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The Determination of Phenol, *o*-Cresol and *p*-Cresol in Aqueous Solution by a Kinetic Method

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Certain phenols can be determined in aqueous solution by a kinetically controlled bromination in which the only measurement is the time taken for the bleaching of an indicator. This time is proportional to the concentration of the indicator. Since no specialised apparatus is needed, the method is not restricted to the laboratory.

PHENOLIC substances are often determined by bromination in aqueous solution.[1,2,3] One method is to add an excess of a standard solution of bromate and bromide ions to an acidified solution of the phenol. After a suitable interval of time, during which the bromination reaction proceeds to completion, an excess of iodide ions is added, and the iodine liberated is back-titrated with standard thiosulphate solution. Phenol has also been determined in micro amounts by using the electrochemical generation of bromine.[4]

This paper shows that phenol, *o*-cresol and *p*-cresol can be determined bromometrically in dilute aqueous solution, without the necessity of using a titration or an electrochemical technique. Analytical use is made of the kinetic characteristics of the following two reactions—

(*a*) the production of bromine in an aqueous solution containing bromide, bromate and hydrogen ions;
(*b*) the nuclear mono-bromination of the phenol.

The observed variable is the time of bleaching of an indicator, and the conditions are chosen so that the observed time is directly proportional to the concentration of phenol used.

The theoretical basis of the method is that when a mixture of bromide and bromate ions to which phenol has been added is acidified, a stationary-state concentration of bromine is set up in accordance with the following equations—

$$H^+BrO_3^- + H^+Br^- \xrightarrow{k_1} \text{products (ultimately bromine)} \quad \ldots \quad (1)$$

$$ArH_3 + Br_2 \xrightarrow{k_2} ArH_2Br + H^+Br^- \quad \ldots \quad (2)$$

where Ar represents an aromatic nucleus.

The rate constant for reaction (2) is large, as would be expected from the fact that the addition of bromine water to aqueous phenol produces an immediate precipitate of tribromophenol. Bell and Rawlinson[5] found the value of k_2 for phenol, at 25° C, to be $1{\cdot}8 \times 10^5$ litre per mole per second.

Because of the large rate constant for nuclear bromination, the concentration of bromine is so low that the stationary-state hypothesis may be applied to the system until the point is reached at which the phenol is completely converted into tribromophenol. Consequently, at all stages of the reaction, both before and after the mono-bromination stage, the rate of nuclear bromination equals the rate of generation of bromine from bromide and bromate ions. Under these stationary-state conditions, the rate of nuclear bromination is independent of the chemical nature and the concentration of the phenol, for it is determined only by the rate of reaction (1).

A further consequence of the stationary state is that, during mono-bromination, the concentration of bromine is so low that an azo dye, such as methyl orange, is not bleached significantly in the course of a few minutes.

The essential feature of the analytical method proposed is that the de-activating effect of the bromine atom on the aromatic nucleus causes the rate constant for di-bromination to

be much less than that for mono-bromination. As a result, the stationary-state concentration of the bromine rises rapidly as the mono-bromination stage is approached, when it reaches a level at which methyl orange is rapidly bleached. This is confirmed potentiometrically for, at the time when the methyl orange bleaches, there is a sharp increase in the slope of the curve of redox potential against time. The time of bleaching for given initial concentrations of bromate, bromide and hydrogen ions at a given temperature depends only on the concentration of the phenol.

