides are precipitated in neutral or alkaline solution and necessitates their removal or the addition of suitable complexing



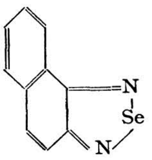
(I)

3′,4′-Diaminophenylpiazselenol



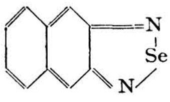
(II)

3,4-Benzo-1,2,5-selenodiazol (piazselenol)



(III)

3,4-Benzopiazselenol



(IV)

4,5-Benzopiazselenol

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* Presented at the Feigl Anniversary Symposium, Birmingham, April 9th, 1962.

agents, which have to be purified to a high degree. It would clearly be desirable to use a reagent reacting with selenous acid in acid solution to produce a selenodiazol derivative extractable from acid solution. *ortho*-Diamines containing only two amino-groups produce either neutral or very weakly basic selenodiazols and would therefore be expected to fit these requirements. The luminescence of three such compounds was therefore investigated, namely, those derived from *o*-phenylenediamine, and 1,2- and 2,3-diaminonaphthalene (**II**, **III** and **IV**, respectively). The first of these compounds was used by Ariyoshi, Kiniwa and Toei[6] for the absorptiometric determination of selenium, and the second was prepared by Hinsberg,[7] but the third does not appear to have been reported previously.

EXPERIMENTAL

APPARATUS—

For measurement of the luminescence emission spectra, a sensitive recording spectrophosphorimeter[8,9] fitted with an E.M.I. 9558QB red-sensitive photomultiplier was used. This instrument was capable of distinguishing between short-lived fluorescence emission and phosphorescence emission of lifetime longer than about 0·25 milli-second. For measurement of the spectra shown in Fig. 5 (p. 564), the chopper was removed from the beam of exciting light, so that the phosphorescence bands were recorded at their true intensities relative to the fluorescence bands.

Absorption spectra were measured with a Beckman DK2 recording spectrophotometer.

PREPARATION OF SELENODIAZOLS—

3,4-*Benzo*-1,2,5-*selenodiazol* (*piazselenol*)—A 0·75-g portion of selenium (as selenous acid) was dissolved in 50 ml of water, and the solution was added to a solution of 1 g of *o*-phenyldiamine in 250 ml of water. The pale buff-coloured precipitate formed was separated by filtration, dried by suction and recrystallised once from water at 70° C. It was then sublimed three times to give colourless needle-shaped crystals melting at 75° C (corrected); Hinsberg[10] recorded a melting-point of 76° C.

Naphtho-1′,2′,3,4-[1,2,5-*selenodiazol*] (3,4-*benzopiazselenol*)—Commercial 1,2-diaminonaphthalene was recrystallised twice from aqueous solution to give silvery leaf-shaped crystals melting at 96° C. A 0·5-g portion of selenium (as selenous acid) was dissolved in 50 ml of hot water, and the solution was added to a solution of 1 g of the recrystallised amine in 250 ml of hot water. The precipitate was separated from the hot solution by filtration, washed with hot water, dried by suction and recrystallised twice from ethanol, yielding pale buff-coloured needles melting at 128° C (corrected); Hinsberg[7] recorded a melting-point of 128° to 129° C.

Naphtho-2′,3′,3,4-[1,2,5-*selenodiazol*] (4,5-*benzopiazselenol*)—Commercial 2,3-diaminonaphthalene was recrystallised from water to give buff-coloured leaf-shaped crystals melting at 190° C (corrected). A 1-g portion of the recrystallised amine was dissolved in 250 ml of 0·1 N hydrochloric acid, and 0·5 g of selenium (as selenous acid) dissolved in 100 ml of 0·1 N hydrochloric acid was added; a bright-red precipitate appeared almost immediately. After 10 minutes, the precipitate was separated by filtration, dried over silica gel and recrystallised from light petroleum (boiling range 40° to 60° C) to give large red needles melting, with decomposition, at about 290° C. Analysis showed the compound to contain 50·3 per cent. of carbon, 2·7 per cent. of hydrogen, 11·8 per cent. of nitrogen and 32·7 per cent. of selenium; the theoretical contents for $C_{10}H_6N_2Se$ are, respectively, 51·5, 2·6, 12·0 and 33·9 per cent. (The selenium content was determined by combustion in oxygen as described previously,[5] but with use of a 500-ml conical flask). Dilute solutions of the compound in cyclohexane or dekalin were stable, but concentrated solutions in toluene deposited a white insoluble substance. This was separated, dried, and analysed; it was found to contain 50·9 per cent. of carbon, 2·7 per cent. of hydrogen, 11·9 per cent. of nitrogen and 32·6 per cent. of selenium. It was concluded that the white compound was a dimer or polymer of the 4,5-benzopiazselenol.

PURIFICATION OF SOLVENTS—

Cyclohexane—The grade sold as "special for spectroscopy" was used without further purification.

Dekalin—Commercial dekalin (boiling range 186° to 194° C) is a mixture of *cis* (b.p. 194° C) and *trans* (b.p. 186° C) isomers and contains appreciable amounts of tetralin (b.p.

207° C) and naphthalene (b.p. 218° C). The boiling-point of tetralin is sufficiently near to that of the *cis* isomer to make purification by fractionation difficult. *cis*-Dekalin can be converted into the *trans* isomer by means of aluminium chloride,[11] and this treatment was adopted before subjecting the liquid to fractionation.

A 500-ml portion of commercial dekalin was stirred in a closed flask with 125 g of anhydrous aluminium chloride for 7 days. The solvent was then decanted and treated for a further 7 days with a fresh 125 g of aluminium chloride; the dekalin was then fractionated in a heated column. About 300 ml of solvent boiling over the range 186° to 188° C were collected. This contained only a trace of tetralin and gave negligible fluorescence when irradiated with light of wavenumber 2·73 μ^{-1} (366 mμ).

CHOICE OF CONDITIONS FOR FLUORIMETRY—

Preliminary tests, in which 100-μg amounts of selenium (as selenous acid) were allowed to react with 100-mg portions of 2,3-diaminonaphthalene in 500-ml volumes of solutions of various acidities, showed that the rate of reaction decreased with increase of acidity and that, for concentrations of hydrochloric acid greater than 0·1 N, reaction was not complete, even after 2½ hours at room temperature.

Further tests were carried out in 1·0, 0·1 and 0·01 N hydrochloric acid at 50° C, the concentration of selenium being decreased to 5 μg per 500 ml. Portions (50 ml) of solution were periodically removed, cooled to 20° C and extracted with 5-ml amounts of cyclohexane; the amount of 4,5-benzopiazselenol was then determined fluorimetrically. With 0·1 N hydrochloric acid, reaction was complete after 15 minutes at this temperature, although still incomplete after 1 hour in N acid solution. It was found that, by increasing the time of reaction to 20 minutes at 50° C in 0·1 N hydrochloric acid, the concentration of reagent could be decreased by one half, reaction of 0·5 μg of selenium per 50 ml of solution still being complete. These conditions were therefore chosen for the fluorimetric determination.

PURIFICATION OF 2,3-DIAMINONAPHTHALENE—

It was found that recrystallised 2,3-diaminonaphthalene gave rise to a comparatively high blank fluorescence when treated as described in absence of selenous acid. This fluorescence did not arise from selenium, but from traces of fluorescent impurity present in the reagent and extracted by the organic solvent from solution in 0·1 N hydrochloric acid. To minimise this blank fluorescence, the reagent was freshly prepared each day as described below.

> Recrystallised 2,3-diaminonaphthalene (0·05 g) was dissolved in 50 ml of 0·1 N hydrochloric acid, and the solution was heated at 50° C for 20 minutes. It was then cooled to 20° C, extracted twice with 10-ml portions of dekalin to remove the fluorescent impurities, and spun in a centrifuge. This procedure, and that described below for determining selenium, was carried out in a room lit only by yellow "safe" lights.

FLUORIMETRIC DETERMINATION OF SELENIUM

Volumes of standard solutions of selenous acid in 0·1 N hydrochloric acid, containing between 0·005 and 0·025 μg of selenium, were transferred to separate 60-ml beakers, and each solution was diluted to 45 ml with 0·1 N hydrochloric acid. The beakers were covered with watch-glasses and placed in a water bath maintained at 50° C. After 5 minutes, 5 ml of 2,3-diaminonaphthalene reagent solution were added to the contents of each beaker, and the solutions were mixed and left in the bath for 20 minutes. Each was then cooled to 20° C, transferred to a separating funnel and vigorously shaken with 5 ml of purified dekalin for 1 minute. Each dekalin extract was shaken with two successive 25-ml portions of 0·1 N hydrochloric acid to remove the last traces of reagent, spun in a centrifuge for 2 minutes and transferred to a 1-cm spectrofluorimeter cuvette for measurement. The intensity of the fluorescence excited by light of wavenumber 2·73 μ^{-1} was found to be proportional to the concentration of selenium up to at least 0·5 μg, although the normal range for measurement was 0·002 to 0·03 μg of selenium per 5 ml of dekalin. The reagent blank reading at the wavenumber corresponding to the uncorrected peak in the fluorescence emission spectrum of the selenium compound was equivalent to 0·002 μg of selenium in 5 ml of dekalin. Comparison of the spectra with those obtained from known concentrations of 4,5-benzopiazselenol in dekalin showed that the over-all recovery of selenium was 95 per cent. (see Fig. 1).

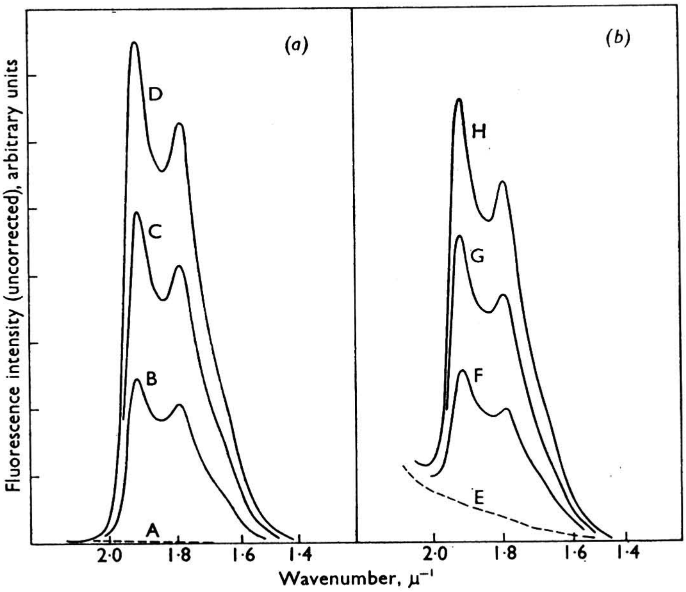

Fig. 1. Fluorescence emission spectra of 4,5-benzopiazselenol in aerated dekalin. (*a*) Pure compound at concentration of: curve A, 0·0 μg per ml; curve B, 0·0053 μg per ml; curve C, 0·0106 μg per ml; curve D, 0·0159 μg per ml. (*b*) Solutions derived from selenous acid by the prescribed procedure and containing selenium equivalent to: curve E, 0·0 μg per ml; curve F, 0·0014 μg per ml; curve G, 0·0028 μg per ml; curve H, 0·0042 μg per ml.

Excitation with 2·73-μ^{-1} (366 mμ) light; half-band width 0·025 μ^{-1} at 2·5 μ^{-1}

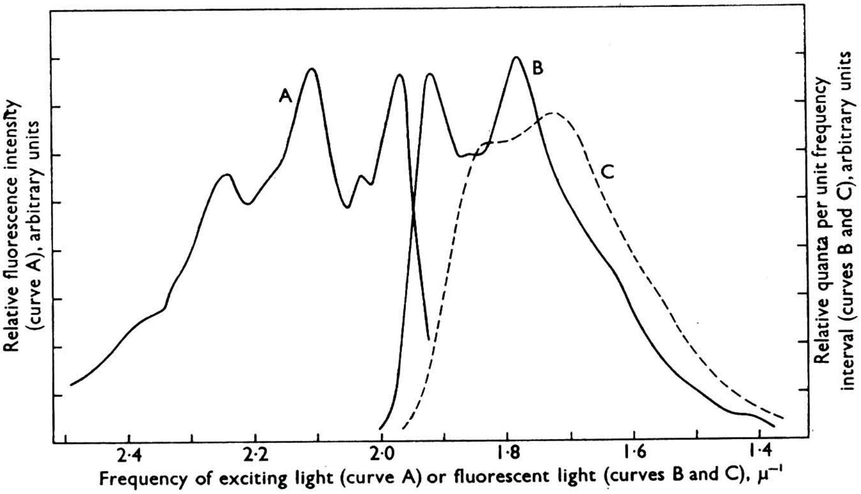

Fig. 2. Corrected fluorescence excitation and emission spectra of 4,5-benzopiazselenol at concentration of 0·7 μg per ml: curve A, excitation spectrum in cyclohexane; curve B, emission spectrum in cyclohexane; curve C, emission spectrum in toluene containing 10 per cent. v/v of cyclohexane.

Excitation with 2·73-μ^{-1} (366 mμ) light for curves B and C; half-band width 0·025 μ^{-1} at 2·5 μ^{-1}

ABSORPTION AND FLUORESCENCE SPECTRA

Preliminary examination showed that solutions of 4,5-benzopiazselenol were far more fluorescent than those of the other selenium compounds. Tests were first made in toluene, as this solvent had proved satisfactory for extracting the piazselenol derivative previously investigated.[5] In toluene, or toluene containing a small amount of cyclohexane, the 4,5-benzopiazselenol exhibited yellow fluorescence (see Fig. 2, curve C), but the solutions were not stable and deposited a white amorphous solid that appeared to be a polymer (see p. 559). It seemed that some kind of association effect occurred in the toluene solutions, even before appreciable decomposition had taken place, since the absorption and fluorescence spectra in this solvent were much more diffuse and shifted to lower wavenumbers compared with the spectra of solutions in cyclohexane. In the latter solvent, the compound exhibits green fluorescence (see Fig. 2, curve B), the fluorescence emission spectrum showing fine structure similar to the rather weak low-frequency absorption band occurring in the blue region of the spectrum in this solvent (see Fig. 3, curve C). A much more intense absorption band appears in the near-ultraviolet region and yet a third band in the middle-ultraviolet region (see Fig. 3, curve C). Excitation in all three absorption bands gives rise to fluorescence, and the complete excitation spectrum (Fig. 4) is similar in shape to the absorption spectrum.

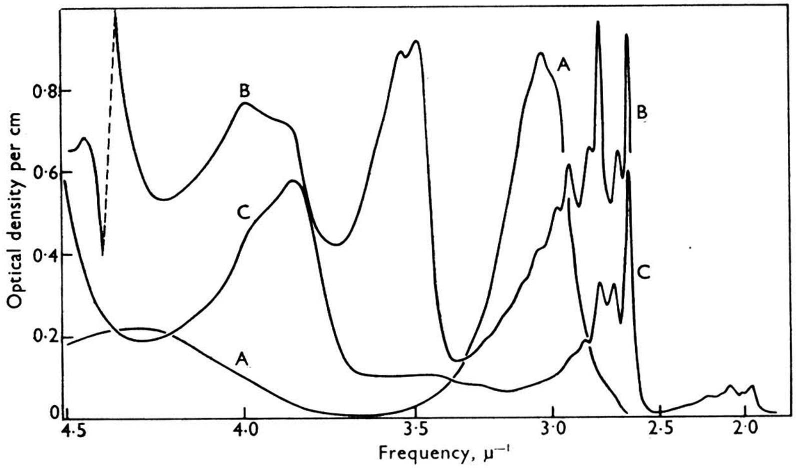

Fig. 3. Absorption spectra of piazselenols in cyclohexane: curve A, 9·5 μg of piazselenol per ml; curve B, 14·9 μg of 3,4-benzopiazselenol per ml; curve C, 4·4 μg of 4,5-benzopiazselenol per ml

In contrast, the fluorescence from the other two compounds (**II** and **III**) was weak. 3,4-Benzopiazselenol gave rise to a recognisable emission spectrum when excited with light of wavenumber 2·73 μ^{-1} (366 mμ). Piazselenol did not absorb appreciably at 2·73 μ^{-1} and, when excited with light of wavenumber 3·19 μ^{-1} (313 mμ), gave only very weak fluorescence that may have arisen from traces of impurity.

The fluorescence efficiencies of the three compounds, determined by comparision with a solution of quinine bisulphate in 0·1 N sulphuric acid, are compared in Table I with that of the piazselenol derivative formed from 3,3′-diaminobenzidine, which was previously used in determining selenium. Values of the fluorescence sensitivity index[12] are also shown in Table I; the sensitivity attained for 4,5-benzopiazselenol with excitation at 2·73 μ^{-1} was some twenty times greater than that attained for 3′,4′-diaminophenylpiazselenol.

Owing to its high volatility, cyclohexane is not an ideal solvent for use in a method involving extraction, particularly if experiments including de-aeration by passage of nitrogen are contemplated. Dekalin is much less volatile, and absorption and fluorescence spectra in this solvent are similar to those in cyclohexane. This solvent was therefore chosen for the fluorimetric method ultimately adopted. The fluorescence efficiency of 4,5-benzopiazselenol in dekalin is shown in Table I. Dekalin has the further advantage over cyclohexane that the quenching of fluorescence by air is less.

OXYGEN QUENCHING OF LUMINESCENCE

De-aeration of solutions of 4,5-benzopiazselenol was found to increase the intensity of the fluorescence band by a factor of about 3 (in cyclohexane) or 2 (in dekalin), without otherwise changing its form. The weak fluorescence band of 3,4-benzopiazselenol was unaffected by de-aeration, but a new band, completely absent with aerated solutions, appeared in the red region. A similar band appeared when solutions of piazselenol were completely de-aerated (see Fig. 5). The quenching effect of oxygen on the latter two bands was so great as to suggest that their origin was an excited state of extremely long lifetime. This was confirmed by taking measurements with the choppers of the spectrophosphorimeter out of phase. The red bands were found to correspond to phosphorescence having a lifetime of about 0·2 to 0·3 milli-second. The phosphorescence efficiencies were determined by comparison with solutions of quinine bisulphate and are shown in Table I.

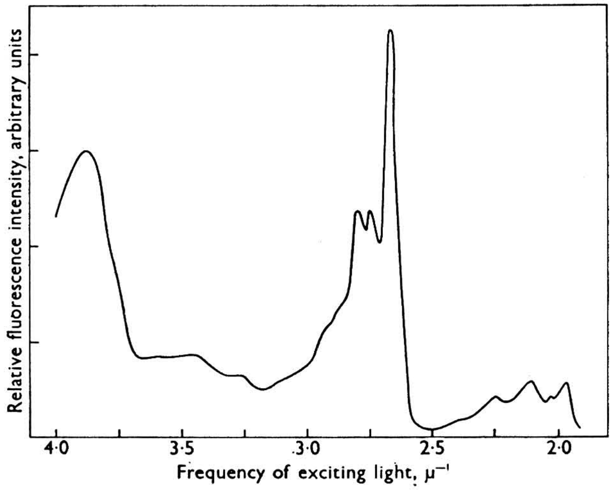

Fig. 4. Corrected fluorescence excitation spectrum of 4,5-benzopiazselenol in cyclohexane at concentration of 1 μg per ml. Half-band width of excitation monochromator 0·02 μ^{-1} at 2·5 μ^{-1}

TABLE I

LUMINESCENCE RESULTS FOR PIAZSELENOLS

Fluorescence efficiency	Fluorescence sensitivity index $\left(\frac{\phi D}{H}\right)$	Phosphorescence efficiency	Phosphorescence sensitivity index $\left(\frac{\phi D}{H}\right)$	Air-quenching factor for fluorescence	Excitation frequency, μ^{-1} (mμ)	Fluorescence emission maximum, μ^{-1}	Phosphorescence emission maximum, μ^{-1}
Piazselenol in cyclohexane—							
Very small	Very small	0·0009	0·00012	—	3·19 (313)	—	1·51
3,4-*Benzopiazselenol in cyclohexane—*							
0·0014	0·00017	0·0052	0·00048	1·0	2·73 (366)	2·50	1·66
4,5-*Benzopiazselenol in cyclohexane—*							
0·52	0·12*	—	—	3·1	2·73 (366)	1·92, 1·78	—
4,5-*Benzopiazselenol in dekalin—*							
0·46	0·094*	—	—	2·1	2·73 (366)	1·92, 1·78	—
4,5-*Benzopiazselenol in toluene containing* 10 *per cent. of cyclohexane—*							
0·53	0·097	—	—	2·8	2·73 (366)	1·72	—
3′,4′-*Diaminophenylpiazselenol in toluene—*							
0·076	0·0045	—	—	1·4	2·29 (436)	1·65	—

* At 1·92 μ^{-1}.

Although the phosphorescence efficiencies are comparatively low, the use of these compounds for determining trace amounts of selenium might have some advantages, because, if a phosphorimeter were used to measure the phosphorescence, all scattered light and fluorescence from traces of impurities in the solution could be completely eliminated,[9] and the blank value arising from other fluorescent impurities would therefore be extremely low. This possibility was not further investigated, since it was found that sufficiently high efficiency and sensitivity could be attained by using the fluorescence of 4,5-benzopiazselenol.

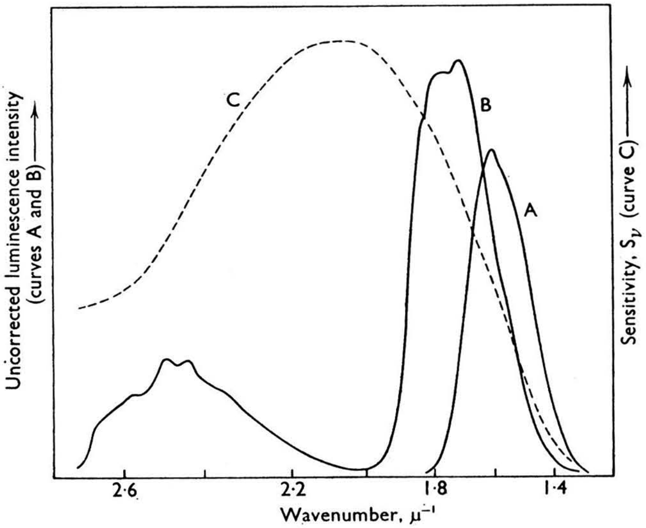

Fig. 5. Luminescence emission from piazselenol (4·4 μg per ml) and 3,4-benzopiazselenol (5·7 μg per ml) in cyclohexane at 20° C. Curve A, phosphorescence band of piazselenol: excitation with 3·19-μ^{-1} (313 mμ) light; half-band width 0·066 μ^{-1} at 2·5 μ^{-1}. Curve B, phosphorescence and fluorescence bands of 3,4-benzopiazselenol: excitation with 2·73-μ^{-1} (366 mμ) light; half-band width 0·018 μ^{-1} at 2·5 μ^{-1}. Curve C, sensitivity (S_ν) curve of quartz-prism spectrometer fitted with E.M.I. 9558QB photomultiplier

DETERMINATION OF SELENIUM WITH 2,3-DIAMINONAPHTHALENE

2,3-Diaminonaphthalene will react with traces of selenium in both acid and neutral solution, but the rate of reaction decreases as the acidity is increased. Rates of reaction were determined at various pH values, and a concentration of 0·1 N hydrochloric acid was finally chosen for the method. At this concentration, the rate of reaction is sufficiently rapid; at the same time, the acidity is sufficient to keep most metals in solution. After reaction, the 4,5-benzopiazselenol can be extracted into a small volume of dekalin.

