

# THE ANALYST

A Monthly Publication  
dealing with all branches  
of Analytical Chemistry:  
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of Public Analysts and  
Other Analytical Chemists

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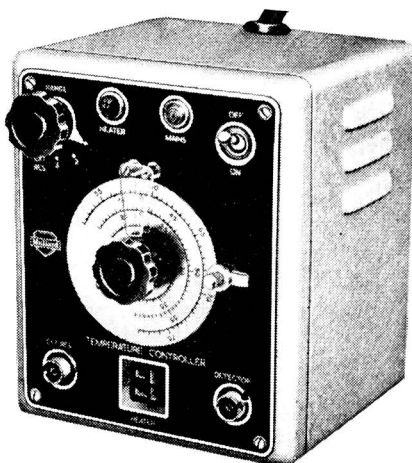
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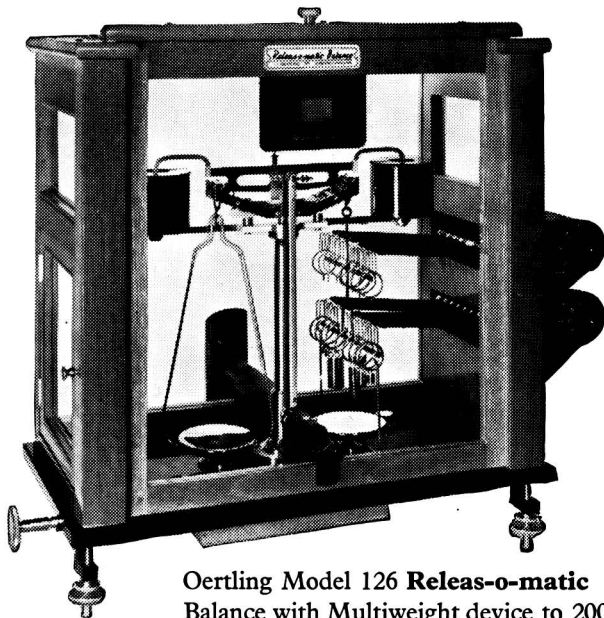
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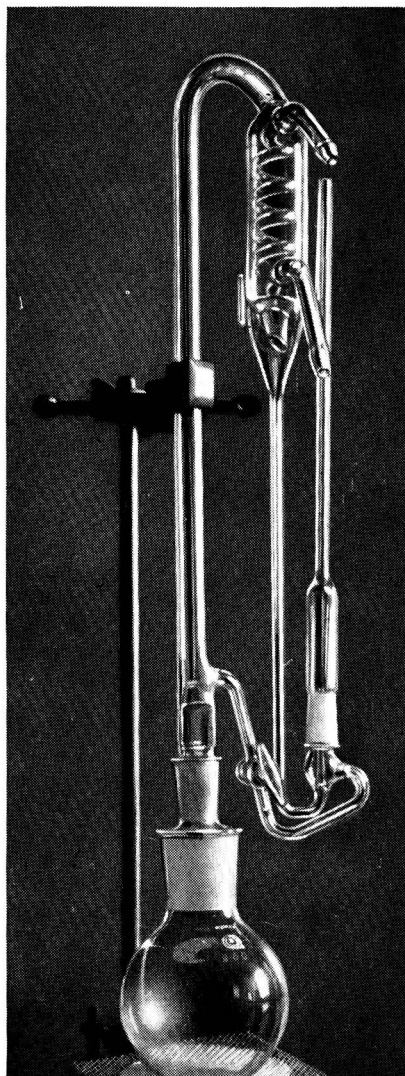
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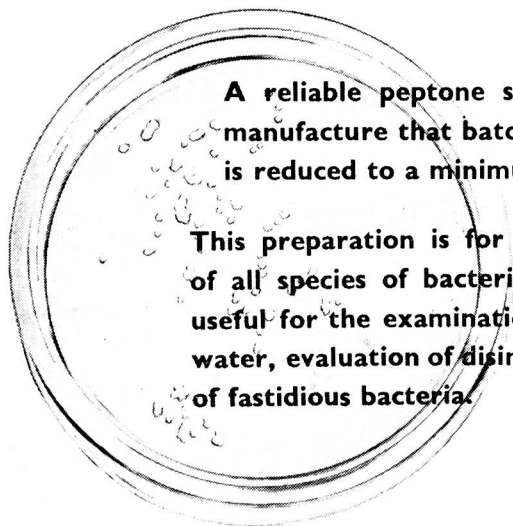
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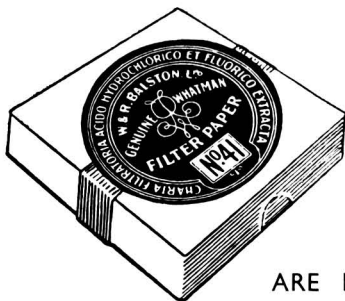
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Ammonia (NH <sub>3</sub> ) .....	0.00005%
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I am,

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# THE ANALYST

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society, organised jointly by the Microchemistry Group and the Scottish Section, was held at 7.15 p.m. on Wednesday, May 6th, 1953, in the Chemistry Department, University of Glasgow, Gilmore Hill, Glasgow. The Chair was taken by the President, Dr. D. W. Kent-Jones, F.R.I.C.

The following papers were presented and discussed: "Geochemistry and Microchemistry," by David T. Gibson, D.Sc.; "Micro-analysis of Silicate Rocks. Part IV. The Determination of Alumina," by Miss Christina C. Miller, Ph.D., D.Sc., F.R.S.E., F.H.-W.C., and Robert A. Chalmers, B.Sc.; "Microchemical Determination of Sulphur in Organic Compounds," by William H. Massie, B.Sc., Ph.D., A.R.I.C.

The meeting was preceded by an afternoon visit to the Clydebridge Steel Works of Colvilles Ltd.

AN Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, May 20th, 1953, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President, Dr. D. W. Kent-Jones, F.R.I.C.

The following papers were presented and discussed: "The Determination of Ergosterol in Yeast. Parts I, II, III and IV," by W. H. C. Shaw, Ph.C., F.R.I.C., and J. P. Jefferies, B.Sc., A.R.I.C.; "The Estimation of Micro Quantities of Calcium," by G. E. Harrison, Ph.D., F.Inst.P., and W. H. A. Raymond; "The Ultra-Violet Spectrophotometric Estimation of the Quality of Mineral Oils Extracted from Bread," by M. A. Cookson, B.Sc., A.R.I.C., J. B. M. Coppock, B.Sc., Ph.D., F.R.I.C., and R. Schnurmann, M.Sc., Dr.Rer.Nat.

### NEW MEMBERS

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### PHYSICAL METHODS GROUP

THE Forty-first Ordinary Meeting of the Group was held at 6 p.m. on Friday, May 8th, 1953, in the Oriental Café, Ipswich. This was a joint meeting with the East Anglian Section of the Royal Institute of Chemistry, and the Chairman of the Group, Dr. J. Haslam, F.R.I.C., was in the Chair.

The following papers on "Emission Spectroscopy" were presented and discussed: "Semi-quantitative Techniques in Spectrochemical Analysis," by R. L. Mitchell, B.Sc., Ph.D., F.R.I.C.; "Some Techniques of Presentation of Sample to the Spectrograph," by A. H. C. P. Gillieson, B.Sc., Ph.D.; "Applications of the Porous Cup Technique," by L. G. Young.

The meeting was preceded by an afternoon visit to the Research Laboratories of B.X. Plastics, Ltd., Manningtree.

# The Determination of Arsenic by B. S. Evans's Method

## With Some Observations on the Separation of Arsenic and Antimony

BY J. HASLAM\* AND N. T. WILKINSON

An improved method for the volumetric determination of arsenic in solutions after its preliminary reduction by means of hypophosphorous acid is described. It is shown that the precipitated arsenic can be filtered on to a medium containing a large proportion of oxy-cellulose and that, after the addition of an excess of standard iodine solution to the arsenic - oxy-cellulose mixture, the excess of iodine can be directly titrated with standard arsenite solution. The end-point in the titration is determined by the disappearance of the yellow colour of the iodine.

The method has been applied successfully to the determination of arsenic in arsenite solutions and, also, to the determination of arsenic in arsenite solutions containing appreciable proportions of antimony. In addition, it is shown that the antimony in a solution containing arsenic and antimony can be determined after a preliminary separation of the arsenic.

Details are given of the application of the method to the determination of arsenic in pig-iron.

RECENTLY we have carried out a considerable amount of work on the volumetric determination of arsenic. The method we have used is based on previous work by Evans<sup>1</sup>; it depends on the reduction of arsenic from either its trivalent or quinquivalent condition by means of hypophosphorous acid in hydrochloric acid solution, and on the iodimetric titration of the resulting elementary arsenic.

A study of Evans's original paper leaves little doubt that he experienced considerable difficulty in titrating the precipitated arsenic; this arsenic was filtered on a pulp filter and arsenic plus pulp were treated with a measured amount of standard iodine solution and water. Evans used the so-called titrated water, which contains a few drops of starch solution and enough 0.01 *N* iodine solution to impart to it a faint permanent blue colour. First, sodium bicarbonate was added to the arsenic, pulp, iodine and titrated-water suspension, and then a slight excess of standard arsenite solution; after addition of further bicarbonate the excess of arsenite was titrated with standard iodine solution until the blue end-point was reached. In this way, Evans claimed to get low "blank" values in experiments with reagents and paper pulp alone.

However, in a subsequent paper,<sup>2</sup> Evans drew attention to the fact that owing to a change in the manufacture of the filter-paper the results in "blank" experiments on the paper pulp were unsatisfactory. For this reason he changed his method of determining precipitated arsenic. In his second method the precipitated arsenic was filtered off on filter-paper pulp that had previously been submitted to a vigorous oxidation with bromine and hydrochloric acid. The arsenic and paper pulp were treated with a slight excess of standard iodine solution, benzene and sodium bicarbonate were added, and then standard arsenite was added in slight excess with intermediate addition of potassium iodide. Further bicarbonate and water were added and the excess of arsenite titrated with standard iodine solution with starch solution as indicator.

Our experiments led us to conclude that the two methods of titrating precipitated arsenic proposed by Evans were unsatisfactory and unnecessarily complicated. First we prepared a white material containing a large proportion of oxy-cellulose by treating filter-paper with bromine and hydrochloric acid; this was thoroughly washed. Using this prepared material as our filtering medium, we filtered the precipitated arsenic, treated the arsenic plus pulp with an excess of standard iodine solution in a stoppered bottle and, after adding potassium iodide and sodium bicarbonate, titrated the excess of iodine with standard arsenite solution; the end-point was indicated by the change from the yellow iodine solution to the white of the oxy-cellulose filtering medium. The end-point was exceedingly sharp, and

\* Present address: Imperial Chemical Industries Limited, Plastics Division, Black Fan Road, Welwyn Garden City, Herts.

"blank" values in experiments on the prepared pulp alone were low. By this method of titrating the precipitated arsenic, results were excellent in determinations of arsenic in sodium arsenite solutions. These arsenite solutions contained various amounts of arsenic between the limits 0.00038 g and 0.1049 g. Full details of the method appear below and the results of this set of experiments are given on p. 392.

In a second set of experiments, the results of which are shown in Table I, the arsenic was determined accurately in sodium arsenite solutions containing appreciable proportions of potassium antimony tartrate. Various combinations of arsenic and antimony solutions were examined, the amount of arsenic being varied up to 0.1049 g and the antimony between the limits 0.0050 g and 0.05 g. In addition, it was shown that, after precipitation of the arsenic in these determinations, the antimony in the filtrates could be determined with high accuracy. This antimony was precipitated as sulphide, the sulphide was dissolved and the antimony in the solution was reduced to the tervalent condition before its determination by oxidation to the quinquivalent condition by means of bromic acid. The method for determining antimony is given on p. 392, and the results are shown in Table II.

The method was extended to the determination of arsenic in the presence of ferric salts. With copper as a catalyst to assist in the speedy reduction of ferric iron by means of hypophosphorous acid, it was shown that between 0.00075 g and 0.0524 g of arsenic could be readily determined in the presence of as much as 5 g of ferric sulphate. The principle of this method was used in the determination of arsenic in pig-iron (p. 393).

#### THE DETERMINATION OF ARSENIC IN ARSENITE SOLUTIONS

##### PREPARATION OF THE STANDARD ARSENITE SOLUTIONS—

Exactly 4.9455 g of AnalaR\*  $\text{As}_2\text{O}_3$  dried at  $105^\circ\text{C}$  were dissolved by heating in a solution containing 2.5 g of pellets of sodium hydroxide (made pure from sodium) in a little water. The arsenic solution was cooled, 66 ml of *N* hydrochloric acid solution were added, and then 10 g of AnalaR sodium bicarbonate. The solution so prepared was diluted to 1 litre with distilled water. This arsenite solution was standardised against iodine solution by the method given in a paper on the standardisation of volumetric solutions.<sup>3</sup> Twenty millilitres of the arsenious solution were equivalent to 20 ml of 0.1 *N* iodine solution; hence 1 ml of this arsenite solution contained 0.003746 g of arsenic. A 0.01 *N* arsenite solution was prepared from the 0.1 *N* solution by dilution.

##### PREPARATION OF THE STANDARD IODINE SOLUTION—

Standard 0.1 *N* and 0.01 *N* iodine solutions were prepared according to the methods given in the paper referred to above.<sup>3</sup>

##### PREPARATION OF THE FILTERING MEDIUM—

About twenty 11-cm Whatman No. 40 filter-papers were digested on a water-bath for about 4 hours with about 400 ml of water containing 4 ml of concentrated hydrochloric acid solution and 20 ml of saturated bromine water. The pulped material thus prepared was stored in a glass bottle and small amounts of it were washed thoroughly with water before use in the filtration of precipitated arsenic.

##### PROCEDURE—

A known volume of the standard arsenite solution was diluted to 65 ml with distilled water. To this solution, in a 600-ml conical flask, were added 10 ml of 3 *M* sulphuric acid solution and 75 ml of concentrated hydrochloric acid. After the addition of 4 g of B.D.H. sodium hypophosphite the solution was warmed gently to effect preliminary reduction; the temperature was not allowed to rise above  $50^\circ\text{C}$  in this operation. A further 10 g of sodium hypophosphite were then added and the mouth of the flask was closed by a cork carrying a length of glass tubing, approximately 80 cm long and 0.5 cm in internal diameter, which acted as a reflux condenser.

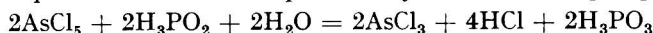
The solution was brought to the boil and boiled gently for 15 minutes. The solution was then cooled and the precipitated arsenic filtered on to a pad of the previously prepared

\* AnalaR  $\text{As}_2\text{O}_3$  contains small amounts of  $\text{Sb}_2\text{O}_3$ , but we have found the proportion, as determined spectrographically, to be of the order of 0.1 per cent. only; this amount is too small to cause interference.

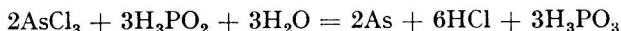
filter pulp. With large amounts of arsenic it is better to mix a little well-washed filter-paper pulp with the precipitate in the conical flask before filtering, in order to keep the precipitate in a finely divided condition so that it will readily dissolve in the iodine solution used for the titration. The precipitated arsenic was washed with an acid hypophosphite solution prepared by adding 2 g of sodium hypophosphite to 100 ml of a solution of diluted hydrochloric acid (1 + 3), and the hypophosphite was removed by repeated washings with 5 per cent. ammonium chloride solution.

The arsenic precipitate and paper pulp filter were transferred to a wide-mouthed 16-oz glass-stoppered bottle to which was added about 50 ml of distilled water. After thorough disintegration of the precipitate and addition of 2 g of potassium iodide and 2 g of sodium bicarbonate, an excess of 0.1 N or 0.01 N iodine solution was added. In practice it was found that the particular iodine solution used was decided by the amount of precipitate. With either solution, an approximately 10-ml excess was used. After the bottle had been thoroughly shaken to ensure complete solution of the arsenic precipitate, the glass stopper was removed, washed with water, and the excess of iodine immediately titrated with either 0.1 N or 0.01 N arsenite solution according to the concentration of iodine solution used. The end-point, *i.e.*, the point at which the yellow of the solution of iodine in potassium iodide changed to the white of the oxy-cellulose pulp, was quite sharp.

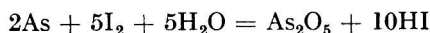
The relevant equations are: for the preliminary reduction of quinivalent arsenic—



for the final reduction of trivalent arsenic—



for the iodine titration—



An experiment on the reagents carried out by the above method, but omitting the known volume of standard arsenite solution, gave a "blank" value of 0.05 ml for a 0.01 N solution.

The following results were obtained by the application of the above method to known arsenite solutions—

Arsenic added, g	..	..	0.00038	0.0011	0.0030	0.0094	0.0524	0.1049
Arsenic found, g	..	..	0.00032	0.0010	0.0030	0.0092	0.0524	0.1048

#### APPLICATION TO ARSENITE SOLUTIONS CONTAINING APPRECIABLE AMOUNTS OF ANTIMONY—

A standard antimony solution was prepared from antimony potassium tartrate; known volumes of this solution were added to known volumes of standard arsenite solution. The arsenic in these solutions was then determined by the method described on p. 391. Results are shown in Table I.

TABLE I  
RECOVERY OF ARSENIC IN PRESENCE OF ANTIMONY

Experiment No.	Arsenic added, g	Antimony added, g	Arsenic found, g
1	nil	0.005	Not detected
2	nil	0.050	"
3	0.00075	0.050	0.00071
4*	0.0026	0.010	0.0026
5	0.00375	0.005	0.00383
6*	0.0054	0.010	0.0056
7*	0.0075	0.010	0.0074
8*	0.0107	0.005	0.0103
9	0.0262	0.010	0.0262
10	0.0524	0.050	0.0521
11	0.1049	0.002	0.1046
12	0.1049	0.010	0.1047

\* In these experiments the amounts of arsenic and antimony present were unknown to the operator.

#### THE DETERMINATION OF ANTIMONY IN FILTRATES OBTAINED AFTER PRECIPITATING ARSENIC WITH HYPOPHOSPHOROUS ACID—

The filtrate from the arsenic precipitation was first boiled down to about 350 ml. Fifty millilitres of concentrated ammonium hydroxide solution were then added in order to neutralise

most of the acid present, after which the antimony was precipitated by the passage of hydrogen sulphide.

The precipitated sulphide was filtered off and washed with water saturated with hydrogen sulphide until the washings were free from chloride. After a hole had been pierced in the bottom of the filter-paper, the bulk of the antimony sulphide was washed into a clean beaker. The trace of antimony sulphide remaining on the filter was then dissolved by pouring on to the filter-paper a hot mixture of 20 ml of concentrated hydrochloric acid, 4 ml of 10-volume hydrogen peroxide and 10 ml of bromine water. The filter was washed with water and the mixture of antimony sulphide and acid, and so on, was brought to the boil. A mixture of 2 ml of 10-volume hydrogen peroxide solution and 5 ml of bromine was added to the boiling solution. The antimony precipitate was completely dissolved by two more additions of peroxide and bromine.

The excess of bromine was then removed by boiling. The solution was cooled and diluted to approximately 250 ml with distilled water, 5 g of AnalaR sodium sulphite were added and dissolved by gentle mixing, and the solution was set aside for about 1 hour.

The solution was then boiled to remove sulphur dioxide, 10 ml of concentrated hydrochloric acid and 1 drop of methyl orange indicator were added and the hot solution was titrated with 0.02 *N* potassium bromate solution until the colour of the methyl orange indicator was just removed.

1 ml of 0.02 *N* potassium bromate solution = 0.001218 g of antimony.  
The results were as shown in Table II.

TABLE II  
RECOVERY OF ANTIMONY IN PRESENCE OF ARSENIC

Experiment No.	Arsenic added, g	Antimony added, g	Antimony found, g
11 (continued)	0.1049	0.0020	0.0023
9 (continued)	0.0262	0.0100	0.0102
3 (continued)	0.00075	0.0500	0.0500

#### THE DETERMINATION OF ARSENIC IN THE PRESENCE OF FERRIC SALTS—

Five grams of B.D.H. ferric sulphate were added to a known amount of standard arsenite solution. Half a gram of AnalaR copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) was added to catalyse the reduction of the ferric salt by the hypophosphorous acid. The subsequent procedure was similar to that given in the method on p. 391; the results obtained were as follows—

Arsenic added, g	.. .. .	nil	0.00075	0.0524
Arsenic found, g	.. .. .	not detected	0.00067	0.0518

#### THE DETERMINATION OF ARSENIC IN PIG-IRON

One gram of copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) was added to a 5-g sample of pig-iron, and the whole dissolved in a mixture of 30 ml of 3 *M* sulphuric acid solution and 15 ml of concentrated nitric acid. The insoluble carbon was filtered off and 2 ml of a saturated aqueous solution of potassium permanganate were added to the filtrate. The liquid was boiled for 5 minutes, after which a little sulphurous acid solution was added in order to remove the excess of permanganate. The solution was evaporated, first on a water-bath and then on a sand-bath, until all the nitric acid was removed. It was necessary to maintain the beaker in constant motion during the evaporation on the sand-bath in order to prevent "bumping."

The pasty mass of ferric sulphate was dissolved in water and the arsenic determined as previously described except that no preliminary reduction was carried out and the final reduction was accomplished by the addition of 14 g of sodium hypophosphite. In this experiment the hypophosphite solution was boiled for half an hour in order to reduce the arsenic completely. The figure for arsenic found, 0.447 per cent., compared well with the figure of 0.44 per cent. found by the ferric chloride distillation procedure.

#### REFERENCES

1. Evans, B. S., *Analyst*, 1929, **54**, 523.
2. ———, *Ibid.*, 1932, **57**, 492.
3. Analytical Chemists' Committee of I.C.I. Ltd., *Ibid.*, 1950, **75**, 577.

# The Determination of Uranium-235 in Mixtures of Naturally Occurring Uranium Isotopes by Radioactivation

BY A. P. SEYFANG AND A. A. SMALES

A method previously used for determining uranium in minerals by neutron irradiation followed by measurement of the separated fission-product barium has been extended to the determination of uranium-235 in admixture with uranium-234 and uranium-238.

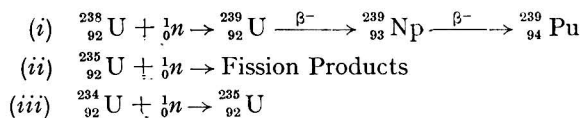
With microgram amounts of uranium-235, short irradiations in the Harwell pile give ample sensitivity. Precision and accuracy of better than  $\pm 2$  per cent. have been achieved for a range of uranium-235 contents covered by a factor of more than  $10^5$ .

THE most frequently used method for measuring isotopic abundance—mass spectrometry—has been applied to uranium by Nier, Inghram and Ney<sup>1</sup> and many other workers. Other methods studied have included fission-fragment counting<sup>2</sup> and a spectrographic technique involving isotopic line shift. Derham and Fenning<sup>3</sup> have described a method depending on the measurement of the growth of  $\beta$ -emitting daughters from the chemically separated uranium, but this seems to be suitable mainly for samples containing much uranium-235 and little uranium-234. Alpha-counting methods have also been used.<sup>4</sup>

Radioactivation analysis, as already pointed out,<sup>5</sup> is essentially a method for measuring isotopes rather than elements, and it has been used for determining individual copper<sup>6</sup> and chlorine<sup>7</sup> isotopes. The application of radioactivation to the determination of uranium in minerals was recently reported by Smales<sup>8</sup> and, as this method gave a measure of the uranium-235 content of the mineral by relying on the constant isotopic content of uranium in nature to give the total uranium, it was a logical step to use it as a basis for the direct determination of uranium-235 in mixtures of the naturally occurring uranium isotopes.

## APPLICATION OF RADIOACTIVATION TO DETERMINATION OF URANIUM-235

Natural uranium contains 99.274 per cent. of uranium-238, 0.72 per cent. of uranium-235 and 0.0061 per cent. of uranium-234. The reactions of these isotopes with slow neutrons can be briefly summarised as follows—



The production of uranium-235 from uranium-234 is negligibly small in the short irradiation periods discussed in this work, owing to the long half-life ( $8.9 \times 10^8$  years) of uranium-235.

From this it follows that the amount of a particular fission-product, measured by counting, is directly related to the uranium-235 content of the sample. Further, if the sample and a standard of normal uranium (known to contain 0.72 per cent. of uranium-235) are irradiated, chemically treated and counted under the same conditions, the following ratio will hold—

$$\frac{\text{Corrected count of standard}}{\text{Corrected count of sample}} = \frac{\text{Weight of } {}^{235}\text{U in standard}}{\text{Weight of } {}^{235}\text{U in sample}}$$

As the choice of barium-140 as a suitable radio-nuclide for isolation and measurement has been fully discussed elsewhere,<sup>8</sup> it is only necessary to mention briefly the following points in its favour.

- (1) High fission yield (6.2 per cent.), convenient half-life (12.8 days) and  $\beta^-$  energy (maximum 1.0 MeV).
- (2) Good chemical separation properties from other radioactive fission products. One valency state in solution, which favours quick and complete exchange with the inactive carrier barium. Good final weighing and counting form (barium sulphate).

The effect of fast neutron fission of uranium-238 will be considered in a later section, but it may be noted here that the effect is negligible for ratios of  $^{235}\text{U}$  to  $^{238}\text{U}$  greater than 1 to 1000, in the "self-serve" positions of the Harwell pile.

In this work only pure uranium oxide or its solution is irradiated; the presence of barium as an impurity, possible in ores, is not a major problem here. Barium-139 (half-life 85 minutes;  $\beta$ -energy 2.3 MeV), which is also a product of fission, may therefore be used instead of barium-140, with certain advantages arising from its shorter half-life (the fission is about the same for both).

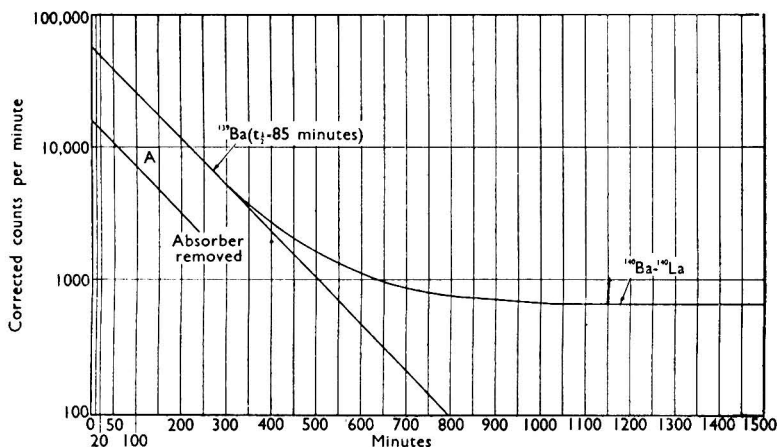


Fig. 1. Decay of fission-product barium. Fifty mg of  $\text{U}_3\text{O}_8$  irradiated for 5 minutes at 9.30 a.m. Barium sulphate precipitated at 11.30 a.m. First count at noon. Curve A, count through absorber (197 mg per sq. cm)

Hence for a given short irradiation time of a few minutes, a much greater relative activity of barium-139 is attained. Also, a decay curve, which can give a valuable check on radio chemical purity, can be obtained more quickly. But apart from a decay curve for the 85-minute barium-139, shown in Fig. 1, all the work described in this paper was carried out with barium-140 because it is more suitable for use in laboratories not conveniently near an atomic pile.

#### NEUTRON SOURCE—

The Harwell pile was used as the neutron source for all the work described here except for one experiment, which was carried out with a 0.5-curie radium - beryllium source. In confirmation of the calculated value, which assumed a neutron flux of  $10^4$  neutrons per sq. cm per second, the barium-140 activity after a 13-day irradiation in this source was only 10 counts per minute per g of natural uranium. The Harwell pile flux is about  $10^{12}$  neutrons per sq. cm per second, which gives ample sensitivity for much shorter irradiations. A useful nomogram for calculating fission-product activities is given by Stang and Hance.<sup>9</sup>

#### STANDARDS—

The comparative method of activation analysis,<sup>5</sup> in which the sample is compared with a standard, was used. For this work, analytical reagent grade uranyl nitrate of natural isotopic composition was further purified by partition chromatography and converted to  $\text{U}_3\text{O}_8$ , which was used as standard.

#### SELF SHIELDING—

If a material undergoing irradiation has a high capture cross-section, the flux at the centre of a mass of such material will be less than at the surface. For solid  $\text{U}_3\text{O}_8$ , of natural isotopic composition and density of 3.5 g per cu. cm, irradiated in cylindrical polythene tubing of 2 mm internal diameter, the self-shielding effect, calculated from the formula of Seaborg, English, Wilson and Coryell,<sup>10</sup> can be shown to be negligible. This conclusion was checked experimentally by irradiating 50-mg portions of  $\text{U}_3\text{O}_8$  diluted uniformly with 0, 1, 2, 5, 10 or 20 volumes of analytical reagent grade magnesium oxide ( $\sigma_{\text{capt.}} < 0.05$  barns) in sealed



short lengths of polythene tubing for 5-minute periods. In this way identical amounts of  $U_3O_8$  were "dispersed" by increasing amounts of magnesium oxide. The separated barium-140 activity, calculated as counts per minute per milligram of  $U_3O_8$ , was identical in all irradiations within the experimental error.

For samples containing significantly greater amounts of uranium-235, in which the total neutron cross-section might be tens or even hundreds of barns, significant effects could appear, which would make irradiation of dilute aqueous solutions of the sample in sealed silica tubing necessary. The effective neutron cross-section of the solution, mainly water, would then be minute.

#### CHEMICAL SEPARATION

The aim of the chemical separation after irradiation is to isolate a radiochemically pure barium compound, *i.e.*, one free from all other radioactive species derived either from trace impurities in the uranium or from the other products of neutron irradiation; these include neptunium-239 as well as other fission products. The chemical separation eventually used is described in full in the procedure on p. 397, but it is similar to that used on the Manhattan Project and described by Coryell and Sugarman<sup>12</sup>; it is also largely that used by Smales<sup>8</sup> for application to minerals. As a known quantity of inactive barium carrier is added there is no necessity for quantitative isolation (except insofar as a loss of sensitivity follows from a low chemical yield). It is desirable to have similar yields from standard and samples, so that corrections for self absorption, and so on, in the counting become negligible.