The over-all stoicheiometry for the mono-bromination of a phenolic molecule (ArH) by an acidified aqueous solution of bromate and bromide ions, is given by the equation—

$$BrO_3^- + 2Br^- + 3H^+ + 3ArH \rightarrow 3ArBr + 3H_2O \quad .. \quad .. \quad .. \quad (3)$$

As has been shown above, the rate of nuclear bromination is independent of the concentration of phenol, and so the reaction shown in equation (3) obeys the kinetic rate law[6] for the bromide - bromate reaction, namely—

$$-d[BrO_3^-]/dt = R = k[BrO_3^-][Br^-][H^+]^2 \quad .. \quad .. \quad .. \quad (4)$$

SELECTION OF OPTIMUM INITIAL CONCENTRATIONS—

Let a be the initial concentration of bromate in the reaction mixture,
b, the initial concentration of the phenol,
R_0, the initial rate of the bromate - bromide reaction,
R_1, the rate of the bromate - bromide reaction when the indicator is bleached,
k, the fourth order rate constant of the bromate - bromide reaction (equation 4),
and t_1, the time of bleaching of the indicator.

To obtain a linear calibration graph of phenol concentration against time of bleaching, the rate of the bromate - bromide reaction (given by equation 4) must be effectively constant. Mathematical analysis of equations (3) and (4) shows that deviations from linearity are minimised if the initial concentrations of bromate, bromide and hydrogen ions are in the ratio in which they are consumed in the bromination reaction, namely 1 : 2 : 3. If this is so, then—

$$R_0 = 18ka^4 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

As 3 molecules of phenol are consumed for each bromate ion consumed, then—

$$R_1 = 18k(a - b/3)^4 \text{ where } b < 3a \quad .. \quad .. \quad (6)$$

Hence
$$R_1/R_0 = (1 - b/3a)^4 \quad .. \quad .. \quad .. \quad .. \quad (7)$$

i.e.
$$R_1/R_0 = 1 - 4b/3a, \text{ if } b \ll 3a \quad .. \quad .. \quad .. \quad (8)$$

Equation (8) shows that the rate at the time of bleaching is always less than the initial rate, but, providing that $b \ll a$, the rate is effectively constant and the approximation $R_1 = R_0$ is nearly exact. If this is so, then, since b mole per litre of the phenol are mono-brominated in time t_1—

$$R_0 = 18ka^4 \simeq b/3t_1 \quad .. \quad .. \quad .. \quad .. \quad (9)$$

i.e.
$$a = \left(\frac{b}{54kt_1}\right)^{\frac{1}{4}} \quad .. \quad .. \quad .. \quad .. \quad (10)$$

Substitution of a known value of k in equation (10) enables the initial value of a to be calculated for any desired value of t_1.

Examination of equation (8) shows that the condition for the rate to be constant up to the time of bleaching is that b/a must be so small that $R_1/R_0 \simeq 1$. However, for a pre-selected time of bleaching, a and b are related by equation (10). This equation shows that for a given time (t_1) and concentration of phenol (b), the value of b/a decreases as the rate constant (k) decreases. Lowering the temperature reduces k and, consequently, also reduces b/a. In practice, a value of t_1 of up to 200 seconds at 0° C proves to be convenient, as this enables an ice-bath to be used for temperature control.

METHOD

REAGENTS—

Bromate - bromide stock solution—Prepare an aqueous solution, 0·1 M with respect to potassium bromate, and 0·2 M with respect to potassium bromide.

Sulphuric acid - methyl orange solution—Prepare an aqueous solution, 0·15 M (0·3 N) with respect to sulphuric acid, containing 10 mg of methyl orange per litre of solution.

PROCEDURE—

Place 25 ml of the sulphuric acid - methyl orange solution in a 50-ml calibrated flask and add an aliquot of the unknown phenol solution. Dilute the contents of the flask to the mark with water. The resulting sample solution should be not more than 0·004 M with respect to the phenol.

Place 10 ml of the bromate - bromide stock solution and 20 ml of the sample solution prepared above, in separate clean, dry boiling-tubes and allow the solutions to cool to 0° C in an ice-bath. Start a stop-clock, and after noting the time, pour the contents of one tube quickly into the other tube. Uniformity of composition is ensured by transferring the resulting solution quickly from one tube to the other twice more. Then place the reaction mixture back in the ice-bath over a white tile, and look vertically down through the solution. Record the time when the last tinge of red colour of the indicator disappears. Calibrate the method by using a solution of phenol of known concentration (0·01 M is suitable), and by varying the amount added in making the sample solution.