The factor limiting sensitivity was the blank fluorescence arising from traces of impurity in the 2,3-diaminonaphthalene reagent. This blank value was minimised by recrystallisation of the reagent in the dark and by pre-extraction with dekalin of a solution of the reagent in 0·1 N hydrochloric acid. To minimise subsequent decomposition, the entire procedure for determining selenium was carried out in a room illuminated by only yellow safe lights. The fluorescence spectra of solutions derived from the reaction of small amounts of selenium, together with that of a typical blank solution, are compared in Fig. 1 with the spectra of dilute solutions of pure 4,5-benzopiazselenol in dekalin. The residual blank fluorescence (Fig. 1, curve E) was due to traces of organic impurity, and, at the frequency of the peak in the fluorescence spectrum of the selenium compound, had a value corresponding to about 0·002 μg of selenium. This blank value was reproducible, and it was estimated that a weight of selenium equivalent to the blank value could reliably be detected.

The solutions yielding the spectra shown in Fig. 1 were not de-aerated. De-aeration increases the fluorescence of the selenium compound by a factor of 2, and it might therefore be expected that the relative magnitude of the blank fluorescence arising from impurities would be correspondingly decreased. Unfortunately, de-aeration produced some increase in the fluorescence of the impurity, and it was decided that the inconvenience of de-aeration was not justified by the relatively small over-all gain in sensitivity. The use of air-saturated solutions was therefore adopted in the final procedure.

INTERFERING ELEMENTS

Preliminary tests have shown that, if the experiment is carried out in the presence of ethylenediaminetetra-acetic acid, relatively few elements interfere. A more detailed investigation of interfering elements is in progress, and it is hoped that the results will be reported later, with an account of the use of the method for determining traces of selenium in high-purity gallium arsenide.

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REFERENCES

1. Hoste, J., *Anal. Chim. Acta*, 1948, **2**, 402.
2. Hoste, J., and Gillis, J., *Ibid.*, 1955, **12**, 158.
3. Cheng, K. L., *Anal. Chem.*, 1956, **28**, 1738.
4. Watkinson, J. H., *Ibid.*, 1960, **32**, 981.
5. Parker, C. A., and Harvey, L. G., *Analyst*, 1961, **86**, 54.
6. Ariyoshi, H., Kiniwa, M., and Toei, K., *Talanta*, 1960, **5**, 112.
7. Hinsberg, O., *Ber.*, 1889, **22**, 866.
8. Parker, C. A., and Hatchard, C. G., *Trans. Faraday Soc.*, 1961, **57**, 1894.
9. ——, ——, *Analyst*, in the press.
10. Hinsberg, O., *Ber.*, 1889, **22**, 2897.
11. Zelinsky, N., and Turowa-Pollak, M., *Ibid.*, 1932, **65**, 1299.
12. Parker, C. A., and Rees, W. T., *Analyst*, 1960, **85**, 587.

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The Micro-determination of Inorganic and Total Sulphate in Urine

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A micro method involving use of ethylenediaminetetra-acetate for determining inorganic and total sulphate in urine has been tested on rat urine. The results were similar to those given by two routine macro methods for determining total sulphate in urine. The micro method offers an advantage in that less than 1 ml of urine is required for a determination.

EXISTING methods for determining sulphate in urine suffer from the disadvantage that a considerable volume of sample is required. Often, only small volumes of urine are available for analysis, particularly in investigations involving small animals. Methods in which disodium ethylenediaminetetra-acetate (EDTA) is used for determining sulphur as sulphate have been reviewed.[1,2] Belcher, Bhasin, Shah and West[3] developed a procedure for the determination of sulphur in organic compounds in which the compound is oxidised, and the sulphate formed is precipitated as the barium salt by adding barium chloride solution. The precipitate is separated by filtration and dissolved in a measured excess of an ammoniacal solution of EDTA, and the excess of EDTA is determined by titration with standard magnesium chloride solution, with Solochrome black T as indicator. This method has been modified in the work described here to permit determination of inorganic and total sulphate in urine. Ethereal sulphate was reported as the difference between the results for inorganic and total sulphate.

METHOD

APPARATUS—

Magnetic stirrer.

Glass-encased rotors, $\frac{3}{16}$ inch long—For use with the magnetic stirrer.

Agla micrometer-syringe burette (0·5 *ml*), *with needles.*

Hypodermic syringe (2 *ml*) *and needles* (*size* 15).

Transfer pipettes—Made from drawn-out Pyrex-glass tubing, with rubber teats to fit.

Micro-filtration tubes—Made from Pyrex-glass tubing 1 cm in diameter, shrunken at one end to leave a hole 1 mm in diameter and cut to a length of 3 cm; the cut end was flanged.

Pyrex-glass tubes—3 inches × 0·5 inch.

Bench centrifuge—To hold six test-tubes.

All glassware was cleaned with Teepol and hot water and then allowed to soak overnight in nitric acid - potassium dichromate cleaning mixture. The glassware was then rinsed successively with tap-water, distilled water and finally de-ionised water. Clean glassware was stored on filter-paper over phosphorus pentoxide in a desiccator.

REAGENTS—

Unless otherwise stated, all materials were of analytical-reagent grade.

Barium chloride solutions—Solutions containing (*a*) 1·5 mg and (*b*) 4·0 mg of $BaCl_2$ per ml.

Hydrochloric acid, 0·1 *and* 3 N—Prepared from acid of M.A.R. grade.

Solochrome black T 150 *indicator solution,* 0·1 *per cent. w/v, in ethanol*—Freshly prepared before use.

EDTA reagent solution, approximately 0·02 M—Standardised against magnesium sulphate heptahydrate by Schwarzenbach's method.[2]

Dimethyl yellow solution, 0·05 *per cent. w/v, in ethanol.*

Magnesium chloride, approximately 0·01 M—Standardised against standard EDTA solution.

Ammonia solution, sp.gr. 0·880.

Sodium sulphate, anhydrous.

Filter-paper pulp, ashless.

PROCEDURE FOR DETERMINING INORGANIC SULPHATE—

Different portions of diluted, freshly filtered rat urine (which had been stored at 4° C) or urine with added sodium sulphate were transferred by means of the micrometer-syringe burette to test-tubes. To the contents of each tube were added 1 ml of 0·1 N hydrochloric acid and then sufficient barium chloride solution to give a 50 per cent. excess over the amount needed to precipitate the sulphate present (the upper limit of sulphate content in urine was assumed to be 5 mg of SO_4^{2-} per ml). Depending on the amount of sulphate present, the solution in each test-tube was diluted to 1 or 2 ml with de-ionised water. The tube was placed in a bath of boiling water for 30 minutes and then allowed to cool. (The bath contained de-ionised water, as tests showed that the tap-water spray contained sulphate.) The suspension of barium sulphate was spun in a centrifuge, and the supernatant liquid was removed with a transfer pipette and filtered through a pad of filter-paper pulp in a prepared micro filter.[4] The precipitate was washed with 1 ml of 0·1 N hydrochloric acid and then with two separate portions of de-ionised water, each washing being removed as previously described after centrifugation. After washing had been completed, the filter-paper pad was impaled on a needle and transferred to the test-tube, together with washings from the transfer pipettes, filter and needles (washing was carried out with use of a 2-ml hypodermic syringe). Standard EDTA solution was added to the contents of each tube from the micrometer-syringe burette, the amount added being about twice as much as that needed to dissolve the barium sulphate present. Two drops of ammonia solution were added, and the tube was heated over a small flame until its contents almost reached boiling-point. At this stage, the tubes were transferred to a bath of boiling water for 5 minutes.

When the solutions were cool, 1 drop of ammonia solution was added to each, and the heating was repeated; at this stage, all the barium sulphate had dissolved. To each cooled solution were added 1 drop of ammonia solution, 2 drops of Solochrome black T indicator solution and 1 drop of dimethyl yellow solution, and a glass-encased rotor was placed in the test-tube. While the solution was stirred magnetically, the excess of EDTA was titrated with standard magnesium chloride solution added from the syringe burette; the end-point was taken as being when the colour of the indicator just changed from green to pink.

PROCEDURE FOR DETERMINING TOTAL SULPHATE—

A 2-ml portion of freshly filtered rat urine was transferred to a small evaporating basin, and 1 ml of 3 N hydrochloric acid was added. The acidified urine was evaporated to dryness on a bath of boiling water, and the residue was extracted with two 5-ml portions of de-ionised water. The combined extracts were filtered through a dry filter-paper, and sulphate was determined in portions of the filtrate (0·30 to 0·80 ml) as described above.

RESULTS AND DISCUSSION OF THE METHOD

A sample of urine was diluted (1 + 4) with de-ionised water, and portions of the diluted sample were analysed for inorganic sulphate by the proposed method. The mean sulphate content found was 593 µg per ml; the results, each of which is the average of duplicate determinations, were—

Volume of diluted sample used, ml	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50
Sulphate found per ml of diluted sample, µg	595	615	598	598	592	594	583	575	601
Deviation from mean, µg	+2	+22	+5	+5	−1	+1	−10	−18	+8

Results for the recovery of inorganic sulphate added to urine are shown in Table I. The proposed method for determining inorganic sulphate was then compared with

TABLE I: RECOVERY OF INORGANIC SULPHATE ADDED TO URINE

A sample of urine was divided into two portions, A and B. Both were diluted (1 + 4) with de-ionised water, and to B was added 1 mg of sodium sulphate per ml. Duplicate determinations were carried out

Volume of diluted sample used, ml	Mean sulphate content found in— urine A, µg per ml	Mean sulphate content found in— urine B, µg per ml	Recovery of added sulphate, µg
0·10	319	1238	919
0·20	305	1357	1052
0·30	331	1316	985
0·40	326	1323	997
0·50	328	1350	1022
Mean ..	322	1317	995

two other methods, namely, Fiske's benzidine method[5] and Folin's gravimetric method.[6] For a sample of urine diluted (1 + 4) with de-ionised water, the results were—

Method	Proposed	Fiske	Folin
Volume of diluted sample used, ml	0·5	5·0	25·0
Sulphate content found, mg per 25 ml	10·65, 10·38	10·67, 10·40	10·70, 10·91

In Table II are shown results for the determination of total sulphate in urine by the proposed method and by that of Fiske.[5]

TABLE II: RESULTS FOR TOTAL AND INORGANIC SULPHATE IN URINE

A portion of urine was hydrolysed by hydrochloric acid for determinations of total sulphate; a further portion of the same urine was used for determining inorganic sulphate. Both portions were diluted (1 + 4) with de-ionised water, and duplicate determinations were carried out

Method	Volume of diluted sample used, ml	Sulphate found in diluted sample: Inorganic (A), μg per ml	Total (B), μg per ml	Ethereal (B − A), μg per ml
Proposed	0·30	604	653	49
	0·40	617	640	23
	0·50	611	627	16
	0·60	593	638	45
	0·70	609	645	36
	0·80	608	648	40
	Mean	607	642	35
Fiske	5·0	610	650	40

Determination of inorganic sulphate in urine diluted (1 + 4) with water was constant for samples in the range 0·1 to 0·5 ml, and results by the micro method are in good agreement with those obtained by the two macro methods (see results above). Further, determinations of known amounts of added sulphate were satisfactory (see Table I). Ethereal sulphate was calculated by difference from the results of parallel determinations of total and inorganic sulphate on amounts of diluted urine varying from 0·3 to 0·8 ml (see Table II); the results obtained compared favourably with those found by Fiske's macro method.[5]

Determinations on undiluted urine were occasionally complicated by retention of colour in the precipitated barium sulphate. This colour could not be completely removed by washing the precipitate and interfered with the sharpness of the colour change in the final titration. Dilution of the urine with 4 volumes of water was found to be sufficient to ensure a sharp end-point with all the urines examined. It was also found that the colour could be removed by boiling the precipitate with a few drops of 100-volume hydrogen peroxide for 2 or 3 minutes after the excess of barium chloride had been removed and the precipitate had been washed once with 0·1 N hydrochloric acid; prolonged boiling with hydrogen peroxide led to difficulties in dissolving the barium sulphate in ammoniacal EDTA solution.

The results obtained suggest that the proposed method can be used for determining inorganic and total sulphate when less than 1 ml of urine is available for analysis.

I thank Professor L. Young, Department of Biochemistry, St. Thomas's Hospital Medical School, for suggesting the possible application of this technique to the problem and for his interest in the subsequent work. A gift of Solochrome black T by Imperial Chemical Industries is gratefully acknowledged.

REFERENCES

1. West, T. S., and Sykes, A. S., "Analytical Applications of Diamino-Ethane-Tetra-Acetic Acid," Second Edition, The British Drug Houses Ltd., Poole, Dorset, 1960, p. 74.
2. Schwarzenbach, G., "Complexometric Titrations," Methuen & Co. Ltd., London, 1957.
3. Belcher, R., Bhasin, R. L., Shah, R. A., and West, T. S., *J. Chem. Soc.*, 1958, 4054.
4. Hawk, P. B., Oser, B. L., and Summerson, W. H., "Practical Physiological Chemistry," Thirteenth Edition, J. & A. Churchill Ltd., London, 1954, p. 949.
5. ——, ——, ——, *op. cit.*, p. 950.
6. Folin, O., *J. Biol. Chem.*, 1905, 1, 131.

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The Paper-chromatographic Separation and Determination of Chlorinated Insecticide Residues

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An investigation into the most suitable conditions for the identification, separation and determination of microgram amounts of the more important chlorinated insecticides and some of their metabolites by reversed-phase paper chromatography is described. Upward displacement on Whatman No. 3 paper with liquid paraffin as fixed phase and aqueous acetone as mobile phase is used. The papers are dipped in a silver nitrate developing reagent and then dried thoroughly, and the spots are rendered visible by irradiation at 2537 A. A separation of eleven insecticides or metabolites is possible. The relationship between the area of the spot and the logarithm of the amount of insecticide present is linear over different ranges for each, and the accuracy of determination for pure insecticides is within ±10 per cent. for amounts from 2·5 μg upwards.

BECAUSE of the increasing number of chlorinated insecticides brought into use in the last decade, many workers have considered general methods for identifying and determining mixed residues. Reversed-phase paper chromatography was originally used by Winteringham, Harrison and Bridges[1] for the separation of ^{82}Br-labelled analogues of DDT.* Later, Moynihan and O'Colla[2,3] adopted the technique for separating BHC isomers, chlordane, toxaphene and DDT. Their solvent system comprised acetic anhydride as fixed phase and n-hexane saturated with acetic anhydride as mobile phase; the insecticides were located by spraying the paper with a mixed reagent prepared from a saturated aqueous solution of ferrous sulphate and glacial acetic acid and then heating. Mitchell,[4] in the first of a series of papers, reported an improvement in the separation of isomers of BHC obtained by using mixed octanes as mobile solvent; after break-down of the isomers by chemical means, he used silver nitrate as the final locating agent. Suitable solvent systems for separating a number of groups of insecticides were later suggested,[5,6] and the method of location was improved by using ultraviolet light of short wavelength to facilitate decomposition of the separated compounds.[7] Subsequently, Mitchell[8] reported on R_F values and sensitivities for 114 chlorinated pesticides in an aqueous sytem (soya-bean oil as fixed phase; 2-methoxyethanol in water as mobile phase) and in a non-aqueous system (2-phenoxyethanol as fixed phase; 2,4,4-trimethylpentane as mobile phase). This technique was applied by McKinley and Mahon[9] to the identification of pesticide residues in food, and Mills[10] described a general method for the detection and semi-quantitative determination of residues in fruits, fats and oils by visual comparison of the unknown spots with standards run concurrently. In a collaborative study of six chlorinated insecticides in milk,[11] the results found by sixteen participating laboratories showed reasonable agreement at the 0·1 p.p.m. level; Major and Barry[12] have recently described a screening technique with semi-quantitative interpretation at the 5 p.p.m. level.

Methods for identifying *lindane* and isomers of BHC[13] and for the identification and semi-quantitative determination of five insecticide residues in dairy products[14] have now been adopted as "first action" by the Association of Official Agricultural Chemists. San Antonio[15] obtained recoveries accurate to within ±10 per cent. by cutting out and weighing the developed spots from untreated soil extracts to which insecticides had been added; McKinley, Savary and Webster[16] attained similar accuracy by paper-chromatographic separation of mixtures of residues, with subsequent elution of the spots and chemical analysis of the eluates.

This paper deals with the separation of the more important chlorinated insecticides and with the determination of the accuracy to be expected from direct examination (measurement of the areas of spots) for amounts of each insecticide in the microgram range.

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* Unless in *italic* type, the names of insecticides conform with the recommendations made in British Standard 1831:1961.

EXPERIMENTAL

IDENTIFICATION—

The spots of insecticide on the chromatogram are treated with a chromogenic reagent consisting of silver nitrate and 2-phenoxyethanol and are then rendered visible by irradiation with ultraviolet light of short wavelength. The mechanism of the reaction, as postulated by Ingold,[17] is that it occurs on the surface of the silver salt in the presence of adsorbed silver ions in an alcoholic medium containing one or more alkoxy groups. A number of reagents in which the insecticides are soluble and silver nitrate is not have been examined; 2-phenoxyethanol was found to be the most suitable. As this compound is only sparingly soluble in water, a 25 per cent. v/v solution of ethanol in water was chosen as the main solvent for the chromogenic reagent. Less diffusion of the spots and more even distribution of the reagent are obtained if the chromatograms are dipped rather than sprayed. The papers must be irradiated with unfiltered ultraviolet light in the spectral region used for bactericidal purposes (2537 A); it is essential that the chromatograms be dry at the beginning of irradiation. The spots of silver chloride initially formed are probably reduced to sub-chlorides or metallic silver, so that, after being washed with distilled water, the spots appear brown against a straw-coloured background.

SEPARATION—

Whatman No. 3 chromatography paper was chosen as the most suitable of the nine grades examined. Pre-treatment of the paper is necessary in order to reduce chloride-bearing impurities on the surface; consistent light-coloured backgrounds are obtained by successive washing with silver nitrate solution, ammonia solution and distilled water.

Because of the low solubility of chlorinated insecticides in water and their consequent unfavourable partition between water and organic solvents, a reversed-phase system involving use of paper previously impregnated with a solvent is necessary. Many combinations of fixed and mobile solvent phases in different proportions were examined for the best individual separation of thirteen of the more important insecticides or their metabolites. The systems investigated were similar to those used by other workers.[8] Two types of solvent system are distinguished: (*i*) aqueous systems, in which the mobile phase is a mixture of water and a miscible organic solvent and the fixed phase a vegetable or mineral oil and (*ii*) non-aqueous systems, in which the partition is between a pair of immiscible or only slightly miscible organic solvents. The relative order of the R_F values found did not vary appreciably with the choice of fixed phase. Liquid paraffin B.P. (applied as a 10 per cent. v/v solution in diethyl ether) and a 70 per cent. v/v solution of acetone in water (unsaturated with respect to the immobile phase) were selected as giving the best separation. Distinction between HHDN (aldrin), *pp'*-DDE, heptachlor, *pp'*-DDT, endrin, HEOD (dieldrin), heptachlor epoxide, *pp'-TDE* (*pp'-DDD*, *Rhothane*), gamma-BHC, methoxychlor and endosulfan alcohol (*thiodan* alcohol) were possible with this system when amounts in the range 1 to 20 μg were present; dehydrochlorinated TDE coincided with heptachlor, endosulfan A with endrin and endosulfan B with gamma-BHC. Attempts to improve separation by using ternary and quaternary water - solvent mixtures were unsuccessful.

It is advisable to develop the chromatogram with the solvent running at right angles to the machine direction of the paper. The descending-solvent technique offers no advantage over ascending chromatography in ease of manipulation or in improved separation; overnight development (16 hours) results in appreciably lower sensitivity and decreased resolution. After measurement, chromatograms can be preserved for qualitative reference by washing them with a 1 per cent. w/v solution of sodium thiosulphate for 10 to 30 seconds and then with distilled water.

DETERMINATION—

Quantitative methods of assessing paper chromatograms have been reviewed.[18] The particular method of interest for insecticides is that described by Fisher, Parsons and Morrison,[19] which is based on the linear relationship between the logarithm of the amount of material on the spot (within a limited range) and its area. Each of the insecticides examined obeys this relationship for the particular solvent system used, but the validity range varies from one insecticide to another. Before accurate determinations can be made, however, it is necessary to obtain a measure of repeatability for the area measurements both on and between chromatograms when two or more papers are run together. To achieve this, it is first necessary to ensure that the technique will give reproducible R_F values both on and between chromatograms developed at the same time and also preferably between those developed on different days.

The variation of R_F values for any given system depends on a number of factors, and some of these, such as the concentrations of mobile and immobile solvent phases, the type of paper and its pre-treatment, the manner of development and the distance of the origin line from the surface of the solvent, are easily controlled. It is important that the tank and its fittings be such that the setting of a suspended paper is accurately reproducible. The most important factors affecting R_F values, however, are the conditions of saturation of the atmosphere within the tank and the degree of equilibration of the papers before development. The former depend on the minimum volume of solvent necessary for complete saturation of the atmosphere and on the number of papers developed concurrently. The critical saturation volume for the 70 per cent. v/v solution of acetone in water in the 20-litre chromatographic tank used is about 200 ml, so that a large volume (400 to 500 ml) of mobile solvent is used to ensure complete saturation. Supersaturation with respect to the more volatile component of the mobile solvent, and consequent "bowing" of the solvent front, may result from the simultaneous development of too many papers; this can be overcome by increasing the proportion of water in the mobile solvent. A comparison between papers equilibrated in a saturated atmosphere and unequilibrated papers shows that, for the acetone - water system, the former are unsatisfactory, *i.e.*, all the solvent vapours must be removed from the chromatographic tank before use. Consistent R_F values are obtained by using 400 to 500 ml of the 70 per cent. v/v solution of acetone for developing two papers or a similar volume of a 67 per cent. v/v solution of acetone in water for four papers within the temperature range 20° to 24° C. A high-walled reservoir should not be used for the solvent, as this leads to compression of the R_F range.