#### METHOD

##### REAGENTS—

*Magnesium oxide*—Analytical reagent grade.

*Nitric acid, sp. gr. 1.42.*

*Barium chloride solution*—Dissolve 18 g of  $BaCl_2 \cdot 2H_2O$  in water and make up to 500 ml.

*Lanthanum nitrate solution*—A 1 per cent. w/v solution of  $La(NO_3)_3 \cdot 6H_2O$ .

*Ammonium hydroxide, sp. gr. 0.880.*

*Strontium carbonate solution*—A 2 per cent. w/v solution.

*Hydrochloric acid - diethyl ether reagent*—A mixture of 5 parts of concentrated hydrochloric acid, sp. gr. 1.18, and 1 part of diethyl ether.

*Sodium tellurate solution*—A 0.4 per cent. w/v solution.

*Zinc metal powder.*

*Methyl orange indicator.*

*Potassium iodide solution*—A 1 per cent. w/v solution.

*Sodium hypochlorite solution*—A commercial solution containing 10 per cent. of available chlorine.

*Hydroxylamine hydrochloride.*

*Ferric chloride solution*—A 1 per cent. w/v solution.

*Sulphuric acid*—A 20 per cent. v/v solution.

##### IRRADIATION—

*Solids*—As mentioned in the discussion on self-shielding, samples containing not much more uranium-235 than natural uranium (say, up to three times more or 2 per cent.) may be irradiated as solid; this is usually  $U_3O_8$ . For these cut a 5-cm length of 2-mm polythene tubing and seal one end by warming and pressing. Introduce freshly ignited analytical reagent grade magnesium oxide to form a compact layer 4 to 5 mm in height at the sealed end of the tube. Weigh the tube and contents, add about 50 mg of  $U_3O_8$  and re-weigh. Add a further similar layer of magnesium oxide on top of the  $U_3O_8$  and then seal the open end. Leave a free space about 1 cm long between the top of the magnesium oxide layer and the seal, for ease of opening. Treat standard and samples similarly. Place the tubes either in a special polythene bottle for irradiation in the pneumatic "rabbit" of the pile or in a 3-inch aluminium can for irradiation in the "self-serve" holes in the pile. Irradiation is carried out for any required time; usually it is about 5 minutes. After irradiating, place the containers in lead shielding for about 15 hours. After this period, tap down the contents of the polythene tube away from one end and carefully cut off the top. Empty the contents into a 50-ml centrifuge tube. (The plug of magnesium oxide serves to "rinse" the sample tube as it is emptied.) Add 2 ml of concentrated nitric acid (sp.gr. 1.42), gently warm to dissolve, and

finally boil off the nitrous fumes. Add 5.00 ml of a barium solution to act as carrier (a solution of 18 g of barium chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , in 500 ml of water).

*Liquids*—For more highly enriched samples or when the amount of sample available is small, solutions containing weighed quantities of solid sample must be irradiated in small silica ampoules. The ampoules, which have a capacity of about 1 ml, are prepared from silica tubing. After one end of each has been sealed, the ampoules are weighed, the sample solution added from a fine-pointed glass dropping-tube and the ampoules re-weighed. Pack the ampoules, after sealing the open ends, in cotton wool in a 3-inch aluminium can and irradiate them in the "self-serve" position of the pile. The time of irradiation necessary can be calculated from the usual activation formula; as an example, 1  $\mu\text{g}$  of uranium-235 irradiated for 24 hours in a flux of  $10^{12}$  neutrons per sq. cm per second gives about 5000 counts per minute of barium-140 at 5 per cent. counting efficiency, 24 hours after the irradiation.

After removing them from the pile, place the samples and standards in lead shielding for about 15 hours; the main activity is due to silicon-31. Transfer the ampoules to 100-ml tall-form beakers containing a few millilitres of water and 5.00 ml of barium carrier solution, carefully break off both ends of each ampoule and warm to ensure thorough mixing. Decant into centrifuge tubes and wash out the ampoules and beakers with further small portions of water.

#### CHEMICAL SEPARATION—

Evaporate the solution containing the irradiated uranium and barium carrier to 5 to 6 ml and add two drops of 1 per cent. lanthanum nitrate solution. Warm if necessary to dissolve any barium nitrate that may have crystallised, add concentrated ammonium hydroxide dropwise until a permanent precipitate is obtained and then two drops in excess. Centrifuge and decant into another centrifuge tube. Add methyl orange indicator, and then hydrochloric acid until the solution is acid. Add 2 drops of 2 per cent. strontium solution, about 25 ml of hydrochloric acid - diethyl ether reagent, mix thoroughly, centrifuge and decant. Wash the precipitate with 5 ml of reagent, centrifuge and decant. Dissolve the barium chloride precipitate in 3 to 4 ml of water, re-precipitate it by adding 20 ml of reagent, centrifuge and decant. Wash with 5 ml of reagent, centrifuge and decant.

Dissolve the precipitate in about 5 ml of water, add 6 drops of lanthanum solution and 6 drops of the 4 per cent. tellurate solution and then about 3 mg of zinc metal powder. When the effervescence ceases, make the solution just ammoniacal to methyl orange, centrifuge and decant into another tube. Add 4 drops of 1 per cent. potassium iodide solution and 2 drops of sodium hypochlorite solution. Warm and set aside for 2 minutes. Acidify with about 1 ml of hydrochloric acid, and add about 0.1 g of hydroxylamine hydrochloride. Boil under a hood until all the iodine appears to be removed and the volume is reduced to 5 to 6 ml. Add 2 drops of strontium solution and 2 drops of lanthanum solution and repeat the double barium chloride precipitation and washing, as above.

Dissolve the precipitate in about 5 ml of water, add 6 drops of lanthanum solution, and 6 drops of 1 per cent. ferric chloride solution. Make ammoniacal to methyl orange, add half a crumbled Whatman accelerator tablet, and heat just to boiling. Filter through a 7-cm Whatman No. 30 filter-paper into a centrifuge tube, wash twice with 2 to 3-ml portions of water. Dilute the filtrate to about 20 ml and make slightly acid with hydrochloric acid. Heat nearly to boiling and add dropwise 2 ml of 20 per cent. v/v sulphuric acid. Allow the precipitate to settle, decant, wash with 10 ml of water, centrifuge, decant and repeat the washing procedure to complete removal of the excess of acid.

Transfer as much as possible of the precipitate, by means of a dropping tube and a few drops of water, to a tared aluminium counting tray. Dry under an infra-red lamp and finally heat in a muffle furnace at  $500^\circ\text{C}$  for 15 minutes. Cool, weigh and reserve for counting.

#### COUNTING TECHNIQUE—

The counting equipment for this work consists of (i) a power unit (type 1082A or 200 is suitable), (ii) scaling unit (type 200 or 1009B), (iii) time accessory unit (type 1003B), (iv) probe unit (type 200B or 1014A). Time pulses can be obtained from a master electric clock serving several units. A mica end-window Geiger - Müller counter (2 mg per sq. cm), of type EHM2, is suitable; it is mounted in a lead castle with a Perspex lining and shelves.

Check the counting equipment in the normal fashion with a suitable beta-emitter, such as natural uranium oxide in equilibrium with  $\text{UX}_1$  and  $\text{UX}_2$ . Place the sample to be counted

in a Perspex carrier and insert it in a shelf at a suitable distance from the Geiger - Müller tube to attain a counting rate of 2000 to 3000 counts per minute. Count for a sufficient time to obtain at least 10,000 counts for each barium sulphate precipitate, counting the precipitates one after another without undue delay. Correction for growth of lanthanum-140 is unnecessary if samples and standards are counted within, say, 60 minutes of each other, provided the barium sulphate precipitations are carried out on each nearly simultaneously.

#### CALCULATION OF RESULTS—

Correct all counts for background, coincidence loss and chemical yield and express as the results in counts per minute.

$$\text{Then } \frac{\text{Weight of } ^{235}\text{U in standard}}{\text{Weight of } ^{235}\text{U in sample}} = \frac{\text{Corrected count of standard}}{\text{Corrected count of sample}}$$

$$\text{and } \frac{\text{Weight of } ^{235}\text{U in sample}}{\text{Weight of sample}} \times 100 = \text{percentage of uranium-235 in sample.}$$

#### “DECONTAMINATION” EXPERIMENTS

Some idea of the separation requirements, or decontamination necessary, can be obtained from the calculated activities of the fission products of uranium after various decay times. A useful paper by Hunter and Ballou<sup>11</sup> gives these details; Table I shows a few relevant figures taken from the graph in that paper.

TABLE I

RELATIVE ACTIVITIES OF SOME NUCLIDES PRODUCED BY SLOW NEUTRON FISSION OF URANIUM-235 AS PERCENTAGE OF ORIGINAL TOTAL FISSION-PRODUCT ACTIVITY

One day after irradiation		Ten days after irradiation	
Nuclide	Relative activity	Nuclide	Relative activity
<sup>140</sup> Ba	1.25	<sup>140</sup> Ba	12.5
<sup>135</sup> Xe	12.5	<sup>140</sup> La	12.5
<sup>97</sup> Nb	9.8	<sup>133</sup> Xe	11.5
<sup>97</sup> Zr	9.0	<sup>143</sup> Pr	10.0
<sup>93</sup> Y	7.5	<sup>131</sup> I	7.0
<sup>133</sup> I	7.5	<sup>99</sup> Mo	7.0
<sup>91</sup> Sr	6.8	<sup>141</sup> Ce	6.5
<sup>142</sup> Ce	6.8	<sup>132</sup> I	5.5
<sup>135</sup> I	4.7	<sup>132</sup> Te	5.5
<sup>99</sup> Mo	4.7	<sup>147</sup> Nd	4.8
<sup>92</sup> Y	4.1	<sup>95</sup> Zr	3.4
<sup>145</sup> Pr	3.0	<sup>91</sup> Y	3.3
<sup>91</sup> Y	3.0	<sup>89</sup> Sr	3.0
<sup>132</sup> I	2.7	<sup>103</sup> Ru/Rh	2.6
<sup>132</sup> Te	2.7		
<sup>149</sup> Pm	1.5		
<sup>105</sup> Rh	1.5		
<sup>141</sup> La	1.5		

To test the efficiency of the separation scheme for relevant fission product elements whose behaviour was not certain, experiments were carried out to determine decontamination factors as follows. (In these experiments the radio-nuclide may not necessarily be in exactly the same chemical form as in the actual fresh fission products present in a sample after irradiation. Nevertheless they are of some value.) A solution of a suitable radio-nuclide was prepared, an aliquot added to 50 mg of U<sub>3</sub>O<sub>8</sub> dissolved in nitric acid and, after barium carrier had been added, the chemical separation was carried out. The activity of the solution, before the final barium sulphate step, was measured in a type M6 Geiger - Müller tube. After precipitation, the activity of the barium sulphate was measured with an end-window Geiger - Müller tube of type EHM2. Details of the nuclides used and results obtained are given in Table II.

Decontamination was satisfactory for zirconium, molybdenum and ruthenium - rhodium and for iodine when a specific removal step was included in the procedure. Earlier workers

have found that fission-product iodine is liable to be present in different forms; so to ensure exchange with added carrier an oxidation reduction step was necessary. Oxidation by sodium hypochlorite in ammoniacal solution followed by reduction to elementary iodine by hydroxylamine satisfactorily overcomes this difficulty.

TABLE II

## "DECONTAMINATION FACTOR" EXPERIMENTS

Tracer and mode of preparation	Activity added, counts per minute	Activity of solution, counts per minute	Activity of BaSO <sub>4</sub> , counts per minute	Decontamination factor	Remarks
<sup>96</sup> Zr ( <i>n,γ</i> ) <sup>97</sup> Zr (zirconium nitrate)	2.3 × 10 <sup>6</sup>	11	3	> 10 <sup>5</sup>	
<sup>98</sup> Mo ( <i>n,γ</i> ) <sup>99</sup> Mo (MoO <sub>3</sub> )	1.6 × 10 <sup>6</sup>	3	1	≈ 10 <sup>6</sup>	
<sup>131</sup> I carrier-free fission product	1.1 × 10 <sup>6</sup>	4 to 12	20	≈ 10 <sup>5</sup>	No specific iodine removal step included
	1.1 × 10 <sup>6</sup>	—	1 to 4	≈ 10 <sup>6</sup>	
<sup>106</sup> Ru/Rh (separated fission product)	2.02 × 10 <sup>6</sup>	1	1	≈ 2 × 10 <sup>6</sup>	
<sup>88</sup> Sr ( <i>n,γ</i> ) <sup>89</sup> Sr ("Specpure" SrCO <sub>3</sub> )	0.8 × 10 <sup>6</sup>	6000	3000	≈ 10 <sup>2</sup>	

For strontium it was found that 99 per cent. of the activity was removed by the first double barium chloride precipitation step, but little more by the remaining steps. Examination of the decay and absorption curves of the residual activity of the barium sulphate showed it to be due almost certainly to barium-135 (half-life 29 hours) and barium-131 (half-life 12.0 days) derived from trace barium impurity in the "Specpure" strontium carbonate irradiated. This trouble will not arise in the usual determination of uranium-235, and there is little doubt that the decontamination from strontium is quite adequate.

## SEPARATION FROM OTHER RADIO-NUCLIDES—

*Sodium*—Any contamination of the uranium sample before irradiation could give rise to radio-nuclides; one possibility is sodium-24. A decontamination factor of  $2 \times 10^6$  was obtained for this nuclide, on starting with  $2.7 \times 10^6$  counts per minute.

*Impurity in analytical reagent grade magnesium oxide*—The activity accompanying the barium sulphate from 10 mg of magnesium oxide after irradiation for 58 hours amounted to about 30 counts per minute 18 hours after irradiation; again it was shown to be from barium impurity in the magnesia. As the normal irradiation time used for samples of nearly natural isotopic composition is 5 minutes any interference from the 20 mg of magnesium oxide used in packing the U<sub>3</sub>O<sub>8</sub> in the polythene tubing can be neglected, but a check should be made on possible interference from each fresh batch of magnesium oxide used. For samples containing little uranium-235, for which long irradiation periods are necessary, the magnesium oxide should be dispensed with.

*Barium*—The interference from barium has been thoroughly discussed by Smales.<sup>8</sup> Only serious contamination, such as from several per cent. of barium, can affect the determination of uranium-235 when the latter is present at almost normal isotopic composition. A simple preliminary separation is then desirable.

A check on the over-all radiochemical purity of the isolated barium-140 can be made by plotting the growth and decay curve, but experience has shown that, if the chemical separation described in the procedure is carried out correctly, this check is usually superfluous. A typical growth - decay curve is shown in Fig. 2.

## RESULTS

## PRECISION—

Eight accurately weighed portions of the standard U<sub>3</sub>O<sub>8</sub> were irradiated for 5 minutes as described above. After 4 days each portion was chemically treated and counted as already described. The results are shown in Table III. For each a total count of about 20,000 was taken, which gave a standard deviation, on the counting only, of about 0.7 per cent. It

can be seen that under favourable conditions a precision of better than 2 per cent. at the 66 per cent. confidence level is possible.

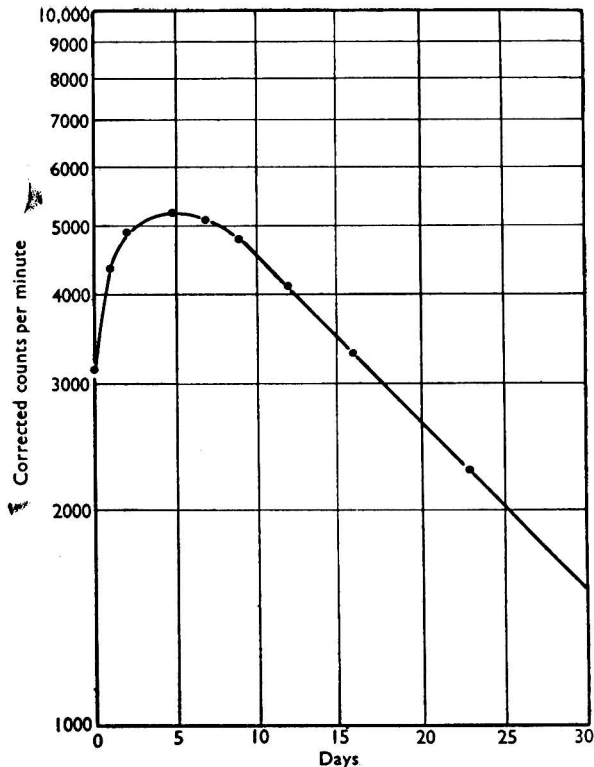
TABLE III

PRECISION OF PROPOSED METHOD WITH STANDARD  $U_3O_8$ 

$U_3O_8$ portion	Time after $BaSO_4$ precipitation		
	4 days, counts per minute per mg of $U_3O_8$	23 days, counts per minute per mg of $U_3O_8$	28 days, counts per minute per mg of $U_3O_8$
1	136	160	122
2	136	159	122
3	141	161	123
4	138	157	121
5	137	160	123
6	141	163	125
7	141	159	121
8	140	159	121
Standard deviation . . .	$\pm 2.3$	$\pm 1.8$	$\pm 1.4$
Coefficient of variation	1.7%	1.1%	1.2%

## ENRICHED SAMPLES—

*Sample No. 1*—About 12 mg of a sample of  $U_3O_8$  were available, whose uranium-235 content, according to a mass spectrometric determination, was about 14.7 per cent. of the total uranium. It was examined in solution by the activation method after igniting, weighing and dissolving the oxide and diluting to 250 ml. The standard was a solution of

Fig. 2. Typical growth - decay curve for  $^{140}Ba$  —  $^{140}La$

0.5000 g of the chromatographically purified  $U_3O_8$  of normal isotopic composition (uranium-235, 0.72 per cent. of total uranium) diluted to 250 ml. Portions of between 0.2 and 0.4 ml of each were irradiated for 11 hours; the results are shown in Table IV.

TABLE IV

## RESULTS BY THE ACTIVATION METHOD FOR SAMPLE NO. 1

Uranium-235 according to mass spectrometric method = 14.7 per cent.

Standards		Sample	
Amount of $^{235}U$ equivalent to 1 count per minute Ba activity, $\mu g$		Portion	$^{235}U$ , %
	0.000317	1	15.0
	0.000315	2	15.3
	0.000316	3	15.2
	Mean 0.000316	4	14.9
		5	14.9
		Mean	15.0 $\pm$ 0.2

*Sample No. 2*—This material had been analysed by Derham and Fenning<sup>3</sup> by their  $\beta$ -counting method, by which it gave 80.7 ( $\pm$  0.4) per cent. of uranium-235; by Palmer's mass spectrometric method<sup>13</sup> it gave 81.2  $\pm$  0.1 per cent. After ignition and nitric acid leaching, which separated uranium from a small amount of a red insoluble material (possibly  $Fe_2O_3$ ), the solution was diluted to 250 ml; it contained 51.4 mg of the  $U_3O_8$ . Approximately 0.2-ml portions were irradiated in silica for 4 hours; the results are shown in Table V.

TABLE V

## RESULTS BY ACTIVATION ON HIGHLY ENRICHED SAMPLES

Standards		Sample	
Amount of $^{235}U$ equivalent to 1 count per minute Ba activity, $\mu g$		Portion	$^{235}U$ , %
	0.00348	1	82.4
	0.00335	2	82.4
	0.00336	3	82.6
	Mean 0.00340	4	81.2
		5	80.8
		Mean	81.9 $\pm$ 0.8

*Synthetic samples*—Less enriched samples were also prepared by diluting samples No. 1 and 2 with natural uranium. For these, portions of the solution were mixed with the standard solution so that each mixture contained about 50 mg of  $U_3O_8$ ; those from sample 1 contained exactly 1.40, 1.07 and 0.87 per cent. of uranium-235 and those from sample 2 contained 0.89 and 1.05 per cent. of uranium-235, according to the determined figures of 15.0 per cent. and 81.9 per cent. for samples 1 and 2, respectively. The solutions were then treated with ammonium hydroxide, and the precipitates filtered and ignited to  $U_3O_8$ . Each precipitate was divided into two approximately equal portions, which were weighed accurately and irradiated for about 5 minutes in polythene tubes as described above. Results are shown in Table VI.

TABLE VI

## RESULTS BY ACTIVATION ON SYNTHETIC SAMPLES PREPARED BY DILUTION OF SAMPLES NUMBERS 1 AND 2 WITH NATURAL MATERIAL

Synthetic oxide				Nominal amount of $^{235}U$ , %	$^{235}U$ found, %
From sample 1	A	..	..	1.40	1.38
	B	..	..	1.07	1.06
	C	..	..	0.87	0.86
From sample 2	D	..	..	0.89	0.90
	E	..	..	1.05	1.07

## DEPLETED MATERIAL—

So far it has been assumed that the neutron flux in the pile is composed entirely of slow neutrons and that only the uranium-235 isotope undergoes fission. Nevertheless there is a proportion of fast neutrons at almost any point in the pile. Fast neutrons cause fission of the uranium-238 isotope and so give rise to barium-140 that cannot be differentiated from the barium-140 arising from uranium-235; this may therefore cause spurious results. Fast fission

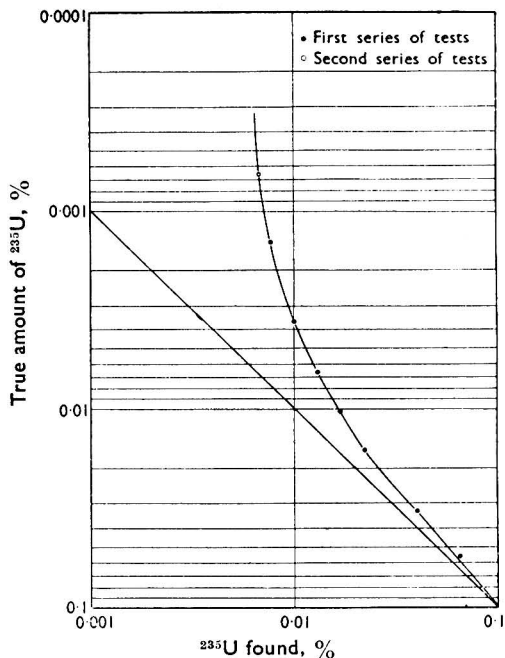


Fig. 3. "Spurious"  $^{235}\text{U}$  effect due to fast fission of  $^{238}\text{U}$

of uranium-235 can be neglected (*i*) because it is a small effect compared with slow fission, and (*ii*) because its effect is compensated for in the standard. The calculation of such a "spurious" contribution is made difficult because the fast-fission cross-section of uranium-238 is energy dependent; the neutron energies in the pile cover a wide "spectrum" and consequently the term "fast neutron flux" is difficult to define and measure. Fortunately, however, the practical determination of the "spurious" contribution is simpler, provided a sample containing little uranium-235 is available.

A sample of uranium oxide stated to contain 0.00065 per cent. of uranium-235 was used for an examination of the extent of this fast fission effect and portions of this material were mixed (via solution and precipitation) with natural  $\text{U}_3\text{O}_8$  to give a range of uranium-235 contents below 0.1 per cent. These samples were then irradiated in a self-serve position of the pile (E1/7) together with the natural  $\text{U}_3\text{O}_8$  standard; the results are shown in Table VII.

The constancy of the "spurious" uranium-235 figure that arises from fast fission of uranium-238 is satisfactory and serves not only to help measure this effect but also to confirm the analysis figure of 0.00065 per cent. for uranium-235 given with the sample, although it should be noted that since the actual uranium-235 content of the sample is only about one-tenth of the "spurious" effect, the value obtained for the latter is not entirely dependent on the original analysis.

The significance of this "spurious" figure is best seen in Fig. 3, where the experimental and actual values are plotted; it shows that as the uranium-235 content becomes greater than 0.1 per cent., the fast fission effect becomes negligible.

If, however, the analysis of samples at or below the 0.1 per cent uranium-235 level becomes necessary, and irradiation is to be carried out in the "self-serve" or "rabbit" positions in the pile, it will be necessary to irradiate, along with the samples, not only a standard of natural

isotopic composition uranium, but also one that contains very little uranium-235 so that the "spurious" effect due to fast fission can be measured in the actual position of the samples in the pile. Even so it is clear that determinations on samples containing much less than 0.01 per cent. of uranium-235 will not be satisfactory, owing to the magnitude of the correction.

Fortunately, use may be made of the thermal column of the pile in which, although the slow neutron flux is less than in the "self-serve" or "rabbit" positions and thus sensitivity is lower, the relative decrease in the effective fast neutron flux is much greater (possibly by a factor  $10^4$  compared with a decrease of 10 to 100 for slow neutron flux).<sup>14</sup>

TABLE VII  
EFFECT OF FAST FISSION OF <sup>238</sup>U

Irradiation date	Length of irradiation hours	<sup>235</sup> U present	<sup>235</sup> U found	Spurious <sup>235</sup> U, %
		(assuming value of 0.00065 per cent. for initial material), %	(assuming value of 0.72 per cent. in standard), %	
22.5.52	50	0.00065	0.00675	0.0061
		0.001415	0.00775	0.0063
		0.00652	0.0130	0.0065
5.6.52	6	0.00359	0.0100	0.0064
		0.01038	0.01676	0.0064
		0.01608	0.0221	0.0060
		0.0327	0.0400	0.007

A 128-hour irradiation of the sample mentioned above, which was said to contain 0.00065 per cent. of uranium-235, was carried out in the thermal column (T.E.14, 10 feet down) together with the standard  $U_3O_8$ ; the results for uranium-235 were 0.00059 and 0.00061 per cent. in the duplicate experiments. This satisfactory result shows that the fast fission effect must be extremely small under these circumstances.

#### HEALTH ASPECTS—

The decay of the unshielded total  $\gamma$ -activity of 0.1 g of normal  $U_3O_8$ , together with 20 mg of magnesium oxide, irradiated in polythene tubing for five minutes in the "self-serve" position of the Harwell pile, is illustrated in Fig. 4. If the normal radiation tolerance is taken as 0.06 roentgens per day, it can be seen that the radiation at one foot from a single sample has dropped to below this tolerance dose after a decay period of only 1 hour. Since most of the remaining activity is removed in the first ammonium hydroxide precipitate the radiation dosage is small, particularly when the normal overnight decay period is included in the procedure. During the whole of the experimental work described no excessive radiation dose, as shown by the standard film badge, has occurred. (All exposures of over one-fifth tolerance in any week would have been reported.)

If aluminium cans are irradiated, appreciable activity is emitted for a short time after their removal from the pile, but these cans are normally transferred by experienced pile operators to lead castles to allow the 2.3-minute aluminium-28 to decay. Little activity is found after irradiation of polythene. As mentioned earlier the silica ampoules after irradiation are quite active, but emit only  $\beta$ -activity (with a 170-minute half-life) and may be handled with tongs or behind Perspex, especially after 15 hours decay.

It is advisable to wear surgical gloves at least until after the completion of the double barium chloride step. The opening of irradiated polythene and silica tubing should be done carefully because slight pressure builds up during the irradiation. This step, together with that of the initial dissolving in nitric acid, and that of removing free iodine, should be carried out in a fume cupboard.

A portable monitor should always be used under the actual working conditions, in order that a safe working time may be decided upon.

#### CONCLUSIONS

The activation method described has been shown to have high sensitivity and to give generally an accuracy and precision of better than  $\pm 2$  per cent. This might be improved by paying particular attention to increasing weighing and, particularly, counting accuracy.



Even as it stands the method is of value, possibly not so much at close to the natural uranium-235 level, but because the precision quoted should be attainable over a wide range of uranium-235 contents; in fact, if the thermal column of the pile is used for the lower range, the precision quoted should be attained for samples containing from 0 to 100 per cent.

Nevertheless at high uranium-235 contents, it may be preferable to determine the uranium-238 content directly, *e.g.*, by separating and counting uranium-239 or neptunium-239. This and similar applications of the method to isotopic analysis of the heavy elements, such as uranium-238 in uranium-233, are at present under consideration.

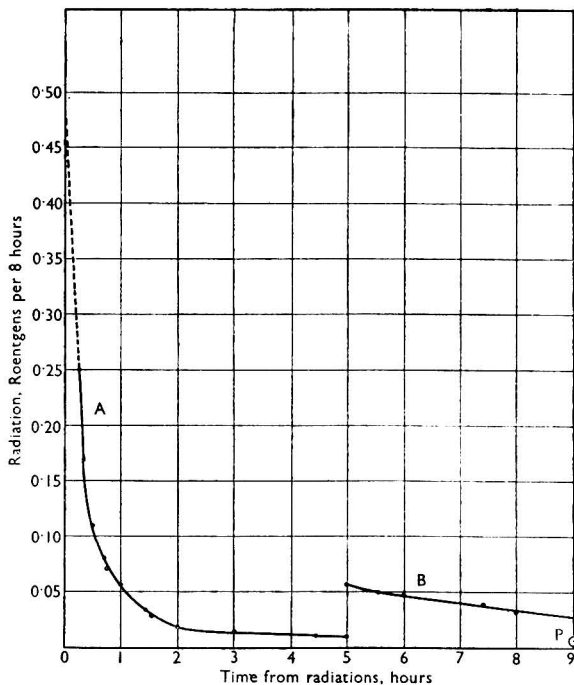


Fig. 4. Decay of total  $\gamma$ -activity of 0.10 g of  $U_3O_8$  irradiated for 5 minutes. Curve A, at 1 foot; curve B, at 3 inches; P, radiation after 24 hours at 3 inches

Apart from the use of the Harwell pile, in which facilities may be made generally available, no special apparatus other than that found in a modern laboratory is required. The actual manipulation and technique can readily be acquired by any competent laboratory chemist even without previous radiochemical experience.

Our thanks are due to Dr. R. H. Dawton, Mr. P. Egelstaff and Mr. F. W. Fenning for providing some of the samples used; to Mr. Fenning for valuable discussion; to the Chief Chemical Inspector for giving leave of absence from Springfields to one of us (A.P.S.) during the period January to June, 1952, in order that the experimental work could be carried out at Harwell; to Chemical Inspectorate, Springfields, for the provision of the purified normal  $U_3O_8$ ; to members of the Pile Operating Group for their unfailing assistance; and finally to the Director, A.E.R.E., for permission to publish.