The bleaching of the indicator occurs over the course of a few seconds. To standardise the timing procedure, a blank experiment is made with the mixed solutions of sulphuric acid - methyl orange and bromate - bromide, but without phenol. This gives a bleaching time of about 3 seconds. The value for the blank is subtracted from the values obtained in the determination, and corrected times are used.

RESULTS AND DISCUSSION

The results of 18 measurements on phenol, *o*-cresol and *p*-cresol are shown in Fig. 1. The continuous line was calculated by the "least squares" method. The standard deviation from this line is 3·3 seconds.

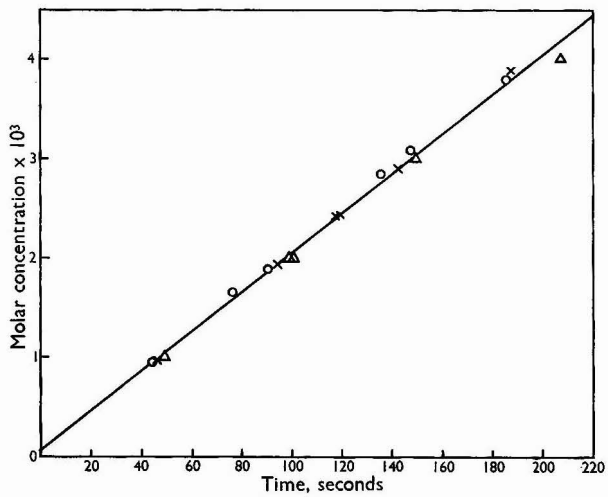

Fig. 1. Time of bleaching for various concentrations: ○, phenol; △, *o*-cresol; and ×, *p*-cresol

These results suggest that the method is capable of giving rapid analyses to an accuracy of ±3 per cent.

Equation (10) requires the slope of the calibration graph, shown in Fig. 1, to be $54ka^4$. The observed slope is $2{\cdot}0 \times 10^{-5}$ mole per litre per second, whereas the calculated value under the quoted experimental conditions is $2{\cdot}8 \times 10^{-5}$ mole per litre per second, assuming k to be 0·42 litre³ per mole³ per second. This agreement is acceptable, bearing in mind, (*a*), that this value of k has been extrapolated from a value[7] at 25° C by using the Arrhenius equation, and, (*b*), that the rate constant for this reaction varies considerably with ionic strength.[8]

In the examples quoted in Fig. 1, the time for the first precipitation of di-brominated or tri-brominated products was greater than that for the bleaching of the indicator. However, with *m*-cresol, precipitation occurred before the indicator was bleached. Examination of the structures of *o*-cresol, *m*-cresol and *p*-cresol shows that it is only in the meta isomer that the

methyl group is ortho or para to the site of substitution. As the methyl group activates strongly at the ortho and para positions and has little effect at the meta position, the rate constant for the bromination of *m*-cresol is much higher than that of *o*-cresol and *p*-cresol. Hence, the mono-brominated *m*-cresol can be di-brominated at a rate comparable to that for mono-bromination of *o*-cresol and *p*-cresol, and consequently the indicator method fails for *m*-cresol.

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A Continuous Monitor for Hydrogen in Gases

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The construction and use of an instrument for the continuous monitoring of hydrogen in gas streams is described. The principles upon which the instrument is based are the catalytic oxidation of hydrogen to water, and the subsequent determination of the water with an electrolytic hygrometer. Factors relevant to the efficient operation of the instrument for laboratory and plant conditions are discussed. Results indicate a coefficient of variation of the order of ± 5 per cent. for the 80 to 1000-v.p.m. hydrogen range.