Transference of residues to the chromatography paper with several portions of ethyl acetate gave low recoveries, owing to losses during successive evaporations of the solvent. Solution of the residue in 20-μl portions of several less volatile solvents and use of an aliquot of the solution for transference was satisfactory. Of the solvents so used, dioxan is preferred, as it gives satisfactory results, provided that the volume taken does not exceed 6 μl applied in not more than two aliquots. If the total weight of residue does not exceed 12·5 μg, an alternative procedure is to transfer all of the dioxan solution, but recoveries in these circumstances are limited by the ability to transfer completely such small amounts and are in practice about 75 per cent.

METHOD

APPARATUS—

Chromatographic tank—Accurate control of the setting of the suspended papers is achieved by ensuring that the supporting unit is rigid and truly horizontal. All-glass tanks (21 cm × 26 cm × 37 cm) fitted with flat ground-glass lids are used; these can conveniently be prepared from suitable accumulator tanks. The internal fittings are made from stainless steel (6- and 12-mm rod and 1-mm sheet) and consist of (*a*) a solvent tray (15 cm × 21 cm × 2 cm) having a flat base mounted on three adjustable screw-legs and supported in the tank on three cup sockets, (*b*) a pair of brackets (15 mm × 15 mm × 15 cm) mounted 2 to 3 cm from the top edge of the tank with bolts (fitted with polythene washers) passing through holes drilled in the short sides of the tank and (*c*) a rigid frame comprising four parallel 6-mm rods set 3·3 cm apart and each fitted with a pair of stainless-steel photographic clips, held between a pair of 12-mm rods. The frame is supported in the tank by the brackets.

Ultraviolet lamp—Two Philips TUV 15-watt germicidal strip lamps mounted parallel with centres 5 cm apart and 15 cm above the chromatographic strips and housed in a light-proof box, the door of which is "guarded" by a microswitch in the lamp circuit; these precautions are necessary to prevent exposure of the eyes to radiation.

Oven for drying chromatograms—Set to operate at 40° to 45° C. A domestic hair-drier can be used, but is less convenient.

Dipping trays—Glass trays approximately 20 cm × 8 cm × 4 cm for the immobile solvent and the chromogenic reagent. Polythene trays 35 cm × 25 cm × 4 cm are suitable for washing the papers.

Micropipettes—Of capacity 2 and 20 µl; the former can be conveniently made from drawn-out capillary tubing and should be calibrated to a tolerance of ±1 per cent. at 1 and 2 µl.

REAGENTS—

Materials should be of analytical-reagent grade when available.

Silver nitrate solution, 0·5 per cent. w/v.

Ammonia solution—Approximately 6 per cent. w/w of NH_3.

Immobile solvent—A 10 per cent. v/v solution of liquid paraffin B.P. in diethyl ether.

Mobile solvent—Mix 7 volumes of acetone with 3 volumes of water.

Chromogenic reagent solution—Dissolve 3·4 g of silver nitrate in 130 ml of water, and add 20 ml of redistilled 2-phenoxyethanol and 50 ml of 95 per cent. ethanol; add a little more ethanol to clarify if necessary.

Sodium thiosulphate solution, 1 per cent. w/v.

Ethyl acetate, redistilled.

Dioxan.

Standard pesticides—The insecticides HHDN (aldrin), m.p. 103·5° to 104° C, HEOD (dieldrin), m.p. 175·5° to 176·5° C, endrin, m.p. 247° C (decomp.), heptachlor, m.p. 95·5° to 96° C, heptachlor epoxide, m.p. 163·5° to 164° C, gamma-BHC, m.p. 112·6° to 112·8° C, *pp'*-DDT, m.p. 109° to 109·5° C, endosulfan A, m.p. 109·5° to 110° C, *pp'*-TDE, m.p. 111° to 111·5° C and methoxychlor, m.p. 88·5° to 89° C, were used. Purify the technical materials, when necessary, by elution with hexane from a column of magnesia and recrystallisation to constant melting-point from ethanol or aqueous ethanol. *pp'*-DDE, m.p. 88·5° to 89° C, dehydrochlorinated *pp'*-TDE, m.p. 66° to 67° C and endosulfan alcohol, m.p. 206·5° to 207·5° C, were prepared from the corresponding insecticides and recrystallised as above. (All melting-points are corrected.)

Insecticide solutions—Prepare standard solutions containing 2·5 and 3·5 mg of insecticide per ml in ethyl acetate; test solutions should contain 25 µg of insecticide per ml in hexane.

PROCEDURE—

Cut Whatman No. 3 chromatography paper into sheets 19 cm × 30 cm, with the machine direction of the paper parallel to the short edge. Wash the sheets with silver nitrate solution, then with ammonia solution and finally twice with distilled water, allow to dry in a chloride-free atmosphere, and store flat under black paper. Immediately before use, lightly mark (graphite pencil) a pair of papers with a line 20 mm from and parallel to one short edge; divide this line with marks at 17·5-mm intervals, starting 15 mm from one edge. Immerse each paper carefully in the immobile solvent (100 ml per paper) up to a line about 25 mm from the marked edge, taking care that the solvent front remains parallel to the origin line, and draw the paper through the solution to the unmarked edge. Dry in a stream of warm air; when dry, place on a flat sheet of glazed paper.

Apply a series of standards comprising 2·5-, 3·5-, 5-, 7-, 10- and 14-µg amounts of insecticide to each paper (or divided between the papers). Introduce a measured volume of a hexane test solution containing up to 140 µg of the insecticide to be examined into a 10-ml flask, remove the solvent with a stream of dry air at a temperature not exceeding 40° C, and concentrate the residue at the bottom of the flask; use a separate measured volume of test solution for each determination. Dissolve the residue in 20 µl of dioxan, and transfer not more than 4 µl of this solution, in not more than two applications, to an origin spot on the chromatographic sheet. Each single application should not exceed 2 µl; when two aliquots are applied to the same origin spot, apply the second after the dioxan from the first has evaporated, but do not allow the time between solution of the residue in dioxan and transfer of the second aliquot to exceed 3 minutes. When the total amount of residue dissolved in hexane is less than 12·5 µg, it is preferable to transfer all the dioxan solution, provided that each 2-µl application is allowed to evaporate before the next is applied.

Ensure that the chromatographic tank is firmly supported and that the fittings are horizontal. Remove any solvent vapours present in the tank from a previous experiment by flushing with dry air. Immediately before use, place 400 to 500 ml of mobile solvent in the tray. Clip the papers on to the outer rods of the frame, and lower the frame on to the brackets so that each paper is immersed to a depth of 1 cm in the mobile solvent. Place the lid on the tank, and allow the chromatograms to develop for 4 to 4½ hours. Carefully remove the papers, mark the position of the solvent front, and allow to drain for 10 minutes.

Immerse completely in the chromogenic reagent solution, remove, and allow to drain. Support the papers in the oven at a temperature not exceeding 45° C for 1 hour or until completely dry. Irradiate the marked sides of the papers with ultraviolet light for 30 minutes or until the spots are well developed; treat both papers identically. Wash in distilled water for 10 minutes, and allow to dry overnight.

Assess the R_F values of the spots (use the leading edges) with a simple Perspex proportional scale (see Fig. 1), and measure the areas by taking the product of the average widths at right angles for both the standard and test spots. Plot a standard graph showing the relationship between the areas of the standard spots and the logarithm of the amount of insecticide in each, and use this graph to assess the amounts of insecticide present in the test spots.

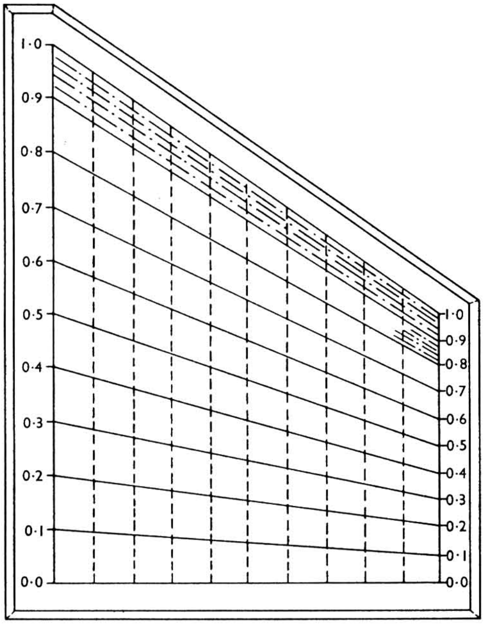

Fig. 1. Proportional scale for measuring R_F values (one-quarter full size)

DISCUSSION OF RESULTS

VARIATION OF R_F VALUES—

The R_F values in Table I are the averages of ten results for each of the insecticides or their metabolites, each result being the average of values from eight to ten individual spots. The coefficients of variation for the R_F values ranged from ±2 per cent. for HEOD to ±3·4 per cent. for *pp*′-DDE; the over-all average for the thirteen compounds was ±2·6 per cent. For any of the insecticides subjected to chromatography under the conditions stated, therefore, the R_F value found should be within the range ±5·2 per cent. of the value in Table I.

REPEATABILITY OF AREA MEASUREMENT—

The variation in area measurement obtained by the technique described above was determined for equal amounts of individual insecticides in the range 2·5 to 10 µg. These amounts were applied in equal 1- or 2-µl portions of standard solution in ethyl acetate to from eight to ten origin spots per paper. The average coefficients of variation of the measured area for single amounts are shown in Table II. Satisfactory agreement was obtained with these coefficients of variation of measured areas for papers with an equal number of applications of standard solutions of both dioxan and ethyl acetate. Two chromatograms developed simultaneously gave a satisfactory level of repeatability and permitted twelve to fourteen unknown pesticides to be determined by comparison with a standard series of six spots.

The variance of the area measurement was calculated for equal amounts of several insecticides applied in different volumes (1, 2, 2 × 1, 2 × 2, 4 × 1 and 1 × 4 μl) to single papers developed in pairs. The *F*-ratio test of variance indicated a difference that was significant when readings from the 4-μl applications were included; otherwise, the areas measured did not differ significantly with the manner of application. The volume used for each application should therefore not exceed 2 μl; since it is obviously desirable that the number of individual applications should be kept to a minimum, not more than two were used.

TABLE I

PAPER-CHROMATOGRAPHIC CHARACTERISTICS OF SOME CHLORINATED PESTICIDES AND THEIR METABOLITES

Insecticide	R_F value	Lower limit of detection, μg	Upper limit for linearity, μg
HHDN (aldrin)	0·24	∼ 1	17
pp′-DDE	0·29	0·5	17
Dehydrochlorinated *pp*′-TDE	0·34	∼ 2	22
Heptachlor	0·34	0·5	19
pp′-DDT	0·39	0·5	26
Endosulfan A (*thiodan* A)	0·43	∼ 1	17
Endrin	0·44	0·5	9·5
HEOD (dieldrin)	0·47	∼ 1	26
Heptachlor epoxide	0·50	0·5	16
pp′-TDE	0·55	0·5	9
Endosulfan B (*thiodan* B)	0·65	∼ 1	—
gamma-BHC	0·66	0·5	7·5
Methoxychlor	0·69	0·5	8
Endosulfan alcohol (*thiodan* alcohol)	1·0	∼ 1	—

TABLE II

COEFFICIENTS OF VARIATION

No. of papers developed together	Average coefficient of variation of measured area—		
	on single paper, %	on two papers, %	on four papers, %
2	5·1	5·7	—
4	5·6	—	7·6

LINEARITY RANGE FOR RELATIONSHIP BETWEEN AREA AND log(AMOUNT)—

Area measurements from six or seven individual determinations of six fixed amounts in the range 2·5 to 14 μg were recorded for each insecticide. An analysis of variance of the correlation figures from these measurements for each insecticide indicated a linear relationship between area and log(amount) within this range, except for amounts of dehydrochlorinated *pp*′-TDE less than 5 μg, of endrin more than 10 μg and of *pp*′-TDE and methoxychlor more than 7 μg. It was not possible to apply this statistical test to gamma-BHC, but a graphical examination indicated linearity for amounts up to 7·5 μg. Accurate measurement of area is difficult for amounts less than 2·5 μg, although levels down to 0·5 μg can be detected by the technique described. The upper limits of linearity in Table I were obtained graphically and appear to be greatest for R_F values between 0·34 and 0·47; this apparent relationship to the R_F value is not strictly adhered to, and the upper limit may also be a function of the relative areas obtained for equal amounts of the various insecticides.

ACCURACY OF METHOD—

Recoveries from test solutions in hexane of all the pure insecticides were determined at three measured levels (2·5, 5 and 10 μg), 2- and 4-μl portions from 20 μl of dioxan solution being used. The average recovery in over 100 determinations was 109 per cent. (mean deviation, 9 per cent.; standard deviation, 11·7 per cent.; coefficient of variation 10·8 per cent.). An analysis of variance of these results indicated that there was no significance in the slight differences between the average recoveries for different amounts or for different volumes of application. The recovery for a measured amount of 1·5 μg was 107 per cent.; although this was satisfactory, an alternative procedure was used for determining total residues of less than 12·5 μg because of the uncertainty involved in area measurement at levels below 2·5 μg. In this alternative method, all the dioxan solution is transferred to an origin spot on the chromatography paper; the mean recovery, limited by the ability to transfer such small volumes completely, was 78 per cent. (mean deviation, 7 per cent.; standard deviation, 8·1 per cent.; coefficient of variation, 10·4 per cent.).

CONCLUSIONS

A practical system for the separation of eleven insecticides or their metabolites has been devised. Satisfactory experimental conditions leading to reproducible R_F values and area measurements have been determined, and the values of reproducibility for these factors have been calculated. The relationship between area of spot and log(amount of insecticide present) is linear for most of the insecticides over the range 2·5 to 14 μg for the solvent system used; the limits of detection and overloading have been estimated. Amounts of pure insecticide from 2·5 μg upwards can be determined by taking suitable aliquots to bring the amount measured within the range of linearity; the method is accurate to within ± 10 per cent.

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REFERENCES

1. Winteringham, F. P. W., Harrison, A., and Bridges, R. G., *Nature*, 1950, **166**, 999.
2. Moynihan, P., and O'Colla, P., *Chem. & Ind.*, 1951, 407.
3. O'Colla, P., *J. Sci. Food Agric.*, 1952, **3**, 130.
4. Mitchell, L. C., *J. Ass. Off. Agric. Chem.*, 1952, **35**, 920.
5. Mitchell, L. C., and Patterson, W. I., *Ibid.*, 1953, **36**, 553.
6. Mitchell, L. C., *Ibid.*, 1953, **36**, 1183 and 1187; 1954, **37**, 530 and 996; 1956, **39**, 985.
7. ——, *Ibid.*, 1956, **39**, 980; 1957, **40**, 294.
8. ——, *Ibid.*, 1958, **41**, 781.
9. McKinley, W. P., and Mahon, J. H., *Ibid.*, 1959, **42**, 725.
10. Mills, P. A., *Ibid.*, 1959, **42**, 734.
11. ——, *Ibid.*, 1961, **44**, 171.
12. Major, A., jun., and Barry, H. C., *Ibid.*, 1961, **44**, 202.
13. Horwitz, W., *Editor*, "Official Methods of Analysis," Ninth Edition, The Association of Official Agricultural Chemists, Washington, D.C., 1960, p. 338.
14. *J. Ass. Off. Agric. Chem.*, 1961, **44**, 141.
15. San Antonio, J. P., *Ibid.*, 1960, **43**, 721.
16. McKinley, W. P., Savary, G., and Webster, C., *Ibid.*, 1961, **44**, 193.
17. Ingold, C. K., "Structure and Mechanism in Organic Chemistry," G. Bell & Sons Ltd., London, 1953, p. 357.
18. Block, R. J., Durrum, E. L., and Zweig, G., "A Manual of Paper Chromatography and Paper Electrophoresis," Second Edition, Academic Press Inc., New York and London, 1958, p. 85.
19. Fisher, R. B., Parsons, D. S., and Morrison, G. A., *Nature*, 1948, **161**, 764.

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Determination of Strontium in Biological Materials and Exchangeable Strontium in Soils by Atomic-absorption Spectrophotometry

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An examination has been made of factors affecting the determination of strontium in biological materials and soil extracts by atomic-absorption methods. Calcium and phosphate together in solution seriously depress absorption of the 4607 A strontium resonance line, but neither calcium alone nor phosphate alone produces serious depression. Aluminium seriously depresses strontium absorption, but its effect is eliminated by the presence of excess of calcium in solution.

In all sample solutions tested, except those from some acid soils, adequate natural calcium was present to suppress the interference from aluminium.

The method recommended for biological materials consists in the removal of phosphate by means of De-Acidite FF anion-exchange resin and then atomic-absorption spectrophotometric analysis by the "addition" method. Ammonium chloride extracts of soils, with the exception of those from some acid soils (to which the addition of calcium may be necessary), require no pre-treatment to suppress interferences, but it is sometimes necessary to remove the ammonium chloride and concentrate the solutions in order to improve accuracy.

The results are given of experiments to determine the efficiency of anion exchange in separating phosphate from strontium and to assess the accuracy and reliability of the application of the addition method to atomic-absorption analysis.

THE use of flame methods in the determination of strontium in naturally occurring materials such as biological samples and soils has, in the past, been difficult owing to its low concentration in these materials, the lack of a means of complete separation from calcium and interference from other constituents present in the sample. In flame-emission methods in which the strontium line at 4607 A is used,[1,2] correction must be made for calcium emission occurring at the strontium wavelength. The same difficulty arises, but to a lesser extent, when the strontium band at 6810 A is used.[3] At both wavelengths the sensitivity is insufficient to allow the accurate determination of strontium at concentrations lower than about 1 p.p.m. in solution, and difficulties are experienced if silicate, iron, aluminium, magnesium, sulphate or phosphate is present.

Neutron-activation[4] and X-ray fluorescence[5] methods are reasonably free from interferences and possess adequate sensitivity for the analysis of biological materials, soils and plants. However, the equipment required for both techniques is expensive, and the neutron-activation procedure is long and difficult.

Since the application of atomic absorption to chemical analysis was suggested and its advantages first demonstrated by Walsh *et al.*,[6,7] no detailed examination of the practical determination of strontium has been published, and reference to strontium has been confined to statements of detection limits in solutions of pure strontium salts.

The method described here for determining strontium is adequately sensitive and rapid; it requires relatively inexpensive equipment and is free from interference arising from extraneous light emitted from the flame at the strontium wavelength. However, as in flame-emission analysis, extraneous ions in the sample solution can restrict the conversion of strontium into free atoms in the flame; an investigation into the effects of ions that seriously affect sensitivity in this way was carried out, and means were found of safely removing them or suppressing their influence. Automatic compensation for the effects of those ions that have only slight influence on sensitivity is achieved by use of the "addition" method of analysis.[8,9]

APPARATUS

The apparatus used in this investigation was the same as that described by David,[10] except that a strontium hollow-cathode discharge tube was used. The cathode of this tube consisted of a copper cylinder, closed at one end, of wall thickness $\frac{1}{16}$ inch, internal diameter $\frac{3}{8}$ inch and internal depth $1\frac{3}{8}$ inches, into the bottom of which was pressed a disc of metallic strontium of thickness $\frac{1}{8}$ inch. The tube was filled in the usual manner[11] with spectrally pure argon at a pressure of 3·5 cm of Silicone oil as measured by the differential manometer. It was operated at a current of 25 mA and modulated at 50 cycles per second in all the work described.

The scale expansion system read from zero to full-scale deflection (50 scale divisions) over the range 0 to 20 per cent. absorption; that is, each division on the expanded scale equalled 0·4 per cent. absorption. All atomic-absorption measurements reported in this paper were made at the wavelength of the strontium resonance line (4607 A) and are stated in divisions on the expanded scale.

A clear blue flame 8 cm high, having a sharp inner cone of height 1·5 mm, was used throughout the work described. This flame was produced at an air pressure of 30 lb per sq. inch and an acetylene pressure of 25 cm of water on the apparatus used.

EXPERIMENTAL

STUDY OF INTERFERENCES—

By analogy with the interferences occuring in the determination of calcium by atomic-absorption methods,[12,13] it was expected that the most serious interferences with strontium absorption would arise from the presence of one or more of the ions PO_4^{3-}, Al^{3+}, SO_4^{2-} and SiO_3^{2-}. The effects of each of these ions, both in the presence and absence of calcium, was tested with solutions containing 2 p.p.m. of strontium. The results are given in Table I.

TABLE I

EFFECTS OF PHOSPHATE, SULPHATE, ALUMINIUM AND SILICATE ON ABSORPTION OF STRONTIUM RADIATION

The effects of phosphate, sulphate, aluminium and silicate, both in the presence and absence of calcium, on the absorption of strontium radiation at 4607 A. Each solution contained 2·0 p.p.m. of strontium, as strontium chloride

				Strontium absorption—	
Phosphate present, as P, p.p.m.	Silicate present, as Si, p.p.m.	Sulphate present, as S, p.p.m.	Aluminium present, p.p.m.	alone, divisions on expanded scale	in presence of 200 p.p.m. of calcium, divisions on expanded scale
—	—	—	—	21·5	24·5
40	—	—	—	20·0	17·0
160	—	—	—	19·5	6·0
—	16	—	—	3·5	20·5
—	64	—	—	0·0	15·5
—	—	40	—	21·5	24·5
—	—	160	—	21·5	23·5
—	—	—	40	6·5	18·0
—	—	—	160	7·0	17·0

The results in Table I indicated that, in the absence of calcium, both silicate and aluminium seriously depressed the strontium absorption. If, however, calcium was present, the effects of these two ions were decreased, but phosphate, which did not significantly depress strontium absorption in the absence of calcium, then seriously depressed it. Figs. 1 and 2 show, respectively, the results of a close examination of the interference of aluminium in the absence of calcium and the combined interference of calcium and phosphate.

The similarity of the curve in Fig. 1 to that of the interference of phosphate with calcium absorption[12] suggested that the depression of the strontium absorption was caused by the formation of strontium aluminate in the flame. The depression caused by phosphate in the presence of calcium (see Fig. 2) may have been the result of the strontium entering the calcium phosphate lattice and therefore being subject to the limited dissociation of calcium phosphate in the flame.