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## The Amperometric Titration of Traces of Ammonia with Hypobromite at the Rotated Platinum Wire Electrode

### Application to the Determination of Nitrogen in Organic Compounds

BY I. M. KOLTHOFF, W. STRICKS AND L. MORREN

Current - voltage curves of sodium hypobromite solutions at the rotating platinum electrode as indicator electrode have been determined in buffer solutions of pH values between 8.3 and 13.0, both in the absence and presence of oxygen. In air-saturated sodium bicarbonate solution the current measured at +0.2 volt with respect to the saturated calomel electrode is proportional to the concentration of hypobromite. Use of this is made in the amperometric titration of arsenic trioxide and ammonia. Procedures are given for the rapid titration of arsenite, of ammonia and of nitrogen in organic compounds after a Kjeldahl digestion. Ammonia can be determined at concentrations between  $6 \times 10^{-4}$  and  $4 \times 10^{-5} M$  with an accuracy and precision better than 2 per cent. At high dilutions the amperometric titration methods with hypobromite are simpler, more rapid and more accurate than previous methods. The methods described in this paper should find application to the amperometric titration of many substances that react stoichiometrically with hypobromite.

SODIUM hypobromite is a well-known volumetric reagent, but it has never been used in amperometric titrations. In this paper the voltammetry of hypobromite at the rotated platinum electrode is described and conditions are established under which traces of ammonia can be titrated rapidly, simply and accurately with hypobromite by the amperometric technique.

Analytical use has been made of the oxidation of ammonia by hypobromite for almost 50 years. Artman and Skrabal<sup>1</sup> and, independently, Rupp and Rossler<sup>2</sup> showed that ammonia and urea can be titrated with hypobromite. A critical study of these titrations has been reported by Kolthoff and Laur.<sup>3</sup> Titrations with hypobromite found wide application to the determination of nitrogen in biological materials, so obviating a distillation of the Kjeldahl digest (for examples see references 4 to 10). The determinations were carried out by adding an excess of hypobromite and titrating with thiosulphate after addition of iodide or by potentiometric titration.

From current - voltage curves for hypobromite solutions at the rotating platinum electrode it was inferred that it should be possible to carry out titrations with hypobromite amperometrically. In practice it was found that, with the rotated platinum electrode as

indicator electrode, traces of ammonia can be titrated more simply, rapidly and accurately than by any other titration method. The end-point in amperometric titrations with hypobromite can be detected very sharply.

The method has been successfully applied in this laboratory to routine determinations of protein nitrogen in blood sera and their albumin and globulin fractions.

#### EXPERIMENTAL

##### MATERIALS USED—

Water was made ammonia-free by redistillation from dilute sulphuric acid medium in an all-Pyrex glass apparatus, air being excluded.

Glutathione in the reduced state was a Pfanstiehl product. The purity of this product was 99 per cent. as determined by titration with cupric copper.<sup>11</sup> The stock solution used was 0.024 *M* in glutathione, which corresponded to 1 mg of nitrogen per 1 ml of solution.

Crystallised bovine plasma albumin was an Armour product. The water content of this product was found to be 6.0 per cent. by heating at 110° C to constant weight. A 10<sup>-3</sup> *M* stock solution of albumin was prepared, containing 1.02 mg of nitrogen in 0.1 ml.

Stock solutions of ammonium chloride and ammonium sulphate were 0.003 *M*.

Stock solutions of sodium hypobromite (0.06 *M* in hypobromite and 0.1 *M* in sodium hydroxide) and of arsenious oxide (0.025 *M*) were prepared according to conventional procedures.<sup>12,13</sup> The stock solution of hypobromite was stored in a dark bottle in a refrigerator at 4° C. Under these conditions the titre of this solution was found to decrease by about 10 per cent. within three months.

Stock solutions of sodium bicarbonate and of borax were 0.6 *M* and 0.1 *M*, respectively.

The titrations were carried out with solutions prepared from stock solutions by appropriate dilution with ammonia-free water.

##### EXPERIMENTAL METHODS—

Current-voltage curves were prepared with a Heyrovský self-recording polarograph and with a manual apparatus and circuit,<sup>14</sup> which was also used for amperometric titrations. Potentials were measured against the saturated calomel electrode. Amperometric titrations were also carried out with the simplified apparatus and circuit described by Kolthoff and Harris.<sup>15</sup> In the present work with this apparatus a reference electrode was used that has a potential of +0.18 volt against the saturated calomel electrode. The electrolyte of the reference half-cell is a saturated mercurous chromate in *M* potassium chromate. Mercurous chromate was prepared as described by Gmelin and Kraut<sup>16</sup> by precipitation from an excess of a slightly acid mercurous nitrate solution with potassium dichromate. The product was filtered, washed with water and suspended in a *M* potassium chromate solution. A layer of mercury serves as the electrode of the half-cell. In order to protect the titration mixture from contamination with chromate, a vessel filled with saturated potassium nitrate was interposed between each half-cell and the titration vessel, the solutions in the two half-cells being connected by means of an agar-potassium chromate and an agar-potassium nitrate bridge, respectively.

A motor provided rotation at 1800 r.p.m. for the platinum electrode. An unused platinum electrode must be cleaned with concentrated nitric acid and rinsed with water. If not in use, the electrode is kept in distilled water.

One- and two-millilitre semi-micro burettes graduated at each 0.01 ml were used in the titrations.

The pH was measured with a Beckman pH meter, Laboratory Model G.

Oxygen was removed from hypobromite solutions by a stream of pure nitrogen, which was passed through two wash-bottles containing hypobromite solutions of the same composition as that in the test mixture.

##### CURRENT-VOLTAGE CURVES AT ROTATING PLATINUM WIRE ELECTRODE—

Current-voltage curves were prepared for hypobromite solutions of various concentrations of sodium hypobromite and pH, both in the absence and presence of oxygen.

Hypobromite is reduced at the rotating platinum electrode and gives a reduction wave which, under proper conditions, exhibits a well-defined diffusion current region in the absence of oxygen. Current-voltage curves of hypobromite at different concentrations in air-free

medium at pH 10.3 are shown in Fig. 1. Current - voltage curves for each concentration were plotted from measurements of the current while the potential was varied first from positive to negative values and then in the reverse direction. It is seen from Fig. 1 that the curves plotted in these two ways are different in shape, which indicates that the electrode

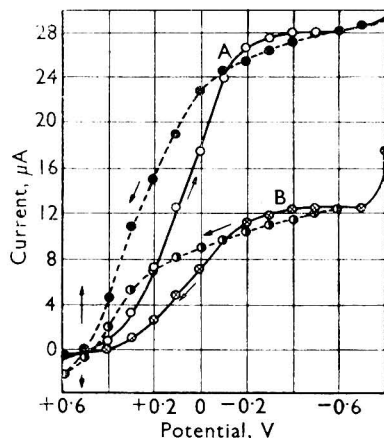


Fig. 1. Current - voltage graphs of hypobromite in the absence of oxygen, at different concentrations in a carbonate - bicarbonate buffer solution (pH 10.35). Curve A,  $1.45 \times 10^{-4} M$  sodium hypobromite; curve B,  $0.65 \times 10^{-4} M$  sodium hypobromite

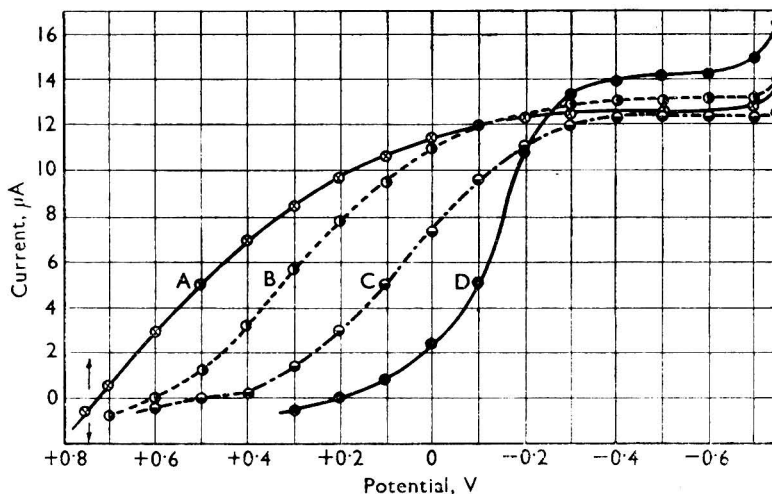


Fig. 2. Current - voltage graphs of  $0.65 \times 10^{-4} M$  hypobromite in air-free solutions at various pH values. Curve A,  $0.24 M$  bicarbonate solution (pH 8.3); curve B,  $0.05 M$  borax solution (pH 9.2); curve C,  $0.15 M$  carbonate -  $0.05 M$  bicarbonate solution (pH 10.35); curve D, approximately  $0.1 M$  sodium hydroxide solution (pH 13.0)

has become polarised during the electrolysis. The curves plotted in the usual way (from positive to negative potentials) show diffusion currents that are proportional to the concentration of hypobromite. It can be seen from Fig. 1 that, for  $0.65 \times 10^{-4}$  and  $1.45 \times 10^{-4} M$  solutions, the diffusion currents are  $12.5$  and  $28.2 \mu A$ , respectively, which corresponds to a current of about  $19.3 \mu A$  for a  $10^{-4} M$  hypobromite solution. Fig. 2 shows current - voltage curves for hypobromite in air-free solutions at various pH values. It is seen that the hypobromite wave is shifted to more negative potentials as the pH of the medium is increased.

Hence at pH 8.3 (bicarbonate), 9.2 (borax), 10.35 (carbonate - bicarbonate), 13 (0.1 *M* sodium hydroxide) the waves start at +0.72, +0.60, +0.50 and +0.20 volt, respectively.

As hypobromite in bicarbonate medium is reduced at the rotating platinum electrode at more positive potentials than is oxygen, it should be possible to detect the reduction wave of sodium hypobromite in air-containing media also. This is demonstrated in Fig. 3, which shows the cathodic waves of hypobromite in a 0.24 *M* sodium bicarbonate solution (pH 8.3) in the absence and presence of air, and the current - voltage curve of the air-saturated

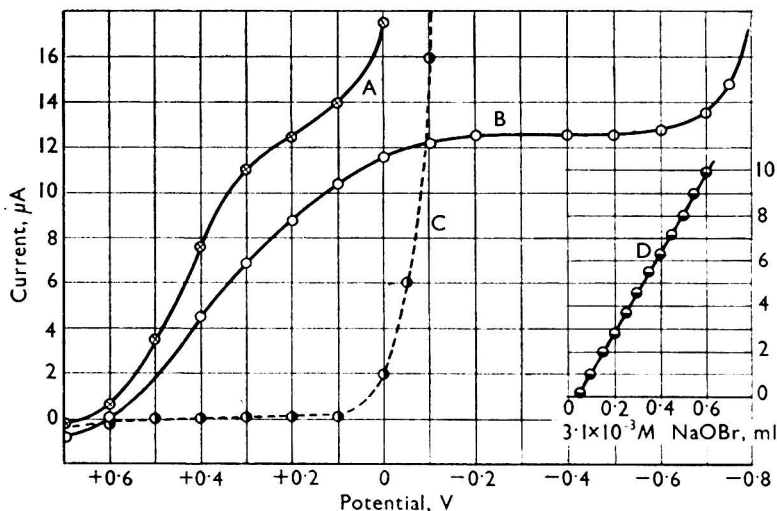


Fig. 3. Current - voltage graphs of  $0.75 \times 10^{-4}$  *M* hypobromite solution in 0.24 *M* sodium bicarbonate solution (pH 8.3). Curve A, in presence of air; curve B, in absence of air; curve C, with supporting electrolyte (0.24 *M* sodium bicarbonate solution, no hypobromite, air saturated); curve D, current at +0.2 V against amount of  $3.1 \times 10^{-3}$  *M* sodium hypobromite solution added to 30 ml of 0.24 *M* sodium bicarbonate solution (pH 8.3)

supporting electrolyte. It is of interest that, in the presence of oxygen, the hypobromite wave (Fig. 3, curve A) starts at a more positive potential and is steeper than that in the absence of oxygen. This effect has not been subjected to a detailed study because of the poor reproducibility of the hypobromite wave at the platinum electrode, the ascending part of the wave being greatly affected by the pre-treatment of the electrode. The diffusion current in the presence of oxygen is not well defined. From the point of intersection of the steep and slowly rising part of the current - voltage curve it is estimated that the current between +0.25 and 0.20 volt corresponds to the diffusion current. In the absence of air, a well-defined diffusion current is found and is equal to the current at +0.2 volt in the presence of air (compare curves A and B, Fig. 3). The straight line in Fig. 3 (curve D), which was constructed by plotting the current at +0.2 volt against the volume of a  $3.1 \times 10^{-3}$  *M* hypobromite solution added to 30 ml of an air-saturated bicarbonate solution, is evidence that the current for sodium hypobromite at +0.2 volt is strictly proportional to the hypobromite concentration.

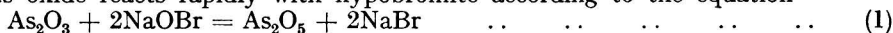
Use of these observations was made in the development of amperometric titrations with hypobromite.

#### AMPEROMETRIC TITRATION WITH HYPOBROMITE

Amperometric titrations with hypobromite were carried out in carbonate - bicarbonate and borax buffers at pH values varying from 8.2 to 10.0. The end-point was found to be best defined in a 0.2 *M* sodium bicarbonate solution (pH 8.2), and this buffer was used in most of the titrations described below.

## TITRATION OF ARSENIOS OXIDE—

Arsenious oxide reacts rapidly with hypobromite according to the equation—



This reaction can be used for the standardisation of the hypobromite solution.

The titration of 3 ml of a  $5 \times 10^{-4} M$  arsenite solution in 30 ml of bicarbonate with hypobromite is shown graphically in Fig. 4, curve A. It is seen that arsenite gives a small anodic current at the rotated platinum electrode at +0.2 volt against the saturated calomel electrode. This current decreases upon addition of hypobromite and is zero before the end-point is reached. On further addition of hypobromite a cathodic current is observed, and this increases along a curved line at first and then linearly with the volume of hypobromite

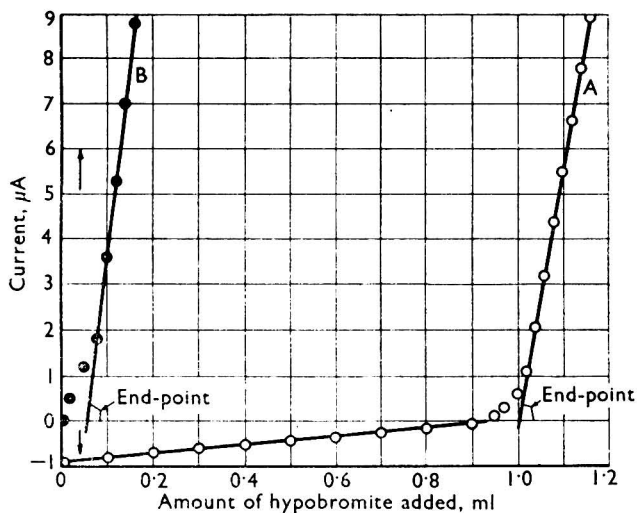


Fig. 4. Curve A, titration of 3 ml of  $5 \times 10^{-4} M$   $\text{As}_2\text{O}_3$  solution in 30 ml of 0.2  $M$  sodium bicarbonate solution with an unknown hypobromite solution at +0.2 V (S.C.E.) at the rotating platinum wire electrode; curve B, blank titration of 30 ml of 0.2  $M$  sodium bicarbonate solution with the same hypobromite solution

added. The end-point is at the intersection of the straight reagent line with the zero current line, which corresponds to the residual current measured at +0.2 volt with the supporting electrolyte in the absence of arsenite. The curved part of the reagent line, which is observed after the zero current is reached, does not correspond to the reaction between arsenite and hypobromite but to a slow reaction between hypobromite and impurities (most likely ammonia) in the bicarbonate solution. This is substantiated by Fig. 4, curve B, which represents a blank titration of the supporting electrolyte (in the absence of arsenite). The blank value is equal to the amount of hypobromite that corresponds to the curved part of Fig. 4, curve A. In a mixture of arsenite and ammonia, the hypobromite apparently reacts first with arsenite and then slowly with ammonia.

## TITRATION OF AMMONIA—

Ammonia reacts with hypobromite according to the equation—



This reaction is slow and therefore, in the classical titration method, an excess of hypobromite must be added and titrated back. Amperometric titrations can be carried out directly and rapidly in spite of the sluggishness of reaction (2). From Fig. 5, curve A, which represents an amperometric titration of ammonium chloride in a 0.2  $M$  bicarbonate solution, it is seen that the first increments of hypobromite added give rise to a considerable cathodic current, which decreases on standing and so indicates a slow reaction. On further addition of reagent the current first increases slowly and then decreases. The reaction is complete after a slight excess of hypobromite has been added, when further addition of hypobromite gives a current that is stable and increases linearly with the volume of reagent added. The intersection

of this line with the zero current line or original residual current gives the end-point. For the performance of a titration it is, therefore, only necessary to measure the current before addition of hypobromite and to record this as the residual current, and then to add reagent until a stable current is observed. A few more increments are then added and the current measured.

Fig. 5, curves B and C, shows the excess reagent lines in ammonia titrations in bicarbonate-carbonate buffers of different pH values. It is seen that a pH higher than 8.2 leads to higher results and also a decrease in the slope of the reagent lines. The results were corrected for the blanks determined for supporting electrolytes of the same pH as those

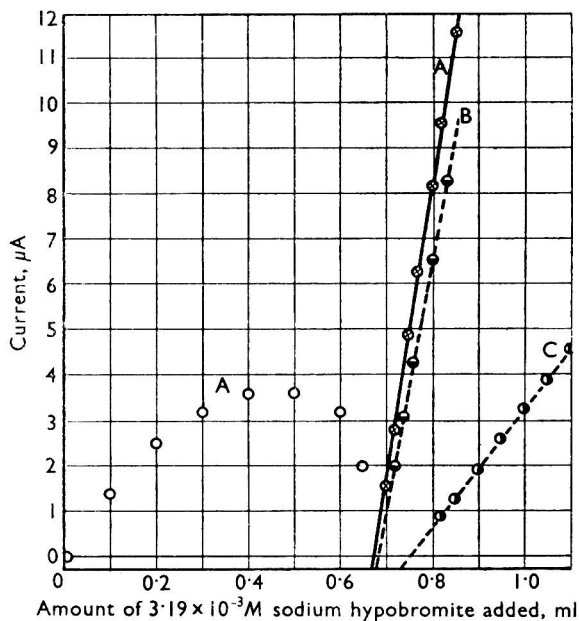


Fig. 5. Amperometric titration at the rotating platinum wire electrode at +0.2 V (S.C.E.) of 30 ml of  $4.43 \times 10^{-6} M$  ammonium chloride in: A, 0.2 M sodium bicarbonate solution (pH 8.23); B, 0.2 M sodium bicarbonate solution and 0.01 M sodium hydroxide solution (pH 8.78); C, 0.2 M sodium bicarbonate solution and 0.1 M sodium hydroxide solution (pH 9.98), with  $3.19 \times 10^{-3} M$  sodium hypobromite

used in the titrations. Because the hypobromite wave is shifted to more negative potentials at higher values of pH, titrations were carried out at +0.2 as well as at +0.1 volt. At both potentials results were high at the higher pH values. A pH of  $8.6 \pm 0.3$  is recommended for the titration.

The amperometric titration of ammonia has been applied to the determination of nitrogen in glutathione, bovine plasma albumin and human sera. The Kjeldahl digestion was carried out with concentrated sulphuric acid and persulphate in a way similar to that suggested by Scott and Myers,<sup>17</sup> and by Willard and Cake.<sup>4</sup> This Kjeldahl digestion was applied to known amounts of ammonium sulphate. It was found that ammonia is not oxidised by persulphate if the procedure is carried out under proper conditions. Thus in one instance 0.886 mg of ammonium sulphate was subjected to the Kjeldahl digestion and the amount recovered, as found by titration with hypobromite, was 0.899 mg, which corresponds to a positive error of 1.5 per cent.

#### METHOD

##### REAGENTS—

*Sodium arsenite solution*—Dissolve 1.2363 g of arsenious trioxide (primary standard) in 10 ml of M sodium hydroxide and make the solution slightly acid by addition of 0.5 M sulphuric acid (use litmus as indicator). Transfer the solution to a 250-ml calibrated flask

and fill it to the mark with ammonia-free water. Dilute part of this solution to one-tenth of its strength to produce a  $2.5 \times 10^{-3} M$  standard solution of arsenious trioxide.

*Sodium hypobromite solution*—Slowly add 20 g of bromine to a solution of 12 g of sodium hydroxide in 500 ml of water with constant thorough shaking. Make the solution up to 2 litres. Dilute this solution, which is about 0.06 *M* in sodium hypobromite and 0.1 *M* in sodium hydroxide, to half strength and standardise it with sodium arsenite solution.

#### STANDARDISATION OF HYPOBROMITE AGAINST ARSENITE—

Place 10 ml of 0.6 *M* sodium bicarbonate solution and 15 ml of ammonia-free water in a 100-ml beaker. Immerse the rotating platinum-wire electrode and a glass tube with a sintered-glass bottom that is covered with a potassium nitrate - agar plug. Into this tube insert the tip of the potassium nitrate - agar bridge, which, by way of a saturated potassium nitrate solution, is connected to a mercurous chromate half-cell. Connect the two electrodes directly through a microammeter. A spotlight galvanometer or a direct-reading Leeds and Northrop microammeter can be used. Record the value of the current, which usually is nearly zero. Add 5 ml of  $2.5 \times 10^{-3} M$  standard sodium arsenite solution and titrate with a hypobromite solution that is approximately  $3 \times 10^{-2} M$  in sodium hypobromite. As long as the hypobromite is not present in excess, the current is negative or zero. After the end-point, the cathodic current increases rapidly on further addition of hypobromite. When the ammeter indicates that the end-point has been passed, measure the current after the addition of a few more increments of hypobromite. Plot the ammeter readings against the volume of hypobromite added. Draw a horizontal line through the point corresponding to the residual current of the supporting electrolyte (before the addition of sodium arsenite). The point of intersection between this line and the line drawn through the points recorded in presence of an excess of reagent corresponds to the end-point.

Carry out a blank titration with the supporting electrolyte (10 ml of 0.6 *M* sodium bicarbonate plus 15 ml of ammonia-free water) under the same conditions as for the standardisation. Deduct the blank from the volume of hypobromite used in the standardisation. The molarity of the sodium hypobromite is given by—

$$\frac{2 \times (\text{volume of arsenite}) \times (\text{molarity of arsenite})}{\text{volume of hypobromite}}$$

The hypobromite solution should be standardised daily.

#### PROCEDURES—

*Titration of ammonia*—Place bicarbonate solution and water in a 100-ml beaker and measure the current through the supporting electrolyte in the cell as described in the standardisation. Add a volume of the sample that will make the solution  $4 \times 10^{-5}$  to  $6 \times 10^{-4} M$  in ammonia. Titrate with a hypobromite solution of suitable concentration ( $3 \times 10^{-3}$  to  $3 \times 10^{-2} M$  in sodium hypobromite). As long as the hypobromite is not present in excess, the current increases at first and then decreases in the last stage of the titration before the end-point. As soon as the end-point is reached, the current increases regularly on the addition of reagent. Determine the end-point as described for the standardisation and subtract the blank determination.

1 ml of  $3 \times 10^{-2} M$  hypobromite solution  $\equiv$  0.34 mg of ammonia ( $\text{NH}_3$ ) or 0.28 mg of nitrogen

*Determination of nitrogen in organic materials*—Heat 0.1 to 1 ml of the sample, containing approximately 1 mg of nitrogen, with 1 ml of concentrated sulphuric acid in a 100-ml Kjeldahl flask until the escaping vapour is transparent. Continue heating for 15 minutes and then allow the flask to cool. To the cold solution add 150 mg of dry potassium persulphate through a long-stemmed thistle funnel, taking care to prevent the powder from sticking to the neck of the Kjeldahl flask. The solution as well as the persulphate must be water-free, otherwise some ammonia will be oxidised. Heat the flask gently for about 1 minute, at the end of which time the mixture should be colourless. If not, add more persulphate. Generally the amount of persulphate required is not more than 10 times the weight of organic matter in the sample. Boil the colourless solution for 5 minutes to destroy the excess of persulphate. Allow the solution to cool and add 5 ml of ammonia-free water. Boil the solution again to remove sulphur dioxide and then transfer it completely to a 25-ml calibrated flask and allow it to cool. Neutralise it carefully with sodium hydroxide, at first partly



with 10 *M* sodium hydroxide and then with a 0.1 *M* solution, using a drop of bromocresol green as indicator. Make up the cold neutral solution to the mark with ammonia-free water. Titrate 5 ml of this solution amperometrically with approximately  $3 \times 10^{-2}$  *M* hypobromite solution as described for the titration of ammonia. Make a blank Kjeldahl digestion and titration with ammonia-free water in place of the sample.

## RESULTS

The results of standardisation of hypobromite solutions of different concentrations against arsenite are summarised in Table I. It is seen that the results are more reproducible

TABLE I

## STANDARDISATION OF HYPOBROMITE AGAINST ARSENITE

Supporting electrolyte: 30 ml of 0.2 *M* sodium bicarbonate if not otherwise stated  
Results are corrected for blank

Concentration of arsenite, <i>M</i>	Total volume of hypobromite used, ml	Hypobromite used in blank, ml	Concentration of hypobromite found, <i>M</i>	Remarks
$3.32 \times 10^{-5}$	0.670	0.043	$3.19 \times 10^{-3}$	Fresh hypobromite solution
$3.32 \times 10^{-5}$ (a)	0.695	0.060	$3.15 \times 10^{-3}$	
$3.32 \times 10^{-5}$	0.688	0.060	$3.18 \times 10^{-3}$	
$3.32 \times 10^{-5}$	0.692	0.060	$3.16 \times 10^{-3}$	Hypobromite solution one day old
$5.00 \times 10^{-5}$	1.005	0.060	$3.17 \times 10^{-3}$	
$5.00 \times 10^{-5}$	1.005	0.060	$3.17 \times 10^{-3}$	
$5.00 \times 10^{-5}$	0.986	0.053	$3.21 \times 10^{-3}$	Hypobromite solution two days old
$5.00 \times 10^{-5}$	0.984	0.053	$3.22 \times 10^{-3}$	
$5.00 \times 10^{-5}$ (a)	1.000	0.055	$3.17 \times 10^{-3}$	
$2.07 \times 10^{-4}$	0.837	0.008	$1.51 \times 10^{-2}$	Fresh hypobromite solution
$2.07 \times 10^{-4}$	0.837	0.008	$1.51 \times 10^{-2}$	
$4.18 \times 10^{-4}$	0.853	0.005	$2.95 \times 10^{-2}$	
$4.18 \times 10^{-4}$	0.952	0.006	$2.64 \times 10^{-2}$	
$4.18 \times 10^{-4}$ (b)	0.953	0.005	$2.64 \times 10^{-2}$	
$4.18 \times 10^{-4}$ (c)	0.970	0.011	$2.61 \times 10^{-2}$	
$8.25 \times 10^{-4}$	1.697	0.005	$2.95 \times 10^{-2}$	

(a) Supporting electrolyte: 0.05 *M* borax (pH 9.2).

(b) Supporting electrolyte: 0.2 *M* sodium bicarbonate, approximately 0.01 *M* in sodium hydroxide (pH 8.68).

(c) Supporting electrolyte: 0.2 *M* sodium bicarbonate, approximately 0.1 *M* in sodium hydroxide (pH 9.87).

TABLE II

## AMPEROMETRIC TITRATIONS OF AMMONIA WITH HYPOBROMITE

Supporting electrolyte: 30 ml of 0.2 *M* sodium bicarbonate

Results are corrected for blank

Titre of hypobromite solution, <i>M</i>	Ammonium salt added	Approximate molarity in ammonia of mixture, <i>M</i>	Blank of ammonia, mg	Ammonia added, mg	Ammonia found, mg	Error, %
$3.19 \times 10^{-3}$	NH <sub>4</sub> Cl	$4.43 \times 10^{-5}$	0.0016	0.0227	0.023	+ 1.3
$3.19 \times 10^{-3}$	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	$4.46 \times 10^{-5}$	0.0016	0.0228	0.023	+ 0.9
$1.52 \times 10^{-2}$	NH <sub>4</sub> Cl	$2.77 \times 10^{-4}$	0.0017	0.1419	0.147	+ 3.4
$1.51 \times 10^{-2}$	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	$2.22 \times 10^{-4}$	0.0014	0.1140	0.116	+ 1.8
$1.51 \times 10^{-2}$	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	$2.22 \times 10^{-4}$	0.0014	0.1140	0.117	+ 2.9
$2.97 \times 10^{-2}$	NH <sub>4</sub> Cl	$5.60 \times 10^{-4}$	0.0017	0.2840	0.286	+ 0.5
$2.97 \times 10^{-2}$	NH <sub>4</sub> Cl	$5.60 \times 10^{-4}$	0.0017	0.2840	0.287	+ 1.0
$2.99 \times 10^{-2}$	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	$5.60 \times 10^{-4}$	0.0017	0.2855	0.288	+ 0.9
$2.99 \times 10^{-2}$	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	$5.60 \times 10^{-4}$	0.0017	0.2855	0.290	+ 1.4
$2.64 \times 10^{-2}$	NH <sub>4</sub> Cl	$5.60 \times 10^{-4}$	0.0018	0.2840	0.287	+ 1.0
$2.97 \times 10^{-2}$	NH <sub>4</sub> Cl (a)	$5.60 \times 10^{-4}$	0.0017	0.2855	0.291	+ 1.7
$2.97 \times 10^{-2}$	NH <sub>4</sub> Cl (b)	$5.60 \times 10^{-4}$	0.0135	0.2855	0.300	+ 4.9
$2.64 \times 10^{-2}$	NH <sub>4</sub> Cl (b)	$5.60 \times 10^{-4}$	0.0033	0.2840	0.300	+ 5.5

(a) Supporting electrolyte: 0.2 *M* sodium bicarbonate, 0.01 *M* in sodium hydroxide (pH 8.78).