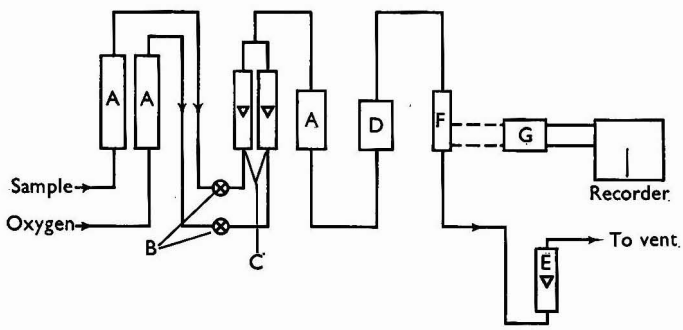
In a previous paper[1] a technique was outlined for the continuous monitoring of hydrogen in carbon dioxide based gas mixtures. The work reported here is a description of the construction, operation and performance of an instrument used for monitoring hydrogen, both in the laboratory and under plant conditions.

The principles upon which the instrument are based is the catalytic oxidation of hydrogen to water, and the determination of the latter with an electrolytic hygrometer. The instrument may be used for hydrogen monitoring of inert-gas streams other than carbon dioxide.

Experimental

Apparatus—

The apparatus is shown schematically in Fig. 1. It is housed in an $18 \times 18 \times 9$-inch aluminium cabinet. The front panel contains a variable auto-transformer and pyrometer for controlling and indicating the temperature of the catalytic furnace, gas-input connections, flow controllers, rotameters and the hydrogen concentration meter. Two molecular-sieve 5 Å driers, the electrolytic cell and the catalytic furnace are fixed on the rear panel. The concentration of hydrogen is recorded continuously by means of a 10-mV potentiometric recorder.



A = Molecular sieve, 5Å, 1/16-inch pellets, ambient temperature
B = Millaflow flow controllers
C = Rotameters for sample and oxygen
D = Catalyst tube and furnace, 300° C
E = Total-flow volameter
F = Electrolytic cell
G = Electronics

Fig. 1. Schematic diagram of hydrogen monitor

The catalytic furnace consists of a stainless-steel vessel that is resistance heated and packed with small pieces of platinum ribbon. The heater is rated to give a maximum temperature of 800° C at the platinum surface. At the time of assembly, the stainless-steel pipework, desiccant containers and catalyst tube (together with its platinum) must be cleaned according to a standard procedure,[1] and all gas lines must be thoroughly dried. All couplings are of the de-mountable O-ring or compression-seal type.

PROCEDURE—

Connect the sample gas and oxygen supply to their respective positions on the front panel of the instrument, and adjust the gas pressure to 20 p.s.i. The optimum flow-rates are 100 ml per minute and 10 ml per minute for sample and oxygen, respectively, at a furnace temperature of 500° C. With a new instrument it has been found that clean-up periods of 3 days are required, with argon as the purge gas. A blank reading for the instrument is determined by passing oxygen or helium through the system. Under the above operating conditions, hydrogen values of less than 5 v.p.m. are observed, which are considered to be negligible.

Replace the sample gas periodically with a standard hydrogen - carbon dioxide mixture to check the efficiency of the catalyst and electrolytic cell. Exposure of the electrolytic cell to an excess of moisture (most likely to occur during the commissioning of the instrument) leads to "flooding" and, possibly, to damage of the phosphorus pentoxide film. Rapid re-coating of the cell may be carried out according to the manufacturer's instructions.

RESULTS AND DISCUSSION

The following important factors were considered in the design and operation of the instrument.

Cleanliness of surfaces—

It is of paramount importance to ensure that all internal stainless-steel surfaces in contact with the sample gas or gases are thoroughly clean with respect to grease and oxide. Surfaces not subjected to the cleaning technique previously described[1] may act as a "sponge" to moisture and a high instrument blank may result. This stricture particularly applies to the catalytic unit and the tubing between the latter and the electrolytic cell.