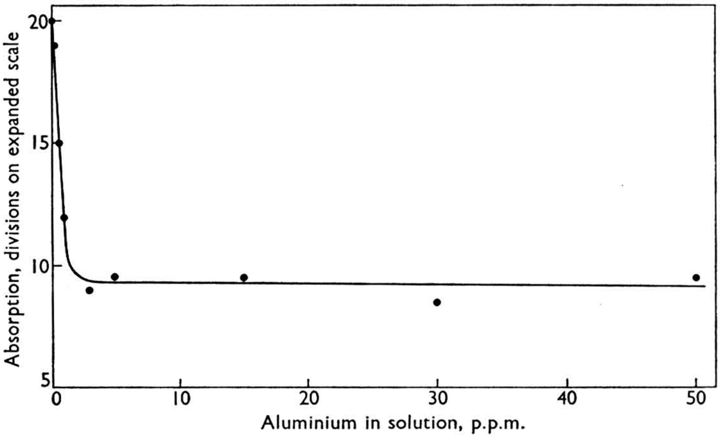

Fig. 1. Effect of aluminium on the absorption of the strontium resonance line at 4607 A. Each solution contained 2·0 p.p.m. of strontium as strontium chloride

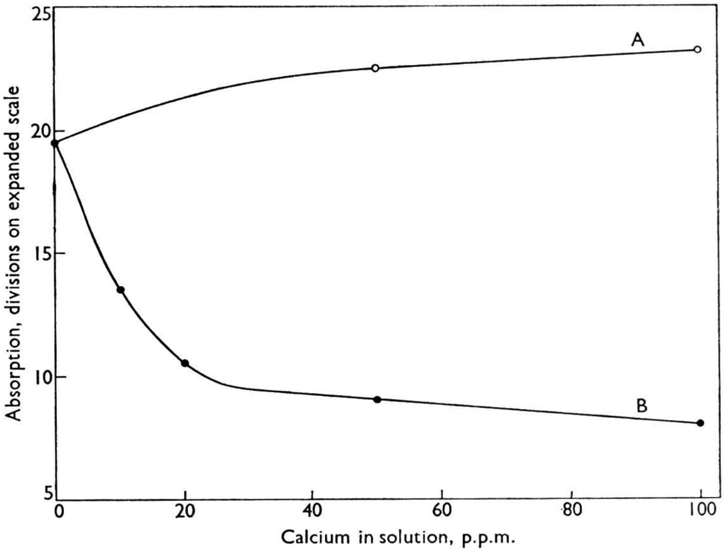

Fig. 2. Effect of calcium (as calcium chloride), in presence and absence of phosphate, on the absorption of the strontium resonance line at 4607 A. Each solution contained 2·0 p.p.m. of strontium as strontium chloride: curve A, phosphate absent; curve B, 160 p.p.m. of phosphorus present as orthophosphoric acid

As calcium and phosphate are major constituents of most biological material, it was important that their effects should be overcome. The best means of achieving this was considered to be either suppression of the interference, by the addition of ions that would compete with strontium for the interfering ions, or the removal of one of the interfering ions. Suppression proved unsuccessful, because the low concentration of strontium in the samples made it necessary to use solutions containing high concentrations of the major constituents of the samples, and insolubility problems were encountered. A combination of removal of phosphate by anion exchange and the determination of strontium by the addition method proved successful. By these means, high sensitivity was achieved by the removal of phosphate from, and the retention of calcium in, the solutions analysed, and accuracy was assured by the use of the addition method, which automatically corrected for any minor interferences remaining.

ADDITION METHOD—

If x is the concentration of an element in a sample and A is the instrumental reading obtained, and if the relationship between reading and concentration is linear, then—

$$x = \mathrm{K}A \quad \ldots \quad (1)$$

where K is the constant of proportionality.

If an addition of known magnitude, a, of the element is made to the sample solution and an instrumental reading again taken, we have—

$$(x + a) = \mathrm{K}A_1 \quad \ldots \quad (2)$$

In these equations, K and x are the only unknown quantities, and x can therefore be calculated.

The addition method is applied in this particular instance by taking three equal portions of a sample solution, adding equal volumes of water to one and solutions containing known concentrations of strontium to the other two, and then taking atomic-absorption readings on all three solutions at 4607 A. The preparation and measurement of two solutions is essential. The inclusion of a third provides a duplicate analysis and confirms the linearity of the relationship between absorption and concentration.

ANION-EXCHANGE COLUMNS—

The resin used was De-Acidite FF (100 to 200 mesh). It was converted to the acetate form by washing with an excess of 2 N sodium hydroxide and then with an excess of 3·5 N sodium acetate solution, and finally with 0·1 N acetic acid until free from sodium. It was loaded into columns of capacity 50 ml and having an internal diameter of 1·8 cm.

Measurements carried out on 10 ml of a solution containing 5 p.p.m. of strontium showed that the interstitial space in the resin bed was about 12 ml and that, if the first 9 ml of solution were rejected, the effluent was free from strontium at a volume well within the next 25 ml, if successive small (about 3 ml) amounts of 0·1 N acetic acid were used in washing.

EFFICIENCY OF ANION EXCHANGE AND DETERMINATION BY THE ADDITION METHOD—

Seven samples of dry plant material, one sample of milk powder, one sample of rock phosphate and one sample of superphosphate were used in these tests. For milk powder and plant material, 10-g portions of the samples were placed in silica dishes and ashed in a muffle furnace at 500° C for 4 hours. These ashes and 1 g of the rock phosphate and 2 g of the superphosphate were each evaporated to dryness twice with 6 N hydrochloric acid; the residues were dissolved in 10-ml portions of N hydrochloric acid, filtered, and the filtrates collected in 200-ml calibrated flasks. The dishes and filters were washed with small volumes of hot water, and the washings were added to the contents of the appropriate flasks; the procedure was continued until each filtrate amounted to about 150 ml. The contents of the flasks were allowed to cool and were then adjusted to the mark with water. The solution prepared from one sample of dry plant material (forest litter) was found to contain too high a concentration of strontium for the subsequent treatment; 3 ml were therefore diluted to 100 ml with 0·05 N hydrochloric acid. These solutions will be referred to as the "sample stock solutions."

Two 10-ml portions of each sample stock solution were taken. One portion of each solution was passed through a column of the anion-exchange resin, and the column was washed with small volumes of 0·1 N acetic acid. The first 9 ml of effluent were rejected and the next 25 ml collected. The other portion was mixed with an equal volume of a solution of strontium chloride containing 2·5 p.p.m. of strontium; 10 ml of this mixture was then passed through a column, and 25 ml of effluent were collected as before. Three 4-ml portions of each of these effluent solutions were taken. One was mixed with 1 ml of water, the second with 1 ml of solution containing 2·5 p.p.m. of strontium and the third with 1 ml of solution containing 10 p.p.m. of strontium. Atomic-absorption measurements were made on each, and the concentration of the strontium solution originally mixed with one of the 10-ml portions of sample stock solution was calculated. Comparison of the calculated with the known concentration (2·5 p.p.m.) gave a value for the recovery of strontium after passage through the column and also an indication of the reliability of the addition method in analysis. Table II shows these recoveries as well as the values from which they were calculated.

TABLE II

RECOVERY OF STRONTIUM ADDED TO SAMPLE SOLUTIONS, AFTER PASSAGE THROUGH DE-ACIDITE FF RESIN

		Mean of two readings—		
Sample	Effluent (4 ml) mixed with 1 ml of—	a, divisions on expanded scale	b, divisions on expanded scale	Recovery,* %
Milk powder	A	1·75	5·38	
	B	7·75	11·0	101
	C	25·0	29·0	95
Pine needles	A	0·0	4·38	
	B	5·25	9·75	102
	C	20·8	27·0	97
Clover	A	18·1	16·5	
	B	25·2	24·4	102
	C	43·8	46·5	101
Rye grass	A	2·63	6·88	
	B	9·25	13·5	104
	C	30·3	33·5	105
Oat straw	A	3·63	7·5	
	B	10·9	14·6	100
	C	30·9	34·9	104
Oat grain	A	0·50	4·88	
	B	6·63	11·0	95
	C	24·9	29·0	96
Forest litter	A	1·63	5·75	
	B	7·63	11·8	103
	C	28·2	30·9	99
Wheat straw	A	7·0	8·88	
	B	13·5	15·7	94
	C	32·5	34·7	103
Superphosphate	A	4·50	6·75	
	B	10·0	13·2	103
	C	28·0	30·6	93
Rock phosphate	A	6·75	8·38	
	B	12·5	14·4	101
	C	31·5	32·5	105

A = Water.
B = Solution containing 2·5 p.p.m. of strontium.
C = Solution containing 10 p.p.m. of strontium.
a = Sample stock solution (10 ml) passed through anion-exchange resin, the column washed and the washings added to the effluent to a final volume of 25 ml.
b = Sample stock solution mixed with equal volume of solution containing 2·5 p.p.m. of strontium, as SrCl$_2$, and 10 ml of mixture treated as in a.

* The first recovery for each sample was calculated from the results for the solution containing added water and the solution containing added B, and the second from the results for the solution containing added water and the solution containing added C.

The recoveries of added strontium shown in Table II indicated that strontium passed quantitatively through the columns and that the addition method was reliable, at least with respect to precision. The zero reading shown in column "a," Table II, for the addition of water to the pine needle sample solutions, is evidence of the absence of effects from spurious absorption in the flame or emission from the flame. The difference between the reading obtained for the addition of water to a sample solution and that obtained for a given addition of strontium indicates the efficiency of conversion of strontium to the free atomic state in the flame. In column "a," Table II, for instance, the increment in absorption reading resulting from an increase of 0·5 p.p.m. of strontium in the sample solutions varies from 5·25 divisions on the expanded scale for the pine needle sample solution to 7·27 for the oat straw sample solution. Whereas such a variation could produce errors of up to 40 per cent. if conventional standards were used, no error results from the use of the addition method, because the efficiency of conversion of strontium to the free atomic state in the flame will be the same for the sample solution with added strontium as it is for that without it.

LINEARITY OF RELATIONSHIP BETWEEN ABSORPTION AND CONCENTRATION—

Linearity between concentration and the quantity measured is important in the use of the addition method. If linearity exists, the concentration of the element in the original sample can be arrived at by simple calculation from only two readings. If linearity does not exist it is necessary first to determine the equation of the curve for each sample, then to apply at least three readings to the equation in order to calculate the original concentration. Such a procedure would be too time-consuming for routine analysis.

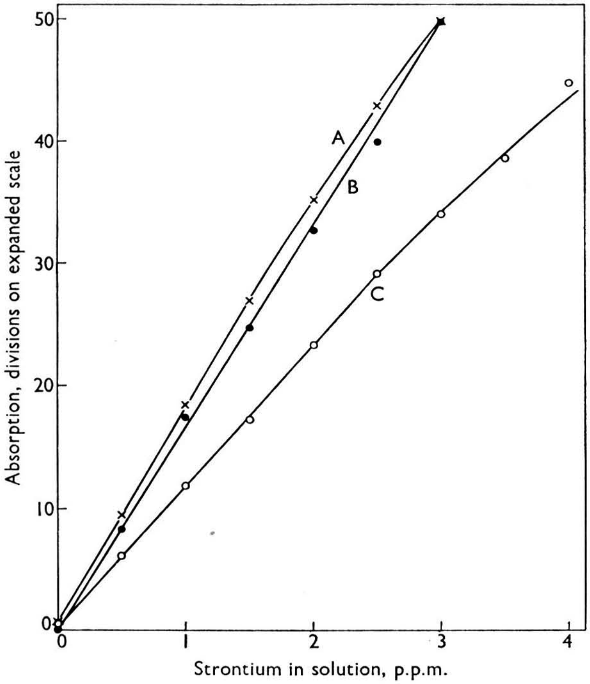

Fig. 3. Curves relating absorption of the strontium resonance line at 4607 Å to concentration of strontium in three aqueous media: curve A, solution prepared from analytical-reagent grade salts to simulate plant ash; curve B, water; curve C, solution prepared from pine-needle ash

The results of an experiment designed to give a critical test of linearity between absorption and concentration in the determination of strontium by atomic absorption are shown in Fig. 3. For this test it was important to use solutions having strontium contents close to, or beyond, the limit of detection of the equipment. The stock solution prepared from the pine needle sample and a solution prepared from analytical-reagent grade salts to give concentrations of the major plant elements similar to those contained in a 200-ml solution of the ash from 10 g of plant dry matter of average composition were therefore used. The solutions were passed through an anion-exchange column, and the effluent was adjusted to volume with washings from the column as previously described. Portions of these solutions were mixed with water and with strontium chloride solutions in the proportion 4 + 1 to give for each a series of solutions containing strontium at concentration intervals of 0·5 p.p.m. These, as well as a series based on water, were measured and the results plotted.

The curves indicate linearity, within the limits of experimental error, up to an absorption of 20 scale divisions and only small departure from linearity, with the pine needle and synthetic solutions, between 20 and 30 scale divisions. Further evidence on linearity over a range of samples is contained in Table II. No departures from linearity greater than these have been found in the determination of strontium in some hundreds of biological samples and soil extracts.

The procedure adopted has been to make additions giving concentrations of strontium of 0·0, 0·5 and 2·0 p.p.m. above that already present in each sample solution, and to calculate the result from both the 0·0 and 0·5 p.p.m. pair and the 0·0 and 2·0 p.p.m. pair. If the two results do not differ seriously and if that from the 0·0 and 0·5 p.p.m. pair is the smaller, it is accepted, because the difference between the two is probably at least partially due to curvature setting in between the lowest and highest additions of strontium. If the result from the 0·0 and 2·0 p.m. pair is the smaller, the average of the two results is accepted, provided they do not differ seriously, because the difference is probably due to experimental error. Serious differences between results calculated from the lowest and highest additions of strontium have seldom occurred, and repeat determinations have always shown them to be due to errors in procedure or calculation.

Once it is established that an atomic-absorption unit gives a linear relationship between absorption and concentration of strontium in solution, the use of two different additions of strontium can be dispensed with, and duplicate additions of 1·0 p.p.m. of strontium used.

ACCURACY, PRECISION AND SENSITIVITY—

A statistical examination of the results in Table II and those from which Fig. 3 was prepared showed that the coefficient of variation of a determined concentration of strontium decreased with an increasing initial (no addition) reading and with increasing amounts of strontium added to the sample. Coefficients of variation are shown in Table III for initial readings of 3 and 9 divisions on the expanded scale and additions of strontium producing concentrations of 0·5, 1·0, 1·5 and 2·0 p.p.m. above that already present.

TABLE III

COEFFICIENTS OF VARIATION OF THE ESTIMATED AMOUNT OF STRONTIUM PRESENT IN SOLUTION AT THE INITIAL READING (NO STRONTIUM ADDED) FOR TWO INITIAL READINGS AND FOR VARIOUS ADDITIONS

Initial reading, division on expanded scale	Strontium added, p.p.m.	Reading, divisions on expanded scale	Coefficient of variation, %
3	0·0	3·0	—
	0·5	9·9	9·24
	1·0	16·8	7·83
	1·5	23·7	7·38
	2·0	30·6	7·17
9	0·0	9·0	—
	0·5	15·9	5·50
	1·0	22·8	3·90
	1·5	29·7	3·35
	2·0	36·6	3·08

The statistical analysis showed that little additional precision would be gained if an initial reading greater than 8 to 10 divisions on the expanded scale were used and that no gain in precision would result from the use of initial readings greater than 13 scale divisions. The use of an initial reading of 8 to 10 scale divisions was more satisfactory with respect to accuracy than were higher initial readings; the higher the initial readings, the more were the readings on the samples with added strontium moved up towards regions where large and variable departures from linearity between absorption and concentration could occur.

The statistical analysis further indicated that the optimum addition of strontium for use with the apparatus described was 1·0 p.p.m. and that, by assuming linearity equal to that evident in Fig. 3, duplicate additions of 1·0 p.p.m. were preferable to two different additions.

Apart from observing the linearity of the relationship between instrumental reading and concentration, the only way of assessing the accuracy of determinations involving the use of the addition method is comparison of the results with those by other methods. In Table IV a comparison is shown of atomic-absorption results with those by X-ray fluorescence analysis carried out on both ash and dry matter of a set of samples. The agreement existing in Table IV is evidence of the accuracy of both methods.

TABLE IV

COMPARISON OF RESULTS BY DIFFERENT METHODS

	Concentration of strontium in dry sample as determined by—		
	X-ray fluorescence on—		
Sample	dry material,* p.p.m.	ash,* p.p.m.	atomic absorption, p.p.m.
Rye grass	13·5	13·6	13·1
Milk powder	9·8	9·7	9·4
Pine needles	1·8	1·3	<3·0
Wheat straw	36·6	35·9	33·6
Clover	88·2	87·6	86·3
Forest litter	165	160	152
Oat straw	14·3	16·0	15·9
Oat grain	3·6	3·0	3·2
Rock phosphate	—	330	341
Superphosphate	—	320	311

* Determinations carried out by K. Norrish and T. R. Sweatman of C.S.I.R.O. Division of Soils, Adelaide.

If ions that depress strontium absorption are absent, the limit of detection is about 0·05 p.p.m. of strontium in solution. This concentration results in an absorption reading of between 0·5 and 1 division on the expanded scale, depending on the extent of enhancement of strontium absorption by calcium in the solutions (see Fig. 2). Short-term fluctuation of the meter pointer produces an uncertainty in reading of 0·1 to 0·2 of a division on the expanded scale.

PROPOSED METHOD

PREPARATION OF SAMPLE—

Biological samples—Take sufficient material, accurately weighed, to give 0·3 to 0·5 g of ash. Place the material in a silica dish, and ash by ignition at 500° C for 4 hours in a muffle furnace. When the ash is cool, evaporate to dryness twice with 5 ml of 6 N hydrochloric acid. Dissolve the residue in 10 ml of 0·1 N hydrochloric acid, and filter through a 7-cm Whatman No. 42 filter-paper into a 50-ml calibrated flask, washing with small volumes of hot water until the volume of filtrate is about 45 ml. Cool the filtrate, and dilute to the mark with cold water.

Pass 10 ml of the solution through a column of De-Acidite FF anion-exchange resin, and wash with small volumes of 0·1 N acetic acid. Reject the first 9 ml of effluent, and collect the next 25 ml in a calibrated flask. Measure the absorption of this solution with the atomic-absorption apparatus; dilute with water, if necessary, to give an absorption reading of 12 divisions, or less, on the expanded scale.

Soils (exchangeable strontium)—Extract 10 g of soil with 200 ml of N ammonium chloride as described by Piper.[14] Measure the absorption of the extract with the atomic-absorption apparatus. If it gives a reading in excess of 12 divisions on the expanded scale, dilute appropriately with water. If the extract gives a reading of less than 2 scale divisions, remove the ammonium chloride from a 100-ml portion of the extract, evaporate to dryness as described by Piper,[14] and then dissolve the residue in exactly 20 ml of 0·5 N hydrochloric acid.

ATOMIC-ABSORPTION PROCEDURE—

Take three 4-ml portions of each solution prepared for analysis; by pipette place 1·0 ml of water into one portion, 1·0 ml of strontium chloride solution containing 2·5 p.p.m. of strontium into the second and 1·0 ml of solution containing 10·0 p.p.m. of strontium into the third. Mix each solution thoroughly, and measure the absorption of each at the strontium resonance wavelength (4607 A) on the expanded scale with the atomic-absorption apparatus.

(If the reading for the addition of water to a solution prepared from a soil extract is low, one of two possibilities exist: either the strontium content is low and no steps can be taken to improve sensitivity, or the strontium absorption is being depressed by the presence of aluminium in solution; the latter can be detected by observing the increment in atomic-absorption reading produced by the additions of strontium. If these increments are markedly less than those observed on solutions known to be substantially free from depressing ions, a considerable gain in sensitivity can be achieved by carrying out the determination in the presence of 200 p.p.m. of added calcium, as calcium chloride, in the solutions.)

Apply equations (1) and (2), see p. 579, to calculate the concentration of strontium in the solution containing the added water; use both the pair of readings obtained from the solution with added water and the solution with the lowest addition of strontium and the pair obtained from the solution with added water and the solution with the highest addition of strontium.

From the concentration in the solution containing added water, calculate the concentration of strontium in the original sample by taking into account the weight of sample taken, the volume of solution prepared from it and the dilutions effected during the procedure.

Care should be exercised in the extraction of samples containing high concentrations of both calcium and sulphate, such as superphosphate. If too large a sample is taken, some strontium is retained in the calcium sulphate left undissolved. The extraction and washing of a 0·5-g sample of superphosphate to a final volume of 50 ml was satisfactory.

CONCLUSIONS

In the use of the addition method in atomic-absorption analysis, elimination of interferences is important only in so far as it improves sensitivity. Whether or not such improvement is necessary depends on the concentration of the element in the sample and the sensitivity of the apparatus for that element. Whereas suppression of interference is unnecessary in the determination of calcium in biological materials by the addition method, the determination of strontium is often impossible unless interferences are suppressed.

The ashing of biological samples in a furnace is known to render a small proportion of the cations insoluble in hydrochloric acid. The amount of strontium lost in this manner has been found here to be generally less than 10 per cent. If determination of it is deemed necessary, the silica in the residue after extraction of the ash with hydrochloric acid can be removed by treatment with hydrofluoric acid and the strontium determined by the proposed method.

In the determination of exchangeable strontium in soils by extraction with N ammonium chloride, experience with the atomic-absorption apparatus has shown that concentration of the solutions by evaporation and removal of ammonium chloride is necessary only when the concentration of strontium is low and that adequate sensitivity exists for direct analysis of most extracts. Basaltic soils contain relatively high concentrations of exchangeable strontium, and dilution of extracts prepared from them is often necessary. Suppression of the effect of aluminium has been found necessary only in the analysis of extracts of highly acidic soils; all others are substantially free from ions that depress strontium absorption.

In the use of the addition method with a single-beam instrument, some gain in accuracy compared with analysis by using conventional standards must arise from the fact that what are effectively sample and standard are measured in quick succession. In the analysis of a large batch of samples by using conventional standards, a considerable time lapse can occur between measurement of sample and standard, and any instrumental drift occurring during this period will adversely affect the accuracy. On the other hand, the use of the addition method involves extrapolation that would make it inherently less accurate than analysis with the use of conventional standards, in which the result is arrived at by interpolation. However extrapolation errors are easily detected if two additions are made to a sample solution and a result is calculated from each.

Modulated atomic-absorption apparatus is particularly suited to the application of the addition method, because, within limits, it measures only the concentration in the flame of atoms of the element being determined; that is, absorption or emission by other atomic species is overcome. One effect that must, however, be taken into consideration is the scattering or interruption of the hollow-cathode beam by excessive concentrations of salts in the sample solutions sprayed into the flame.[10] Provided the concentration of salts (other than ammonium salts) in the sample solution does not exceed 1 per cent., they produce no measurable reduction of intensity in the hollow-cathode beam on its passage through the flame, and any absorption reading obtained can be reliably ascribed to the presence in the flame of free atoms of the element being determined. Determination of an element can then be achieved by simple calculation from only two measurements.