(b) Supporting electrolyte: 0.2 *M* sodium bicarbonate, 0.1 *M* in sodium hydroxide (pH 9.98).

in titrations with more concentrated solutions ( $10^{-2}$  to  $3 \times 10^{-2} M$  sodium hypobromite). At these concentrations the blank correction is less than 1 per cent. of the total volume of hypobromite used. From Table I it is also seen that the results of titrations in a borax buffer (pH 9.2) and in a carbonate buffer of about pH 9.9 are from 1 to 2 per cent. lower than those found with bicarbonate as supporting electrolyte. Hypobromite solutions kept for one or two days in a refrigerator show hardly any change in titre. Table II shows results for amperometric titrations of ammonia. It is seen that  $23 \mu\text{g}$  of ammonia at a concentration of about  $4 \times 10^{-5} M$  can be determined with an error of less than 1 per cent. The accuracy and precision of the ammonia titrations is better than 2 per cent. All errors are positive. This must be attributed to formation during the titration of nitrogen oxides, as found by Kolthoff and Laur.<sup>3</sup> At any pH markedly higher than 8.6 the result is high, as is seen from the last two experiments shown in Table II. Table III gives results for the nitrogen content of reduced glutathione and albumin as found after Kjeldahl digestion and titration of the digest with hypobromite. The nitrogen content of glutathione is found to be 13.72 per cent., which compares favourably with the theoretical value of 13.68 per cent. The nitrogen content of albumin is generally assumed to be 16 per cent.,<sup>18</sup> a value which is in fair agreement with our average result of 16.22 per cent. It is also seen from Table III that the blank corrections are not larger than 3 per cent. of the titration results, a factor that is of importance for the accuracy of the method.

TABLE III

AMPEROMETRIC DETERMINATION OF NITROGEN IN REDUCED GLUTATHIONE AND IN BOVINE PLASMA ALBUMIN AFTER KJELDAHL DIGESTION

Supporting electrolyte: 30 ml of 0.2 M sodium bicarbonate

Concentration of hypobromite used: approximately  $3 \times 10^{-2} M$

Results are corrected for blanks

Quantity of material used for Kjeldahl digestion, mg	Blank of nitrogen, mg	Theoretical amount of nitrogen in the titration mixture, mg	Nitrogen found, mg	Average error, %	No. of determinations
7.37 mg of glutathione	0.0058	0.2016	0.2022	+ 0.3	4
6.98 mg of albumin ..	0.0035	0.2232 (a)	0.2264	+ 1.4	2

(a) This value corresponds to a nitrogen content of 16 per cent. in albumin.

Nitrogen determinations in normal and pathological blood sera and in their albumin and globulin fractions are being carried out in this laboratory by the Kjeldahl digestion and titration method described in this paper. The results of these determinations will be reported elsewhere.

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## The Micro-determination of Traces of Gaseous Elements in Metals by the Vacuum Fusion Method

BY J. N. GREGORY, D. MAPPER AND J. A. WOODWARD

A vacuum fusion method is described for the micro-determination of gases in metals. The experimental work involved in the development of the method and details of the proposed apparatus are fully described. Steel and uranium can be rapidly analysed for oxygen, nitrogen and hydrogen with an accuracy of better than  $\pm 10$  p.p.m. with 50 to 200-mg samples.

An unsuccessful attempt to determine oxygen and nitrogen in zirconium on a micro scale is also recorded.

In recent years much attention has been directed towards the effects of traces of gaseous elements on the properties of metals. A considerable amount of work has been carried out on various steels and, more recently, attention has been directed towards such metals as zirconium, titanium, uranium, molybdenum, thorium and vanadium. Sloman<sup>1</sup> and Sloman and Harvey<sup>2</sup> have successfully determined oxygen, hydrogen and nitrogen in these metals with the aid of a relatively large-scale vacuum fusion apparatus. In Sloman's method, metal samples ranging in weight from 5 to 25 g are required and the 2 to 10 ml of gas produced is analysed by conventional macro methods.

We believed that some improvement and greater simplicity of operation could be attained by carrying out vacuum fusion analyses on a much smaller scale. There is no theoretical reason why the principles applied in Sloman's method cannot be applied to the extraction and collection of gas volumes one-thousandth the size of those handled in the macro system. The gas could then be extracted from samples of 100 mg or even smaller and analysed by one of the recently devised micro-analytical methods or by mass spectrometry.

In general, the vacuum fusion method as applied to the determination of oxygen, hydrogen and nitrogen consists in introducing the metal sample into an outgassed graphite crucible at high temperature in a continuously evacuated system. The graphite is usually heated by high-frequency induction by means of an external coil. The operating temperature is determined by the particular metal and gas; it can be as high as 2200° C. The theoretical principles involved are discussed in detail by Sloman and Harvey<sup>2</sup> and Brewer.<sup>3</sup> In general, the oxygen is evolved as carbon monoxide containing a small proportion of carbon dioxide, and the nitrogen or hydrogen in the elemental state. These elements are often combined with the metal, so the operating temperature should be such that the dissociation pressure for the reactions involved would be substantially greater than the pressure maintained in the system, namely, about  $10^{-5}$  mm of mercury. For rapid evolution of the gas the dissociation pressure should be about 2 to 3 mm of mercury.<sup>2</sup>

Metals that have refractory oxides and nitrides are liable to cause considerable difficulties at the high temperatures involved. It is difficult to outgas the graphite to give a sufficiently low blank value for gas at the high temperature, and considerable evaporation of the metal can also occur. The condensation of metal on the cold walls of the furnace jacket or on the graphite crucible at intermediate temperatures can, with certain metals, cause considerable

chemisorption losses of gas. Sloman reduces the amount of evaporation by diluting the metal in an iron bath in order to reduce its activity. This, he claims, also facilitates oxide or nitride dissociation, particularly with metals having high melting points. We have found the metal-bath technique to be of little or no advantage in micro-analytical work.

Gas analysis of metals on a micro scale has several marked advantages. The small sample required has particular value in determinations involving the rarer metals; it also facilitates the study of homogeneity in metal specimens. However, for samples with gross inhomogeneities and inclusions, sampling difficulties may arise. Efficient heating of the large crucibles used in macro-analysis, without large and expensive induction heating units, requires careful design of the crucible and considerable skill in its construction and assembly. All this is time-consuming and is rendered unnecessary by the micro system in which simple disposable crucibles can be used in conjunction with an 8-kilowatt heater. The micro method involves no more difficulties than the large-scale method and it is considerably more rapid, so making it suitable for routine work.

Micro-scale vacuum fusion has several applications. A number of papers have described various systems operating on more or less the same fundamental principles, but which vary somewhat in detail, specific purpose, and method of gas analysis.

The determination of oxygen in uranium has been given considerable attention by a number of workers. Rice<sup>4</sup> and Lipkin and Perlman<sup>5</sup> have described equipment suitable for this purpose, and Seifert, Gilpatrick, Phipps and Simpson<sup>6</sup> describe a similar system in which the gas is extracted from cupric oxide, silica, uranium trioxide, uranium dioxide or uranium nitride.

Little detail is given in these papers of methods of analysis, and in some work the evolved gas is assumed to be all carbon monoxide. This assumption, as will be shown later, can lead to serious errors.

Guldner and Beach<sup>7</sup> and Walter<sup>8</sup> also describe in detail another variation of the vacuum fusion method on a small scale, but they use a somewhat unnecessarily complicated crucible and furnace system. In the work described below, the apparatus incorporates ideas taken from all these previous investigators, but also has new features that lead to simpler construction and facilitate speedy manipulation with no loss of accuracy.

#### DESCRIPTION OF THE APPARATUS

##### GENERAL CONSTRUCTION—

Fig. 1 illustrates the apparatus in its finally developed form. The heavily outlined part indicates the main line along which the gas sample is transported. In this part, mercury cut-offs are used instead of taps, so that the gas sample does not come into contact with grease at any stage. The parts of the system lightly outlined are the ancillary units required for operating the cut-offs, and so on. All ground joints are sealed with black wax, which is applied lightly so that it is not extruded into the interior of the vacuum line on assembly. All the mercury cut-offs except D are of the normal type and are set at approximately barometric height above the reservoirs; they have stainless steel balls fitting into ground seats to ensure good sealing. In cut-offs B and C the ball seal ensures collection of a constant volume of gas on the backing side of the pump, 13.

The cut-off, D, is of special wide bore to allow fast pumping. The all-glass ball seals are carefully ground to withstand a pressure of at least two atmospheres when mercury-sealed. This enables a pressure of 15 lb per sq. inch more than atmospheric to be applied to the reservoir of this cut-off. By doing this, it is possible to open the system to atmosphere on either side of the cut-off without disturbing the vacuum on the opposing side. This is useful when crucibles and samples are being charged, as the furnace side alone need be opened to the atmosphere and the subsequent outgassing of the mercury pumps is avoided. Before opening cut-off D, after having had the furnace open to the atmosphere, it is essential to evacuate the furnace side again. This can be readily done via the auxiliary lines shown, *i.e.*, through taps G, H and J, or K and L.

The whole system is evacuated by the all-glass two-stage mercury diffusion pump, 19, backed by the two-stage rotary pump, 20. The other pumps, as described later, are for gas handling only.

At the furnace end of the system a small gas burette, 11, is provided, by which small amounts of gas introduced via the mercury lift, 21, can be measured. The gas is measured by a pressure, volume and temperature determination when compressed into the precision

bore capillary, 22, which is 2 mm in diameter. The gas can be released into the system by drawing down the mercury to the position shown in Fig. 1, and can be used for calibration purposes or for adding known amounts of other gases to the gas sample.

#### FURNACE DESIGN AND SAMPLE-ADDING MECHANISM—

The apparatus and graphite crucible must be thoroughly outgassed as described below before the metal sample is added. Once outgassed the graphite must be kept under high vacuum at a temperature of at least 1100° C, or the blank gas value will not remain constant. It is essential to have the metal samples already in the system, so that they can be added to the crucible when required. It is possible to analyse successively five separate samples with one graphite crucible in this system.

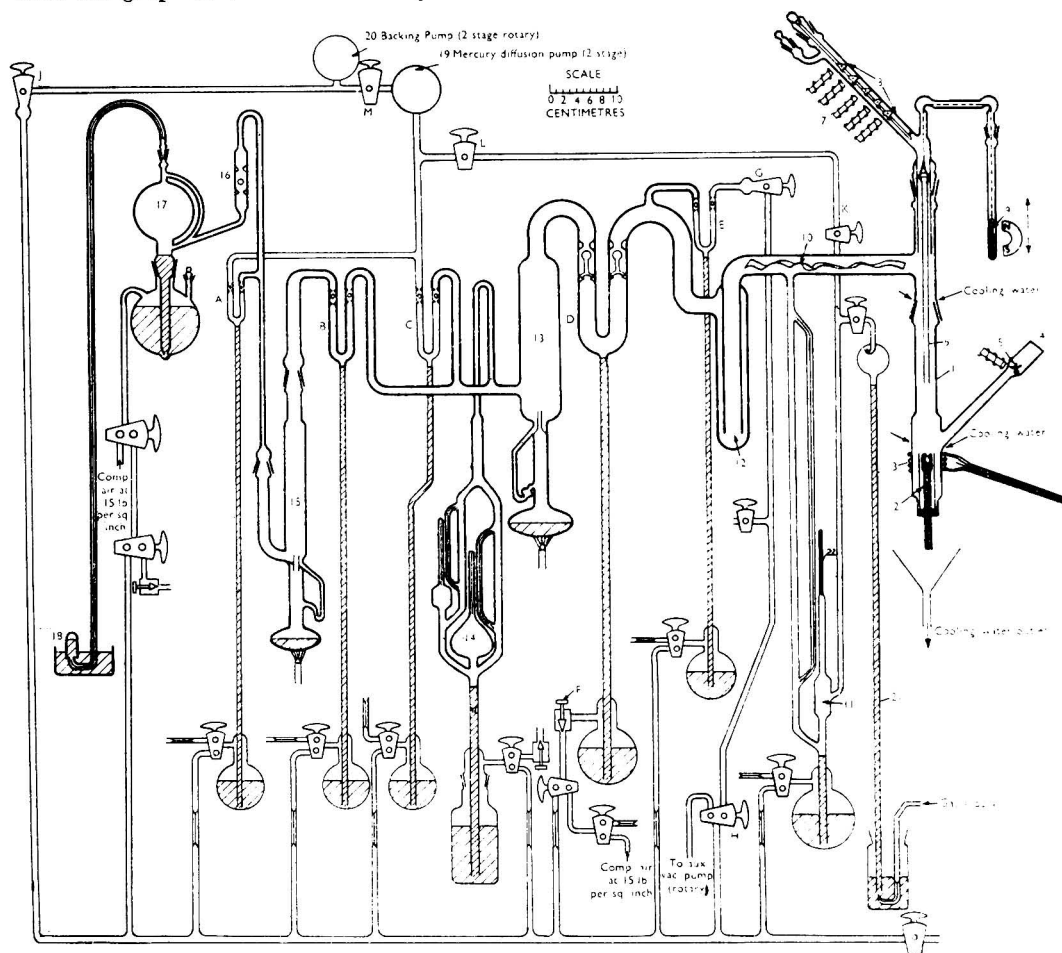


FIG. 1. Vacuum fusion apparatus for micro-scale gas analysis

- |  |  |   |
|--|--|---|
| 1 Silica furnace tube  | 10 Gold foil for protection of furnace from mercury      | 18 Gas collecting thimble for analyses in Blacet - Leighton apparatus |
| 2 Graphite crucible and heat shield                              | 11 Gas burette for testing purposes                      | 19 Two-stage all-glass mercury diffusion pump                         |
| 3 H.F. heating coil  | 12 Safety trap   | 20 Two-stage rotary backing pump                                      |
| 4 Silica window for viewing with disappearing filament pyrometer | 13 Two-stage all-glass mercury diffusion pump            | 21 Mercury lift for introduction of other gases                       |
| 5 Solenoid-operated trap door for protecting viewing window      | 14 McLeod gauge, double range, for measuring evolved gas | 22 Gas burette measuring capillary (made from precision bore tubing)  |
| 6 Movable silica funnel for sample addition                      | 15 Two-stage mercury diffusion pump (small silica)       |   |
| 7 Solenoids  | 16 Mercury non-return valve for Toepler pump             |   |
| 8 Solenoid-operated trip buckets for sample storage              | 17 Toepler pump  |   |
| 9 Soft-iron-in-glass counterweight for funnel (6)                |  |   |
- A, B, C, D, E, Cut-offs  
 F, Constriction  
 G, H, J, K, L, M, Taps

The samples are held in the hinged trip buckets, 8 (Fig. 1), which are suspended between two glass-covered tungsten rods attached to the stopper at the top. Each of these buckets has sealed into its base a small piece of soft iron by which it can be tipped up by a solenoid, 7, so projecting the contents into the inclined tube. The solenoids are actuated through a selector switch with press-button control so that any particular sample can be chosen. The metal sample falls into the silica funnel, 6, which, during the addition, is lowered by magnetic neutralisation of its counterweight, 9, so that its tip projects into the mouth of the crucible. As soon as the sample is introduced into the crucible the funnel is raised magnetically by

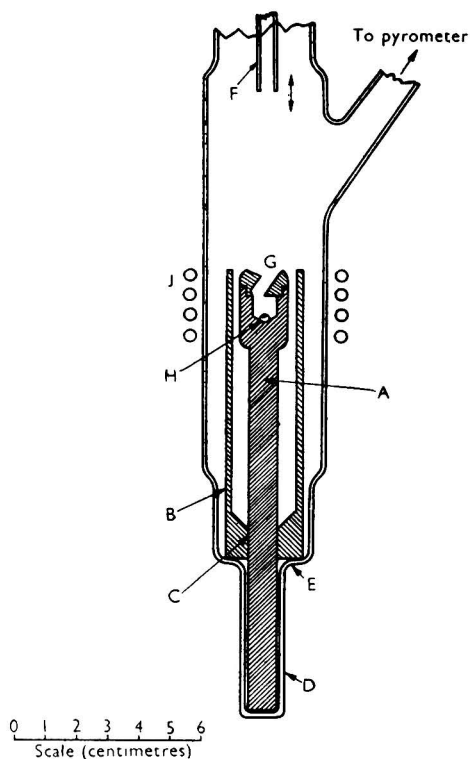


Fig. 2. Graphite crucible, heat shield and silica furnace assembly. A, crucible; B, heat shield; D, constriction; E, shelf; F, funnel; G,  $\frac{3}{16}$ -inch hole; H, sample; J, heating coil

the counterweight, which is attached to the funnel by a stainless steel chain and is adjusted so that friction will hold the funnel stationary in any position. The crucible is kept at a temperature between  $1100^{\circ}$  and  $1200^{\circ}$  C while the silica is in contact with it.

In Fig. 2 the detailed construction of the crucible and lower part of the clear silica furnace jacket is shown. The crucible and heat shield are made separately from best-grade fine-grained graphite; there is a good tight sliding fit at C for assembly.

The stem of the crucible is held firmly in the lower constriction, D, of the silica jacket and the heat shield rests on the shelf, E. All the components described here are circular in section. The top of the crucible must be flush with the top of the heat shield. The tightly fitting cap of the crucible has a shallow recess at the top to take the funnel, F, and has a hole, G,  $\frac{3}{16}$  inch in diameter, drilled at approximately  $45^{\circ}$  through it. The hole is drilled so that the sample at H is invisible from the exterior. In this way, effusive evaporation of metal is reduced to a minimum without seriously hindering gas evolution.

The crucible is heated by means of the high-frequency heating coil, J. To minimise high-frequency heating of the heat shield, the shield is split vertically for about 7 to 8 cm by two fine saw cuts diametrically opposite each other.

In constructing a furnace of this type, care must be taken to match the work to be heated

and the work coil to attain maximum heating efficiency. The greater the sectional area of the coil occupied by the work the greater is the efficiency, but this consideration must be balanced against the necessity for having reasonable clearance between the walls of the silica vessel and the graphite shield. If this clearance is too little the temperature gradient in the silica becomes dangerously high. The work coil should have the requisite number of turns for maximum efficiency; this can only be finally determined by experiment. The temperature of the graphite is measured by a disappearing-filament pyrometer, which directly faces the inclined mouth of the crucible through the window, 4 (Fig. 1), in the side-arm. The side-arm has a magnetically operated flap, 5, to prevent condensation of metal and graphite on the window.

The silica vessel is cooled by four jets of water; two impinge on the area around the cone and socket joint between the silica and glass parts of the apparatus and two are directed just above the coil. The water flow must be arranged so that a continuous film of fast-flowing water covers the whole of the silica vessel. The free flow of water over the heating coil does not give rise to any difficulty with the type of heater used in this work. The work coil should have just enough clearance to enable a free flow of water around the silica jacket. It should not touch the jacket at any point. A "Radyne" heater, with a maximum continuous rating of 8 kilowatts, operating at 450 kilocycles and specially adapted for graphite heating, was used in this apparatus. With a specially constructed transmission line, 6 kilowatts could be dissipated in the graphite to produce a maximum temperature of 2200° C. The high-frequency heater is provided with a control unit that gives a continuous range of temperature from about 1100° to 2200° C. Fig. 3 shows a general view of the whole apparatus in operation and Fig. 4 shows the details of the furnace and sample-adding device. For safety, the furnace is surrounded on the three working sides by firmly held sheets of "Triplex" glass (front removed in Fig. 4).

The principle use of the trap, 12 (Fig. 1), is to prevent water being sucked back into the diffusion pump in the event of a fracture of the furnace tube. It is unnecessary to cool this trap, as mercury vapour does not appear to interfere with the operation of the furnace. However, as a precaution, a strip of gold foil, 10 (Fig. 1), was inserted to collect any mercury diffusing back. This foil is regularly cleaned by ignition.

#### OPERATION OF THE APPARATUS

##### INITIAL EVACUATION AND OUTGASSING—

After the crucible and samples have been set in position, the initial evacuation is carried out by the rotary pump, 20 (see Fig. 1), via the auxiliary vacuum line, through taps J, H and G and cut-off E. The reservoir taps of the cut-offs, McLeod gauge, Toepler pump, and so on, are all turned to this line so that the reservoirs are at the same pressure as the system. In this way, no mercury can fly over. When evacuation is complete, these taps are closed, H is switched to the auxiliary vacuum pump (not shown) and M is opened. At this stage, the mercury in the cut-offs is set at the positions shown in the diagram, except for E, which is closed. The three mercury diffusion pumps are started and left until the pressure indicated by the McLeod gauge is less than  $10^{-5}$  mm of mercury.

With the cooling water flowing, the graphite crucible is raised slowly to the outgassing temperature and maintained at that temperature for several hours. To minimise evaporation of the graphite this temperature should not exceed 2000° C. Any gas evolved from the graphite or the pumps is extracted continuously through the main pump, 19. During this process and at any other time when not in use, the mercury in the burette, 11, should be maintained at barometric height, so sealing off this unit from the main system.

The gas evolved from the furnace is measured by the increase in pressure on the backing side of the diffusion pump, 13, with cut-offs B and C closed. The gas is pumped into a constant volume, which is determined by releasing measured amounts of gas into the system via the burette, 11, and pumping it into the measuring space. The mercury pump is capable of operating against a backing pressure of several millimetres of mercury; the increase in pressure produced by 0.03 cu. cm is of the order of 0.10 mm of mercury (on the backing side), so that the system can pump effectively several hundred cubic millimetres into the measuring space. The McLeod gauge, 14, has a double scale; one is calibrated from 0 to 0.10 mm of mercury and the other from 0 to 3 mm. The volume enclosed between traps B and C and the pump in this apparatus is 244 cu. cm, giving a calibration factor of 0.0321 cu. cm for

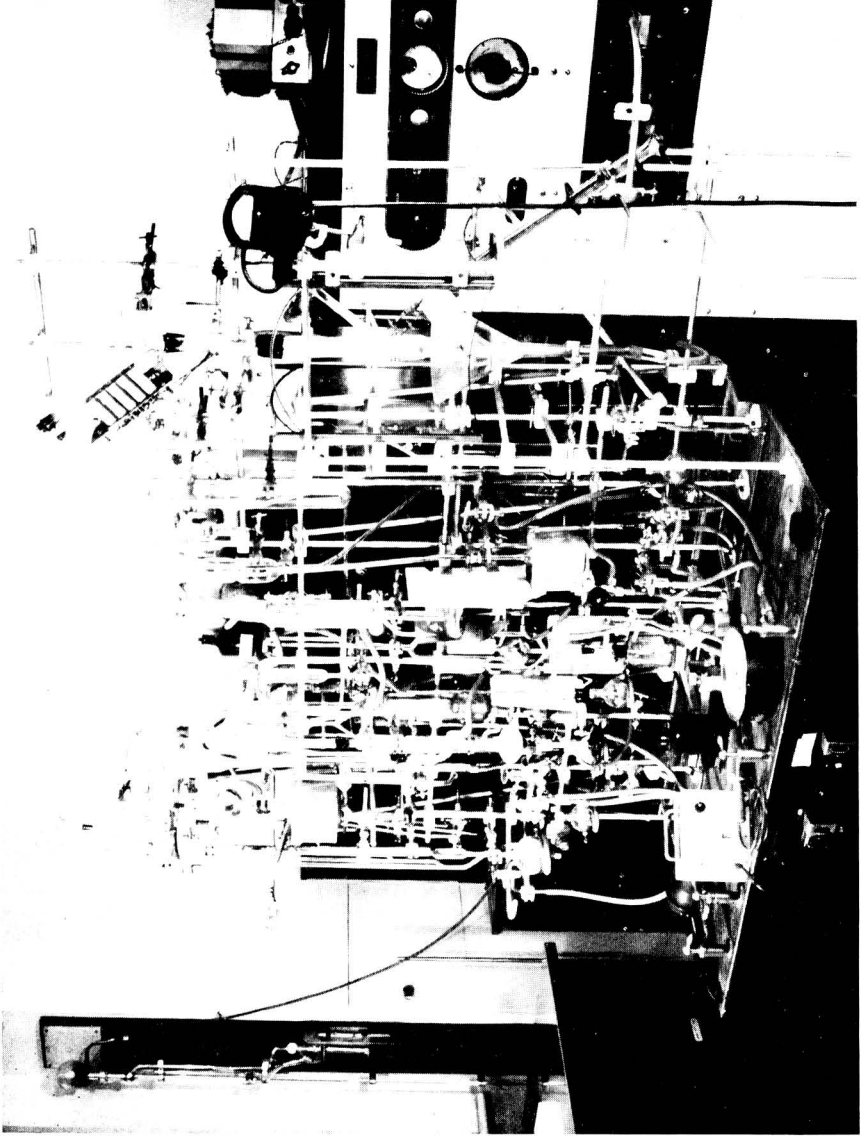


Fig. 3. General view of apparatus



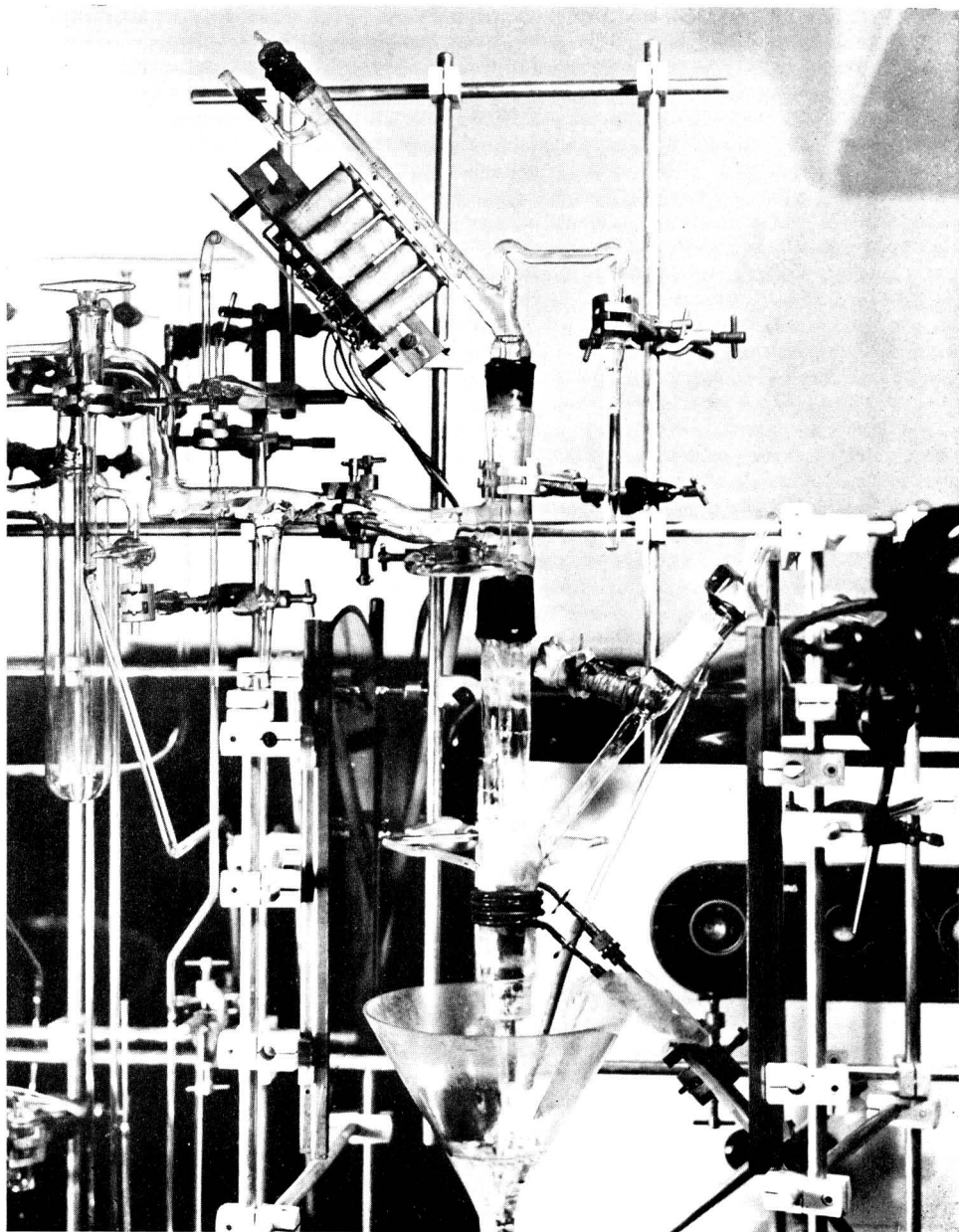


Fig. 4. View of furnace and sample-adding mechanisms

a pressure rise of 0.10 mm of mercury. Calibration graphs show that the accuracy of this measurement is limited only by the experimental error in reading the McLeod gauge, which is unlikely to exceed  $\pm 5$  per cent.

The progress of the graphite outgassing can be followed by closing B and C, setting the graphite at the operating temperature and collecting the gas during a period of about 5 minutes. The acceptable blank rate depends on the expected volume of gas from the metal sample and the time taken for it to be evolved. In general, the operating temperature should be high enough to give complete evolution of the gas in less than 5 minutes; with a gas volume of more than 10 cu. mm a blank rate of between 0.05 and 0.1 cu. mm per minute is negligible. With high working temperatures it may not be possible to produce a negligible blank rate, so a sample must be collected and analysed. The contribution of the blank value must then be allowed for in the gas sample.

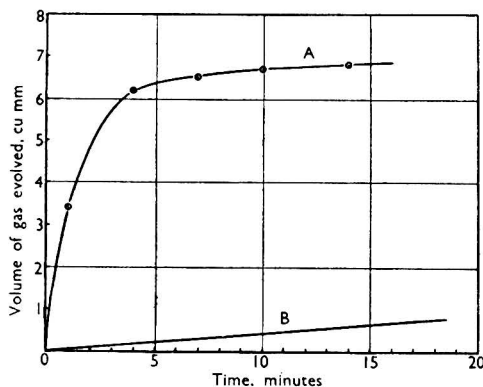


Fig. 5. Gas evolution of uranium sample at 1600° C. Curve A, gas from uranium plus blank value; curve B, blank value for graphite at 1600° C

As the blank rate increases with temperature, whereas the time for gas evolution decreases, it is obvious that there is a temperature at which the proportion of blank in the sample is at a minimum. If practicable this temperature should be used; in general, this seems to be the temperature at which the gas is evolved in about 5 minutes.

Another factor that determines the maximum operating temperature is the volatility of the metal. The maximum volatility permitted will vary with each metal and will depend on the chemisorptive properties. Some guidance can be obtained from the fact that uranium can be extracted satisfactorily at 1800° C, at which temperature its vapour pressure is about 0.01 mm of mercury.<sup>9</sup>

Some workers take great trouble to flame and outgas all the glass parts of their apparatus. This is unnecessary, as the final criterion of the contribution of extraneous gas sources is the blank rate produced by test. After outgassing hardly any gas is collected when the graphite is cold, so that any other effect is negligible.