Minimum delay time—

The time required to register an alteration of hydrogen concentration in the sample gas is dependent on the delay volume and the flow-rate of sample gas. This delay volume of the pipework, valves and catalyst vessel must be as small as possible, consistent with efficient operation of the instrument. In the present design, the sample gas drier, immediately prior to the Millaflow flow controller, constitutes 95 per cent. of the delay volume. The equilibration time required for the instrument described is of the order of 10 minutes.

Minimum maintenance—

The instrument has been used over plant operating periods of several weeks during which time no maintenance has been required. The equilibrium moisture capacity of molecular sieve 5 Å at 25° C and inlet moisture concentration[2] of 100 v.p.m. is approximately 20 per cent. w/w. Therefore, for a sample gas flow-rate of 100 ml per minute, containing 100 v.p.m. of moisture, the life of the sample gas drier will be of the order of 5 years. Frequent reduction in oxidation efficiency of the catalyst, for example, by the deposition of carbon from thermally unstable organic compounds or irreversible poisoning by sulphur compounds, must be avoided. In addition, potential catalyst poisons, such as sulphur compounds, are polar molecules and are therefore likely to be retained firmly on the molecular-sieve drier.

Calibration—

Although the electrolytic hygrometer is a quantitative instrument and, therefore, frequent calibration is not necessary, the provision of a standard hydrogen gas supply facilitates rapid calibration of both the platinum catalyst and the electrolytic cell.

A series of four hydrogen - carbon dioxide gas mixtures was prepared and analysed by means of helium gas chromatography.[3] The hydrogen concentrations were 80, 160, 510 and 920 v.p.m. The effect of varying the catalyst temperature over the range of 150° to 500° C and halving the sample gas flow-rate to 50 ml per minute was investigated with the 920 v.p.m. hydrogen standard-gas mixture. The results (shown in Table I) indicate that complete oxidation of the hydrogen was achieved over the temperature range 300° to 500° C for a 100 ml per minute sample flow-rate and 200° to 500° C for a 50 ml per minute sample flow-rate. In addition, it was shown that varying the oxygen flow-rate from 2 to 30 ml per minute did not affect the indicated hydrogen concentration.

TABLE I

VARIATION OF CATALYST TEMPERATURE AND SAMPLE FLOW-RATE

Catalyst temperature, ° C	Standard gas flow-rate, ml per minute	Hydrogen monitor reading, v.p.m.	Indicated hydrogen concentration, v.p.m.
500	50	470	940
500	100	910	910
450	50	480	960
450	100	910	910
400	50	470	940
400	100	930	930
350	50	470	940
350	100	890	890
300	50	470	940
300	100	900	900
250	50	460	920
250	100	359	359
200	50	465	930
200	100	138	138
150	50	83	166
150	100	83	83

A typical calibration of the instrument over the range 0 to 1000 v.p.m. of hydrogen, for a sample flow-rate of 100 ml per minute, oxygen flow-rate of 10 ml per minute and catalyst temperature of 300° C, is shown below—

Hydrogen in standard gas, v.p.m.	920	513	160	80
Hydrogen monitor, v.p.m. ..	930	490	170	85

Calibration of this type, together with the determination of hydrogen in a gas mixture that had been analysed by helium gas chromatography, have indicated a maximum error of ±5 per cent. for the instrument.

INTERFERENCE—

Any hydrogenous compound that passes through the molecular sieve and is oxidised to water on the catalyst will create a positive error in the recorded hydrogen content. The lower alkanes and alkenes are examples. The four lowest alkanes were used to investigate the interference effect on the instrument. Methane, ethane, propane and butane were added to carbon dioxide to provide four sources of the basic gas with 500 v.p.m. of alkane as impurity. A mixture of alkane and carbon dioxide, flow-rate 100 ml per minute, together with oxygen, flow-rate 10 ml per minute, were passed through the instrument at a catalyst temperature of 300° C. The results are shown below—

	Methane	Ethane	Propane	Butane
Percentage of oxidation	<0·001	0·5	1·0	2·0

On the basis of these results, the operating temperature of 300° C was selected in order to minimise interference by oxidation of higher hydrocarbons.