The use of the addition method in atomic-absorption analysis is not confined to the determination of strontium. Its application to the determination of other elements depends on the stability of emission from the light source and the linearity of the relationship between absorption and concentration. The stability and linearity for sodium, potassium, calcium, magnesium, iron, manganese and molybdenum is such that the determination of these elements in a variety of samples has been successfully carried out here with the apparatus described. The addition method is probably suited also to the determination of other elements detectable by atomic absorption, but these elements could not be examined owing to lack of light sources.

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REFERENCES

1. Harrison, G. E., *Nature*, 1958, **182**, 792.
2. Diamond, J. J., *Anal. Chem.*, 1955, **27**, 913.
3. Taylor, A. E., and Paige, H. H., *Ibid.*, 1955, **27**, 282.
4. Loveridge, B. A., Webster, R. K., Morgan, J. W., Thomas, A. M., and Smales, A. A., *Anal. Chim. Acta*, 1960, **23**, 154.
5. Roberts, W. M. B., *Nature*, 1959, **183**, 887.
6. Walsh, A., *Spectrochim. Acta*, 1955, **7**, 108.
7. Russell, B. J., Shelton, J. P., and Walsh, A., *Ibid.*, 1957, **8**, 317.
8. David, D. J., *Nature*, 1960, **187**, 1109.
9. Willis, J. B., *Spectrochim. Acta*, 1960, **16**, 273.
10. David, D. J., *Analyst*, 1961, **86**, 730.
11. Jones, W. G., and Walsh, A., *Spectrochim. Acta*, 1960, **16**, 249.
12. David, D. J., *Analyst*, 1959, **84**, 536.
13. Willis, J. B., *Spectrochim. Acta*, 1960, **16**, 259.
14. Piper, C. S., "Soil and Plant Analysis," University of Adelaide, Adelaide, South Australia, 1942.

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A Colorimetric Method for determining Total Sulphur in Soils

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The soil is ignited with vanadium pentoxide in a current of nitrogen, and oxidation of volatile products of decomposition is completed by passage over hot cupric oxide. Hot metallic copper converts sulphur trioxide to the dioxide, which is absorbed in a solution of sodium tetrachloromercurate and determined colorimetrically with *p*-rosaniline and formaldehyde.

In the classical method for determining total sulphur in soils, sulphur compounds are converted into sulphate, which is then extracted from the other constituents of the soil. The overwhelming preponderance of silica and sesquioxides normally present makes this a tedious procedure, and subsequent determination of the small amounts of sulphate extracted is difficult. Further, as the barium contents of most soils are between 100 and 3000 p.p.m.,[1] considerable amounts of barium sulphate may be retained in the discarded residue.

To overcome these difficulties, Smittenberg and his co-workers[2] and Little[3] heated soils with reduced iron powder and determined the sulphide liberated on acidification. St. Lorant[4] proposed a method in which sulphate was converted into hydrogen sulphide by heating with a mixture of red phosphorus and hydriodic acid, and Johnson and Nishita[5] applied this method to soils. Japanese[6] and Russian[7] workers have used a solution of stannous chloride in concentrated orthophosphoric acid instead of St. Lorant's reagent, and Steinbergs and his co-workers[8] used a mixture of hydriodic and hypophosphorous acids to liberate hydrogen sulphide from soils previously heated with either sodium hydrogen carbonate or metallic magnesium. Kiba, Takagi, Yoshimura and Kishi[6] and Volkov and Ostroumov[7] reported that their methods gave low results in the presence of copper, and no doubt this is true for any method based on the formation of hydrogen sulphide; in view of the normal copper contents of soils (up to 100 p.p.m.[1]), this would probably not usually be a source of serious error.

An alternative approach was suggested by the work of Hagerman and Faust,[9] who expelled sulphur from refractory materials by heating with vanadium pentoxide. Larsen, Ross and Ingber[10] adapted this method to the micro scale by converting oxides of sulphur into the dioxide and determining this colorimetrically as described by West and Gaeke.[11] The proposed method is an adaptation of this procedure.

EXPERIMENTAL

The expulsion of sulphur from inorganic compounds by heating with vanadium pentoxide was first investigated. Samples were mixed with the oxide and heated in an empty quartz tube in a current of air; oxides of sulphur were collected in 5 per cent. hydrogen peroxide, and the resulting sulphuric acid was titrated with standard alkali. The vanadium pentoxide produced a liquid melt, and consequently the evolution of oxides of sulphur was prohibitively

TABLE I

RECOVERY OF SULPHUR FROM INORGANIC COMPOUNDS

Sample	Sulphur content, %	Sulphur found, %	Sample	Sulphur content, %	Sulphur found, %
Potassium sulphate	18·4	18·3	Pyrites†	47·6	48·1
Hydrated ferrous sulphate	11·9*	11·9	Zinc concentrates†	31·2	30·6
Hydrated ferric sulphate	24·2*	23·9	Burnt pyrites†	2·02	1·97
Hydrated aluminium sulphate	18·5*	18·5	Portland cement†	1·17	1·23
Hydrated calcium sulphate	18·6*	18·5	Basic slag†	0·16	0·16
Barium sulphate	13·7	13·7			

* Determined gravimetrically as barium sulphate.

† Obtained from the Bureau of Analysed Samples Ltd.

slow; the inclusion of 0·2 g of acid-washed kieselguhr (analytical-grade Celite obtained from L. Light and Co. Ltd.) per gram of vanadium pentoxide overcame this difficulty, and heating for 30 minutes then sufficed.

Sulphur trioxide tended to condense in the outlet of the combustion tube, and so a 15-cm quartz adapter was included between the outlet and the absorption vessel, thereby permitting the end of the combustion tube to be heated without damage to the absorber. Apart from this modification the apparatus was as shown in Fig. 1. Sulphur trioxide that condensed in the adapter was rinsed into the hydrogen peroxide after each combustion. Table I shows the results of these experiments.

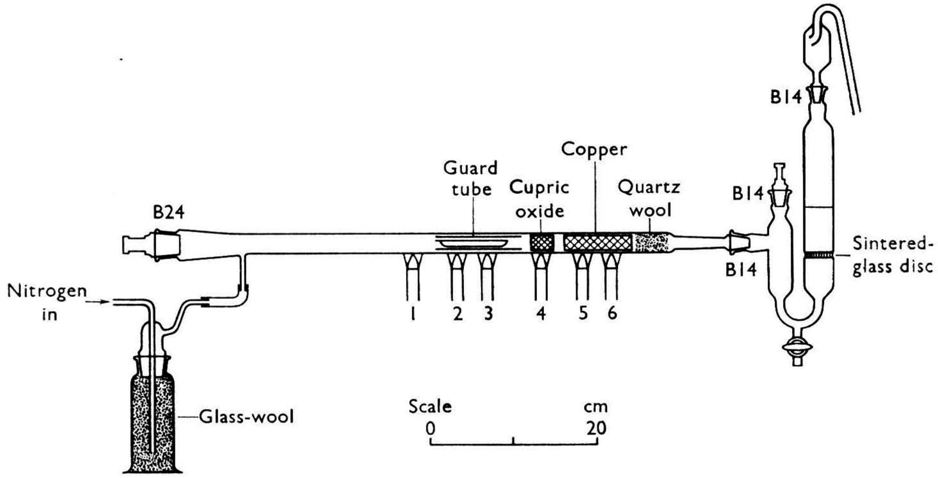

Fig. 1. Details of combustion tube and absorber

Larsen, Ross and Ingber[10] prepared vanadium pentoxide sufficiently low in sulphur for their micro method by fusing the oxide overnight at 1000° C. The pentoxide can be readily prepared from ammonium metavanadate; as this, unlike the pentoxide, is avilable in analytical-reagent grade, it seemed a more suitable source of the pure oxide. Pentoxide of sufficient purity can be prepared by heating the metavanadate in an electric furnace for 3 to 4 hours at 500° to 550° C, which suffices to remove all the ammonia; as the oxide does not fuse at this temperature, the product does not need to be ground. Blank values not exceeding 5 p.p.m. of sulphur are obtained by this method and can be further decreased by fusing the oxide, but this refinement is hardly necessary in the analysis of soils.

TABLE II

EFFECTS OF VARIOUS IONS ON RECOVERY OF SULPHUR FROM POTASSIUM SULPHATE

Sulphur present, µg	Ion added	Sulphur found, µg
60	None	58, 60
100		105, 104
200		207, 200
100	PO_4^{3-} (1200 µg)	100
	NO_3^- (100 µg)	100
	Cl^- (1000 µg)	98
	NH_4^+ (100 µg)	101

Table II shows that recovery of sulphur from potassium sulphate by Larsen, Ross and Ingber's colorimetric method[10] was satisfactory and that relatively large amounts of nitrate, phosphate, ammonium and chloride ions had no effect. In these determinations, 10 to 12 cm of reduced copper, heated by two bunsen burners, served to reduce sulphur trioxide to the dioxide, nitrogen instead of air being used as carrier gas.

Results were erratic when the method was applied to organic sulphur compounds, apparently owing to incomplete oxidation of the volatile products of decomposition of the organic matter. This was overcome by including a roll of oxidised copper immediately before the reduced copper in the combustion tube.

Table III shows that the method is applicable in the presence of considerable amounts of organic nitrogen. Table IV shows the degree of reproducibility attained in applying the method to soils; for the last three of these soils, Steinbergs and his co-workers[8] found 74, 292 and 450 p.p.m., respectively, of total sulphur by their sodium hydrogen carbonate method and 73, 284 and 424 p.p.m. by reduction with metallic magnesium.

TABLE III

RECOVERY OF SULPHUR FROM ORGANIC COMPOUNDS

Sample	Nitrogen present, µg	Sulphur present, µg	Sulphur found, µg
Sulphonal	—	100	97, 99
Methionine	50	100	98, 104
Methionine *plus* glycine	1000	100	94, 99
S-Benzylthiouronium chloride ..	90	100	99, 98

TABLE IV

REPRODUCIBILITY OF RESULTS FOR TOTAL SULPHUR IN SOILS

Soil	Sulphur found, p.p.m.
Broadbalk plot No. 2B (farmyard manure since 1843) ..	478, 492, 488, 484, 472
Broadbalk plot No. 3 (no fertiliser since 1839)	186, 184, 184, 182, 186
Yellow podzolic (Australian)	82, 82, 84, 82
Lateritic red earth (Australian)	275, 274, 288, 291
Heavy textured grey-brown soil (Australian)	438, 441, 438, 437

METHOD

APPARATUS—

The combustion tube (see Fig. 1) is a 60-cm transparent-quartz tube of 22 mm internal diameter, fitted with standard joints and a side-arm. The side-arm permits more rapid operation in a series of determinations, as, if the outlet of the combustion tube is sealed, the boat can be replaced against a current of nitrogen, thereby avoiding the necessity of allowing the copper to cool.

The quartz guard tube protects the combustion tube against possible sputtering of the charge during the initial heating.

A sintered-glass disc (porosity No. 2; 30 mm diameter) is incorporated in the Pyrex-glass absorption vessel.

Closely fitting rolls of oxidised and reduced copper gauze, 30 mm and 90 mm, respectively, in length, constitute the tube filling.

Before entering the combustion tube, nitrogen is bubbled successively through solutions of sodium hydroxide and tetrachloromercurate and finally through glass-wool.

REAGENTS—

Vanadium pentoxide—Heat analytical-reagent grade ammonium metavanadate, with occasional stirring, in a silica basin at 500° to 550° C in an electric furnace for 3 to 4 hours.

Sodium tetrachloromercurate solution—Dissolve 27·2 g of mercuric chloride and 11·7 g of sodium chloride in water, and dilute to 1 litre.

p-*Rosaniline hydrochloride reagent solution*—Triturate 0·5 g of *p*-rosaniline hydrochloride with water, dilute to 100 ml, and filter. To 40 ml of the filtrate add 60 ml of concentrated hydrochloric acid, and dilute to 1 litre with water.

Formaldehyde solution, 0·2 per cent. v/v, aqueous.

PREPARATION OF COMBUSTION TUBE—

Insert the two rolls of copper gauze into the combustion tube, keeping them a short distance apart, and heat both gently in a stream of air. Allow to cool, displace air from the tube with nitrogen, pass hydrogen through the tube, and heat the second spiral until the copper is completely reduced; burn the excess of hydrogen at the outlet. Discontinue heating, allow to cool in a current of nitrogen, push the oxidised copper into the position shown in Fig. 1, and heat the tube strongly, with the nitrogen still flowing, until a negligible blank value for sulphur is obtained with *p*-rosaniline and formaldehyde.

PROCEDURE—

Weigh 0·5 to 2·0 g of the finely ground soil (equivalent to not more than 500 μg of sulphur) into an agate mortar, and mix with 1 to 2 g of vanadium pentoxide by gentle grinding. Transfer to a quartz combustion boat (10 mm × 15 mm × 75 mm), and place boat and contents in the combustion tube. Connect the absorber, and flush the apparatus with nitrogen for 5 to 10 minutes. Place 40 ml of sodium tetrachloromercurate solution in the absorber, and fit the splash trap in position. Adjust the flow of nitrogen to 3 to 4 bubbles per second, and light burners 1, 4, 5 and 6. When the copper spirals are at red heat, light burners 2 and 3, and heat the boat gently for about 5 minutes and then at full heat for a further 30 minutes. Disconnect the absorber, and transfer its contents to a calibrated flask; use distilled water for washing and dilution to the mark. Transfer an aliquot of the solution containing not more than 20 μg of sulphur to a 50-ml calibrated flask, add 5 ml each of *p*-rosaniline hydrochloride reagent and formaldehyde solutions, and dilute to the mark with distilled water. Set aside for 35 minutes, measure the optical density at 550 mμ (Ilford No. 606 filter) against a reagent blank solution, and determine the amount of sulphur present from a calibration curve. Maximum intensity of colour develops in about 30 minutes and does not diminish significantly over the next 30 minutes.

Plot the calibration curve from the results obtained for a solution of sodium sulphite (standardised against iodine and diluted with sodium tetrachloromercurate solution) or, preferably, for a stock solution of sulphur dioxide in tetrachloromercurate prepared from a solution of potassium sulphate by the procedure described above. With a Spekker absorptiometer and a 1-cm cell, the working range is from 2 to 25 μg of sulphur per 50 ml of solution, but the relationship between optical density and sulphur content is not strictly linear above 10 μg of sulphur per 50 ml. A calibration curve should be plotted for each batch of *p*-rosaniline reagent solution.

With organic or calcareous soils, the period of gentle heating should be prolonged by a few minutes; with calcareous soils, it may be necessary to increase the proportion of vanadium pentoxide in the charge.

Sulphur dioxide in sodium tetrachloromercurate solution is not readily oxidised by atmospheric oxygen, so that solutions can be accumulated and a series of determinations completed at the end of the day.

I thank Drs. N. J. Barrow and J. R. Freney for supplying details of their method and for a gift of soils.

REFERENCES

1. Swaine, D. J., "The Trace-Element Content of Soils," *Technical Communication No.* 48, Commonwealth Bureau of Soil Science, Harpenden, 1955.
2. Smittenberg, J., Harmsen, C. W., Quispel, A., and Otzen, D., *Plant & Soil*, 1951, **3**, 353.
3. Little, R. C., *J. Sci. Food Agric.*, 1957, **8**, 271.
4. St. Lorant, I., *Hoppe-Seyl. Z.*, 1929, **185**, 245.
5. Johnson, C. M., and Nishita, H., *Anal. Chem.*, 1952, **24**, 736.
6. Kiba, T., Takagi, T., Yoshimura, Y., and Kishi, I., *Bull. Chem. Soc. Japan*, 1955, **28**, 641.
7. Volkov, I. I., and Ostroumov, E. A., *Zhur. Anal. Khim.*, 1958, **13**, 686.
8. Steinbergs, A., Iismaa, O., Freney, J. R., and Barrow, N. J., in the press.
9. Hagerman, D. B., and Faust, R. A., *Anal. Chem.*, 1955, **27**, 1970.
10. Larsen, R. P., Ross, L. E., and Ingber, N. M., *Ibid.*, 1959, **31**, 1596.
11. West, P. W., and Gaeke, G. C., *Ibid.*, 1956, **28**, 1816.

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The Determination of Oxygen by Fast-neutron Activation

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A method is described for determining oxygen in most elements by fast-neutron activation. Nitrogen-16 produced in the reaction ^{16}O (*n,p*) ^{16}N by irradiation with 14·5-MeV neutrons is detected by counting high-energy gamma rays. A wide variety of metals has been analysed, and results generally agree with those obtained by vacuum fusion. At present, the limit of detection is about 10 p.p.m. of oxygen.

THERE is a constant need for determinations of oxygen in almost all metals, and this topic has been reviewed by Elwell[1]; the most widely used method for determining trace impurities of oxygen is by vacuum fusion. Pearce and Masson[2] adapted the isotope-dilution technique to the determination of oxygen in iron and steel and obtained results indicating that vacuum fusion did not remove all the oxygen from the sample. As vacuum fusion has been accepted in the past as the most reliable method of determining traces of oxygen in metals, it was decided to develop an independent method to attempt to resolve this discrepancy. Such a method (fast-neutron activation) had been applied to the determination of oxygen in beryllium[3]; a modification of the technique, entailing the counting of high-energy gamma-rays instead of beta-particles, permitted oxygen to be determined in almost all elements with a detection limit of about 10 p.p.m.

DESCRIPTION OF METHOD

As before,[3] the sample was irradiated in a flux of 14·5-MeV neutrons, and the 7·4-second activity from nitrogen-16 produced in the reaction ^{16}O (*n,p*) ^{16}N was then compared with the activity from a sample of similar size containing a known amount of oxygen.

Neutrons of 14·5 MeV were obtained by bombarding a tritiated zirconium target with 250-keV deuterons. The total neutron output from the target was from 1 to 2×10^{10} neutrons per second. Irradiation was for 10 seconds, with the samples in a standard position close to the source of neutrons. The neutron output was monitored by a fission counter, and the pulses were fed via a ratemeter into a fast pen recorder and also into a scaler; the total counts recorded by the scaler was proportional to the number of neutrons received by the sample.

After irradiation, the samples were rapidly transferred to a standard position near a 2·5-inch × 2·5-inch sodium iodide crystal. A special non over-loading amplifier (Nuclear Enterprises No. 5202) was used, and its output was fed into a scaler biassed to count pulses from photons more energetic than 3·5 MeV. About 75 per cent. of the nitrogen-16 atoms produce 6-MeV gamma-rays on decay, and, as gamma rays of energy greater than 3·5 MeV are rare, the counting system is specific for nitrogen-16; at the same time, it has a fairly high efficiency (approximately 10 per cent.). A timing unit was available that printed the counts recorded in successive 4-second periods, and these results could be used to produce decay curves. It was found, however, that the decay curves always consisted solely of a pure 7·4-second emitter and a constant counter background, so the procedure was modified to record counts between 15 and 35 seconds and between 90 and 110 seconds. In this second period only the counter background was recorded, so that, when the second count was subtracted from the first, the result was proportional to the activity of the sample. This technique considerably decreased the time needed for calculating the oxygen content.

CALIBRATION OF METHOD

In order to make the calibration as easy and as accurate as possible, the samples to be irradiated are of standard size (1 cm in diameter and 0·5 cm long); in this way the neutron and counter geometries are constant. Standard samples of beryllium containing known amounts of added oxygen were available, but these could only be used as standards for other materials if the corrections for neutron and gamma absorption were known.

The variation in neutron flux for many different metals was calculated from the known total cross-sections for 14·5-MeV neutrons and shown to be small. However, to check these calculations a thin disc of Perspex (oxygen compound) was irradiated with neutrons that had passed through a 0·5-cm disc of various materials and was then counted in the usual way. The Perspex experienced an attenuated flux corresponding to that at the back of the sample; the results were—

Absorber	Air	Perspex	Beryllium	Aluminium	Zirconium	Iron	Copper
Activity of Perspex	2785	2770	2730	2790	2739	2680	2690
Absorption of neutrons, % ..	0	0	1	0	1	3	3

These figures showed that the maximum absorption for the materials tried was 3 per cent.; the mean absorption was approximately 1 per cent. and hence negligible.

The variation in gamma absorption was also measured. Again, a thin disc of Perspex was irradiated many times and counted with various thicknesses of each material to be investigated between it and the counter; the relationship between the percentage of activity transmitted and the thickness of the absorber was derived.

As the sample is irradiated in a position close to an almost point source of neutrons, the fluxes of neutrons at the back and front of the sample differ by a factor of 4. Also, because the sample is counted by placing one of its faces in contact with the sodium iodide crystal, there is a large difference in counting geometry between back and front of the sample. Both these variations have been determined and must be taken into consideration when calculating the absorption of the sample. In calculating the absorption correction, the sample is theoretically divided into sections such that the variations in flux and counter geometry through them are small. Some results are shown in Table I; absorption corrections for other materials are found by interpolation.

TABLE I

CORRECTIONS FOR GAMMA-RAY ABSORPTION

Section No.	Position of section,* cm	Counter geometry (relative)	Neutron flux (relative)	Activity transmitted by— Be, %	Al, %	Zr, %	Fe, %	Cu, %
1	0·0 to 0·04	1·54	4·08	99	98·5	94	94	94
2	0·04 to 0·1	1·46	3·22	97	96·5	83	83	83
3	0·1 to 0·2	1·33	2·26	94	90	75	74	73
4	0·2 to 0·3	1·22	1·53	91	84	70	69	67
5	0·3 to 0·4	1·11	1·14	88	81	67	66	65
6	0·4 to 0·5	1·00	1·00	86	78	65	65	65
Activity transmitted from whole sample, % ..				93·5	89·5	78	77	76

* Measured from the face of the sample placed nearer to the source of neutrons and to the counter.

Because of the difficulty of preparing homogeneous mixtures of beryllium and beryllium oxide, the standard deviation of the oxygen determinations on the standard sample of beryllium is about 12 per cent. To improve the accuracy of the method, pure compounds of known oxygen content were used, but the choice was severely limited by the need to fashion them into a standard shape; silica, hydroquinone and cholesterol were used, the silica being machined to size and the organic compounds compacted in a small press. These samples and the standard beryllium were irradiated many times, and the nitrogen-16 activity was counted as before. The measured activity was normalised to a standard flux of neutrons (10^{10} neutrons per second) and a standard weight of sample; the results are shown in Table II.