#### EVOLUTION AND COLLECTION OF GAS FROM METAL SPECIMEN—

When the blank rate is reduced to a satisfactory value, all the cut-offs are opened and the whole system pumped for a few minutes. The graphite is cooled to about 1200° C and the silica funnel lowered. Cut-offs B and C are closed, the sample is immediately introduced into the crucible and the funnel raised. The temperature is then raised quickly to the operating value and the progress of the collection of the evolved gases observed at regular intervals by the McLeod gauge. Gas is collected until the rate of evolution is equal to the original blank rate. A typical gas evolution graph for a uranium sample is shown in Fig. 5. From this it is clear that all the gas in the metal is evolved in 5 to 6 minutes and thereafter only the gas blank is collected. The factor controlling the rate at which the gas appears in the McLeod system is almost always the rate of evolution. The pumping speed is high; 30 cu. mm of gas can be transferred from the measuring burette to the McLeod gauge in less than 1 minute. It is essential to have a fast removal of the evolved gas to avoid reverse reactions (see below, p. 422).

When gas evolution is complete, the cut-off, D, is closed, the McLeod gauge pressure and temperature are read carefully and the crucible is cooled to 1200° C to await the next sample. Once a sample has been added it is essential to maintain the crucible at the working temperature for the minimum possible time and never to exceed this temperature, otherwise excessive metal evaporation will cause chemisorption losses in subsequent samples.

By closing cut-off A and opening B, the gas is then transferred completely within a few minutes to the backing side of pump 15. This portion includes the bulb of the Toepler pump, 17, which constitutes the greatest proportion of the backing volume because the line between pumps 15 and 17 is made as narrow as possible. About 3 or 4 strokes of the Toepler pump suffice to transfer over 99 per cent. of the gas to the thimble, 18; it can then be analysed

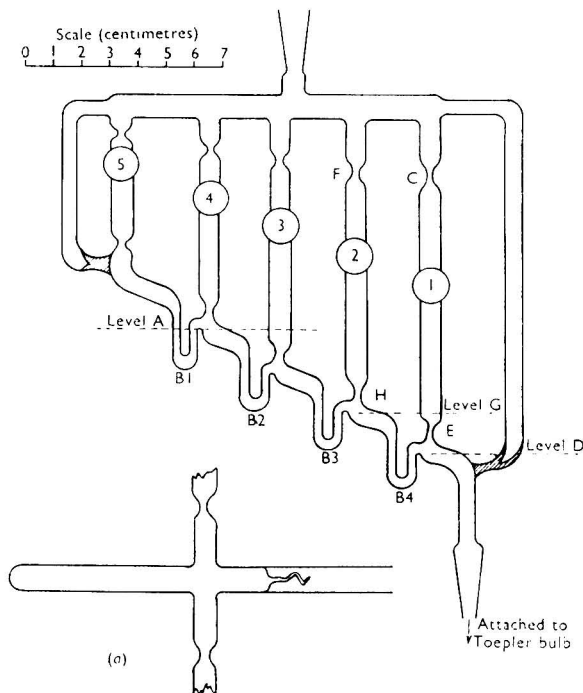


Fig. 6. Multiple breaker-seal unit (front view). Inset (a), side view of one breaker-seal tube. B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub>, B<sub>4</sub>, U-tubes; C, E, F, H, constrictions

by the Blacet - Leighton method.<sup>10</sup> As soon as the gas is pumped through by pump 15, B can be closed and C and D opened for a few minutes to clear the system, and the whole procedure can be repeated with a second sample in the crucible. In this way it is possible to collect the gas evolved from five separate samples in less than 2 hours. The greatest delay occurs in the gas analysis and the preliminary outgassing of the graphite.

There are several advantages in carrying out the extractions in rapid succession, apart from speed. If an appreciable interval occurs between two extractions, the blank rate rises, particularly if the crucible is cooled to room temperature, and considerable heating at temperatures greater than the operating temperature is necessary to lower the blank rate. This procedure can cause appreciable evaporation of the metal. Once a negligible blank rate has been established it will remain negligible if not more than 5 to 15 minutes elapse between each extraction and the temperature is maintained at about 1100° to 1200° C in this time interval.

Alternatively, the gas evolved can be analysed by a mass spectrometric method, in which event a collecting bulb of about 15 ml capacity, with a breaker-seal, is attached via a constricted arm to the top of the Toepler pump. The gas contained in the Toepler bulb is compressed into it and the constriction is sealed off with a flame. By further heating at the

constriction, the tube containing the gas sample can be removed without breaking the vacuum. As the Toepler bulb contains over 80 per cent. of the gas, the remainder being in the line to pump 15, a considerable fraction of the gas is taken as a sample for complete analysis.

To enable the five gas samples to be collected in breaker-seal tubes successively, without reducing the vacuum when replacing the tube, a special multiple breaker-seal unit has been designed; it is shown in Fig. 6.

This unit is fitted to the top of the Toepler pump by the A10 cone; a small tap with a capillary bleed line to atmosphere is fitted to the top socket. The five successive gas samples are collected in the breaker-seal tubes 1 to 5. After B and C (Fig. 1) are closed, the Toepler pump and this unit can still be evacuated continuously through A (Fig. 1). Just before A is closed for collection of sample 1, the mercury in the Toepler pump is allowed to rise to the level A (Fig. 6) and then drawn back again. Since the pressure is the same on either side of the small U connections, B, mercury remains behind in each of them and seals off the breaker-seal tubes from each other at the lower end. The constriction at C is then closed and separated from the upper manifold. Cut-off A (Fig. 1) is closed and the gas sample transferred via pump 15, with B (Fig. 1) open to the Toepler bulb, as described earlier. On raising the mercury in the Toepler pump to the level D (Fig. 6) nearly all the contents of the bulb are compressed into the breaker-seal tube 1, which is sealed off at E and removed for mass-spectrometric analysis. As the total pressure of the gas in the tube is never more than 2 or 3 mm, the mercury in B<sub>4</sub> effectively seals tube No. 1 from the succeeding ones.

Gas sample No. 2 should be ready for collection and is stored on the backing side of pump 13, with B and C (Fig. 1) closed. Cut-off A is opened for a few minutes to flush out the residue of the previous sample. During this period the mercury must be cleared from B<sub>4</sub> to open the path to breaker-seal 2. This is achieved by slowly increasing the pressure of air via the bleed line on the top of the unit. This blows the mercury in B<sub>4</sub> back into the Toepler bulb but does not affect B<sub>1</sub>, B<sub>2</sub> and B<sub>3</sub>, since the pressure will be equal on either side of these U-tubes. When this is effected and all the added air has been removed via A (Fig. 1), the constriction, F, is closed, as was C previously. Cut-off A is then closed and the second gas sample pumped into the Toepler pump. On raising the mercury to the level G, sample 2 is pushed into tube 2, which can then be sealed off at H, and removed as was tube 1. The procedure is repeated for each of samples 3, 4 and 5. In this way the gas from all the samples is evolved and collected without breaking the vacuum in any part of the apparatus at any stage and with little delay between samples. The frame holding the breaker-seal tubes is so constructed that new tubes can be readily fitted by a competent glass-blower.

#### ANALYSIS OF GAS—

*Mass spectrometry*—This method is speedy and highly sensitive; it has an over-all accuracy of about  $\pm 10$  per cent. Gases other than those present in the graphite can be determined at concentrations equivalent to about 0.1 part per million in 100-mg samples of metal.

The main disadvantage of this method is the great difficulty in differentiating between the two major components, carbon monoxide and nitrogen, which are of equal mass. This can be overcome with some considerable loss of accuracy by determining the fraction of mass 29, which is principally the monoxide of <sup>13</sup>C, and multiplying the value found by the <sup>12</sup>C/<sup>13</sup>C abundance ratio (88.5) to obtain an estimate of the total carbon monoxide in the fraction of mass 28. But as the fraction of mass 29 is so small, considerable errors arise if any impurity of mass 29 is present in the gas. Impurities of mass 29 are quite likely to be met, as traces of hydrocarbons are frequently present in the graphite.

*Blacet - Leighton method*—The Blacet - Leighton method<sup>10</sup> of gas micro-analysis has been applied with considerable success and is now generally used when the gas sample is larger than 10 cu. mm. The collection of the gas in a Blacet - Leighton thimble requires much simpler apparatus than the mass spectrometer breaker-seal; manipulation is also easier. Nevertheless, for samples smaller than 10 cu. mm, the mass spectrometer is more reliable.

#### EXPERIMENTAL

##### CRUCIBLE AND FURNACE DESIGN—

In the earlier work a heat shield was not used and the furnace tube had an internal diameter of only 30 mm. This was similar to the system used by Rice<sup>4</sup> and Lipkin and Perlman.<sup>5</sup> At 2000° C there was considerable evaporation of graphite on to the walls and on

two occasions the furnace tube cracked during a temperature change. The radiant heat absorption of the graphite film probably caused intolerable thermal gradients in the silica. To eliminate the danger, the heat shield was added and the furnace tube widened to 40 mm. The heat shield also gave better thermal efficiency and partly compensated for the loss in coil efficiency at the larger diameter.

The first heat shields projected about 1.5 cm above the top of the crucible, but it was noticed that the gas recovery in a batch of uranium samples consistently decreased in the third, fourth and fifth samples. This was found to be due to chemisorption by uranium, which had evaporated and become condensed on the upper part of the heat shield; its temperature (1100° to 1300° C) was ideal for rapid reversal of the reaction.  $\alpha$ -Counting tests on parts of the heat shield showed that the evaporation was effusive, as no part of the heat shield hidden from the uranium was appreciably contaminated.

A simple way of testing the system for losses of this type is to add known amounts of carbon monoxide or nitrogen via the burette, 11, while maintaining the furnace containing the metal at the operating temperature (after thoroughly outgassing the metal) and with cut-off D closed. The gas is left in contact with the system for a few minutes and then pumped off, and the amount recovered is compared with the amount added.

TABLE I

## RECOVERY OF ADDED GAS WITH DIFFERENT TYPES OF HEAT SHIELD

Type of heat shield	Gas	Temperature of crucible, ° C	Volume of gas added, cu. mm at S.T.P.	Volume of gas recovered, cu. mm at S.T.P.	Recovery, %
Old design projecting above crucible	CO	1600	45.7	6.0	15
	CO	1600	16.3	4.5	30
	CO	20	22.2	20.2	90
	N <sub>2</sub>	1600	55.0	0.0	0
	N <sub>2</sub>	1600	30.6	0.7	2
	N <sub>2</sub>	20	57.4	60.0	100
With top of heat shield flush with crucible top	CO	1600	6.5	5.7	90
	CO	1600	21.4	22.6	100
	N <sub>2</sub>	1600	18.8	10.7	60
	N <sub>2</sub>	1800	37.8	34.6	90
	N <sub>2</sub>	1800	12.1	11.1	90

Measured amounts of nitrogen and carbon monoxide were introduced into the system after 100 mg of uranium had been heated in the crucible for about 1 hour at 1800° C, so that considerable evaporation would have been expected. After a few minutes in contact with the furnace the gas was pumped away and measured in the usual manner. From the first part of Table I, with the projecting heat shield, it is clear that both the nitrogen and the carbon monoxide were substantially absorbed. Since it is well established that the formation of carbon monoxide from uranium oxide and graphite is rapid at 1600° C (Sloman and Harvey<sup>2</sup>), it is clear that the loss of carbon monoxide was due to chemisorption by the evaporated uranium on the heat shield, which was at about 1200° C. As it is not certain whether the decomposition of uranium nitride was complete under these conditions at 1600° C, it is probable that some of the nitrogen was lost by formation of nitride in the crucible. This is confirmed by the results at 20° C, which indicate that cold evaporated films do not cause loss and show also that the graphite when cold does not absorb appreciable amounts of the gas at the prevailing pressure. For the rest of the experiments the heat shield described on page 417 was used. The top of the shield was flush with the crucible top and out of the range of effusive evaporation. The much better recoveries with carbon monoxide at 1600° C confirm that the loss probably occurred by the reaction with evaporated uranium, whereas the reduced loss with nitrogen at 1600° C seems to confirm that some of the original effect was due to reaction of the nitrogen with uranium in the crucible. However, recoveries were good at 1800° C for nitrogen, which confirmed that this temperature is essential for complete dissociation of the nitride. The results shown in the second part of Table I indicate that for efficient recovery of oxygen and nitrogen from uranium a working temperature of about 1800° C must be used and the heat shield should be designed so that it does not collect evaporated uranium.

In these experiments an open graphite crucible was used. Subsequently it was found

that the results with uranium were improved even further by use of the crucible with the detachable cap with the inclined entry port, as described above (p. 417).

The conditions in these experiments with regard to concentration of gas in contact with the evaporated film and the time of exposure were much more severe than those met with in actual gas determinations, in which the gas is pumped away as soon as it is evolved and the pressure is always low compared with the static conditions in the gas addition experiments.

Hydrogen is completely lost from uranium at quite low temperatures<sup>11</sup> and its quantitative evolution should not produce any difficulties. Nevertheless, Sloman and Harvey<sup>2</sup> mention

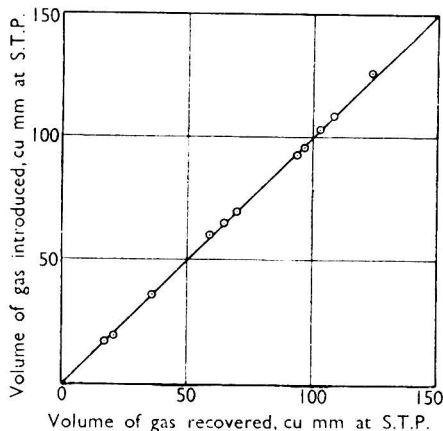


Fig. 7. Gas transfer efficiency

an anomalous effect with hydrogen; its solubility in uranium increases with increase in temperature. As they use a steel bath they must maintain a temperature of at least 1550° C; at this temperature hydrogen is appreciably soluble. In our apparatus the sample is added at about 1200° C and all the hydrogen is released and pumped away before the temperature is raised.

#### GAS TRANSFER EFFICIENCY—

To test the gas transfer efficiency, the delivery of the Toepler pump was connected to a gas burette identical to burette II in Fig. 1. Measured volumes of air were introduced into the system by the burette, II, and transferred by the pumps and Toepler pump to the collecting burette. The graph (Fig. 7) shows that no significant amount of gas is lost or gained during the procedure. In tests carried out without the second pump, 15, in the system, about 10 strokes of the Toepler pump reduced the pressure in the McLeod gauge to about 0.0001 mm, which is equivalent to a residue of less than 0.05 cu. mm of gas at S.T.P. To attain this efficiency it was necessary for the delivery capillary of the Toepler pump to have an internal diameter of 0.5 mm.

In tests with a sample of approximately 30 cu. mm, with the system in its present form, it was shown that more than 99.5 per cent. of the gas was pumped into the McLeod gauge from the furnace in about 1.5 minutes. The second pump, 15 (Fig. 1), left less than 0.1 cu. mm in the McLeod gauge after 3 minutes, and 5 strokes of the Toepler pump accounted for 99.9 per cent. of the gas accumulated on the backing side of pump 15.

#### APPLICATION

The preparation of standard samples containing known amounts of gas is an extremely difficult problem in vacuum fusion work. The obvious method of approach is to use oxides and nitrides of the particular metal, since with many of them the gases do exist in chemical combination with the metal. However, it has been found that oxides and nitrides, even in an extremely fine state of subdivision, are much more difficult to decompose than when the elements are distributed throughout the metal. Also, in micro work, unweighable amounts of oxides or nitride would be required for a comparable standard. Satisfactory oxygen standards can be prepared for uranium by a quantitative surface oxidation process and it

has been found that a thin surface film decomposes readily at the normal working temperature for uranium.

#### URANIUM—

The apparatus used for preparing the standards is shown in Fig. 8. It is a constant-volume system, in which the amount of oxygen absorbed by the heated uranium specimen at A is measured by the change in pressure involved.

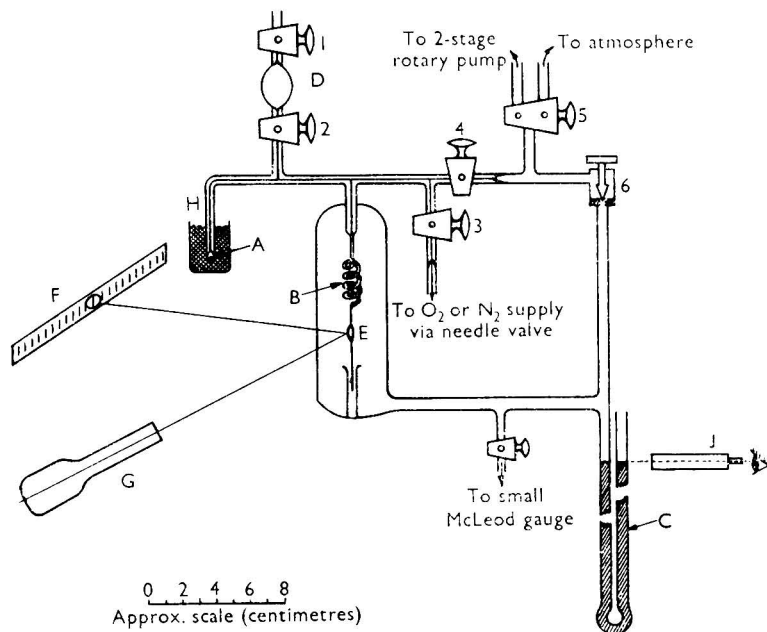


Fig. 8. Apparatus for preparation of uranium standards. A, sample; B, Bourdon-type gauge; C, manometer; D, calibrated bulb; E, mirror; F, scale; G, lamp; H, seal; J, cathetometer

The constant volume is that part closed off by the taps 2, 3 and 4 and includes the spiral of the all-glass Bourdon-type gauge, B. For maximum sensitivity this volume should be small. This part is mainly constructed from 1.5-mm diameter capillary tubing. About 30 to 50 mg of carefully cleaned uranium is sealed in at A by a joint at H, and the whole system is evacuated. Pure oxygen is then introduced at a pressure of about 30 to 40 cm of mercury into the small volume via 3. The pressure of the system is measured by using the Bourdon gauge (mirror, E, lamp, G, and scale, F) as a null-point instrument. The pressure in the outer jacket is adjusted by the taps 5 and 6 until the reading on the scale is zero; the pressure is determined by the open manometer C. With 2, 3 and 4 closed, the gauge is carefully balanced, the mercury level is then read by the cathetometer, J, and the uranium is carefully heated electrically on a small sand-bath. The amount of reaction is controlled by time and temperature; with experience this can be judged semi-quantitatively by the movement of the light spot on the scale. A temperature of 180° to 200° C gives a steady and controllable reaction rate. Removal of the sand-bath stops the reaction when required and the system is carefully brought back to within 0.2° C of its original temperature. The pressure change due to oxygen absorbed is measured by the change in the manometer pressure required to return the light spot to zero. The amount of oxygen absorbed for a given pressure change is independent of the absolute pressure of the oxygen and it is only the small pressure change, which can be accurately determined by the cathetometer, J, that is quantitatively significant.

It is essential to know the magnitude of the constant volume and this is found by measuring the pressure change on admitting air at atmospheric pressure to the evacuated

volume from the calibrated bulb, D. Specimens with as little as 10 cu. mm of added oxygen could be prepared with an accuracy of  $\pm 1.0$  cu. mm by this method.

The gas was extracted from a number of samples prepared in this way and also from the same uranium containing no added oxygen, and was then analysed by the mass spectrometric method. The uranium samples containing added oxygen were kept as small as possible so that the contribution of their normal oxygen content was a minimum.

In Table II the oxygen calculated from the carbon monoxide and dioxide of the gas in excess of that obtained from the same uranium unoxidised, is compared with the amount of oxygen added. The oblique-entry crucible was used in these experiments as before.

TABLE II

## RECOVERY OF OXYGEN FROM PREPARED URANIUM OXIDE STANDARDS

Order of analysis of sample	Operating temperature, 1800° C		Recovery %
	Volume of oxygen added, cu. mm at S.T.P.	Volume of oxygen recovered, cu. mm at S.T.P.	
1	15.0	14.5	97 $\pm$ 10
2	13.7	13.3	97 $\pm$ 10
3	18.0	16.7	93 $\pm$ 8
4	20.2	21.6	107 $\pm$ 5

The recoveries were all 100 per cent. within the experimental error and it is obvious that the system, operated as previously described, is satisfactory for oxygen in uranium. However, if relatively large uranium samples are used in an analysis the adsorption losses still appear in the fourth and fifth sample. If the sample weights are greater than 150 mg, it has been found that a maximum of three analyses can be carried out accurately in one determination.

Some similar experiments were carried out with an open crucible, 1 cm in internal diameter; the effect of uranium evaporation can be seen from the results shown in Table III. Between samples 1 and 2 the crucible was kept for about 30 minutes at 1800° C; subsequent recoveries were accordingly low.

TABLE III

## EFFECT ON OXYGEN RECOVERY OF URANIUM EVAPORATION FROM AN OPEN CRUCIBLE

Order of analysis	Operating temperature, 1800° C		Recovery, %
	Oxygen added, cu. mm at S.T.P.	Oxygen recovered, cu. mm at S.T.P.	
1	7.7	7.3	95 $\pm$ 15
2	14.0	10.8	77 $\pm$ 10
3	14.3	10.9	76 $\pm$ 10
4	24.2	18.0	74 $\pm$ 10

Artificially severe conditions were applied before samples 2, 3 and 4 were analysed, but Table III illustrates the effect of chemisorption by evaporated uranium even when the heat shield is flush with the top of the crucible. Greater consistency in normal samples has also indicated that the oblique-entry crucible is more reliable.

Many attempts were made to prepare nitrogen standards by this method, but the vacuum fusion analysis always gave a gas that was substantially carbon monoxide in spite of elaborate purification of the nitrogen. This failure was probably due to the high temperature required for the reaction of uranium and nitrogen (about 400° C), which caused considerable outgassing of oxygen from the capillary walls even when silica was used. Preliminary vacuum outgassing of the heated part of the system was useless; it caused spurious effects owing to re-absorption on admission of nitrogen followed by desorption at the reaction temperature.

## ANALYSIS OF URANIUM OF KNOWN GAS CONTENT—

A few analyses were carried out with a small piece of uranium taken from the same source as some immediately adjacent samples that were examined by Sloman by the macro method. Sloman's results showed that this sample was reasonably homogeneous, so that



the gas content of adjacent samples can be said to represent the true composition of the piece used in our analyses.

Table IV shows the results by the two methods of analysis. In the micro-determination, samples ranging in size from 120 to 190 mg were used. The results by the micro method are, within experimental error, similar to the results by the well-established macro method. The slight differences may be due to small-scale inhomogeneities, which are more likely to influence the micro method.

TABLE IV  
COMPARISON OF THE PROPOSED METHOD WITH SLOMAN'S METHOD  
FOR URANIUM

Analysis by micro-method				Analysis by Sloman's macro-method			
Sample No.	Oxygen, % w/w	Nitrogen, % w/w	Hydrogen, ml per 100 g	Sample No.	Oxygen, % w/w	Nitrogen, % w/w	Hydrogen, ml per 100 g
1	0.0078	0.0018	0.9	A	0.0070	0.0010	1.04
2	0.0095	0.0005	1.1	B	0.0083	0.0012	0.84
Mean ..	0.0087	0.0012	1.0	Mean ..	0.0077	0.0011	0.94

A and B are samples from either side of the micro-analysed metal. The gas evolved in these samples was analysed for carbon monoxide, carbon dioxide, hydrogen and nitrogen by the Blacet - Leighton method.

#### STEEL SAMPLES—

Steel and most other ferrous alloys have never given any real difficulties when their gas contents have been determined by the macro vacuum fusion method. The analysis of several standard steels provided by the British Iron and Steel Research Association was carried out in our apparatus and the results are shown in Table V.

At 1700° C the gas evolution was complete within 5 minutes and further heating or higher temperatures produced no more gas than that expected from the graphite blank rate, which was negligible in these analyses. Steel samples of 50 to 200 mg were used in this work, according to their total gas content.

TABLE V  
GAS DETERMINATION IN STEEL

Sample No.	B.I.S.R.A. Identification No.	Analysis by micro-method			B.I.S.R.A. analyses	
		Oxygen, % w/w	Nitrogen, % w/w	Hydrogen, % w/w	Oxygen, % w/w	Nitrogen, % w/w
1	784	0.007	0.004	0.0003	0.010	0.0045
2		0.010	0.002	0.0004		
3		0.006	0.006	0.0005		
Mean ..		0.008	0.004	0.0004		
1	4654	0.007	0.008	0.0003	0.004	0.0085
2		0.003	0.005	0.0001		
Mean ..		0.005	0.007	0.0002		
1	8652	0.006	0.04	0.0002	0.0145	0.016
2		0.01	0.03	0.0004		
3		0.02	0.02	0.0002		
4		0.01	0.05	0.0007		
Mean ..		0.012	0.035	0.0004		

The results by the micro method shown in Table V, although showing some scatter, are regarded as satisfactorily close to the standard figures, considering the small amounts of gas involved. Again the scatter may be due to inhomogeneities sufficiently large to give differences in samples a few hundred milligrams in weight, but small enough to have negligible effect on the 5 to 20-g macro samples commonly used in the standardisation of these ingots.

We consistently found a small percentage of hydrogen in the samples, but no figures for this gas were reported in the B.I.S.R.A. analyses.

#### ZIRCONIUM—

Macro-analysed zirconium was supplied by Mr. H. A. Sloman, and an attempt made to analyse this metal on the micro scale met with little success. Sloman<sup>2</sup> reports that oxygen and nitrogen are readily evolved from zirconium at 1750° C, but in the micro system no gas could be collected at temperatures below 2000° C. At this temperature and even up to 2200° C gas evolution was slow and incomplete. As the furnace of the micro system is not designed to operate above 2000° C for prolonged periods, the work on zirconium was discontinued. The use of an iron bath did not effect any improvement. It is difficult to say why our experience with this metal differs so much from that of Sloman.

The difficulties with zirconium could probably be overcome by the use of a furnace designed to operate at considerably higher temperatures.

#### CONCLUSIONS

The results have shown that analysis of trace amounts of gases in steel and uranium can be carried out on the micro scale with an accuracy almost equal to the conventional macro method. The apparatus is in many ways simpler to operate at the micro level, particularly in regard to furnace design and assembly, and is probably more rapid.

The procedure has been reduced to a reliable routine and it has obvious advantages in application to analysis of rare and valuable metals.

The authors wish to thank Mr. A. A. Smales for his interest and valued advice in this work. Acknowledgments are also due to Mr. G. Palmer and his group for considerable assistance in mass spectrometric analysis of gas samples, and to Mr. J. Wright for advice in the Blacet - Leighton analyses. The excellent glass blowing of Mr. B. George was a decisive factor in the success of this work.

Finally, the authors wish to thank the Director, Atomic Energy Research Establishment, Harwell, for permission to publish this paper.

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## Apparatus for Automatic Control of Cathode Potential in Electro-analysis

BY J. F. PALMER AND A. I. VOGEL

Full details are given of an electronic instrument that has been constructed for the automatic control to within  $\pm 1$  millivolt of the potential at the cathode with respect to a standard reference electrode in electro-analysis. The parts of the apparatus include a D.C. output unit working from the A.C. mains for the supply of current at low voltage, a valve voltmeter and a high-tension power-pack: these can be used independently and should be of value in an analytical laboratory.

It is now generally accepted that an apparatus for the automatic control of cathode potential is very useful in an analytical laboratory, and many instruments have been designed for this purpose.<sup>1,2,3,4,5,6,7,8</sup> The instrument described has been built by the authors and was exhibited at the International Congress on Analytical Chemistry at Oxford, September, 1952. It is based on the principle originated by Harvey Diehl<sup>4</sup> in 1948, and is believed to

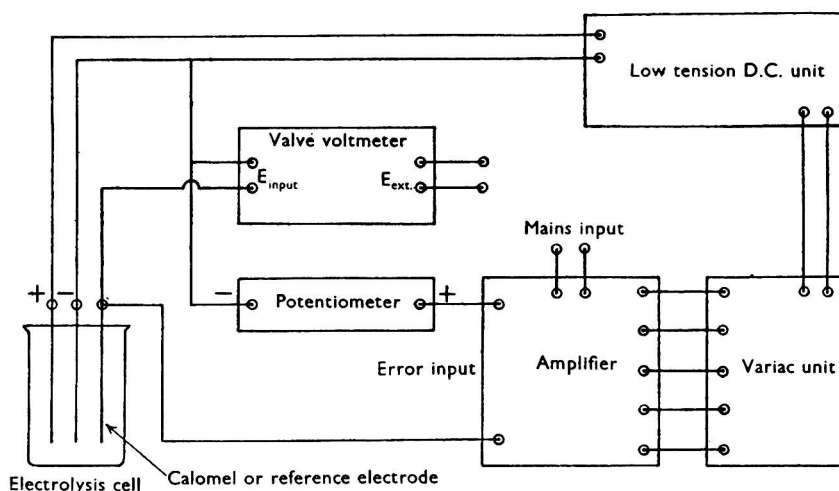


Fig. 1. Diagrammatic scheme of the apparatus assembly

be a great improvement on previous instruments; moreover, all the components used are obtainable in Great Britain. The prototype of this apparatus was described in the second edition of Vogel's "Textbook of Quantitative Inorganic Analysis."<sup>9</sup> In the form in which it was first devised, the operation of the circuits as described in the textbook did not give complete satisfaction, and in its present form many improvements have been incorporated.

The apparatus maintains the cathode potential constant at a pre-determined value in the range of 0 to 2.0 volts during electro-analysis. The current used in the electrolytic cell can vary from 10 amperes to a few milliamperes. A potentiometer that can be read directly in millivolts and a valve voltmeter are incorporated in the apparatus: both are directly calibrated against a built-in standard Weston cell.

The potential difference between the cathode and a reference electrode (usually a saturated calomel half-cell) can be set and automatically maintained within  $\pm 1$  millivolt of the set value. The ultimate sensitivity of the apparatus depends on the efficiency of stirring, the rigidity of the electrodes, and on any other factors that may contribute to mechanical instability. This maximum sensitivity is higher than is usually necessary for most applications of controlled-potential electro-analysis; a variation of  $\pm 10$  millivolts is generally sufficient.