OPERATION UNDER PLANT CONDITIONS—

The hydrogen content of the gas coolant in the Advanced Gas-Cooled Reactor at Windscale was continuously monitored by gas chromatography and hydrogen monitor for a period of 6 weeks. The gas chromatograph and hydrogen monitor values were compared for a nominal 400-v.p.m. hydrogen concentration. A relative deviation of 7 per cent. was found for 137 paired determinations. The difference between this deviation and the deviation obtained with hydrogen standards (*i.e.*, 5 per cent.) was attributed to a slight difference in coolant-sampling position and to the deviation normally found in routine helium ionisation chromatography.

CONCLUSION

An instrument has been devised for the continuous monitoring of hydrogen in carbon dioxide and inert gases. Operation parameters have been determined for maximum efficiency and specificity. An assessment for continuous monitoring under plant conditions has been made and the instrument found to be satisfactory.

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The Determination of Helium-3 in Argon at Levels of 10^{-12}

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The helium in the argon is first concentrated by removing the argon on an activated charcoal trap at −190° C. The helium is then transferred to a modified A.E.I. Ltd., MS2 mass spectrometer equipped with a Vibron amplifier, in which the volume of the helium-3 (and helium-4) is measured. With 1-litre samples the limit of detection is approximately 2×10^{-5} p.p.m. by volume.

Current experience on establishing the level of helium-3 in the argon blanket gas of the Dounreay Fast Reactor is outlined.

THE measurement of the level of helium-3 and its day-to-day variation in the argon "blanket" gas of the Dounreay Fast Reactor has been carried out. Helium-3 is produced within the reactor from the radioactive decay of tritium, which is produced by two nuclear reactions: (*i*), ${}^{6}_{3}\mathrm{Li}$ (n, α) ${}^{3}_{1}\mathrm{H}$ on the lithium present as an impurity in the sodium - potassium metal (primary coolant), and (*ii*), ternary fission in the uranium fuel of the driver charge. The driver charge fuel elements are vented so that fission-product gases escape into the argon gas blanket.

Calculations showed that the volume of helium-3 produced from tritium decay should be from about 0·3 to 0·6 ml per year. Therefore, as the argon blanket gas has a volume of about 10^{8} ml, in order to detect the day-to-day change in the helium-3 level it was necessary to measure about 1 to 2×10^{-5} p.p.m. by volume.

By using refined techniques with a conventional mass spectrometer, the detection limit for the direct determination of helium in argon can be lowered to about 5 p.p.m. by volume and by a simple impurity-concentration technique[1] to 0·05 p.p.m. by volume. Therefore, in order to achieve the required 1 to 2×10^{-5} p.p.m. by volume, a superior concentration procedure was required and, as the sample size was limited to 1 litre, arising from the associated radioactive fission-product gases (radiation levels up to 1 Roentgen per hour per litre), improved spectrometric sensitivity was also required. The determination of 10^{-8}-ml amounts of rare gas is usually only undertaken with special instruments and techniques, *e.g.*, as used on rare gases from meteorites.[2]

EXPERIMENTAL

MASS SPECTROMETRIC DEVELOPMENT—

A standard A.E.I. Ltd., MS2 mass spectrometer and a Vibron Mass Spectrometer Amplifier Type 51A were made available for the work.

By using the standard d.c. amplifier equipped with a 4×10^{10}-ohm resistor the limit of detection for helium was about 5×10^{-5} ml. The Vibron amplifier was then fitted (the Vibron head being fitted with a 10^{12}-ohm resistor and 3-pF condenser). This lowered the detection limit to about 2×10^{-6} ml, but the noise level was appreciable and the time constant of the detection system long (about 3 seconds) for normal peak-scanning techniques to be used. Measurements had to be made with the instrument controls already "tuned" to the required mass number, and the stability of various voltage and current supplies was of paramount importance.