TABLE II

COMPARISON OF STANDARDS

Sample	Normalised activity (A), counts per 20 seconds per g	Oxygen content (C), %	Absorption correction (B)	Value of AB/C
Mixture of beryllium and beryllium oxide	2914	0·38 ± 0·05	1·07	8205 ± 960
Silica	354,000	53·2	1·09	7252
Cholesterol	28,900	4·14	1·04	7270
Hydroquinone	198,000	29·1	1·04	7075

Possible interfering elements

The change from counting beta particles to counting high-energy gamma-rays has permitted many other metals to be analysed and has also decreased the number of possible interfering elements. The most serious interference is from fluorine, which produces nitrogen-16 by the reaction $^{19}\text{F}\ (n,\alpha)\ ^{16}\text{N}$ (which has a cross-section of the same order as that of the oxygen reaction). As both elements yield the same reaction product, it is not possible to distinguish between them; obviously, therefore, if it is not to cause interference, fluorine must be present to a considerably lesser extent than is oxygen. In the samples so far analysed, the fluorine content has been negligible. If fluorine is present at about the same level as oxygen, it would be possible to determine it by another reaction, *e.g.*, $^{19}\text{F}\ (n,2n)\ ^{18}\text{F}$, and then to correct the result for oxygen.

Boron also interferes through formation of beryllium-11 by the reaction $^{11}\text{B}\ (n,p)\ ^{11}\text{Be}$. Beryllium-11 has a half-life of 13·7 seconds, and about 10 per cent. of the atoms produced decay with a photon more energetic than 3·5 MeV. The cross-section for this reaction is of an order of magnitude less than that of the oxygen reaction, so that boron can be present in a concentration ten times that of oxygen before it interferes appreciably.

Neutrons of 14 MeV cause fission of uranium and thorium, and some short-lived fission products emit gamma rays more energetic than 3·5 MeV; this makes it impossible to determine trace amounts of oxygen in these metals. However, about 1 per cent. of uranium and thorium can be tolerated in other elements without interference with the determination of oxygen.

Comparison of fast-neutron activation with other methods

Several different metals previously analysed by vacuum fusion (and, for two samples, by isotope dilution) were also analysed by fast-neutron activation; the results are shown in Table III. The agreement between results by vacuum fusion and neutron activation was good for nearly all the samples, but the activation results were significantly different from those obtained by isotope dilution.

Table III

Comparison of results for oxygen

Sample	Oxygen content found by—			Source of sample and of results by vacuum fusion†
	activation, p.p.m.	vacuum fusion, p.p.m.	isotope dilution,* p.p.m.	
Beryllium 3/1	4300	4400	—	A
Beryllium 3/7	4300	4700	—	
Steel BNL 11	160	145	254	B
Steel BPL 15	37	30	63	
Steel BOL 25	120	100	—	
Steel CRL 15	54	35	—	
Copper NPE	330	320	—	C
Titanium	1070	1200	—	
Zirconium	970	1000	—	D
Niobium	310	340	—	
Stainless steel	65	70	—	

* Results found by Pearce and Masson.[2]

† Samples were obtained from: A, U.K. Atomic Energy Authority, Atomic Weapons Research Establishment; B, British Iron and Steel Research Association; C, British Non-ferrous Metals Research Association; D, U.K. Atomic Energy Authority, Production Group, Springfields Works.

Oxygen has also been determined by neutron activation in aluminium, tantalum, tungsten, tin, molybdenum, vanadium and rhenium, and the method is considered to be applicable to all elements except boron, fluorine, thorium and uranium.

The error of the method varies with the oxygen content of the sample; for oxygen contents of about 1000 p.p.m., the error is estimated to be about 7 per cent., between 100 and 1000 p.p.m., about 10 per cent. and between 20 and 50 p.p.m., about 15 per cent.

CONCLUSIONS

Improvements in the method of detecting nitrogen-16 have permitted oxygen to be determined in most elements by fast-neutron activation. Even the determination of oxygen in beryllium, for which beta-particle counting was previously used,[3] can be better carried out by gamma-ray counting, because, although the efficiency of detection is decreased, interference from impurities in the beryllium is overcome. The limit of detection of the method is about 10 p.p.m. when a total fast-neutron output of 10^{10} neutrons per second is used. The method is specific and rapid; once the counting equipment has been set up and the sample prepared, about fifteen samples can be analysed per hour.

I thank the British Iron and Steel Research Association, the British Non-ferrous Metals Research Association and the Production Group of the U.K. Atomic Energy Authority for supplying analysed samples. I also thank Mr. J. Gray for operating the Cockcroft - Walton machine.

REFERENCES

1. Elwell, W. T., *in* "The Determination of Gases in Metals," *Special Report No.* 68, The Iron and Steel Institute, London, 1960, p. 19.
2. Pearce, M. L., and Masson, C. R., *in* "The Determination of Gases in Metals," 1960, p. 121.
3. Coleman, R. F., and Perkin, J. L., *Analyst*, 1959, **84**, 233.

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Notes

THE DETERMINATION OF CARBON DIOXIDE AND NITROUS OXIDE IN SOLUTIONS OF MONOETHANOLAMINE

STUDIES at this Laboratory of the kinetics of mass-transfer rates in chemical reactions have necessitated the determination of carbon dioxide and nitrous oxide in aqueous solutions of monoethanolamine.

DETERMINATION OF CARBON DIOXIDE

Our recent work on the application of gas chromatography to the determination of carbon dioxide in samples of rocks and minerals[1] led to the supposition that a somewhat similar technique could be used for determining carbon dioxide in solutions of monoethanolamine. Use of the apparatus and technique described previously[1] was suitable for this determination.

Samples were transferred by pipette to the reaction vessel, and the carbon dioxide was liberated by boiling with diluted orthophosphoric acid. The determination was completed as before, except that the 6-foot column of silica gel was replaced by a 2-foot column of activated charcoal. (This permitted nitrous oxide to be determined with basically the same apparatus, only the reaction vessel being changed.) The apparatus was calibrated as before, *i.e.*, by weighing pure calcium carbonate into the reaction vessel and decomposing it by boiling with orthophosphoric acid.

DETERMINATION OF NITROUS OXIDE

Although nitrous oxide is appreciably soluble in aqueous solutions of monoethanolamine (a 10 per cent. w/v solution of monoethanolamine saturated with the gas contains approximately 1 g of nitrous oxide per litre), chemical reaction does not occur, and special precautions are needed to prevent loss of dissolved gas.

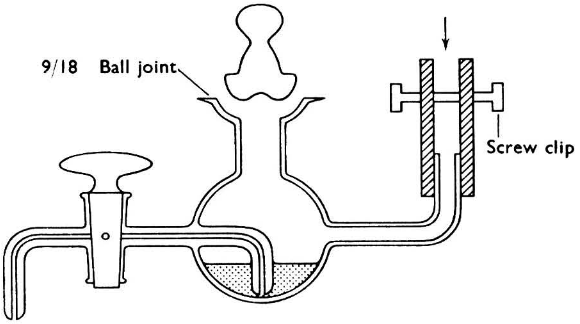

Fig. 1. Reaction vessel used in determining nitrous oxide

The reaction vessel used for this determination is shown in Fig. 1 and consists of a round-bottomed flask of capacity about 12 ml fitted with a ball joint for connection to the apparatus used previously.[1] The tap funnel used when determining carbon dioxide is not required, but provision is made for removing the liquid material from the flask after evolution of the nitrous oxide. The tap shown in Fig. 1, although not depicted as such, is spring-loaded, as is also the 9/18 ball joint.

Evolution of nitrous oxide is readily achieved by boiling the solution in the reaction vessel. When such boiled monoethanolamine samples are left in the vessel, a small amount of the gas re-dissolves on cooling, and it is therefore preferable to remove the sample immediately after it has been boiled. When samples so removed are replaced in the reaction vessel and boiled again, no further nitrous oxide can be recovered.

A graph of peak area against volume of nitrous oxide is a straight line passing through the origin. The peak areas obtained from nitrous oxide injected with a by-pass injector[2] were identical with those obtained by injecting the same volumes into the reaction vessel through the rubber tubing, although the peak heights were not the same. The admission of a standard volume of gas through the by-pass injector was therefore adopted as a means of calibrating the katharometer response.

PROCEDURE—

In order to avoid loss of nitrous oxide during the sampling operation, a graduated 5-ml pipette is used to transfer the monoethanolamine sample from the mass-transfer reaction apparatus to the flask shown in Fig. 1. Only the solution contained in the lower part of the pipette, amounting to 2 ml, is transferred to the reaction vessel. The reaction vessel is then connected to the apparatus described previously.[1] Duplicate samples taken at the same time are stored until required, a screw clip and a ball-joint stopper lubricated with Apiezon T grease being used to prevent loss of nitrous oxide.

With the reaction vessel in position and the screw clip closed, the sample is gently boiled for 2 minutes over a microburner. The monoethanolamine solution is removed by carefully opening the tap. The nitrous oxide evolved is then swept on to the chromatographic column in the manner described for carbon dioxide. The area of the peak corresponding to nitrous oxide is measured and compared with that of the peak produced by injecting a known volume of pure nitrous oxide.

The work described in this Note forms part of a research programme of Warren Spring Laboratory, D.S.I.R., and is published by permission of the Director.

REFERENCES

1. Jeffery, P. G., and Kipping, P. J., *Analyst*, 1962, **87**, 379.
2. Kipping, P. J., and Jeffery, P. G., *Ibid.*, 1961, **86**, 680.

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DETERMINATION OF VOLATILE IMMISCIBLE LIQUIDS IN WATER AND EFFLUENTS

IN a method proposed for the approximate determination of small concentrations of volatile immiscible liquids in river waters and effluents,[1,2] a direction is given to remove with acetone traces of oil adhering to the inside of the sample bottle. The acetone solution is then added to the main sample in the reagent flask.

More extensive experience of this method has shown that acetone may interfere with adsorbtion of the volatile oil on certain types of activated carbon. The direction to rinse out the sample bottle with acetone should be deleted and replaced by the sentence: "Wipe out the inside of the bottle with two or three pieces of filter-paper, and add them to the contents of the flask."

REFERENCES

1. Sherratt, J. C., *Analyst*, 1956, **81**, 518.
2. Joint Committee of the Association of British Chemical Manufacturers and the Society for Analytical Chemistry, "Recommended Methods for the Analysis of Trade Effluents," W. Heffer and Sons Ltd., Cambridge, 1958, p. 15; *Analyst*, 1957, **82**, 123.

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THE DETERMINATION OF URANIUM DIOXIDE WITH A HYDROCHLORIC ACID - ETHYL ACETATE SOLVENT

METHODS for determining uranium dioxide, UO_2, generally involve use of specialised equipment,[1,2] and a search of the literature failed to disclose a simple procedure in which common laboratory reagents and apparatus were used. Larsen[3] has described the solution of uranium metal with hydrogen chloride in ethyl acetate in separating it from oxides of uranium. In order to avoid use of hydrogen chloride, a solution of hydrochloric acid in ethyl acetate was tried. This solvent proved to be satisfactory for separating uranium dioxide from U_3O_8, uranium trioxide, uranium carbide and uranium metal.

EXPERIMENTAL

Hydrochloric acid is completely miscible with ethyl acetate at a concentration of approximately 25 per cent. (3 M). Uranium metal, uranium carbide (a mixture of UC and UC_2) and uranium trioxide were found to be readily soluble in this solvent under conditions of reflux; U_3O_8 was also soluble, a 0·5-g sample requiring approximately 2 hours of heating under reflux for complete solution.

The solubility of uranium dioxide in this solvent was found to be dependent on the composition of the oxide. As the ratio of uranium to oxygen was increased from 1 to 2 ($UO_{2\cdot00}$) to 1 to 2·667 ($UO_{2\cdot667}$ or U_3O_8), the solubility increased from zero to 100 per cent. When the percentage of soluble uranium was plotted against the ratio of uranium to oxygen (determined by thermogravimetric analysis), a direct relationship was obtained, as shown in Fig. 1. Ratios of uranium to oxygen, determined on the residues after extraction, were always less than 1 to 2·01. Table I shows results for the recovery of uranium dioxide from prepared mixtures of the metal, its oxides and its carbide.

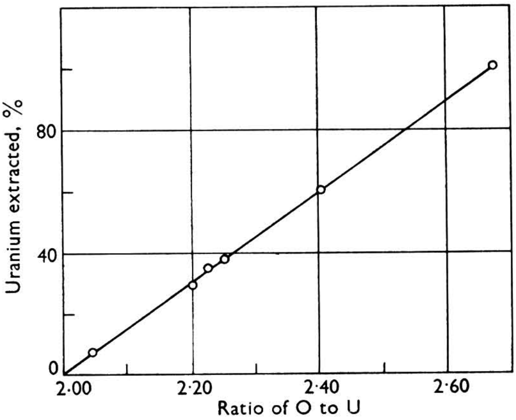

Fig. 1. Relationship between uranium extracted from UO_2 and the ratio of oxygen to uranium

TABLE I

RECOVERY OF URANIUM DIOXIDE FROM PREPARED MIXTURES BY PROPOSED METHOD

Composition of sample					
Uranium dioxide, %	Uranium metal, %	Uranium trioxide, %	U_3O_8 %	Uranium carbide, %	Recovery of uranium dioxide, %
0·5	31·6	20·2	43·7	4·0	102·0
2·4	48·6	37·7	11·3	—	101·9
5·2	—	59·1	35·7	—	99·1
10·3	34·4	43·5	11·8	—	102·7
20·6	41·3	5·7	21·2	11·2	100·3

METHOD

PROCEDURE—

Weigh a suitable sample into a round-bottomed 250-ml flask fitted with a ground-glass neck and a water-cooled condenser; the weight of sample will depend on its UO_2 content and the procedure used for the final determination of uranium. Add 100 ml of a 25 per cent. v/v solution of hydrochloric acid in ethyl acetate, and heat gently under reflux for 2 hours. Cool, filter through a Whatman No. 50 filter-paper, with suction, and wash the flask and residue thoroughly with the solvent. Ignite the residue, and weigh as U_3O_8, or dissolve it in nitric acid, and determine uranium by any suitable procedure. Calculate the UO_2 content of the sample.

Discussion of the method

Uranium dioxide sintered at high temperature in an atmosphere of hydrogen cannot be determined by the proposed method, as such treatment renders it almost insoluble in the solvent.

The method provides a fairly rapid means of determining the ratio of uranium to oxygen in samples of uranium dioxide with good accuracy and without the use of specialised equipment.

Samples were filtered under suction with use of a Millipore filter holder (obtained from the Millipore Filter Corporation, Bedford, Mass., U.S.A.) fitted with a Whatman No. 50 filter-paper. The hard nature of this paper made it unsuitable for collecting fine residues when supported on a Buchner funnel, erratic results being caused by the residue creeping under the paper.

References

1. Silverman, L., Houk, W. W., and Moudy, L., *Anal. Chem.*, 1957, **29**, 1762.
2. Murray, P., and Tackray, R. W., U.K. Atomic Energy Research Establishment Report AERE–M/R–632, Harwell, 1958.
3. Larsen, R. P., *Anal. Chem.*, 1959, **31**, 545.

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THE COLORIMETRIC DETERMINATION OF DIALKYLTIN COMPOUNDS DISSOLVED IN FATS AND OLIVE OIL

Included with other test solutions, olive oil containing 2 per cent. of added oleic acid is recommended in the 1958 report of the British Plastics Federation (and a liquid food fat, such as a vegetable oil or lard oil, is suggested in the Food Additives amendment of the U.S. Food and Drug Administration) as suitable for testing the migration of substances from plastics packaging. In this connection, it was desired to determine small amounts of dialkyltin compounds added as stabilisers to poly(vinyl chloride) film and extractable in small amounts by fats and olive oil under the conditions of the accelerated tests.

Bagnall[1] gave results for tin found in olive oil, but the method used was not described. Incineration in a platinum dish and subsequent oxidation by mixed acids in a Kjeldahl flask resulted in some loss of volatile tin. Kjeldahl digestion as recommended by the Analytical Methods Committee[2]—Method (I)B, continuation (*b*)1,—in an apparatus modified by the addition of a 12-inch air condenser[3] was prolonged, and, with a 2-g sample, less than 200 μg of a dialkyltin compound could not be detected by the dithiol method.

A solvent capable of extracting small amounts of a dioctyltin compound from olive oil was not found, but, by increasing the concentration of dithizone reagent from 0·008[4,5] to 0·025 per cent. to allow for the interfering reaction of olive oil, and despite rapid fading of colour, comparison with controls of olive oil containing increments of the dioctyl tin compound gave an approximate figure for the amount present in the olive oil extractant.

Catechol violet (catechol sulphonphthalein), although less sensitive and less selective than dithizone, is more stable; it forms a blue complex with quadrivalent inorganic tin and mono- and dialkyltin compounds.[6] It has been used as a spotting reagent for organo-tin compounds in paper chromatography[7] and for determining quadrivalent tin spectrophotometrically.[8] As a 0·1 per cent. solution in 95 per cent. ethanol, it forms a complex with dibutyl- and dioctyltin compounds soluble in ethanol; after being shaken and then set aside for 4 hours, the ethanolic solution separates from the olive oil as a clear brown to violet upper layer.

The method described below has given satisfactory results in this particular application.

Method

Reagents—

Catechol violet solution, 0·1 per cent. w/v, in 95 per cent. ethanol—Freshly prepare before use.

Industrial methylated spirit.

Olive oil, B.P.

PROCEDURE—

Weigh 2 to 10 g, according to the amount of dialkyltin compound expected, of the olive oil extractant into a stoppered, graduated 25-ml glass tube of total capacity at least 30 ml and 7 inches in length. Make the weight up to 10 g with olive oil, and add 0·5 ml of the catechol violet solution and 13·5 ml of industrial methylated spirit. Shake for 2 minutes, inverting the tube occasionally to ensure adequate mixing, set aside for 4 hours to obtain as upper layer an optically clear ethanolic solution. By means of a clean dry pipette, transfer some of the ethanolic extract of the dialkyltin - catechol violet complex to a parallel-sided 1-cm glass cell, and measure its absorption at 550 mμ (a Unicam SP700 spectrophotometer was used) against a blank solution prepared by treating 10 g of olive oil exactly as described above. Similarly, from standards containing 200, 300, 400 and 500 μg of the dialkyltin compound per 10 g of olive oil (0·005 per cent. solution, diluted), plot the maximum absorption at 550 mμ as a calibration curve. As the dialkyltin - catechol violet complex is only partly extracted into ethanol, at least two further extractions are necessary. The residual ethanolic solution is drawn off by pipette or siphon, and further extractions are carried out by repeating the same procedure.

RESULTS

Some typical results obtained by the proposed procedure are shown in Table I.

TABLE I

ABSORPTION AT 550 mμ

	Absorption of standard containing, per 10 g of olive oil—			Absorption of solution derived from—		
Extraction	375 μg of dioctyltin compound, %	400 μg of dioctyltin compound, %	425 μg of dioctyltin compound, %	1·0 g of olive oil extract of dioctyltin compound, %	2·0 g of olive oil extract of dioctyltin compound, %	2·4 g of olive oil extract of dioctyltin compound, %
First	59	60	60	56	58	61
Second	35	37	42	44	54	56
Third	7	7	19	18	38	44
Fourth	—*	—*	Nil	Nil	—*	5

* Not determined.

By making 6 g of sample up to 10 g with olive oil, dialkyltin compounds extracted from poly(vinyl chloride) by butter fat and margarine were determined.

I thank Dr. J. O. Smith and the Directors of British Cellophane Ltd. for permission to publish this Note.

REFERENCES

1. Bagnall, H. H., *Analyst*, 1935, **60**, 820.
2. Analytical Methods Committee, *Ibid.*, 1960, **85**, 647.
3. Price, J. W., *Paint Manuf.*, May, 1958, 147.
4. Aldridge, W. N., and Cremer, J. E., *Analyst*, 1957, **82**, 37.
5. Chapman, A. H., Duckworth, M. W., and Price, J. W., *Brit. Plastics*, 1959, **32**, 78.
6. Burger, K., *Z. LebensmittUntersuch.*, 1961, **114**, 1.
7. Williams, D. J., and Price, J. W., *Analyst*, 1960, **85**, 579.
8. Ross, W. J., and White, J. C., *Anal. Chem.*, 1961, **33**, 421.

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DETERMINATION OF TOTAL WATER IN ROCKS BY A SIMPLE DIFFUSION METHOD

THE determination of the total-water content of a rock simply by measuring the loss on ignition rarely yields an accurate result because of the decomposition of carbonates, oxidation of bivalent ion and sulphides and the volatility of alkali salts; all accurate and reliable methods depend on collection of the water evolved. This may be achieved by circulating dry air or nitrogen over the sample heated in a combustion tube and adsorbing the water evolved on a desiccant. Suitable packings overcome interference by oxides of sulphur and fluorides. Examples of this procedure have been given by Riley[1] and Jeffery and Wilson[2]; these methods, although accurate and reliable, necessitate careful assembly and conditioning of gas-absorption trains and are most suitable for a series of determinations.

For occasional determinations, simple non-circulation methods are useful, the water evolved being collected by condensation,[3] on a filter-paper[4] or by a desiccant.[5] In this last method, a silica test-tube is supported in a rubber bung, which fits into the absorption tube to effect a gas-tight connection. Most of the water expelled from the sample on ignition in the silica test-tube is carried to the desiccant by expansion of gases and vapour, and residual water vapour is removed from the ignition tube by diffusion and convection, so avoiding one source of error in Penfield's method.[3] Further, the silica test-tube permits use of a greater working temperature than is possible in the normal Penfield method, the only limiting factor being the rubber connection.

The method described below is based on the same principle as Harvey's method.[5] The use of ground silica and glass joints sealed with polytetrafluoroethylene sleeves permits greater working temperatures, and the air temperature of the junction between test-tube and absorption tube can be maintained at more than 100° C, thereby avoiding condensation of water at this point; the compact form of this modification leads to lower blank values (0·20 mg or less).

The apparatus used is shown in Fig. 1 and consists of a silica test-tube, an absorption tube filled with magnesium perchlorate and a guard tube containing magnesium perchlorate; Fig. 1 (*a*) shows the apparatus assembled for a determination. The sample (0·1 to 1 g), contained in a platinum boat, is heated in the silica tube by a blast flame (920° C) or an Amal burner (850 °C).