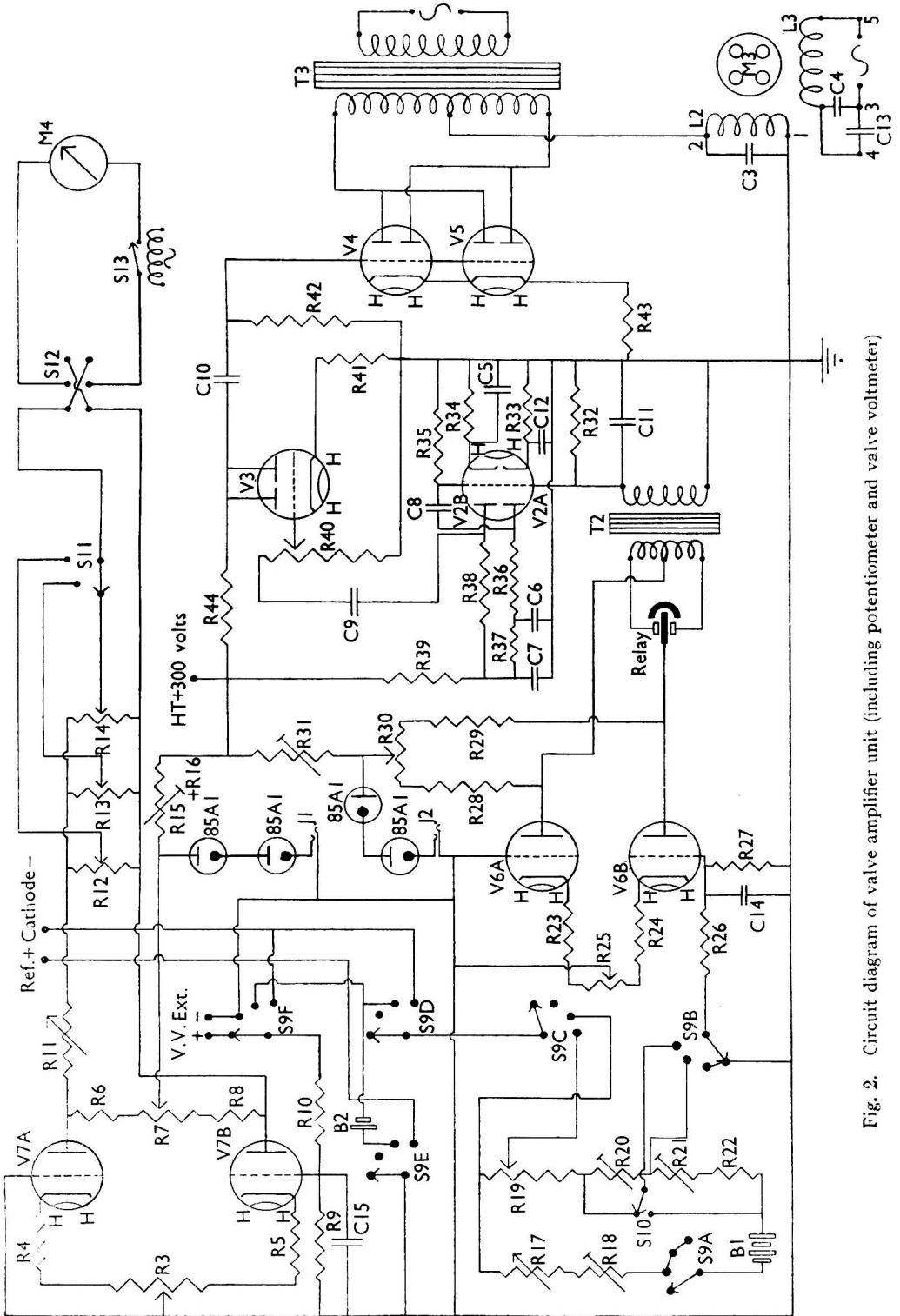


Fig. 2. Circuit diagram of valve amplifier unit (including potentiometer and valve voltmeter)

A diagrammatic representation of the whole assembly is shown in Fig. 1. The operation of the instrument depends on the detection of a D.C. "error voltage" between the potentiometer and the controlled cell (*e.g.*, cathode of the electro-deposition cell and saturated-calomel reference electrode). This "error voltage" is fed into a single-stage balanced D.C. amplifier, which has an input resistance of approximately 11 megohms; this resistance is large enough to ensure that polarisation of the calomel-cathode cell does not occur. The output of the D.C. amplifier is fed into a polarised relay, which converts the D.C. "error voltage" into 50-cycle square-topped alternating current. The alternating voltage is passed into a mu-metal step-up transformer and then into a three-stage resistance-capacity-coupled amplifier. The output of this amplifier is connected to the grids of two 12AU7 valves, joined in parallel, the anodes (plates) of which are joined directly to the secondary winding of the centre-tapped power transformer,  $T_3$  (Fig. 2). These valves therefore act as phase-discriminating power amplifiers; the phase relationship between the amplified pulse and that of the secondary winding of the transformer produces a rectified impulse in the motor winding  $L_2$ . The phase relationship between this impulse and its counterpart through the motor winding  $L_3$  determines the direction of rotation of the motor.

The reversible induction motor, geared to 1 r.p.m., is coupled to a 6-ampere capacity "Variac" transformer controlling the A.C. input to the electrolysis unit (Fig. 3). When a D.C. "error voltage" is present, the motor (which controls the variable arm of the "Variac" transformer) will rotate slowly and so alter the potential difference between the anode and cathode until the "error input" is reduced to zero, when the motor will cease to rotate. Hence by variation of the potential difference between the anode and cathode, the potential of the cathode in relation to the saturated-calomel reference electrode is maintained at a constant value.

The apparatus, excluding the electro-deposition cell and associated electrodes, is composed of six units—

1. A D.C. output unit, working from the A.C. mains, to supply the necessary current at low voltage to the electro-deposition cell.

2. A motor-driven "Variac" transformer to control the A.C. input to the D.C. output unit.

3. A potentiometer that can be set to the algebraic sum of the desired potential drop between the cathode and the potential of the reference electrode, or to any other pre-determined value.

4. A valve amplifier unit operating on a minimum stimulus of 1 millivolt D.C., which is connected to a reversible motor controlling the "Variac" transformer.

5. A valve voltmeter for measuring the cathode - reference cell potential ( $E_{\text{input}}$ ; Fig. 1) and also, if required, for external use ( $E_{\text{ext}}$ ).

6. A valve-stabilised power-pack for supplying the necessary high-tension and low-tension voltages for units 4 and 5.

#### D.C. OUTPUT UNIT—

The direct current required for the electrolysis is drawn from the A.C. mains by the use of the step-down transformer  $T_1$  (10 amperes, 15 volts), a selenium bridge rectifier, SE, and a smoothing filter circuit. Current at 3, 6, 9, 12 or 15 volts may be drawn from the transformer secondary by setting the switch  $S_1$ . The bridge rectifier can handle up to 20 volts, and the switch  $S_1$  ensures that there is an adequate margin with due regard to the maximum possible input from the "Variac" transformer.

The rectifier, SE (see Fig. 3), is followed by an inductance - capacity smoothing filter, consisting of a 3000- $\mu\text{F}$ , 24-volt, paper condenser,  $C_1$ , a 40 millihenry choke,  $L_1$ , and a 9000- $\mu\text{F}$ , 24-volt, condenser,  $C_2$  (three 3000- $\mu\text{F}$  condensers wired in parallel). Meter  $M_2$  is a triple-range ammeter (0 to 0.1, 0 to 1.0 and 0 to 10 amperes), and meter  $M_1$  is a triple-range voltmeter (0 to 1.0, 0 to 5.0 and 0 to 20.0 volts); these indicate the electro-deposition current and voltage, respectively. (The low-tension unit is fed from the socket  $P_2$  on the "Variac" transformer unit.)

#### "VARIAC" TRANSFORMER UNIT—

The mains input to the low-voltage unit, Fig. 3, is controlled by the "Variac" transformer, the variable arm of which is attached to a geared-down reversible two-phase four-pole induction

motor,  $L_2$  and  $L_3$ , Fig. 4. The motor, developing 5 ft.-lb torque per 1 r.p.m., is geared down to rotate at 1 r.p.m. Provision is made in this unit for controlling the motor either manually or by the amplifier. With the double-pole change-over switch,  $S_5$ , in the position shown

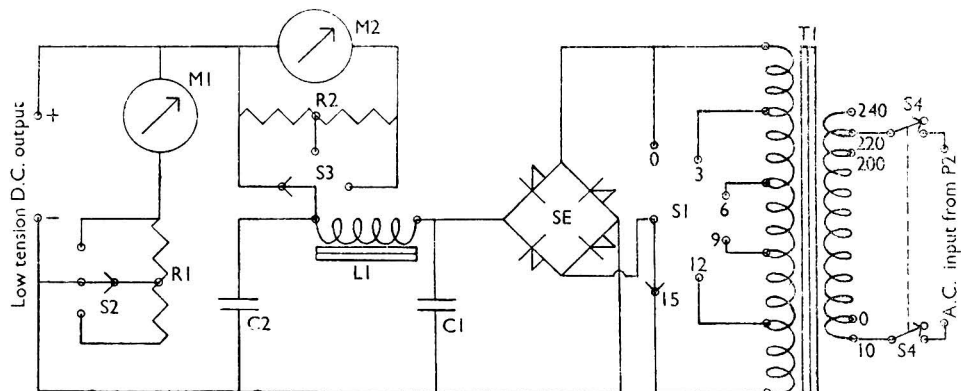


Fig. 3. D.C. low-tension unit circuit

in Fig. 4 and the six-pin plug from the amplifier inserted, the motor  $M$  will be controlled by the amplifier. With switch  $S_5$  in the alternative position, and the two-way manual motor-direction control unit, Fig. 5, plugged in at  $P_1$  in lieu of the six-pin plug from the amplifier, the "Variac" transformer can be set manually. The safety switches,  $S_6$  and  $S_7$ , are fitted to the "Variac" transformer unit to prevent the moving contact arm of the "Variac" transformer from rotating too far and so damaging the carbon brush. If the automatic

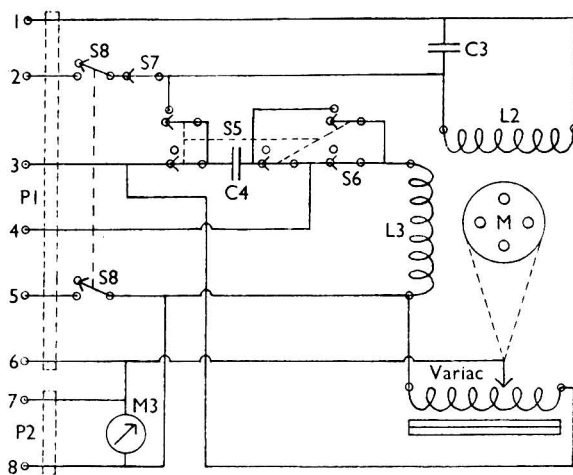


Fig. 4. Circuit diagram of motor-driven Variac unit

control, for some reason or another, does not operate correctly and, in consequence, either of the safety switches  $S_6$  or  $S_7$  is brought into action, the motor will cease to function. To bring the moving arm of the "Variac" transformer back to its normal working range, it is then necessary temporarily to connect the manual unit, Fig. 5. With the instrument working correctly, over-running of the moving arm of the "Variac" transformer should not occur.

The possibilities should be borne in mind that, if the standard reference electrode circuit is broken during the analysis owing to the presence of an air bubble, or if the switch,  $S_1$ , on the transformer, Fig. 3, is set at too low a value initially, either of the safety switches may come into operation. Switch  $S_8$ , Fig. 4, disconnects the windings when the motor is idle between determinations, and so prevents overheating of its windings.

The A.C. output of the "Variac" transformer is brought out to a socket,  $P_2$ , which is connected to the A.C. input of the low-tension unit, Fig. 3. The rotation of the motor in either direction will be indicated by the movement of the needle of the voltmeter,  $M_3$ .

#### THE POTENTIOMETER UNIT—

This incorporates a direct-reading "Colvern" helical potentiometer,  $R_{19}$ , Fig. 2, of exactly known resistance (about 100,000 ohms). The potentiometer is divided 1 to 1000, and so reads directly in millivolts when exactly 1 volt is placed across it. A resistance network of equal value,  $R_{20} + R_{21} + R_{22}$ , is placed in series with the direct-reading potentiometer,  $R_{19}$ . The toggle switch,  $S_{10}$ , by bringing this network into the circuit, extends the voltage range of the potentiometer,  $R_{19}$ , by 1.000 volt.

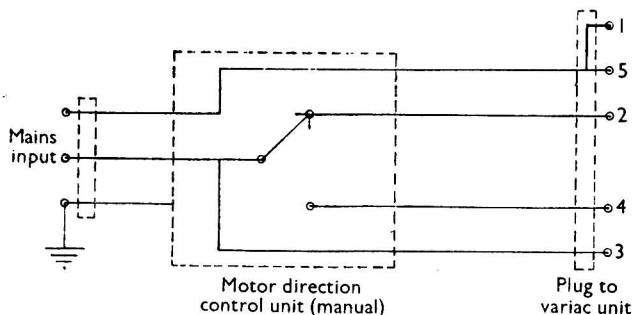


Fig. 5. Diagram of two-way manual motor direction control unit

The potentiometer unit is completed by  $R_{18}$  and the potentiometer calibration control,  $R_{17}$ . With 3 volts supplied by  $B_1$  (2 high-quality dry cells),  $R_{17}$  is adjusted so that there is exactly 1 volt across  $R_{19}$ . This is achieved by balancing the potentiometer unit against a Weston cell incorporated within the apparatus. The circuit is so arranged that if  $R_{19}$  is proportional to 1.000 volt, then  $R_{19} + R_{20}$  will be proportional to the potential of the standard Weston cell, *i.e.*, 1.018 volts. Hence, if the voltage across  $R_{19} + R_{20}$  is balanced against a Weston cell,  $R_{17}$  may be adjusted until an exact equality is attained. This is observed by feeding any "out of balance" voltage via the amplifier to the "Variac" transformer motor; the movement of the latter may be discerned audibly or by observation of the A.C. voltmeter,  $M_3$ , Fig. 4. The total value of the resistances  $R_{20} + R_{21} + R_{22}$  must be equal to  $R_{19}$ , and the pre-set potentiometer,  $R_{21}$ , is adjusted accordingly by measuring the combined resistance of  $R_{20} + R_{21} + R_{22}$  with a sensitive Wheatstone bridge in the initial calibration of the potentiometer.

#### THE VALVE AMPLIFIER UNIT—

The first part of this unit consists of a single-stage D.C. amplifier with two valves in a bridge circuit,  $V_{6A}$  and  $V_{6B}$ , Fig. 2. The input to the D.C. amplifier is introduced via the switch  $S_{9B}$ , which forms one of the sections of the operation selector switch. This switch has four positions: OFF, ZERO, CALIBRATE and USE. In the first two positions the input to the D.C. amplifier is earthed through  $R_{26}$ . During the initial adjustment of the amplifier, the manual zero control,  $R_{30}$ , is set at about the mid-point of its range and the amplifier is adjusted to zero by means of the pre-set zero control,  $R_{25}$ ; the latter need not be touched again unless a valve is replaced. The two valves of the bridge amplifier are shown separately in Fig. 2 for the sake of clarity, but are in reality combined in one glass envelope in the 12AX7 valve. When  $S_9$  is in the CALIBRATE position, the potentiometer will be balanced against the standard Weston cell as previously described; in the USE position, the potentiometer will be balanced against the cathode-reference cell potential.

*Note on the operation selector switch,  $S_9$* —This switch consists of six single-pole 4-way sections. The first section,  $S_{9A}$ , disconnects the potentiometer battery,  $B_1$ , when it is not in use. Section  $S_{9B}$  selects the appropriate input for the D.C. amplifier. Sections  $S_{9C}$ ,  $S_{9D}$  and  $S_{9E}$  are concerned with the inter-connections of the Weston cell, potentiometer unit, and the cathode-reference electrode cell. Section  $S_{9F}$  is the input selector switch of the valve voltmeter.

The operation selector switch,  $S_9$ , controls both the potentiometer - amplifier and the valve-voltmeter circuits. In the first position, OFF and v.v. EXT., the amplifier input is connected to earth, the battery  $B_1$  is disconnected, and the valve-voltmeter input leads are brought out to the valve-voltmeter external terminals on the panel. In the second position, ZERO, the amplifier input and the valve-voltmeter input leads are connected to earth, which permits the zero controls of the amplifier and valve voltmeter to be correctly adjusted. In the third position, CALIBRATE, the potentiometer is connected in opposition to the standard Weston cell; the latter is also connected to the input terminals of the valve voltmeter. In the fourth position, USE and v.v. CELL, the potentiometer is connected so as to oppose the cathode - reference cell potential, whilst the valve voltmeter indicates the magnitude of this potential.

The output of the D.C. amplifier is impressed between the vibrating reed of a polarised relay and the centre-tap of a mu-metal-screened step-up transformer,  $T_2$ . The condenser,  $C_{11}$ , serves to by-pass all higher frequencies to earth and its value is best determined experimentally; the optimum capacity lies between 0.01 and 0.1 microfarad. The output of the transformer,  $T_2$ , is passed into a three-stage A.C. amplifier, which incorporates two stages of resistance-capacity-coupled amplification wired in cascade for which a single 12AX7 valve,  $V_{2A} + V_{2B}$ , is used, followed by another resistance-capacity-coupled stage for which a 12AX7 valve,  $V_3$ , strapped as a single valve, is used. A potentiometer,  $R_{40}$ , is inserted in the grid circuit of the final 12AX7 valve to serve as a sensitivity control for the complete amplifier, and this can be used to prevent "hunting," which would occur if the amplifier were over-sensitive.

The output of the resistance-capacity-coupled amplifier is fed to the grids, connected in parallel, of two 12AU7 valves,  $V_4$  and  $V_5$  in Fig. 2, which act as phase-discriminating amplifiers, as their anodes (plates) are connected directly to the secondary of the centre-tapped mains transformer,  $T_3$ , and so control the direction of rotation of the "Variac" transformer motor through  $L_2$ , Figs. 2 and 4. The condenser,  $C_{13}$ , is coupled in parallel with condenser  $C_4$ , Fig. 2, when the amplifier is connected to the "Variac" transformer unit. This condenser increases the torque of the motor to a satisfactory value when it is under automatic control.

#### VALVE VOLTMETER—

The circuit (Fig. 2, upper left-hand corner extending to  $M_4$ ) is of the Wheatstone bridge type; the two arms consist of equal resistances,  $R_6$  and  $R_8$ , of 30,000 ohms each, whilst the other two arms are formed by the internal resistances of the two parts,  $V_{7A} + V_{7B}$ , of the 12AX7 valve. The control grid of one of the parts,  $V_{7A}$ , is earthed. The voltage to be measured is applied to the control grid of the other part,  $V_{7B}$ ; this causes an unbalance in the circuit, which is indicated on the meter,  $M_4$ , the deflection being linear to well within 1 per cent. As for the D.C. amplifier there is a pre-set and a manual zero control, and the initial adjustment to zero is carried out by setting the manual zero control,  $R_7$ , to about the mid-point of its range and turning the pre-set control,  $R_3$ , to give no deflection on  $M_4$ . The manual sensitivity control,  $R_{11}$ , is used in the CALIBRATE position of the operation selector switch,  $S_9$ , to secure a deflection of 1.018 volts on  $M_4$ . The selector switch,  $S_{11}$ , permits the use of any of the three ranges, 0 to 1.0, 0 to 2.5 or 0 to 5.0 volts; these three ranges are controlled by the potentiometers  $R_{12}$ ,  $R_{13}$  and  $R_{14}$ . The valve voltmeter records directly to 0.001 volt on the 0 to 1.0 range.

The initial calibration of the valve voltmeter is carried out by setting  $R_{11}$  at about its mid-point and adjusting  $R_{12}$  to give a deflection of 1.018 volts on  $M_4$  with  $S_9$  in the CALIBRATE position. This is followed by setting the switch  $S_{11}$  to the 2.5 and 5.0-volt ranges in turn and making the appropriate adjustments to  $R_{13}$  and  $R_{14}$ , respectively. During the initial calibration the zero position of  $M_4$  must be repeatedly checked and adjusted with  $R_7$ , if necessary.

A reversing switch,  $S_{12}$ , is incorporated in the circuit to provide for change in the polarity of the cathode in relation to the reference electrode. The thermal delay switch,  $S_{13}$ , in series with the meter  $M_4$ , protects the latter during the initial warming-up period of the valve  $V_7$ .

#### POWER-PACK—

The circuit for the valve-stabilised power-pack is shown in Fig. 6.\* The VR105 regulators provide a constant reference voltage for the triode component,  $V_{8B}$ , of the 12AU7

\* This is a modification of the circuit given in Fig. 7-15 (p. 219) in "The Radio Amateurs' Handbook," 29th Edition, American Radio Relay League, 1952.



valve. A reduction in the load current produces an increase of the anode voltage on  $V_{8B}$  and an increase of the bias on  $V_{8A}$ ; in consequence more current passes through the 500-ohm resistance  $R_{44}$ , the bias on  $V_9$  (6Y6G) is increased, the voltage across  $V_9$  is also increased and therefore the output voltage falls to the pre-set value of 300 volts.

The high-tension supply for this stabilising circuit is provided by a full-wave rectification circuit. The mains supply is fed into the apparatus via the main on-off switch,  $S_{15}$ , and the fuses, and thence to the A.C. ammeter,  $M_5$ . From the ammeter, mains leads are taken to the stirrer motor, to the transformer,  $T_3$ , Fig. 2, to pins 3 and 5 of  $P_1$  on the "Variac" transformer unit, Fig. 4, and to the input winding of the power-pack transformer,  $T_4$ , and also to  $T_5$ , Fig. 7, if series heating of the valves is used.

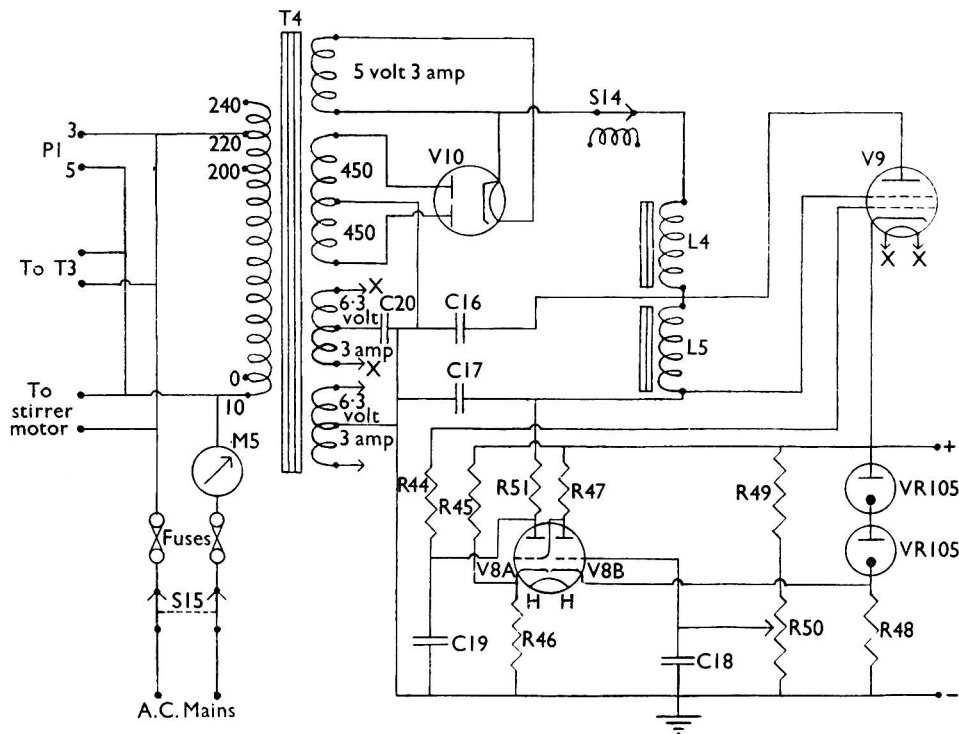


Fig. 6. High-tension power pack circuit

The full-wave rectifier comprises  $V_{10}$  (U52) and the 450-0-450-volt secondary winding on  $T_4$ . The H.T. + supply is taken from the cathode of  $V_{10}$  to the thermal delay switch,  $S_{14}$ . This switch protects the smoothing condensers and the 85A1 regulators of the D.C. amplifier and valve voltmeter, Fig. 2, during the warming up of the valves of the apparatus. After the switch  $S_{14}$  is a two-stage inductance-capacity smoothing filter, consisting of chokes  $L_4$  and  $L_5$  and condensers  $C_{16}$  and  $C_{17}$ .

The valve heaters can be supplied from a 6.3-volt winding on the mains transformer,  $T_4$ , if a stability of  $\pm 5$  millivolts suffices. In any event, valve  $V_9$  must receive its heater supply from an independent winding isolated from the high-tension negative source. In the instrument as built, the valve heaters were wired in series and supplied by the stabilising circuit shown in Fig. 7. This circuit makes use of full-wave rectification, followed by an inductance-capacity filter. The output is then fed into two 6Y6G series valves, a 6AU6 being used as the regulator valve. The cathode potential of the regulator valve is maintained at a constant value by a neon regulator, VR75. The resistances  $R_{55}$  and  $R_{57}$  are adjusted so that a current of 150 milliamperes passes through the heater chain, as detected by a milli-ammeter inserted in the jack,  $J_3$ .

A photograph of the complete assembly is reproduced as Fig. 8. The cabinet on the

left houses the motor and "Variac" transformer unit,\* the adjacent cabinet contains the potentiometer, valve amplifier, valve voltmeter and power packs (this is kept cool by means of a "Vent-Axia" fan installed at the back of the unit), whilst the cabinet on the right incorporates the low-tension D.C. unit. The "Variac" transformer unit is connected by cable supplying alternating current to the low-tension D.C. unit. A 6-wire cable connects the "Variac" unit (1) and the potentiometer, valve voltmeter and power-pack unit (2). The latter

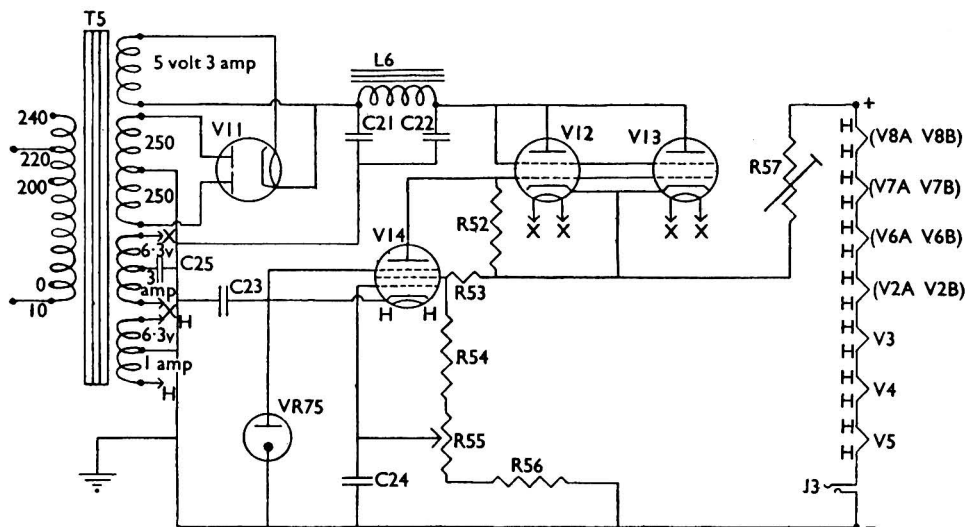


Fig. 7. Low-tension power pack circuit

unit (2) and the cell unit are connected to two wires from the D.C. input terminals (one to the cathode and the other to the reference cell); the anode and cathode are also connected by two wires to terminals on the low-tension D.C. unit.

#### OPERATION OF THE COMPLETE INSTRUMENT FOR CONTROLLED-POTENTIAL ELECTRO-ANALYSIS

The apparatus is first earthed to a water pipe or other suitable earthing conductor; the earthing connection should be soldered. The electro-deposition cell is connected to the apparatus. Two 15-ampere single insulated wires are connected from the D.C. output terminals on the low-tension unit, Fig. 3, to the anode and cathode, respectively. Two more wires from the reference electrode and the cathode are connected to their respective terminals on the potentiometer - amplifier unit, Fig. 2. It is important to use four wires for connecting the cell to the apparatus, for, if the negative output terminal of the D.C. low-tension unit were joined directly to the cathode terminal of the potentiometer - amplifier unit and a common wire were run to the cathode, it would be found that the valve voltmeter would indicate, and the amplifier would respond to, the voltage drop through the common lead superimposed upon the cathode - reference cell potential. The apparatus is plugged into the mains and switch  $S_{15}$ , Fig. 6, is closed. The stand-by switch,  $S_8$ , Fig. 4, and the mains switch,  $S_4$ , Fig. 3, on the low-tension D.C. power unit are kept in the "off" position. The apparatus is allowed to warm up for 10 to 15 minutes.

The operation selector switch,  $S_9$ , Fig. 2, is then turned to the ZERO position. The valve voltmeter is adjusted for zero by means of  $R_7$ . The stand-by switch,  $S_8$ , is turned on, the sensitivity control,  $R_{40}$ , on the amplifier unit is advanced and the amplifier set to zero by  $R_{30}$ , Fig. 2; the zero position is indicated by the cessation of movement of the "Variac" transformer motor and of the pointer of  $M_3$ , Fig. 4. The operation selector switch,  $S_9$ , is now turned to CALIBRATE, and the valve voltmeter is adjusted by  $R_{11}$  to read 1.018 volts. The potentiometer unit is calibrated by manipulating  $R_{17}$  until movement of the "Variac" transformer motor or of the needle of  $M_3$  ceases and  $M_3$  indicates about 20 volts. The apparatus is then ready for use; should any delay occur, the stand-by switch,  $S_8$ , is opened.

\* This description should be read in conjunction with Fig. 1.