For maximum sensitivity the mass-spectrometer ion-source voltages were adjusted (tuned) to the first ion repellor maximum on mass number 3 for the helium-3 determinations and on mass number 4 for early work with "natural" helium-4.

To increase further the sensitivity of the mass spectrometer a 2-litre reservoir of the double-inlet system of the MS2 was replaced with a small reservoir of about 50-ml capacity. Corrections, however, have to be applied to the recorded results to allow for the pumping away of the gas through the mass spectrometer leak valve. (The leak has molecular flow characteristics, and hence the flow is proportional to $M^{-\frac{1}{2}}$ where M is the molecular weight of the gas concerned.) With these modifications, the detection limit should now be approximately 5×10^{-8} ml of helium.

To establish the detection limit of the mass spectrometer, samples of air containing 5·4 p.p.m. by volume of helium were used. Aliquots (0·2 ml) were dispensed into the 50-ml reservoir, and the mass number 4 peak was measured. Five aliquots gave an average reading of 67·2 $\pm$ 1·4 (2σ) divisions on a 10-inch recorder chart (100 divisions = full-scale deflection) with a noise level of approximately 2 divisions. Thus 1×10^{-6} ml of helium-4 could be measured to within ± 2 per cent.; 2×10^{-7} ml is measurable to within ± 10 per cent. and the absolute detection limit, *i.e.*, twice noise level, is about 2×10^{-8} ml. Use of a calibrated helium leak also confirmed the accuracy of these absolute measurements. Taken in conjunction with a 1-litre sample this gave a detection limit of 2×10^{-5} p.p.m. by volume.

The major drawback to the detection of helium-3 was that at mass number 3, the peaks from the hydrogen deuteride ion HD^+ and, if sufficient hydrogen is present, the association ion H_3^+ also occur. To resolve the peaks in the mass doublet requires a resolving power of at least 500.

^3He : 3·01699 a.m.u.

HD : 3·02289 a.m.u.

$$\therefore \text{Resolving power} = \frac{M}{\Delta M} = \frac{3}{0{\cdot}006} = 500$$

The standard MS2 has a resolving power of about 200, with the collector slit at 0·020 inch; this resolving power was insufficient to distinguish the two peaks at mass number 3 in a mixture of helium-3, hydrogen and deuterium (Fig. 1). Decreasing the collector slit width to 0·005 inch gave only sufficient resolving power to distinguish the two peaks (Fig. 2). Decreasing of the collector slit reduced the sensitivity by a factor of four. In view of the poor resolution and the lowered sensitivity a hydrogen-removal stage was added to the concentration procedure, the collector slit being opened out again to 0·020 inch.

It was found that, with volumes of air in excess of 0·2 ml, there was a distinct suppression effect on the mass-4 peak, probably arising from space-charge effects that caused de-focusing of the ion beam. This set the limit for the volume of concentrated gas from the concentration apparatus.

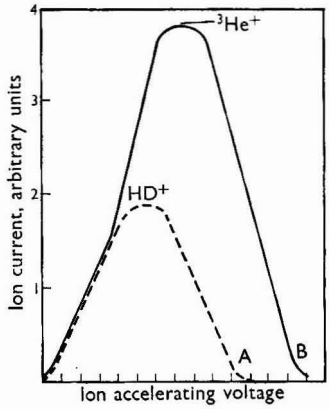


Fig. 1. Peak shape of mass 3 with 0·02-inch collecter slit: graph A, hydrogen deuteride only; graph B, a mixture of helium-3 and hydrogen deuteride