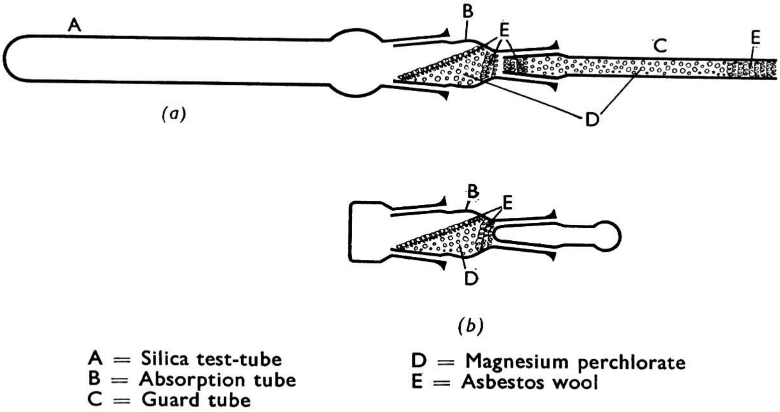

Fig. 1. (*a*) Apparatus assembled for a determination; (*b*) sealed and plugged absorption tube

To avoid condensation of water droplets, which are only slowly vaporised, the tube is gently heated along its length before heat is applied to the sample. The standard period of heating adopted was 1 hour, although transfer of water is complete in as little as 10 minutes; prolonged heating does no harm, as some mineral species may evolve water slowly. When ignition is complete, the absorption tube with its polytetrafluoroethylene sleeves is sealed with a cap and plug, as shown in Fig. 1 (*b*).

The packing of the absorption tube requires special attention, as a large surface area is needed; this is achieved by packing the magnesium perchlorate so that its surface slants and holding it in place by asbestos wool and slight moistening of the surface.

To find the time needed for the transfer of water from the heated silica tube to the desiccant, weighed amounts of magnesium sulphate heptahydrate were introduced into the ignition tube in a platinum boat; the results indicated that the water was completely transferred in 10 minutes. However, such a short time of heating would not be adequate for the complete expulsion of combined water from many minerals. Also, it must be pointed out that this method, although adequate for many rocks, may yield low results for such minerals as talc, topaz, chondrodite and staurolite, which do not always give up their combined water completely, even when heated over a blast flame.[6] In common with Harvey's and Penfield's methods, the proposed procedure is not suitable for rocks containing much sulphur and fluoride without a retainer. Carbon dioxide evolved from certain rocks could also interfere, unless it was displaced from the absorption tube. The results of a series of comparative determinations by the proposed method and the furnace-circulation method (see Table I) show adequate agreement.

TABLE I

COMPARISON OF RESULTS BY PROPOSED AND CIRCULATION METHODS

Samples were taken from the collection of analysed rocks, Geological Survey of Great Britain; the numbers are laboratory serial numbers

	Rock material	Time of heating, minutes	Water found by— diffusion method, %	Water found by— circulation method, %
1771.	Granophyrit granite, Burn of Roerwater, Shetland	60	0·45	0·46
1733.	Tonalite, Cloudlaid, Morvern, Argyllshire	60	1·32	1·35
1628.	Lamprophyre, Salen, Lock Sunart, Argyllshire	120	2·32	2·45
1448.	Picroteschenite, Lugar Sill, Lugar, Ayrshire	60	4·18	4·22
1697.	Rhyolite, Church Stretton, Shropshire	60	3·61	3·62
1698.	Andesite, Middle Hill, near Church Stretton, Shropshire	60	4·45	4·58
1612.	Porphyritic obsidian, Sandy Braes borehole No. 3, Tardree Mountain, Co. Antrim	60	12·83	12·81
1811.	Ash borehole, Earle's Quarry, Derbyshire	15	10·10	10·14
1820.	Altered basalt, Ballygill North, Co. Antrim	25	18·93	18·94
1821.		90	16·86	16·82
1822.		90	17·61	17·52
1823.		60	17·32	17·32

I thank Mr. L. J. Lionnel for assistance with some of the experimental work. This Note is published by permission of the Government Chemist and the Director of the Geological Survey, Department of Scientific and Industrial Research.

REFERENCES

1. Riley, J. P., *Analyst*, 1958, **83**, 42.
2. Jeffery, P. G., and Wilson, A. D., *Ibid.*, 1960, **85**, 749.
3. Penfield, S. L., *Amer. J. Sci.*, 1894, **48**, 31.
4. Shapiro, L., and Brannock, W. W., *Anal. Chem.*, 1955, **27**, 560.
5. Harvey, C. O., *Bull. Geol. Surv. Great Britain*, 1939, **1**, 8.
6. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. L., "Applied Inorganic Analysis," Second Edition, John Wiley & Sons Inc., New York, 1953, p. 828.

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THE SPECTROPHOTOMETRIC DETERMINATION OF TIN IN SOIL WITH GALLEIN

A COLORIMETRIC method for determining tin in samples of soil and sediment by means of its complex with gallein was described by Wood[1] and subsequently modified by us.[2] In a further modification, Marranzino and Ward[3] used a mixture of cyclohexanone and *o*-dichlorobenzene for extracting the complex; these workers determined tin down to 5 p.p.m.

In the procedure described below, the tin - gallein complex is extracted into pentyl alcohol, and tin at a concentration of 1 p.p.m. can be determined in a 1-g sample of soil or sediment.

METHOD

REAGENTS—

Ammonium iodide.

Hydrochloric acid, N—Prepare from analytical-reagent grade acid.

Hydrazine hydrate solution, 10 *per cent. w/w.*

Gallein solution, 0·1 per cent. w/v, in ethanol—Filter before use.

Ethanol, absolute.

Pentyl alcohol—Analytical-reagent grade.

Chloroacetate buffer solution—Prepare a solution 2 M in both chloroacetic acid and sodium chloroacetate.

Standard tin solution—Dissolve 0·1 g of powdered tin in 100 ml of concentrated hydrochloric acid, and dilute to 1 litre in a calibrated flask with water; dilute this solution twenty-fold with N hydrochloric acid.

$$1 \text{ ml} \equiv 5\ \mu\text{g of tin.}$$

PROCEDURE—

Mix 1 g of sample with 1 g of ammonium iodide in a borosilicate-glass test-tube (18 mm × 180 mm), and heat until ammonium iodide ceases to sublime and the residue attains a dull-red heat; keep the top of the test-tube cool to minimise loss of vapour. Leach by bringing to the boil with 10 ml of N hydrochloric acid, filter through a Whatman No. 40 filter-paper, and wash with hot N hydrochloric acid, adding the washings to the filtrate. Dilute the cold filtrate to 50 ml with N hydrochloric acid, and take a suitable aliquot (unless the tin content of the sample is known to be less than 5 p.p.m., in which event continue with the total filtrate).

Add hydrazine hydrate solution until the iodine has been reduced, and then add N hydrochloric acid if necessary until the solution is just acid. (The aluminium present in the soil is usually adequate as an indicator, otherwise use a test paper externally.) Cool the solution, transfer to a 150-ml separating funnel, add 10 ml of chloroacetate buffer solution, and dilute to 100 ml with water. Add 0·4 ml of gallein solution, mix, set aside for 10 minutes, and extract the complex by shaking vigorously with 10 ml of pentyl alcohol for 30 seconds. Discard the aqueous layer, dry the pentyl alcohol solution by passage through a filter-paper, and measure its optical density at 500 mμ in 1-cm cells against pentyl alcohol. Plot a calibration graph for the range 1 to 20 μg of tin from the results obtained by adding 10-ml portions of chloroacetate buffer solution to suitable volumes of standard tin solution in separating funnels, diluting each with water to 100 ml and continuing as described above for the sample.

DISCUSSION OF THE METHOD

Some experience is necessary to achieve efficient decomposition of the sample, and for accurate determination it may be advisable to repeat the attack by mixing a further 1 g of ammonium iodide with the residue and re-heating before leaching with acid. With adequate practice, this becomes unnecessary, but early attempts may give results low by 25 to 50 per cent.

If the sample solution is left overnight before filtration, there is considerable loss of tin from solution; this does not occur when the solution has been filtered immediately, nor if 6 N hydrochloric acid is used for leaching. Wood has suggested that the more basic complexes of the type $[\text{Sn(OH)}_x\text{Cl}_{6-x}]^{2-}$ are probably in colloidal solution and may be slowly flocculated by organic colloids from the soil. Also, there may be some direct adsorption by carbon resulting from degradation of the organic matter.

The optimum pH range for formation of the tin - gallein complex is 2·0 to 2·5. Wood[1] has shown that the complex in aqueous solution contains one atom of tin and two molecules of gallein; although the structure of the complex was not ascertained, halogen was shown to be absent.

The tin - gallein complex has an absorption maximum at 500 mμ, which differs slightly from those of the complexes formed by the interfering elements (see Table I). Beer's law is obeyed over the range 0·1 to 2·0 μg of tin per ml of the pentyl alcohol solution, and solutions of the complex have been kept for 5 days without deterioration.

INTERFERENCES

There was no interference from (*a*) sodium, potassium, ammonium, calcium, strontium and barium ions at a concentration of 100 mg per ml of test solution, (*b*) aluminium and iron$^{\text{II}}$ at a concentration of 10 mg per ml or (*c*) copper$^{\text{II}}$, lead$^{\text{II}}$, zinc, chromium$^{\text{III}}$, manganese$^{\text{II}}$, arsenic$^{\text{III}}$, arsenic$^{\text{V}}$ and vanadium$^{\text{V}}$ at a concentration of 1 mg per ml. Interfering elements are listed in Table I. The reactions of copper, iron, lead, and manganese are prevented by the presence of iodide, and titanium, molybdenum and tungsten are not usually rendered appreciably soluble by the ammonium iodide attack on samples of soil or sediment.

TABLE I

INTERFERING IONS

Element	Absorption maximum, mμ	Amount of element added, μg	Apparent amount of tin found, μg
Antimony^{III}	490	100	1·7
Titanium^{IV}	480	100	2·3
Molybdenum (as molybdate)	480	200	3·2
Tungsten (as tungstate) . .	490	200	0·2

In attempts to mask interfering elements, Wood found that fluoride, citrate, tartrate and ethylenediaminetetra-acetate completely suppressed reaction of tin and that orthophosphate greatly decreased the intensity of colour of the complex; acetate also prevents reaction of the tin, and formate causes great loss of sensitivity.

RESULTS

Standard deviations have been determined for three levels of tin in soil; they are ±0·02, ±0·21 and ±3·8 at the levels 2, 20 and 250 p.p.m. of tin, respectively. Replicate determinations of tin in the U.S. Geological Survey standard sample of diabase, W-1, gave results of 2·6, 2·7, 2·8, 2·6 and 2·8 p.p.m. (mean, 2·7 p.p.m.; standard deviation, ±0·10). This compares well with the results found by Onishi and Sandell[4] (2·5 and 3 p.p.m.). These workers decomposed a 1-g sample with sulphuric, nitric and hydrofluoric acids, separated tin by distillation with hydrobromic and hydrochloric acids and determined tin colorimetrically with toluene-3,4-dithiol. However, application of the proposed procedure to samples of rocks, although encouraging, has not yet been studied in detail.

The work described forms part of the programme of the Geochemical Prospecting Research Centre, which is assisted by a special grant from the Department of Scientific and Industrial Research.

REFERENCES

1. Wood, G. A., Ph.D. Thesis, University of London, 1957.
2. Stanton, R. E., and McDonald, A. J., *Trans. Inst. Min. Metall., Lond.*, 1961/1962, **71**, 27.
3. Marranzino, A. P., and Ward, F. N., paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1958 (abstract No. 58); U.S. Geological Survey Bulletin No. 1152, Washington, D.C., 1962, in the press.
4. Onishi, H., and Sandell, E. B., *Geochim. Cosmochim. Acta*, 1957, **12**, 262.

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Book Reviews

THE ANALYSIS OF TITANIUM, ZIRCONIUM AND THEIR ALLOYS. By W. T. ELWELL, F.R.I.C., and D. F. WOOD, B.Sc., A.R.I.C. Pp. xii + 198. London: J. Wiley and Sons Ltd. 1961. Price 53s.

Much of the basic material of this book appeared originally in the I.C.I. publication "The Analysis of Titanium and its Alloys," the third edition of which was reviewed in *The Analyst* (1960, **85**, 924). This has been revised, and expanded to include methods for analysing zirconium and its alloys. Publication has been widened in that the book is now commercially available and appears under the names of the authors who are responsible for its contents. As they point out in their preface, it is not a treatise on the analytical chemistry of these two metals, but a laboratory compendium containing the information essential to the chemical analysis of the metals and their alloys. The work of revision on titanium has been carefully done, even to the incorporation of suggestions made in the earlier review (*loc. cit.*). The main changes in this section are a different ethylenediaminetetra-acetic acid method for determining aluminium, an extension to the procedures given for determining tungsten when molybdenum is present, the introduction of the mandelic acid method for zirconium in the presence of titanium, and an amplification of the table for interpreting spectra to include six more elements.

References to the literature are comparatively few in number, some 58 in all, but they have been carefully chosen and are probably adequate for a work of this kind.

Curiously enough, there is no index to the subject matter. A description of the mercury-cathode cell used in the authors' laboratory for separating iron and other elements in the determination of aluminium in zirconium alloys would have been interesting and would help the reader to make a choice from the many types of apparatus now available. A diagram showing the set-up in the atomic-absorption spectrophotometric determination of zinc would also be welcome.

Apart from the merits of clear presentation, adequacy of information and convenience of size possessed by this volume, its value lies in the fact that the methods described in it are in use and have had their trustworthiness established. The authors are to be congratulated on producing a laboratory text that must always be consulted when analyses of titanium, zirconium and their products have to be undertaken.

L. S. THEOBALD

ATOMIC-ABSORPTION SPECTROPHOTOMETRY. By W. T. ELWELL, F.R.I.C., and J. A. F. GIDLEY, B.Sc., A.Inst.P. Pp. viii + 102. Oxford, London, New York and Paris: Pergamon Press Ltd. 1961. Price $5.00; 30s.

It is perhaps in the nature of things that when a new technique appears somewhat optimistic claims are made on its behalf by its originator or his enthusiastic disciples. Atomic-absorption spectrophotometry was just such a technique, partly, no doubt, because emission spectroscopy has always been bedevilled by various forms of interference of which the so-called "inter-element" effect is the most serious and the least predictable, and the new technique appeared to offer a chance of exorcism. Since Walsh's original paper in 1955 work in various laboratories has confirmed his views with varying degrees of success. If one could generalise one might perhaps say that the absorption technique occasionally has some advantages to offer but that those interference effects attributable to the difficulty in controlling the vaporisation process remain as a formidable deterrent to the optimist. The authors of this book clearly recognise this and have set out to bring the reader up to date on the subject and at the same time to put it dispassionately into perspective with related techniques. This they have generally succeeded in doing and in support have quoted 66 references of which 24 cover the last 2 years. Only rarely is the perspective lost. We all make mistakes in analysis from time to time, but the authors seem to give undue emphasis to a case of contamination caused by the use of a brass burner, where a terse warning to would-be constructors would have attracted less attention.

The book is divided into two roughly equal parts; the first deals with the theory, instrumentation and general practice of the method and the second with the determination of specific elements, including detailed procedures for zinc, lead and magnesium. The logical treatment of the subject matter permits the reader to assimilate readily the principles and practice of the technique providing he is already reasonably familiar with flame photometry and spectrophotometry.

One might have expected to see, in the first text-book devoted to the subject, more illustrations of apparatus; rather too much is left to the reader's imagination or past experience with related techniques. In particular, less space could have been given to constructional details of hollow-cathode lamps, which are obtainable commercially, and this could have been profitably used to illustrate burner - atomiser systems, with at least one photograph of a complete apparatus.

This book has much to recommend it, and it is a pity therefore that it is marred in places by slipshod composition and punctuation, which should certainly be rectified in a second edition. In contrast, the printing, binding and general lay-out of the book are in accordance with the publishers' usual high standards, and despite its drawbacks the book represents very good value and should find its place in every analytical chemist's library.

F. W. J. GARTON

MÉTHODES SÉLECTIONNÉES DE MICROANALYSE ORGANIQUE QUANTITATIVE. By R. LÉVY and B. COUSIN. Volume I. Pp. x + 122. Paris: Dunod Editeur. 1961. Price 15 NF.

This series of pocket books is intended to provide practical information in a convenient form for bench-side consultation by working organic microanalysts. The first volume deals with the organisation of a routine laboratory, with balances and weighing, and with the general apparatus required for handling samples. The advice given is concise and thoroughly sensible; most admirably, Dr. Lévy lays the necessary stress on refined techniques without making it appear that microanalysts must be born rather than trained. In fact, the format of the book makes it extremely convenient for training purposes, and one regrets that there is no English equivalent. Because microanalysts are notoriously non-conformists, each of whom has the only "right" way, it is not to be expected that everyone will entirely agree with Dr. Lévy's recommendations. Nevertheless, the trainee will learn much from this book, and the old hands will regularly nod in approval.

The series is complementary to Dr. Lévy's monograph, which was reviewed recently (*Analyst*, **1962**, **87**, **511**), therefore little information is given on variations of the recommended methods or on other developments. Further volumes will describe selected methods of elemental and functional-group analysis as practised in the Service Central de Microanalyse; they will be awaited with interest by all organic microanalysts. A. M. G. MACDONALD

PHOTOMETRIC TITRATIONS. By J. B. HEADRIDGE, Ph.D. Pp. x + 131. Oxford, London, New York and Paris: Pergamon Press Ltd. 1961. Price 45s.

This is the fourth volume of a series of monographs on modern developments in analytical chemistry and is bound to be limited in length and scope by the amount of investigation that has been reported in the literature. The author is to be congratulated on the thoroughness of his collection of material and on his organisation of it. The references contain some to work published as recently as mid-1960. It is most refreshing to find an enthusiastic exponent of a technique who does not insist that it be used on all occasions, but who points out that it has its proper place as an analytical tool and should not be used inappropriately. Although a hammer can be used as a screwdriver, the converse is not necessarily true.

Most of the book consists of descriptions of determinations that can be made by the method, and the section on theory is comparatively brief. At times attention to detail lapses. On page 47, the strictures on Bapat and Tatwawadi's work show that the author has not thought out the implications of the way a Spekker absorptiometer works. Had he done so, he would have seen that, though Bapat and Tatwawadi give no details of technique, their results were certainly obtainable by use of a Spekker in the manner implied in their paper. It would, of course, have been less misleading if the writers had used the old-fashioned Spekker term "drum-reading" instead of "optical density." Incidentally, the correct reference to this work (*Anal. Chim. Acta*, 1958, **18**, 334) was omitted, the one given being to another paper by these authors on a different topic. In the section on precipitation reactions it might have been mentioned that it may be found necessary to improve collimation of the light beam after passage through the absorbing medium in order to reduce back-scatter of light on to the photocell (for a discussion of this and other points see *Chemical Age*, 1956, **74**, 24).

On the whole, the book is well put together and is a useful contribution to the specialist literature that is now so necessary to the analyst. In the matter of price, one is left to wonder what costing system is used by publishers. Books of similar length and not too dissimilar construction have appeared at a third of the cost of this one, or less. The high price of the volumes in this series has been criticised before. The effect may be that sales will be restricted to that market (libraries, and other regular buyers) on which the costing is presumably based and that individuals will look twice at their money before parting with it. R. A. CHALMERS

THE CHEMICAL ANALYSIS OF FOODS. Originally written by H. E. COX. Fifth Edition. By DAVID PEARSON, M.Sc., F.R.I.C. Pp. xii + 464. London: J. & A. Churchill Ltd. 1962. 50s.

As soon as Cox published his book in 1929 it was recognised as a standard work, although its scope was somewhat limited. It was clearly and concisely written, and contained analytical results obtained over many years in his laboratory. Before his untimely death in 1951 three revisions had appeared, each an improvement on the previous one. Since that time the food analyst has become concerned with a wider range of products, and newer methods have been developed and come into use. It is therefore of considerable interest that an attempt has been made—and at once be it added a very successful one—to revise the book and bring it up to date. The author, who is on the staff of the National College of Food Technology, Weybridge, and of the Chelsea College of Science and Technology, has tried to retain Cox's style and general arrangement, and this will be appreciated by all who are familiar with previous editions. The general aim has been "to bring the methods into line with current practice in the average food laboratory which is equipped for dealing with routine work." Such laboratories, whether of industrial concerns or of public analysts, have of recent years had to expand their conception of routine work, in order to ensure or to check compliance with legal requirements or official recommendations. As a consequence, many methods regarded as specialised a few years ago are now adapted for regular use when dealing with particular foods. It would not be possible in any reasonably sized book to deal comprehensively with all these methods. The author has, however, given a few in detail and accessible literature references to others.

Chapters 1 to 3 are completely new. The first summarises food legislation in this country, with details of relevant Statutory Instruments and references to Codes of Practice and the Reports of the Food Standards Committee. All this is necessary for selecting the nature of the analysis of any food and for the interpretation of results. The second deals with general methods for the determination of basic constituents of foods, and the third with the detection and determination of additives, such as trace metals, preservatives and colouring matters that may be present in foods.

Chapters 4 to 14 are based on chapters 1 to 11 in the previous edition, but there has been much revision, and additional foods have been included. Chapter 15, the last, covers a number of miscellaneous foods.

Appendix 1 specifies the present Regulations dealing with preservatives and gives the recommendations of the Food Standards Committee on these additives. Appendix 2 deals with emulsifying and stabilising agents and Appendix 3 refers to claims regarding vitamin and mineral contents of foods. Three further Appendixes give useful data.

This volume will be a valuable and essential addition to the library—and the bench—of all food laboratories. The author is to be congratulated on his selection of new material and on the way in which he has incorporated it into the familiar pattern set by Cox. J. R. NICHOLLS

ULTRA-VIOLET AND VISIBLE SPECTROSCOPY: CHEMICAL APPLICATIONS. By C. N. R. RAO, Ph.D., D.Sc., A.R.I.C. Pp. xiv + 164. London: Butterworths Publications Ltd. 1961. Price 30s.

The sub-title of this book is *Chemical Applications* and the purpose of the work is to "introduce the basic concepts of electronic spectroscopy and to present its applications in analytical, structural and physicochemical problems."

Elementary ideas, notation and experimental methods are dealt with briefly. The treatment of chromophores and of electronic transitions in simple and conjugated molecules is on familiar lines, and the presentation is clear within its limitations. The author evidently decided not to overtax his readers with theory, but he may have to discuss intensity of absorption more fully in the next edition.

Applications, including tests for purity, indirect determinations of molecular weight, analysis of mixtures, as well as the correlation of structure and absorption, make up the most comprehensive chapter in the book. Steric effects are given a short chapter to themselves. With the help of collaborators, Dr. Rao provides further Sections on far-ultraviolet absorption spectra of organic molecules, fluorescence, charge-transfer spectra and a number of miscellaneous topics.

The book is well produced and reasonably priced. It has many merits as an introduction to the subject. The first part is, however, barely adequate as a preparation for the later parts. The last three chapters are not fully intelligible to a beginner and are too slight to be of great value to anybody else. The defects could be remedied without seriously altering the character of the book.