The solution to be electrolysed is now placed in the electro-deposition cell. The tip of the saturated-calomel electrode is placed as close as possible to the cathode and at about its middle. If the cathode happens to be positive to the reference electrode, the reversing switch,  $S_{12}$ , Fig. 2, on the valve voltmeter must be thrown into the correct position. The ammeter switch,  $S_3$ , Fig. 3, should now be set to the 10-ampere range and the voltmeter switch,  $S_2$ , to the 20-volt range. The stirrer motor for the electrolysis cell is set in motion, the A.C. input switch,  $S_4$ , Fig. 3, is closed, and the voltage selector switch,  $S_{11}$ , rotated to 15 volts. The stand-by switch,  $S_8$ , on the "Variac" transformer unit, is closed, and the voltage selector switch,  $S_1$ , is re-adjusted so that the A.C. output of the "Variac" transformer unit, as indicated on the voltmeter  $M_3$ , is between 100 and 200 volts. If  $M_3$  reads over 225 volts or less than 5 volts, the safety switches,  $S_6$  or  $S_7$ , Fig. 4, will come into operation and switch off the motor; it will then be necessary to use the manual press-button unit, Fig. 5, to re-start the apparatus.

If the "Variac" transformer is functioning in the upper part of its range, it will exert a smoother and more accurate control on the voltage of the D.C. output of the low-tension unit. This will permit the sensitivity control,  $R_{40}$ , Fig. 2, to be more fully advanced without instability occurring. The voltage selector switch,  $S_{11}$ , should therefore be set so as to keep the A.C. output of the "Variac" transformer unit as high as possible. Once electro-analysis has begun, the sensitivity control should be advanced as far as is compatible with absence of instability; any instability will be revealed by a gentle oscillation of the needle of the A.C. voltmeter,  $M_3$ . The operation of the "Variac" transformer unit is intermittent owing to the dependence of the cathode over-voltage on the current and for other reasons. When the electrolysis current has fallen below 1 ampere, the range of  $M_2$  is changed by  $S_3$  first to 0 to 1.0 ampere and subsequently to 0 to 0.1 ampere. The electrolysis is discontinued when the current falls and remains at between 10 and 30 milliamperes. The switch  $S_9$  is set at ZERO, the electrolyte is removed (*e.g.*, by lowering the electrolysis vessel), and the electrodes are simultaneously washed without interrupting the current. The stirrer motor is then switched off, and switches  $S_8$ ,  $S_4$  and  $S_{15}$  are turned off.

If another electrolysis is to be carried out immediately, the stand-by switch,  $S_8$ , and the A.C. input switch,  $S_4$ , are opened. The ZERO and CALIBRATION positions of the potentiometer unit are checked again; the "Variac" transformer output should be reduced to about 20 volts during the re-calibration. This ensures that the initial cathode - reference cell potential will not exceed that required in the subsequent electrolysis. The potentiometer unit may now be set to the required value and  $S_{11}$  to 15 volts; switches  $S_4$  and  $S_8$  are closed, the stirrer started, and  $S_1$  re-adjusted as described above.

#### CHECKING THE VALVES—

The efficiency of the valves may be checked (*e.g.*, when a breakdown occurs) by inserting a milliammeter (0 to 10 mA) into the cathode leads of all the valves by means of a rotary switch. The failure of a rectifier valve will be apparent by a reduced or zero reading on all the valves supplied by it. When the milliammeter is inserted in the common cathode lead of the phase discriminators  $V_4$  and  $V_5$ —a parallel shunt will be required to prevent over-deflection of the meter—it will serve as a good zero point indicator, as when no signal is being fed to the phase discriminators and consequently the "Variac" transformer motor is stationary, the current reading will be at a maximum.

#### DETAILED LIST OF COMPONENTS

The details of the various components are listed below to correspond with the Figs. The components are those used in the authors' apparatus and are intended as a guide.

##### D.C. LOW-TENSION UNIT (FIG. 3)—

- $R_1$  = shunt supplied with Pullin voltmeter ( $M_1$ ).
- $R_2$  = shunt supplied with Pullin ammeter ( $M_2$ ).
- $C_1$  = 3000- $\mu$ F, 24-volt, paper condenser (M.R. Supplies).
- $C_2$  = 9000- $\mu$ F (3  $\times$  3000  $\mu$ F), 24-volt, paper condenser (M.R. Supplies).
- $L_1$  = 40-millihenry 10-amp. smoothing choke (M.R. Supplies).
- $T_1$  = mains step-down transformer; primary windings 10-0-200-220-240 volts; secondary windings, 0-3-6-9-12-15 volts at 15 amp. (M.R. Supplies).
- $M_1$  = Pullin voltmeter, C30/IV, knife-edge pointer and mirror scale, scaled to read 0 to 1.0, 0 to 5.0 and 0 to 20.0 volts.
- $M_2$  = Pullin ammeter, C30/100M, knife-edge pointer and mirror scale, scaled to read 0 to 0.1, 0 to 1.0 and 0 to 10.0 amp. (Measuring Instruments (Pullin) Ltd.).
- SE = selenium bridge rectifier, funnel type, rated at 15 volts, 15 amps. (M.R. Supplies).
- $S_1$  = two-pole six-way six-bank double-contact rotary switch, wired as one-pole six-way (Oak or Yaxley).

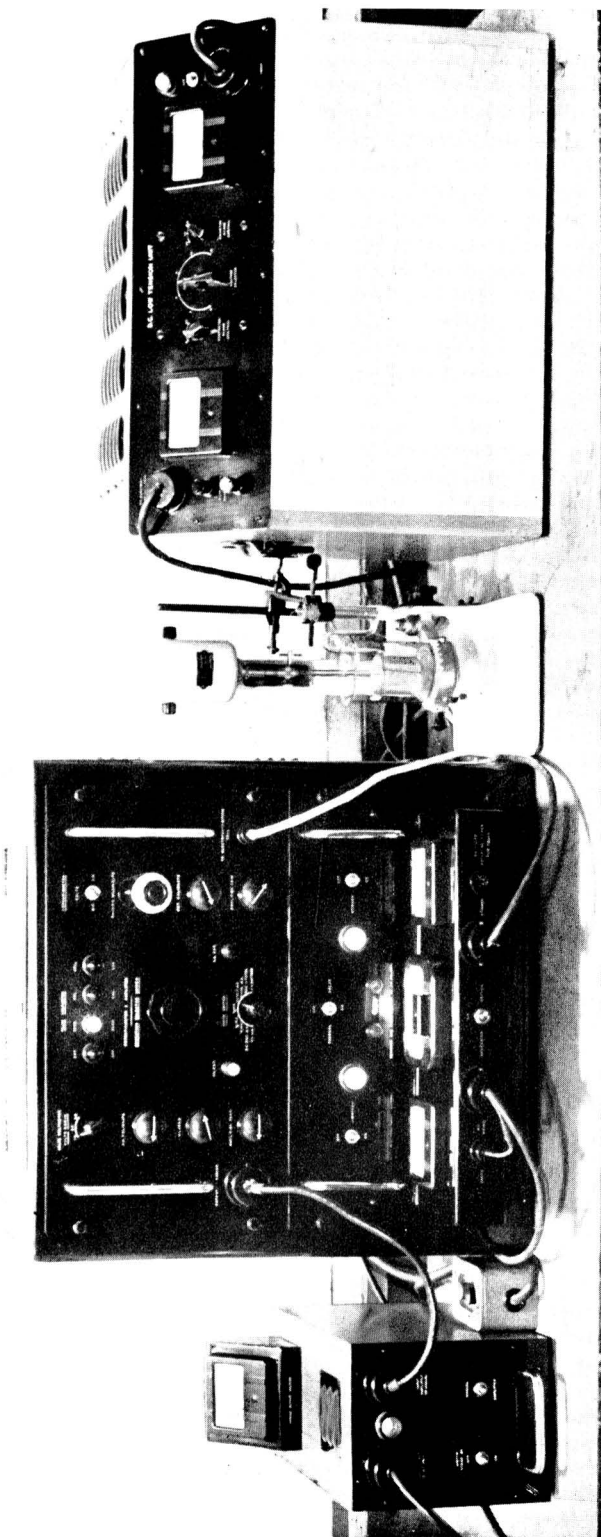


Fig. 8. General view of complete assembly

$S_2$  or  $S_3$  = six-pole three-way switch, wired as one-pole three-way (Bulgin, S.438).

$S_4$  = two-pole on - off switch (Bulgin, S.267).

A mains socket and plug (not shown in Fig. 3) was used to connect the low-tension unit with  $P_2$  on the "Variac" transformer unit (Bulgin, P.162).

#### MOTOR-DRIVEN "VARIAC" TRANSFORMER UNIT (FIG. 4)—

$L_2 + L_3$  = windings of four-pole two-phase reversible induction motor, geared down to 1 r.p.m., attached to a "Variac" transformer of 5 amperes capacity (Zenith). It was necessary to rewire the motor as supplied by the manufacturers to conform with Fig. 4.

$C_3$  = 0.25- $\mu$ F, 500-volt, paper condenser (Webbs Radio).

$C_4$  = 0.4- $\mu$ F condenser, supplied with motor unit (Zenith).

$S_5$  = four-pole change-over switch, required for alternative circuit with manual control (Bulgin, S.301).

$S_6$  and also  $S_7$  = safety switch supplied with motor.

$S_8$  = two-pole on - off switch (Bulgin, S.267).

$M_3$  = Pullin 0-300 volts A.C. voltmeter, R30/300V, knife-edge pointer and mirror scale (Measuring Instruments (Pullin) Ltd.).

$P_1$  = six-pin socket (Bulgin, P.166).

$P_2$  = three-pin socket, one pin not used (Bulgin, P.162).

#### MANUAL MOTOR-DIRECTION CONTROL UNIT (FIG. 5)—

This consists of one press-button two-way switch as supplied by Zenith Electrical Co. Ltd., with the motor-controlled "Variac" transformer. It was necessary to drill another hole at the end opposite to the one already present; the original hole was used for the wires to the six-way plug, which was inserted into  $P_2$ , Fig. 4, and the new hole carried the two wires to the A.C. mains.

#### VALVE AMPLIFIER UNIT (INCLUDING POTENTIOMETER AND VALVE VOLTMETER) (FIG. 2)—

(The resistances and condensers, unless otherwise indicated, were Erie or Dubilier products.)

$T_2$  = mu-metal-screened input transformer, 1 to 100 step-up ratio; primary winding, 400 turns, centre-tapped, D.C. resistance 34 ohms; secondary winding, 10,000 turns, D.C. resistance 2700 ohms; inductance about 2.15 henries (Sowter).

Relay = Carpenter polarised high-speed relay, type 5PA18A (Telephone Manufacturing Co. Ltd.).

$(V_{6A} + V_{6B}) = (V_{7A} + V_{7B}) = (V_{2A} + V_{2B}) = V_3 = 12AX7$ .

$V_4 = V_5 = 12AU7$ .

Four 85A1 Neon regulators (Mullard).

$S_9$  = two-bank six-pole four-way ceramic rotary switch (Webbs Radio).

$S_{10}$  = two-way single-pole toggle switch (Bulgin).

$S_{11}$  = three-way single-pole rotary switch (Bulgin or Yaxley).

$S_{12}$  = two-pole change-over switch (Bulgin, S.270).

$S_{13}$  = thermal delay switch (Bulgin S.364).

$R_3$  = 1000-ohm, 1-watt potentiometer.

$R_4$  =  $R_5$  = 6000-ohm, 1-watt, high-stability ( $\pm 5$  per cent. tolerance) resistance.

$R_6$  =  $R_8$  = 30,000-ohm, 1-watt, high-stability ( $\pm 5$  per cent. tolerance) resistance.

$R_7$  = 1000-ohm, 1-watt, potentiometer (carbon track).

$R_9$  = 10-megohm, 1-watt, high-stability resistance.

$R_{10}$  = 1-megohm, 1-watt, high-stability resistance.

$R_{11}$  = 25,000-ohm, 1-watt, potentiometer.

$R_{12}$  =  $R_{13} = R_{14} = 50,000$ -ohm potentiometer.

$R_{15}$  = 10,000-ohm wire-wound potentiometer with 5000-ohm resistance  $R_{16}$  in series, both 1-watt.

$R_{17}$  = 25,000-ohm potentiometer (carbon track).

$R_{18}$  = 100,000-ohm potentiometer (carbon track).

$R_{19}$  = 100,000-ohm helical potentiometer (Colvern Ltd.).

$R_{20}$  = 2500-ohm pre-set potentiometer.

$R_{21}$  = 20,000-ohm pre-set potentiometer.

$R_{22}$  = 90,000-ohm, 1-watt, high-stability resistance.

$R_{23}$  =  $R_{24} = 2000$ -ohm, 1-watt, high-stability ( $\pm 5$  per cent. tolerance) resistance.

$R_{25}$  = 1000-ohm potentiometer (carbon track).

$R_{26}$  = 1-megohm, high-stability resistance.

$R_{27}$  = 10-megohm, high-stability resistance.

$R_{28}$  =  $R_{29} = 27,000$ -ohm, 1-watt, high-stability ( $\pm 5$  per cent. tolerance) resistance.

$R_{30}$  = 1000-ohm, 1-watt, potentiometer (carbon track).

$R_{31}$  = 10,000-ohm wire-wound potentiometer with 5000-ohm resistance in series, both 1-watt.

$R_{32}$  = 0.25-megohm, 0.5-watt, high-stability resistance.

$R_{33}$  = 15,000-ohm, 0.5-watt, high-stability resistance.

$R_{34}$  = 20,000-ohm, 0.5-watt, high-stability resistance.

$R_{35}$  = 0.25-megohm, 0.5-watt, high-stability resistance.

$R_{36}$  =  $R_{38} = 1$ -megohm, 0.5-watt, high-stability resistance.

$R_{37}$  = 100,000-ohm, 0.5-watt, high-stability resistance.

$R_{39}$  = 50,000-ohm, 0.5-watt, high-stability resistance.

$R_{40}$  = 0.25-megohm potentiometer (carbon track).

$R_{41}$  = 100-ohm, 1-watt, potentiometer (carbon track).

- $R_{42}$  = 0.1-megohm, 1-watt, resistance.  
 $R_{43}$  = 300-ohm, 3-watt, wire-wound resistance.  
 $C_5$  = 25- $\mu$ F, 25-volt working, condenser.  
 $C_6$  =  $C_7$  = 8- $\mu$ F, 500-volt working, condenser.  
 $C_8$  =  $C_9$  =  $C_{10}$  = 0.1- $\mu$ F, 500-volt, condenser.  
 $C_{11}$  = 0.01 to 0.1- $\mu$ F condenser (see text).  
 $C_{12}$  = 25- $\mu$ F, 25-volt working, condenser.  
 $C_{13}$  = 1- $\mu$ F, 1000-volt working, condenser.  
 $C_{14}$  =  $C_{15}$  = 0.01- $\mu$ F, 100-volt working or higher-rated condenser.  
 $B_1$  = two Siemens 1.5-volt T-type cells.  
 $B_2$  = standard Weston cell.

A 6-inch "Vent-Axia" extract unit (grille model) was fitted into the back of the cabinet to control the temperature. It was found that the change in temperature during the initial warming up of the components in the cabinet caused a gradual drift in the calibration of the potentiometer.

The "Variac" transformer motor is shown in outline in Fig. 2; the numbers correspond to those on the 6-pin socket shown in Fig. 4.

#### HIGH-TENSION POWER-PACK (FIG. 6)—

- $T_4$  = mains transformer; primary windings, 10-0-200-220-240 volts; secondary windings, 450-0-450 volts at 150 mA, 5 volts at 3 amperes, 6.3 volts at 3 amperes, centre-tapped, and 6.3 volts at 3 amperes, centre-tapped (optional, not required if series heating is used) (M.R. Supplies).  
 $(V_{8A} + V_{8B})$  = 12AU7 (Webbs Radio).  
 $V_9$  = 6Y6G (Webbs Radio).  
 $V_{10}$  = U52 (Webbs Radio).  
 $S_{14}$  = thermal delay switch (Bulgin, S.363).  
 $S_{15}$  = two-pole on-off switch (Bulgin).  
 $R_{44}$  = 500-ohm, 0.5-watt, resistance.  
 $R_{45}$  =  $R_{46}$  = 33,000-ohm, 2-watt, resistance.  
 $R_{47}$  = 0.25-megohm, 0.5-watt, resistance.  
 $R_{48}$  = 9000-ohm, 1-watt, resistance.  
 $R_{49}$  = 200,000-ohm, 0.5-watt, resistance.  
 $R_{50}$  = 100,000-ohm potentiometer (carbon track).  
 $R_{51}$  = 0.3-megohm resistance.  
 $C_{16}$  =  $C_{17}$  = 16- $\mu$ F, 600-volt working, paper condenser.  
 $C_{18}$  = 0.1- $\mu$ F, 300-volt working, paper condenser.  
 $C_{19}$  = 0.015- $\mu$ F, 300-volt working, paper condenser.  
 $C_{20}$  = 8- $\mu$ F, 600-volt working, paper condenser.

#### LOW-TENSION POWER-PACK (FIG. 7)—

- $T_6$  = mains transformer; primary windings, 10-0-200-220-240 volts; secondary windings, 250-0-250 volts at 200 mA, 5 volts at 3 amperes, 6.3 volts at 3 amperes, centre-tapped, 6.3 volts at 1 ampere, centre-tapped (M.R. Supplies).  
 $R_{52}$  = 0.5-megohm, 0.5-watt, resistance.  
 $R_{53}$  = 10,000-ohm, 3-watt, resistance.  
 $R_{54}$  = 25,000-ohm, 3-watt, resistance.  
 $R_{55}$  = 10,000-ohm, 3-watt, wire-wound potentiometer (Colvern).  
 $R_{56}$  = 5000-ohm, 3-watt, resistance.  
 $R_{57}$  = 1000-ohm, 25-watt, pre-set resistance.  
 $C_{21}$  = 8- $\mu$ F, 350-volt working, paper condenser.  
 $C_{22}$  = 16- $\mu$ F, 350-volt working, paper condenser.  
 $C_{23}$  = 0.1- $\mu$ F, 350-volt working, paper condenser.  
 $C_{24}$  = 0.01- $\mu$ F, 350-volt working, paper condenser.  
 $C_{25}$  = 8- $\mu$ F, 350-volt working, paper condenser.  
 $J_3$  = closed-circuit jack socket.  
 $V_{11}$  = U52 valve.  
 $V_{12}$  =  $V_{13}$  = 6Y6G valve.  
VR 75/30 = neon regulator (Brimar).  
 $L_6$  = 10 to 20-henry, 200-mA smoothing choke (M.R. Supplies).

#### MISCELLANEOUS COMPONENTS—

*Wooden cabinets*—"Variac" transformer motor unit: 7 × 15 × 9 inches. Low-tension D.C. unit: 22 × 15 × 17 inches, asbestos-lined (incorporating an air-cooled selenium rectifier; the size of the low-tension unit cabinet can be reduced slightly if a motor-driven blower is used to cool the rectifier).

*Metal cabinet*—This was a standard Imhof model.

The addresses of the suppliers of the important components are—

Colvern Ltd., Mawneys Road, Romford, Essex.

Alfred Imhof Ltd., 112-116, New Oxford Street, London, W.C.1.

Measuring Instruments (Pullin) Ltd., Winchester Street, Acton, London, W.3.

M.R. Supplies Ltd., 68, New Oxford Street, London, W.C.1.

Dr. G. A. V. Sowter, 1B, Head Street, Colchester, Essex.

Telephone Manufacturing Co. Ltd., Hollingsworth Works, Martell Road, West Dulwich, London, S.E.21.

Webb's Radio, Ltd., Soho Street, Oxford Street, London, W.1.

Zenith Electric Co., Ltd., Villiers Road, Willesden Green, London, N.W.2.

Other components for which manufacturers' addresses are not listed, can be obtained from most suppliers of radio components.

The authors' thanks are tendered to the Governors of Woolwich Polytechnic for liberal grants and excellent facilities, and to Imperial Chemical Industries Ltd. for financial assistance that has helped to defray the heavy cost incurred in the development of the apparatus to its final form.

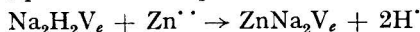
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DEPARTMENT OF CHEMISTRY  
WOOLWICH POLYTECHNIC  
LONDON, S.E.18.

October 29th, 1952

ERRATUM: May (1953) issue, p. 309. The equations on lines 33 and 35 should read:—



where  $\text{V}_e$  is  $[(\text{COO}\cdot\text{CH}_2)_2\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\text{COO})_2]^{''''}$

## Notes

### THE SEPARATION OF RODENT HAIRS AND INSECT FRAGMENTS FROM OAT PRODUCTS

EXAMINATION of cereal products for rodent hairs and insect fragments is complicated, if they contain much bran, by the particles of light branny material that separate out with the extraneous matter during the flotation procedure. This effect makes the subsequent scanning of the separated material with a microscope difficult and unreliable. In the "Official Methods of Analysis of the A.O.A.C."<sup>1</sup> (the standard reference for this test), adjustments to the method are made in order to reduce the amount of bran that separates. These modifications are (i) a reduced digestion period, which has the effect of retaining some of the more dense endosperm attached to the bran (occasionally no digestion is required), and (ii) the use of a liquid of lower density, such as aqueous alcohol.

Oatmeals and rolled oats are not specifically dealt with in the A.O.A.C. method; difficulty in examining these has been noted by Kent-Jones, Amos, Elias, Bradshaw and Thackray.<sup>2</sup> We have found the usual technique unreliable with oat products; this note describes a modified method that gives cleaner separations of extraneous matter from fine, medium, coarse and "pinhead" oatmeal and oat-flakes.

With a product such as rolled oats some digestion is desirable in order to free the extraneous fragments; this is done by boiling the material for a short time with aqueous alcohol and hydrochloric acid. Examination of the residual material has shown that this treatment adequately removes any adhering extraneous matter.

The extraneous matter is separated in a Wildman trap-flask by means of a light mineral oil. Recoveries of rodent hairs from the aqueous alcohol were better with the light mineral oil than with

other, lower, petroleum fractions. The tendency of the oil to adhere to the sides of the trap-flask is reduced by initial thorough cleaning and adequate rinsing of the flask. The sides of the flask should be wetted with aqueous alcohol before the oil is added.

A preliminary extraction of the sample to remove fatty material was found to be necessary; ethyl ether was better than light petroleum for this purpose.

#### METHOD

##### REAGENTS—

*Dilute alcohol, sp.gr. 0.94*—Dilute 500 ml of industrial methylated spirit to 1 litre with water.

*Light mineral oil*—Refined spindle oil, "Vitrea 13," which is supplied by Shell Mex and B.P. Ltd. Viscosity 70 seconds (Redwood No. 1) at 70° F.

##### PROCEDURE—

Extract 100 g of sample with ether in a continuous extractor for 6 hours, evaporate the ether and put the sample in a 2-litre Erlenmeyer flask containing 800 ml of dilute alcohol and 40 ml of concentrated hydrochloric acid (sp.gr. 1.18). Bring to the boil in a water-bath with occasional agitation, and boil under a reflux condenser for 10 minutes (5 minutes for the "pinhead" size). Cool and transfer the mixture to a 2-litre Wildman trap-flask, thoroughly washing out the digestion flask with dilute alcohol. Rinse the sides of the trap-flask with dilute alcohol, and add 50 ml of light mineral oil. Stir this into the alcoholic mixture, fill the flask with dilute alcohol, and set it aside for 1 hour to effect the separation. During this hour, gently stir the mixture at intervals to release any bran at the interface of the two liquids and to free any oil adhering to the sides of the flask. Separate the oil and about  $\frac{1}{4}$  inch of liquid below the interface by means of the trap, and transfer this portion to a beaker in the usual manner, washing successively with dilute alcohol, light petroleum and dilute alcohol. In a similar manner carry out a second flotation with a further 50 ml of oil. Combine the two oil fractions, filter them and wash the filter successively with dilute alcohol, light petroleum and industrial methylated spirit. Transfer the filter-paper to a Petri dish moistened with a mixture of equal volumes of glycerin and alcohol and examine it through a binocular microscope.

We are grateful to Messrs. Shell Mex and B.P. Ltd. for supplying us with a range of mineral oil fractions.

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RESEARCH ASSOCIATION OF BRITISH FLOUR MILLERS  
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October 22nd, 1952

#### A MODIFIED DEAD-STOP END-POINT CIRCUIT FOR TITRATIONS OF FERROUS IRON WITH POTASSIUM DICHROMATE IN APPROXIMATELY *N* SOLUTIONS

An article by Stone and Scholten<sup>1</sup> suggested the use of the dead-stop end-point of Foulk and Bawden<sup>2</sup> for ferrous iron titrations with potassium dichromate. The dead-stop end-point is sharp and definite, but in titrations with *N* solutions it has the defect of giving no warning of the approach of the end-point. By means of the circuit described, warning is given of the approach of the end-point and the amount of warning can be varied to suit any requirements.

The circuit is set up as shown in Fig. 1. A galvanometer can be switched either in parallel with the electrodes (switch  $S_2$ , position 2), to show the drop in potential across them, or in series with the electrodes, to act as a micro-ammeter (switch  $S_2$ , position 1). The galvanometer used is a Unipivot type as manufactured by the Cambridge Instrument Company Limited; it has 100-division readings on either side of the central zero and has an internal resistance of about 800 ohms. With the circuit as shown, the deflections are on one side of the zero when the galvanometer is in series with the electrodes and on the other side when in parallel. The variable resistance  $R_2$  (0.2 M $\Omega$ ) controls the potential difference across the electrodes and is set for each pair of electrodes. The variable resistance  $R_1$  is used as a shunt to control the sensitivity of the galvanometer when it is connected in parallel with the electrodes. The two platinum wire electrodes,



which are of 22 S.W.G. wire and each 1 inch long, are bent into a loop and sealed in glass tubes. A  $1\frac{1}{2}$ -volt dry cell placed in circuit by switch I is used as a source of current. A four-pole three-way single-bank Yaxley switch can be used in place of switches  $S_1$  and  $S_2$ .

#### ADJUSTMENT OF RESISTANCE SETTINGS—

*Setting of  $R_2$* —With the electrodes dipping into about 200 ml of a stirred solution, about 0.5 N with respect to sulphuric acid, containing at least 1 ml of unreacted N potassium dichromate solution, adjust  $R_2$  until the potential drop across the electrodes is about 200 millivolts. Read the current in microamperes and the potential drop across the electrodes in millivolts on either

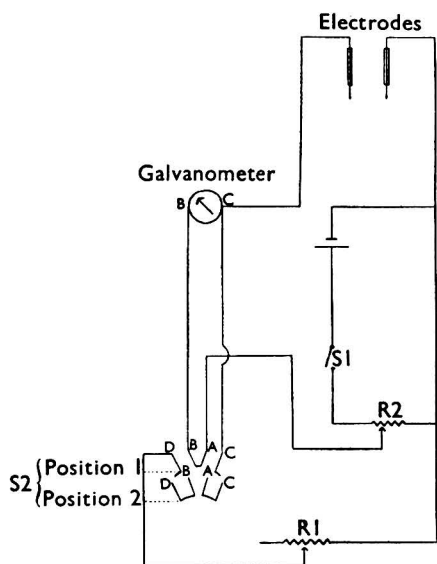


Fig. 1. The modified dead-stop end-point circuit. A, input; B, galvanometer (+); C, galvanometer (-) electrode (+); D, electrode (-);  $S_1$ ,  $S_2$ , switches

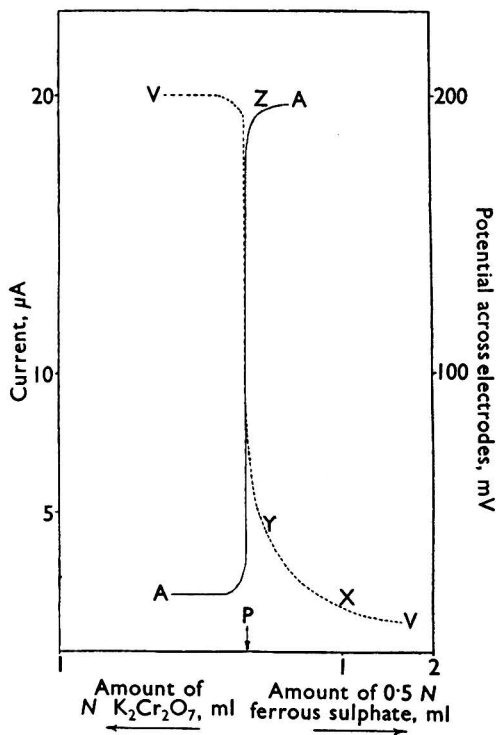


Fig. 2. Titration graphs with N potassium dichromate solution and 0.5 N ferrous sulphate solution

side of the equivalence point and plot graphs (see AA and VV, Fig. 2). Between points X and Y (Fig. 2) the potential increase is measurable for each drop of dichromate solution added. This relatively steady increase is used to show proximity to the end-point.

*Setting of  $R_1$* —With the galvanometer in series, titrate with ferrous iron solution until the end-point is reached as shown by the rapid increase in current. Add an amount of ferrous sulphate solution equal in volume to that required for warning (normally 0.2 ml). Switch the galvanometer and  $R_1$  in parallel with the electrodes and adjust  $R_1$  until the galvanometer gives full-scale deflection.

#### TITRATION PROCEDURE FOR DICHROMATE IN FERROUS SOLUTION—

Close switch  $S_1$  and unclamp the galvanometer. Place  $S_2$  in position 2, *i.e.*, in parallel, and add the dichromate fairly rapidly. Little increase in potential occurs until a point (X in Fig. 2), about 1 ml from the equivalence point, P, is reached, when there is a definite permanent increase in galvanometer reading. Continue to add the dichromate dropwise until the reading on the galvanometer is the maximum, position Y. Re-set  $S_2$  to position 1, when a large deflection is

obtained (see point Z), which indicates an excess of ferrous sulphate solution, and add the dichromate slowly until there is a sudden large drop in deflection, which indicates the end-point.

#### APPLICATION—

The Walkley - Black rapid titration method for the determination of organic carbon can be carried out more quickly with the proposed circuit than with diphenylamine indicator, which, in the presence of finely divided soil, gives a poorly discernible end-point. The proposed circuit should prove useful in titrations of the redox systems mentioned by Stone and Scholten whenever relatively strong solutions are being titrated.

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MINISTRY OF AGRICULTURE AND FISHERIES  
NATIONAL AGRICULTURAL ADVISORY SERVICE  
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September 29th, 1952

#### THE DETECTION OF BORON IN TREATED TIMBER

THE practice of impregnating starch-containing sapwoods with boric acid or borax to render them immune to attack from the powder-post beetle (*Lyctus brunneus* Steph.) has brought about the need for some rapid and simple field method of determining whether such timber has been satisfactorily treated. The most suitable test would be a direct spot-test whereby a pronounced colour change would occur on timber containing the required amount of boron when some chemical reagent was applied to it.

In New South Wales, the Timber Marketing Act of 1945 requires that timber so treated shall contain 0.2 per cent. of boric acid in the core, based on the oven-dry weight of the wood.

Curcumin (turmeric) is a well-known reagent often used for the detection of boron,<sup>1</sup> with which it reacts to form a red compound. However, if an alcoholic solution of curcumin is sprayed or dropped on treated timber containing about 0.2 per cent. of boric acid, no colour reaction can be detected. If the timber is first acidified by spraying with hydrochloric acid before applying the curcumin solution, a light reddish colour can often be seen, which will turn blue-black when a drop of alkali is placed upon it. Experience in our laboratories has shown that with this technique the colour development is not only very erratic but also is not sensitive enough for our purpose.

The addition of oxalic acid<sup>2</sup> or salicylic acid<sup>3</sup> to the curcumin reagent is reported to aid the development of the red colour produced in the reaction of curcumin with boron.

Investigations into the use of these reagents resulted in the development of a satisfactory spot-test for the direct detection of boron in timber. Two reagents are required, the first being an alcoholic solution of curcumin, the second an alcoholic solution of hydrochloric and salicylic acids.

#### REAGENTS—

*Alcoholic curcumin solution*—Add 2 g of turmeric powder to 100 ml of 95 per cent. alcohol and boil the mixture under a reflux condenser for 1 hour. Cool and filter the solution.

*Hydrochloric - salicylic acid solution*—Mix 80 ml of 95 per cent. alcohol with 20 ml of 30 per cent. hydrochloric acid, and saturate the mixture with salicylic acid.

#### PROCEDURE—

Plane or rasp the surface of the timber to facilitate absorption of the reagents. Apply 2 drops of alcoholic curcumin solution to the prepared surface and allow the solution to dry for a few minutes. Then apply 2 drops of the hydrochloric - salicylic acid solution to the same spot. As this second solution dries, a brown to red stain will develop.

The intensity of the colour produced varies with the boron content of the timber in such a way that it is possible not only to detect treated timber, but also to determine whether or not it has been satisfactorily treated. The colour varies from a distinct red-brown stain on timber containing less than 0.1 per cent. of boric acid to a well-defined homogeneous bright red stain on timber containing approximately 0.2 per cent. of boric acid (the amount required for satisfactory treatment in New South Wales). The intensity of the red stain increases with the concentration of boron in the timber, so that with timber containing excessive amounts of boron,

*e.g.*, 0.8 per cent., an intense dark maroon stain is developed. This stain should not be confused with the dark brownish-red stain developed on slightly undertreated timber. It can be distinguished from the latter by its greater intensity and more homogeneous nature. On dry timber each of the solutions takes about 2 minutes to dry, *i.e.*, the stain is fully developed in about 5 minutes from the start of the test. With wet samples from a freshly treated charge the stain takes up to 30 minutes to develop, but it was found that drying could be hastened by the following procedure—

*Modified procedure for wet timber*—Allow several drops of the curcumin solution to soak into the timber for several minutes, then touch it with a lighted match. The alcohol will burn, leaving a relatively dry spot. Repeat this procedure with the alcoholic acid solution. As this second solution burns the stain will develop.

The only other compounds known to turn curcumin red-brown are those of ferric iron, molybdenum, titanium, niobium, tantalum and zirconium.<sup>1</sup> As these either are not found in timber or are present only in very small amounts, this spot-test can be regarded as specific for boron. The test can be made more specific by making use of the fact that the red-brown rosocyanine stain produced by boron in the presence of turmeric will turn greenish-black if treated with alkali and that the original red colour can then be restored by acid. This does not occur with the stain produced by ferric iron, molybdenum, and so on.

This spot-test has been in use by the Division of Wood Technology for more than a year, and has also been used successfully by commercial treatment-plant operators and timber inspectors without any anomalies being reported. It has been found that the curcumin solution deteriorates in about 2 months after its preparation, but that the hydrochloric-salicylic acid solution will keep indefinitely. The most convenient method of using the solutions is from a dropping bottle, TK pattern, with a ground-in slotted stopper, and a capacity of about 60 ml.

I am indebted to the Forestry Commission of New South Wales for permission to publish this Note.

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November 26th, 1952

## Apparatus

### A GUARD VALVE FOR TIN DETERMINATIONS BY THE IODIMETRIC PROCEDURE

In the iodimetric procedure, after reduction of tin, the reduced solution is protected from oxidation by air by an inert atmosphere of carbon dioxide gas that is maintained during cooling and subsequent titration. Gas from a cylinder or generator is used, or the carbon dioxide is generated *in situ*.

For generation *in situ* a number of devices have been proposed; of these, perhaps the most widely used is the Contat-Göckel valve.<sup>1</sup> This consists essentially of a reservoir to which is connected an internal siphon tube. For use, the reservoir is almost filled with sodium bicarbonate solution, and the valve is fixed in the neck of the flask by a rubber bung just before removal of the Erlenmeyer flask from the source of heat at the end of the reduction step. As the reduced tin solution cools, sodium bicarbonate solution is drawn intermittantly into the flask through the siphon tube, the carbon dioxide generated each time breaking the siphon and restoring pressure equilibrium. But with the usual design there is a time lag in the mixing of the two solutions and this causes a large excess of bicarbonate solution to be drawn into the flask at each operation of the siphon.

This disadvantage is overcome with the improved design, diagrammatically illustrated in Fig. 1, in which a constriction in the siphon tube is loosely closed by a glass bead. This device

forms an imperfect seal, which allows the bicarbonate solution to enter dropwise as the pressure in the flask becomes reduced during cooling. Only the amount necessary to maintain pressure

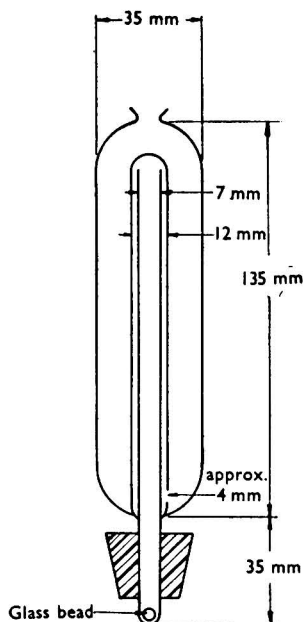


Fig. 1. The guard-valve

equilibrium is drawn into the flask, and this enables a more compact design of valve to be used. A valve constructed to the dimensions shown will hold enough bicarbonate solution in the reservoir for at least three tin determinations.

I express my thanks to the Chief Scientist, Department of Supply, Australia, for his permission to publish this note.

#### REFERENCE

1. Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," Second Edition, Macmillan & Co. Ltd., London, 1950, p. 589.

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W. H. JACKSON  
October 29th, 1952

## Official Appointments

### PUBLIC ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Food since the last record in *The Analyst* (1953, 78, 387).

<i>Public Analyst</i>	<i>Appointment</i>
DEDICAT, Herbert . . . . .	Borough of Bacup.
ELVIDGE, William Farrand (Deputy) . . . . .	County of Northumberland.
HARRIS, Tennyson . . . . .	Borough of Crewe.
HARRIS, Tennyson . . . . .	Borough of Glossop.
SPALDING, Robert Clarence (Deputy) . . . . .	Borough of Erith.
SPALDING, Robert Clarence (Deputy) . . . . .	Borough of Gillingham.
SPALDING, Robert Clarence (Deputy) . . . . .	Urban District of Orpington.
WOODHEAD, John Ezra . . . . .	Metropolitan Borough of Wandsworth.

## OFFICIAL AGRICULTURAL ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Agriculture and Fisheries since the last record in *The Analyst* (1953, 78, 387).

<i>Agricultural Analyst</i>	<i>Appointment</i>
HOUSE, Cecil John .. ..	County Borough of Bury.
SHERRATT, John Graham .. ..	County Borough of Blackpool.

## British Standards Institution

### NEW SPECIFICATION\*

B.S. 718:1953. Density Hydrometers and Specific Gravity Hydrometers. Price 5s.

### DRAFT SPECIFICATIONS

A FEW copies of the following draft specifications, issued for comment only, are available to members of the Society, and can be obtained from the Secretary, Society of Public Analysts and Other Analytical Chemists, 7/8, Idol Lane, London, E.C.3.

Draft Specification prepared by Technical Committee OSC/6—Glycerine.  
CR(OSC)2509—Draft B.S. for Glycerine.

Draft Specification prepared by Sub-Committee RUC/10/9—Tests for Cellular Rubber.  
CR(RUC)2425—Draft B.S. Methods of Testing Cellular Rubber.

Draft Specification prepared by Sub-Committee OSC/24/1—Methods for the Analysis of Glycerine.  
CR(OSC)2511—Draft B.S. for Methods of Sampling and Analysis of Glycerine.

## Book Reviews

FERTILISERS. METHODS OF ANALYSIS USED IN O.E.E.C. COUNTRIES. Pp. 182. Paris: The Organisation for European Economic Co-operation. 1952.

The Organisation for European Economic Co-operation (O.E.E.C.) was constituted in Paris in 1948 to discuss the economic problems of, and work out a common plan of action for, its members. There are eighteen members, that is, nearly all the European countries outside the U.S.S.R., but the United States and Canada are not members, although they participate in the work. The programmes for national recovery have now been co-ordinated so as to ensure the most effective use of American aid, and measures for liberalisation of trade and payments have been agreed. It would appear that one of the objectives is to develop greater uniformity in international trade in fertilisers, and that to assist in the purpose, this "documentation"—as the publication is officially described—gives a survey, authentic to the beginning of 1952, of the methods of fertiliser analysis in fourteen O.E.E.C. countries. The official methods are given in generally adequate, but varying, detail. In this respect the old problem of how far a method of analysis should be given in detail is again emphasised; whereas the official methods of the Netherlands, Belgium and France are given so adequately as to include notes on principles, warnings of snags, and even somewhat elaborate formulae for calculating the results of the analysis, those of Luxembourg are confined to outlines without any details of quantities to be taken or of actual laboratory procedure or technique.

The methods dealt with in this book are concerned with the analysis of nitrogenous, phosphatic and potash fertilisers. With regard to nitrogen, the Kjeldahl method is, of course, standard for all countries. The determination of ammoniacal nitrogen presents many variations: by distillation with soda, magnesia or calcium carbonate, by direct titration after the addition of formaldehyde, and by diffusion from calcium hydroxide. It is interesting to note that although in no country are precautions taken against the loss of nitrogen as nitrosyl chloride when mixtures containing both nitrates and chlorides are made acid with sulphuric acid, the Swiss method for dealing with nitric, "ureic" and ammoniacal nitrogen in mixed fertilisers does, in fact, overcome this difficulty, and, furthermore, in providing special procedures for the determination of ammonia originally present in the form of ammonium salts so that the ammonia evolved from the breakdown of urea

\* Obtainable from the British Standards Institution, Sales Department, 24, Victoria Street, London, S.W.1.

on distillation with alkali does not so count, provides a method for mixtures including fish meal or guano. It is not well known that many fish meals and guanos contain a substantial proportion of their nitrogen in the form of urea. The methods for nitric nitrogen also provide considerable variation, the gasometric procedure curiously enough being comparatively popular.

The techniques used for assessing the solubility of various forms of phosphate in water offer great contrasts in respect of the ratios of weight of sample to weight of water taken for the determination, varying from 1/20 to 1/100. The actual determination of the phosphorus is in general practice confined to two gravimetric methods—as a molybdenum precipitate or as ammonium magnesium phosphate—and a volumetric (Pemberton) method. Considerable attention is given to the conditions necessary for accuracy, and the direct method of single ammonium magnesium phosphate precipitation in the presence of large concentration of citrate has almost disappeared. Doubt still appears to exist with regard to the influence of soluble silica on the determination.

All the countries use the perchlorate method for determination of potassium and many use the chloroplatinate method as an alternative. In the second, some weigh the chloroplatinate, whereas others reduce it to platinum and weigh it as such. In the procedure for preparing the sample, in which phosphates are present, for final treatment with either perchloric acid or platinum chloride, precipitation with barium hydroxide is still frequent, although it has been recognised in England for years that the barium phosphate precipitated by such treatment always includes significant amounts of absorbed potassium. The United Kingdom is the only country that uses any form of cobaltinitrite precipitation at any stage.

From the point of view of review and possible amendments of the official methods under the Fertiliser and Feeding Stuffs Act in this country, the O.E.E.C. document is of considerable reference value as covering so many European countries, but it has little other value. The many methods for different forms of nitrogen offer possible scope for enlarging this section of our methods; the methods for phosphorus cannot be claimed to be any more accurate or precise than ours; and as regards potassium, the real help is that greater attention is paid to ensuring the purity of the final product. Nevertheless, the primary purpose of the publication is fully served. Careful consideration of the details of the various official methods indicates a measure of uniformity and a large area of common ground. It is clear that no satisfactory agreement on international standards can be reached without a conference of representative analysts, but it is equally clear that such a conference might well arrive at a workable conclusion.

GEORGE TAYLOR

SUBSTANCES NATURELLES DE SYNTHÈSE; PRÉPARATIONS ET MÉTHODES DE LABORATOIRE. Volumes I to IV. Edited by LÉON VELLUZ, D.ès S. Pp. xvi + 136; viii + 138; vi + 156; vi + 166. Paris: Masson et Cie. 1951 and 1952.

When reading the first four volumes of "Substances Naturelles de Synthèse" the reviewer was reminded of his student days a quarter of a century ago. At that time textbooks on organic chemistry gave much attention to the dyestuff industry and the student's laboratory work was devoted almost exclusively to reactions in that field. It is a tribute to the advance in our knowledge of the chemistry of natural products that Professor Velluz, assisted by an able team of collaborators, has been able to produce a most readable account of synthetic methods for the preparation of these substances. Four volumes of this work have so far appeared and all follow the same pattern.

Volume I deals with ascorbic acid, adenine, adenine labelled with  $^{15}\text{N}$  and  $^{14}\text{C}$ , adenosine, chloramphenicol, aesculin, DL-histidine and L-tryptophan. For each substance there is an introductory section summarising methods that have been used for its synthesis, and the stereochemical considerations involved. Then follows an account, giving full practical details, of the most satisfactory synthesis. A series of notes dealing with special aspects of the synthesis completes each monograph. For example, the preparation of chloramphenicol from *p*-nitroacetophenone, according to Long and Troutman, is described, whilst an alternative route from  $\alpha$ -acetylaminoacetophenone is indicated in a note. A further note deals with the optical isomers of chloramphenicol, comparison being made with the corresponding problem in the ephedrine series. Final notes refer to the reactions of Tollens and of Sommelet used in the synthesis. Volume I also includes reviews on ring formation in the coumarin and pyrimidine series, as well as practical notes on the preparation of pure solvents. Two full pages of photomicrographs, showing crystals of the substances synthesised, is a pleasing feature.

A summary of the contents of the other volumes is given below.

Preparations in Volume II include adenylic acid, DL-aspartic acid, desoxycorticosterone, DL-lysine, DL-methionine, progesterone, L-threonine and L-thyroxine. There are reviews of the

Oppenauer reaction and the separation of carbonyl compounds by functional derivatives. Practical notes are given of reagents for carbonyl compounds and of the treatment of ketones.

Under preparations in Volume III are those for DL-glutamic acid, DL-dihydroxyphenylalanine, equilenine, oestradiol, oestrone, DL-ornithine, thiamine and oxythiamine. Ring formation in the thiazole series and synthesis of  $\alpha$ -amino-acids are reviewed and practical notes on the determination of melting points are given.

Volume IV contains preparations of D-pantothenic acid, adermin (pyridoxin),  $\beta$ -alanine, androsterone, riboflavine, ribose, testosterone and DL- $\alpha$ -tocopherol. There are reviews of ring formation in the pyridine series and of chromatography (adsorption). The practical notes are also for chromatography (adsorption).

From a detailed study of selected sections, the work of abstracting from the literature appears to have been good and the references quoted reliable. The book is well printed on good paper and is substantially free from typographical errors.

These volumes will form a useful addition to chemical libraries and serve as a source of information to all chemists, including analysts, who are interested in natural products. If the standard of the first four volumes is maintained, the demand for further volumes of the series will be assured.

G. E. FOSTER

SEMIMICRO QUALITATIVE ANALYSIS. By PAUL ARTHUR, Ph.D., and OTTO M. SMITH, Ph.D. Third Edition. Pp. xii + 285. New York and London: McGraw-Hill Book Co., Ltd. 1952. Price 34s.

For those unfamiliar with the second edition of this book, it may be said that it is one of the considerable number of American textbooks that advocates the teaching of qualitative inorganic analysis by semi-micro methods, and was, when the first edition appeared in 1938, one of the pioneers of this subject. It still remains among the soundest of these books and is particularly outstanding in its capable systematic treatment of the identification of anions. It is one of the volumes in the excellent International Chemical Series.

Rather more than half of the book is given over to theoretical treatment of the chemistry required for analytical purposes. Owing to the structure of American education, by which a study of other branches of chemistry is not necessarily a concomitant of a study of analytical chemistry, much of this consists of elementary physical chemistry.

On the practical side the book is competent. The scale of working might be termed large semi-micro, since about 1 ml of solution is used as the starting point, and the sulphides of Group II are precipitated in rather more than 2 ml of solution; one variant described, for example, requires a 25-ml flask to contain this solution.

The present edition shows little change from the previous one; the alterations consist largely in some rearrangement and clarification of the theoretical part and the modification or improvement of some of the tests. Some of the more recently developed techniques for small-scale manipulation might with advantage have been included in the chapter on semi-micro technique, but the remainder of the practical section covers excellently the requirements of a first course in the qualitative analysis of the more familiar cations and anions.

C. L. WILSON

INORGANIC CHEMISTRY. AN ADVANCED TEXTBOOK. By THERALD MOELLER. Pp. x + 966. New York: John Wiley & Sons Inc. London: Chapman & Hall Ltd. 1952. Price 80s.; \$10.00.

During the last thirty years or so the chemist, armed with the knowledge of atomic structure and with methods of investigation gained from the physicist, has been able to probe more deeply into the nature and internal structure of the inorganic compounds he uses. A new lease of life, by no means ended, has been given to inorganic research and much new knowledge has been and remains to be gained. Inorganic chemistry no longer stops at a description of the properties and behaviour of its substances; it seeks to correlate these properties and this behaviour with the internal structure of substances and ultimately with the particulate structures of the atoms themselves.

This book deals in a readable and satisfying way with the new advances that have been made and with the way in which these illumine some of the older, descriptive knowledge. The dust-cover describes it as "a modern, comprehensive treatment of essential theory and fact," and this claim is fully justified.

Any analytical chemist who has not been able to keep abreast of the new knowledge and wants to bring himself up to date can hardly do better than read this book. The going, at times,

may be difficult, but the journey will be worth while. Even those who pride themselves on knowing will find much to enjoy in its pages.

Part I deals with atomic nuclei and related properties, the extranuclear structure of atoms, systematic classification of the elements, characteristics dependent upon extranuclear structures, valency and the chemical bond, complex ions and co-ordination, oxidation - reduction phenomena, acids and bases, and non-aqueous solvents.

Part II is more descriptive and discusses the elements and their compounds, where possible, in terms of the principles developed in Part I.

The printing is good, the diagrams are clear, and the references well chosen and by no means confined to American work.

The author is to be congratulated on writing a book of moderate size that meets a real need for chemists, but it is a pity that the price is so high; it is the one factor that may prevent the book from having, in this country, the success it deserves.

L. S. THEOBALD

## Publications Received

- MODERN MASS SPECTROMETRY. By G. P. BARNARD, B.Sc., Ph.D., A.M.I.E.E., F.Inst.P. Pp. 326. London: The Institute of Physics. 1953. Price 50s.
- CIBA FOUNDATION COLLOQUIA ON ENDOCRINOLOGY. Volume V. BIOASSAY OF ANTERIOR PITUITARY AND ADRENOCORTICAL HORMONES. Edited by G. E. W. WOLSTENHOLME, O.B.E., M.A., M.B., B.Ch., and MARGARET P. CAMERON, M.A., A.B.L.S. Pp. xvi + 228. London: J. and A. Churchill Ltd. 1953. Price 25s.
- APPLIED INORGANIC ANALYSIS. WITH SPECIAL REFERENCE TO THE ANALYSIS OF METALS, MINERALS AND ROCKS. By Dr. W. F. HILLEBRAND and Dr. G. E. F. LUNDELL. Second Edition. Revised by Dr. G. E. F. LUNDELL, H. A. BRIGHT, M.S., and Dr. J. I. HOFFMAN. Pp. xxii + 1034. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1953. Price 120s.; \$15.00.
- RICHMOND'S DAIRY CHEMISTRY. Revised by J. G. DAVIS, D.Sc., Ph.D., F.R.I.C., and F. J. MACDONALD, A.R.I.C. Fifth Edition. Pp. viii + 603. London: Charles Griffin & Co. Ltd. 1953. Price 60s.
- TOXICITY OF INDUSTRIAL ORGANIC SOLVENTS. (Revised in consultation with the Toxicology Committee.) Report No. 80 of the Medical Research Council, Industrial Health Research Board. By ETHEL BROWNING. Second Edition. Pp. viii + 412. London: H.M. Stationery Office. 1953. Price 35s.
- LEYBOLD POLAROGRAPHISCHE BERICHTE. Band I, Heft 1/2, Oktober, 1952, and Heft 3, Januar, 1953. Pp. 54; 52. Köln: Staufien-Verlag. Subscription DM. 10 per annum.  
*Polarographic abstracts.*
- PROTECTIVE DISPLAY LIGHTING OF HISTORICAL DOCUMENTS. National Bureau of Standards Circular 538. Pp. ii + 8. Washington: U.S. Government Printing Office. 1953. Price 15 cents.
- NON-AQUEOUS SOLVENTS. APPLICATIONS AS MEDIA FOR CHEMICAL REACTIONS. By LUDWIG F. AUDRIETH and JACOB KLEINBERG. Pp. xii + 284. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1953. Price 54s.; \$6.75.
- CHEMICAL CONSTITUTION. AN INTRODUCTION TO THE THEORY OF THE CHEMICAL BOND. By Dr. J. A. A. KETELAAR. First English Edition translated by Dr. L. C. JACKSON. Pp. viii + 398. Amsterdam, New York and London: Elsevier Publishing Co.; London: Cleaver-Hume Press Ltd. 1953. Price 40s.

## Papers for Publication in *The Analyst*

THE Editor welcomes Papers and Notes for insertion in *The Analyst*, whether from members of the Society or non-members. They are submitted to the Publication Committee, who decide on their suitability for insertion or otherwise.

A copy of the current Notice to Authors, last published in full in *The Analyst*, 1952, 77, 495, can be obtained on application to the Editor, *The Analyst*, 7-8, Idol Lane, London, E.C.3. All Papers submitted will be expected to conform to the recommendations there laid down and any that do not may be returned for amendment.

A few copies of the tabulated "Nomenclature of Vitamins," reprinted from *The Analyst*, 1953, 78, 72, are also available.



**CHEMIST** required for analytical and preparative research on inorganic chemicals and magnesium. Applicants should have B.Sc. or A.R.I.C. with some practical experience and would be expected to work under the Chief Analyst in a modern and well equipped laboratory. Salary depending on qualification and experience. Apply to the Secretary, Magnesium Elektron Limited, Clifton Junction, near Manchester.

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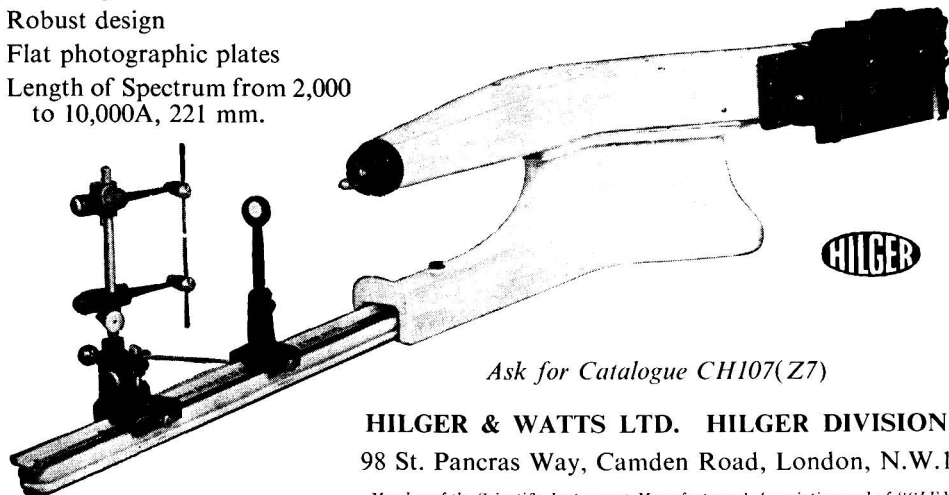
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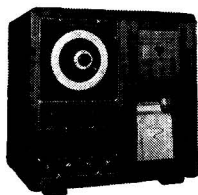
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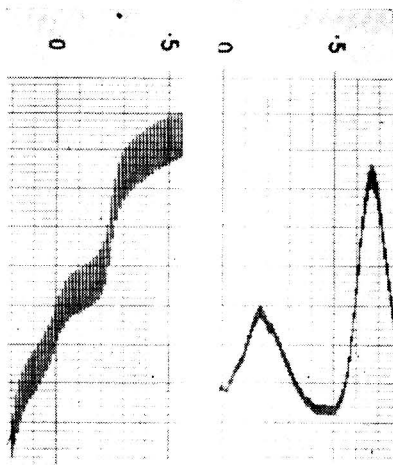
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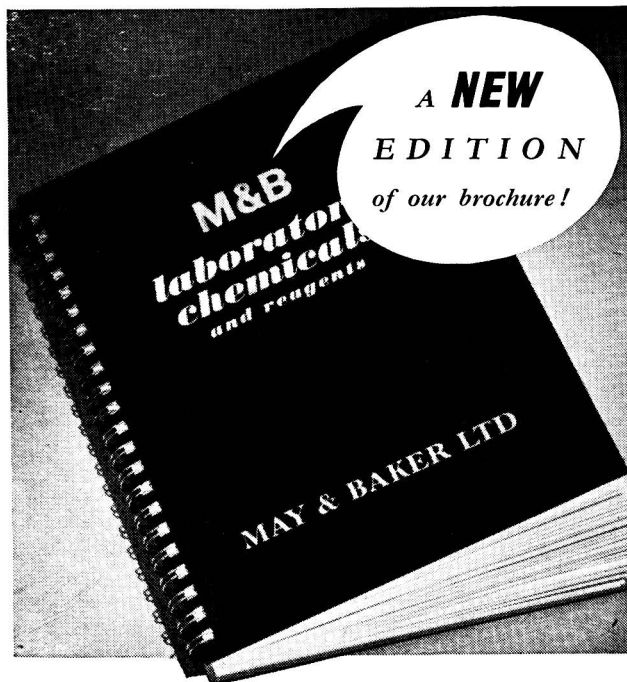
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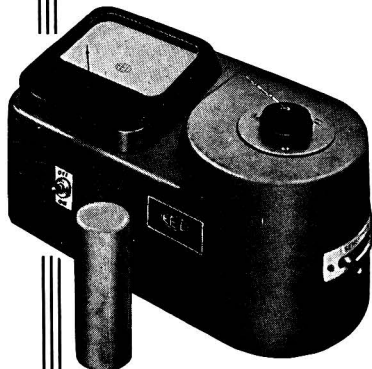
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OXFORD, 4th—9th September, 1952

Pp. xii + 493

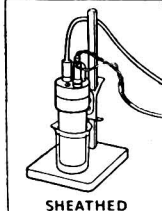
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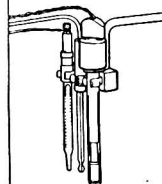
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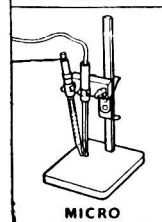
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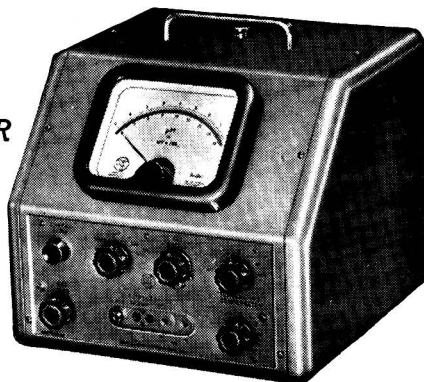
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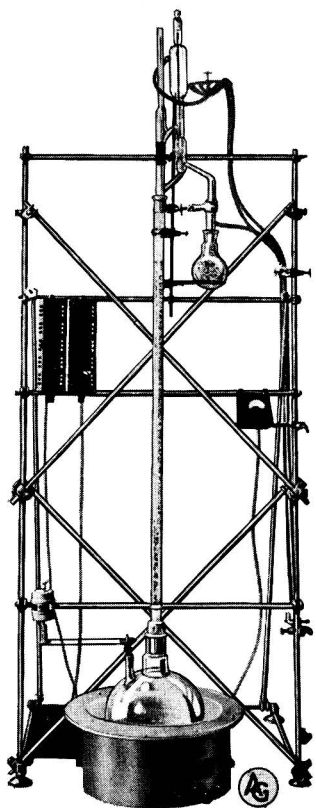
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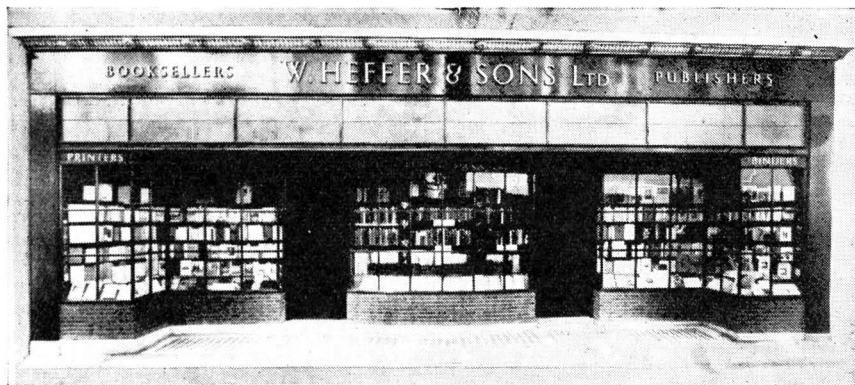
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