Each chapter is well documented and there is a useful bibliography. R. A. MORTON

ADVANCES IN ELECTROCHEMISTRY AND ELECTROCHEMICAL ENGINEERING. Edited by PAUL DELAHAY. Volume I. ELECTROCHEMISTRY. Pp. x + 326. New York and London: Interscience Publishers Inc. 1961. Price $12.00; 90s.

This volume is the first of a series edited by Paul Delahay and Charles W. Tobias. The object of the series according to the Editors is to make available authoritative reviews bridging "the gap between electrochemistry as a part of physical chemistry and electrochemical engineering." It is also their intention to place alternating emphasis in successive volumes on electrochemistry and on electrochemical engineering.

They also announce their intention to exclude specific problems in electroanalytical chemistry, but the analyst will find much valuable information in this first volume.

Five monographs are included: the electrical double layer and its influence on electrode reaction rates by Roger Parsons; hydrogen overvoltage on mercury by A. N. Frumkin; oxygen overvoltage by Manfred Breiter; semi-conductor electrode reactions by H. Gerischer; fast electrode processes by Paul Delahay.

As separate mongraphs each of these is excellent and complete in itself. Each is necessarily brief and one, that on oxygen overvoltage, very brief; but good bibliographies should lead the reader to further studies of value. For each monograph the author has provided a list of the symbols employed in his treatment of the subject, but the lists frequently do not include the same symbols for the same quantity. It is unfortunate that, in new books, authors do not always use the internationally agreed symbols of I.U.P.A.C., and that editors do not impose this uniform system upon their contributors.

The high-quality production always associated with the publishers is maintained in this work.

A. J. LINDSEY

PROGRESS IN NUCLEAR ENERGY. Series IX. ANALYTICAL CHEMISTRY. Volume 2. Edited by CARL E. CROUTHAMEL. Pp. viii + 400. Oxford, London, New York and Paris: Pergamon Press Ltd. 1961. Price 100s.; $15.00.

This second volume of the Analytical Chemistry series is written both for the advanced student and specialist researcher, the various chapters not only reviewing recent advances and innovations in certain fields of investigation, but also, in many instances, presenting in some detail the fundamental principles and theoretical aspects of particular developments.

Some chapters are illustrated by excellent photographs of modern instrumentation as developed commercially in the U.S.A. and the U.K.; others have scale drawings of particularly important items of apparatus. The graphical and diagrammatical illustrations are well selected to embellish the text, and each chapter concludes with an extensive up-to-date bibliography.

Recent advances in counting techniques are reviewed by specialist members of the Argonne Laboratory. The important topic of electron volts - ion pair is clearly discussed for air and many gases on the basis of a constant 26·4-eV value for argon ionised either by electrons or 5·3-MeV alpha particles. The applications of X-ray proportional counters to chemical analysis are described, and a list of calibration isotopes is given. Comment is made on the photosensitivity of aluminised Mylar and the superiority of gold coatings. Constructional details for various counters are given and their resolving powers discussed.

Crystal conduction counters are described as examples of the more recent types of detector instrumentation based on diamond crystals, semi-conductors, etc.; they are shown to have certain advantages in dealing with fission fragments or other heavy nuclear particles.

Scintillation spectrometry has special treatment and the merits of caesium and sodium iodide - thallium activated crystals are described.

A comprehensive chapter by Elion and Shapiro deals lucidly with the general theory and application of electron-spin resonance spectroscopy. The field covered is extremely wide, *e.g.*, free radicals, the specific use of vanadium chelates in E.S.R. monitoring of coronary treatment, the confusing E.S.R. spectrum of graphite at high temperatures, the donor concentrations of semi-conductors, etc., are but a few of the many interesting matters described by the authors.

Hofmann of the Los Alamos Laboratory presents a most useful section on the separation and analysis of the ten transuranium elements from neptunium to element 102. Most separation detail is naturally devoted to the commoner valency states of Np and Pu; solvent extraction, chelates, ion exchange, recoil separations, etc., are all described, and a comprehensive section on chemical and instrumental analysis is presented. Considerable chemical information is, however, given on the heavier transplutonium elements, and the researcher in this field will find this review of much interest.

D. R. Peppard presents an instructive theoretical paper on the liquid - liquid extraction of inorganic substances that is well illustrated by the results of his own practical studies and those of other specialist researchers.

J. W. Robinson describes the basic principles of atomic-absorption spectroscopy and of flame photometry and lists detection limits for the metallic elements of the Periodic Table. Dean's use of preliminary solvent extraction and Vallee's use of the oxy-cyanogen flame are considered as affording the major advances in the application of flame spectrophotometry. Recent advances in ultraviolet, visible and infrared absorption spectrometry are reviewed by J. C. White of the Oak Ridge National Laboratory. Many applications of these techniques to the determination of the actinide elements are described. The modern work on the absorption spectrophotometry of molten salts is justifiably given detailed treatment.

R. H. Miller comments on the fantastic quantities of beta-emitting isotopes now available, and discusses the use of such sources as laboratory tools for the production of bremsstrahlen and characteristic X-rays. Backscattering phenomena are also considered as an analytical tool. X-ray fluorescence analysis has, of recent years, become a powerful analytical method and it may be that the beta source, because of its constancy, may become a serious rival to the X-ray tube as a target bombarder.

The volume ends with a readable chapter by J. E. Salmon on ion-exchange chromatography, considerable attention being paid to the employment of aqueous organic solvents as eluants. Acid salt exchangers and heteropolyacid exchangers are considered as more recent alternatives to the classical resin types. These newer substances are of considerable interest and have been used for the preparation of pure multicurie sources of some fission products, *e.g.*, caesium-137.

This new publication will add to the knowledge of the individual researcher and will provide him with thought-stimulating concepts, valuable information and useful data. It is in every way a most praiseworthy "daughter" volume to the precursors of this celebrated "Progress in Nuclear Energy" series.

D. T. Lewis

Rock-forming Minerals. Volume 1. Ortho- and Ring Silicates. By W. A. Deer, M.Sc., Ph.D., F.G.S., R. A. Howie, M.A., Ph.D., F.G.S., and J. Zussman, M.A., Ph.D., F.Inst.P. Pp. viii + 333. London: Longmans, Green & Co. Ltd. 1962. Price 95s.

This is the first of five volumes planned to deal with the common minerals of igneous, metamorphic and sedimentary rocks. In a description in detail of some forty-five minerals, among them members of the olivine, humite, garnet, epidote and melilite groups, the main topics are atomic structures, optical and physical properties, salient features of the chemistry, including many chemical analyses, and the chief modes of occurrence.

Although designed primarily for the geologist, the volume provides much useful and interesting information for the silicate analyst who wants to know more than the percentage composition of the minerals he has to analyse.

L. S. Theobald

Publications Received

The Radiochemistry of Nickel. By L. J. Kirby. Pp. vi + 52. Washington, D.C.; U.S. Department of Commerce, Office of Technical Services. 1961. Price 50 cents.
Nuclear Science Series: NAS—NS-3051.

The Radiochemistry of Rubidium. By G. W. Leddicotte. Pp. vi + 34. Washington, D.C.; U.S. Department of Commerce, Office of Technical Services. 1962. Price 50 cents.
Nuclear Science Series: NAS—NS-3053.

The Radiochemistry of Sulfur. By G. W. Leddicotte. Pp. vi + 30. Washington, D.C.; U.S. Department of Commerce, Office of Technical Services. 1962. Price 50 cents.
Nuclear Science Series: NAS—NS-3054.

The Radiochemistry of Sodium. By W. T. Mullins and G. W. Leddicotte. Pp. vi + 44. Washington, D.C.; U.S. Department of Commerce, Office of Technical Services. 1962. Price 50 cents.
Nuclear Science Series: NAS—NS-3055.

The Radiochemistry of Phosphorus. By W. T. Mullins and G. W. Leddicotte. Pp. vi + 32. Washington, D.C.; U.S. Department of Commerce, Office of Technical Services. 1962. Price 50 cents.
Nuclear Science Series: NAS—NS-3056.

Absorptionsspektroskopie im ultravioletten und sichtbaren Spektralbereich. By Bruno Hampel. Pp. vi + 109. Braunschweig, Germany: Friedr. Vieweg & Sohn. 1962. Price DM 16.80.

THE ELECTRONIC THEORY OF ACIDS AND BASES. By W. F. LUDER and SAVERIO ZUFFANTI. Second Edition. Pp. xii + 165. New York: Dover Publications Inc. 1961. Price $1.50 (paper).

QUANTITATIVE CHEMICAL ANALYSIS AND INORGANIC PREPARATIONS. By R. M. CAVEN, D.Sc., F.R.I.C. Second Edition. Revised by A. B. CRAWFORD, B.Sc., Ph.D., A.R.C.S.T., F.R.I.C., and W. A. ALEXANDER, B.Sc., F.R.I.C. Pp. viii + 428. London and Glasgow: Blackie & Son Limited. 1962. Price 35s.

RAPID MICROCHEMICAL IDENTIFICATION METHODS IN PHARMACY AND TOXICOLOGY. By FELIX AMELINK, Ph.D. Pp. vi + 121 + 32 pp. Supplement of Drawings. Amsterdam: Netherlands University Press. 1962. Price Dutch Gldrs. 25.

GLOSSARY OF ORGANIC CHEMISTRY: INCLUDING PHYSICAL ORGANIC CHEMISTRY. By SAUL PATAI. Pp. xiv + 227. New York and London: Interscience Publishers, a division of John Wiley & Sons. 1962. Price 57s.

METHODS OF BIOCHEMICAL ANALYSIS. Volume IX. Edited by DAVID GLICK. Pp. x + 452. New York and London: Interscience Publishers, a division of John Wiley & Sons. 1962. Price 109s.

STANDARD METHODS OF CHEMICAL ANALYSIS. Volume 1. THE ELEMENTS. Edited by N. HOWELL FURMAN, Ph.D. Sixth Edition. Pp. xx + 1401. Princeton, N.J., New York, Toronto and London: D. Van Nostrand Company Inc. 1962. Price £9 9s.

A MANUAL OF COSMETIC ANALYSIS. By SYLVAN H. NEWBURGER, Ph.D. Pp. vi + 84. Washington, D.C.: Association of Official Agricultural Chemists Inc. 1962. Price $4.00 domestic; $4.25 foreign.

STANDARDIZATION OF SPECTROPHOTOMETRIC DATA IN THE NEAR ULTRAVIOLET, VISUAL AND NEAR INFRARED. By JØRGEN FOG, Dr.Med. Pp. 64. Oslo: Johan Grundt Tanum Forlag. 1962.

STRAHLUNGSMESSUNG IM OPTISCHEN SPEKTRALBEREICH: MESSUNG ELEKTROMAGNETISCHER STRAHLUNG VOM ULTRAVIOLETT BIS ZUM ULTRAROT. By GEORG BAUER. Pp. viii + 181. Braunschweig, Germany: Friedr. Vieweg & Sohn. 1962. Price DM 16.80.

HYDROBORATION. By HERBERT C. BROWN. Pp. xiv + 290. New York: W. A. Benjamin Inc. 1962. Price $10.00.

HANDBUCH DER KOLORIMETRIE. Band I. KOLORIMETRIE IN DER PHARMAZIE. By Dr. rer. nat. BOHUMIL KAKÁČ and Dipl.-Ing. ZDENĚK J. VEJDĚLEK. Translated by Dipl.-Ing. E. HACHOVÁ. Pp. xvi + 1139 + 12 plates. Jena: Veb Gustav Fischer Verlag. 1962. Price DM 79.20.

Errata

APRIL (1962) ISSUE, p. 302. Replace Legend to Fig. 1 by "Fig. 1. Transmission curves for thymol blue in alkaline solution: curve A, pH 7·8; curve B, pH 8·3; curve C, pH 8·8; curve D, pH 9·3; curve E, pH 9·8".

JUNE (1962) ISSUE, p. 456, 18th line. *For* "0·9 amp" *read* "0·09 amp."

IBID., facing p. 456, Legend to Fig. 1, 2nd line. *For* "C, titration panel; D, sequence-control unit" *read* "C, sequence-control unit; D, titration panel."

IBID., p. 461, top of Fig. 7. *For* "N/C relay Operate" *read* "N/O relay Operate."

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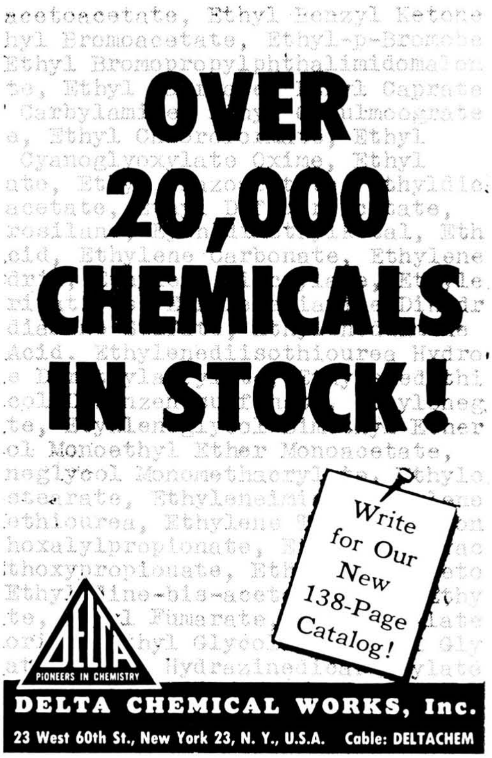

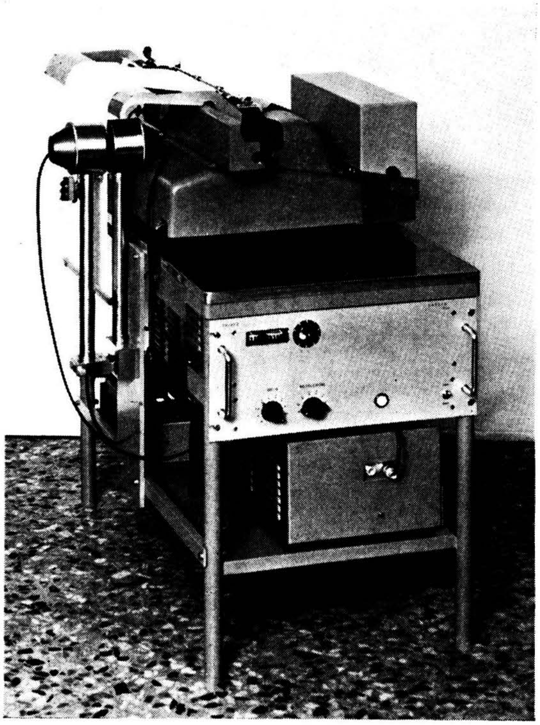

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1. Belcher, R. and Ingram, G., *Analyt. Chim. Acta*, 1950, **4**, 118, 401
2. Clark, S. J., "*Quantitative Methods of Organic Analysis*", pp 42-76, Butterworths Scientific Publications, 1956.

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1. Whitehead, T. H., *J. Chem. Educ.*, 1959, **36**, 297
2. Williams, T. R. and Harley, J. D., *Chemist-Analyst*, 1961, **50**, 114
3. Davies, M. T., *Analyst*, 1959, **84**, 248

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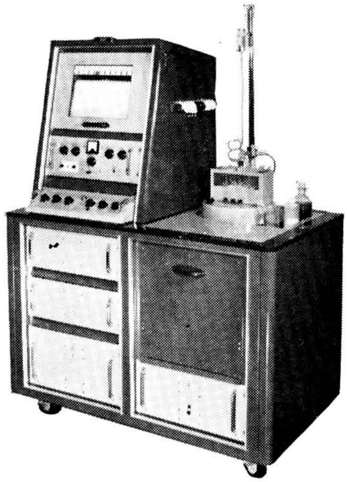

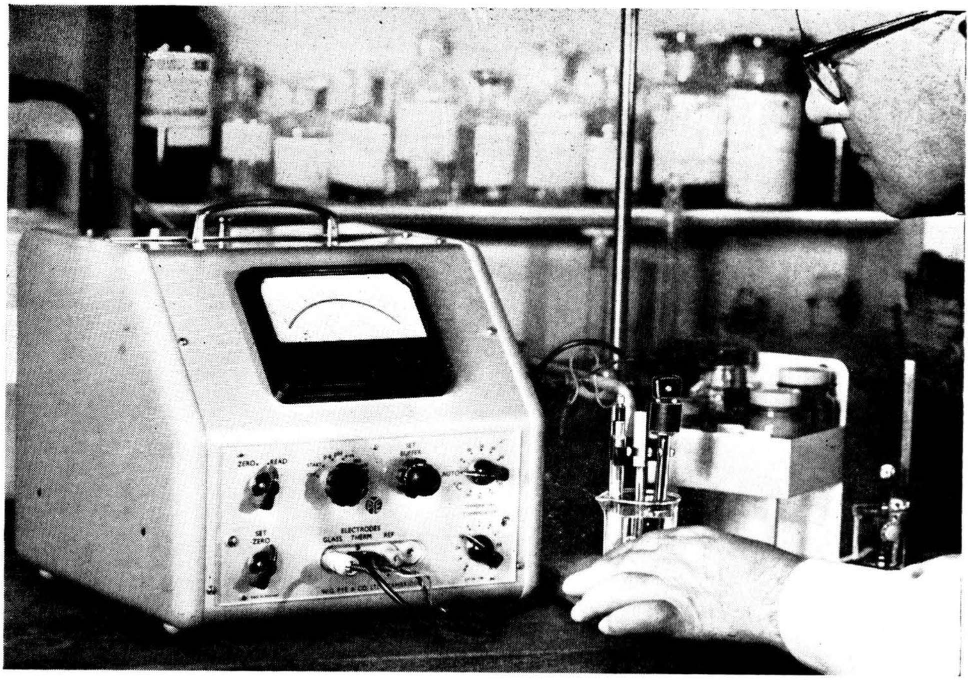

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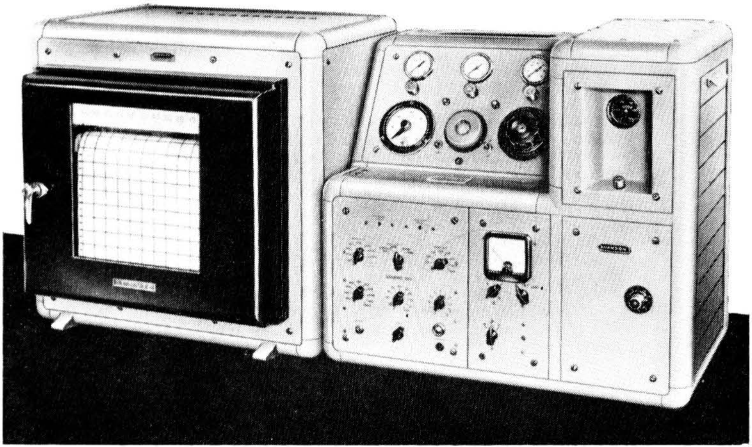

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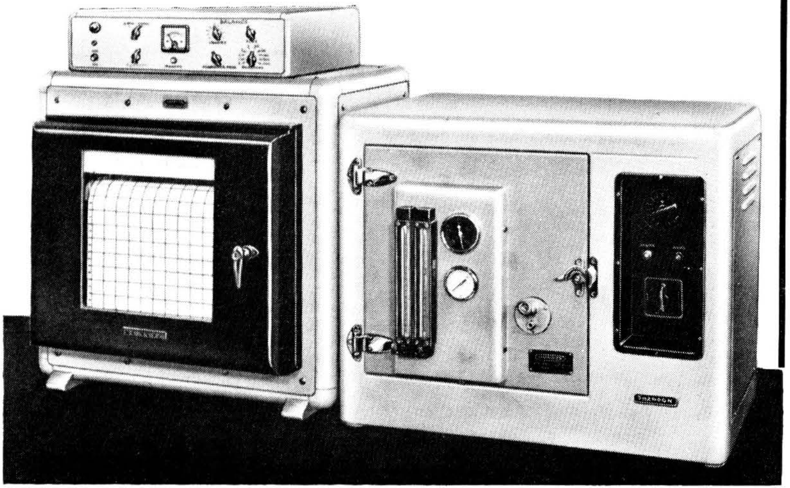

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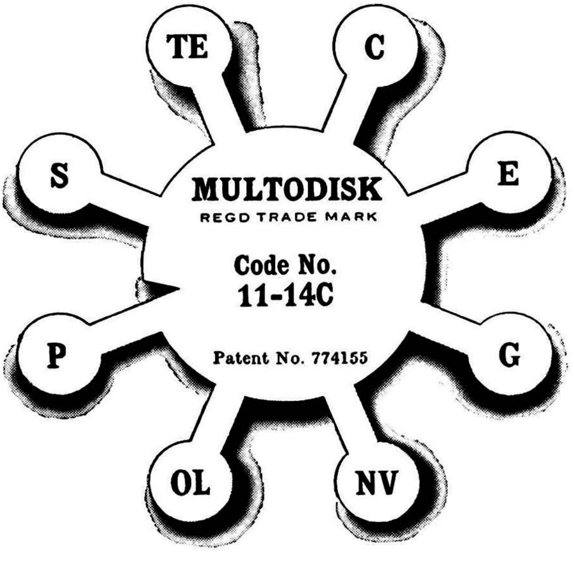
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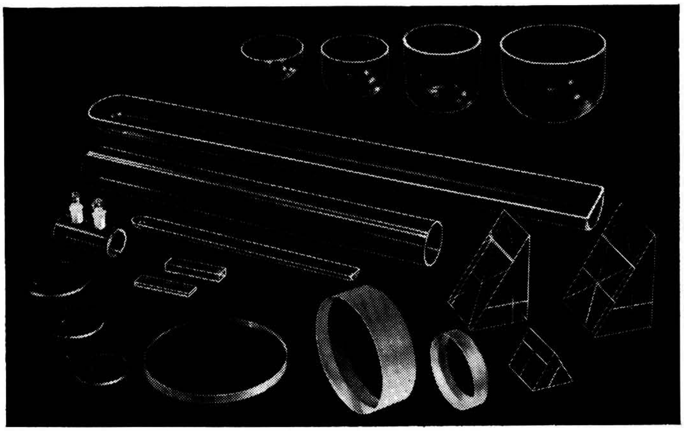


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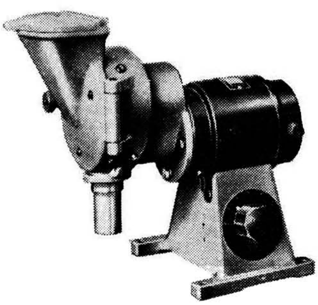

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