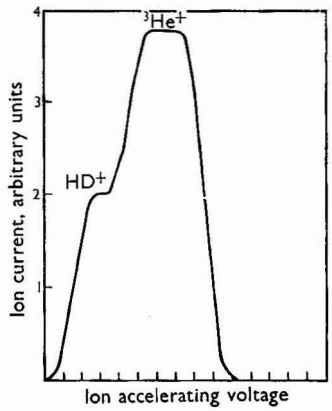


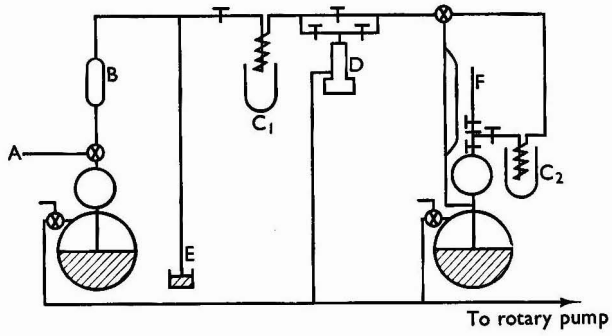
Fig. 2. Peak shape of mass 3 with 0·005-inch collecter slit; mixture of helium-3 and hydrogen deuteride showing partial resolution of mass-3 doublet

CONCENTRATING THE HELIUM—

Helium and argon are both members of the "inert"-gas family, therefore they cannot be separated by chemical procedures, and use must be made of variations in their physical properties.

The boiling-point of argon is —185·7° C and that of helium is —268·9° C, so the argon can be condensed at liquid nitrogen temperature (—195·8° C) leaving helium as a gas.

A few experiments were made with a simple apparatus, the argon was condensed in a cold-trap containing an absorbent and the helium was recovered by pumping. It was established that activated charcoal held the argon better than a molecular sieve, and an apparatus was constructed (Fig. 3).



A = Sample attachment point
B = B.T.S. reagent container
C_1, C_2 = Cold traps (−196° C)
D = Mercury diffusion pump
E = Simple manometer
F = Concentrate sample tube
⊗ = 3-way taps
T = Taps
\+ = Ground-glass joint

Fig. 3. Schematic diagram of the helium concentration apparatus

A series of experiments was carried out to determine the recovery of helium. The helium was added by using known volumes of air (5·4 p.p.m. by volume of natural helium)—the main constituents of air, *i.e.*, oxygen and nitrogen, are retained on the liquid-nitrogen cooled charcoal, the helium being pumped from trap 1 to trap 2 and finally into the sample tube.

The results of the first series of experiments are summarised in Table I. These are results on concentrates from 50-ml aliquots of air that should contain $2{\cdot}7 \times 10^{-4}$ ml of helium. The analyses were carried out on a standard MS2 gas mass spectrometer.

TABLE I

RECOVERIES OF HELIUM FROM 50 ml OF AIR

Aliquot No.	Total volume of concentrated gas, ml	Volume of helium found, ml	Helium added, ml	Recovery, per cent.
1	—	$2{\cdot}7 \times 10^{-4}$	$2{\cdot}7 \times 10^{-4}$	100
2	$3{\cdot}6 \times 10^{-4}$	$2{\cdot}6 \times 10^{-4}$	$2{\cdot}7 \times 10^{-4}$	96
3	$3{\cdot}7 \times 10^{-4}$	$2{\cdot}8 \times 10^{-4}$	$2{\cdot}7 \times 10^{-4}$	103
4	$4{\cdot}1 \times 10^{-4}$	$2{\cdot}8 \times 10^{-4}$	$2{\cdot}7 \times 10^{-4}$	103

A second series of experiments was then undertaken, in which the samples consisted of 1 litre of helium-free argon and 25 ml of air, *i.e.*, $1{\cdot}35 \times 10^{-4}$ ml of helium. Results are summarised in Table II.

TABLE II

RECOVERIES OF HELIUM FROM 25 ml OF AIR IN 1 LITRE OF ARGON

Sample No.	Total volume of concentrated gas, ml	Volume of helium found, ml	Helium added, ml	Recovery, per cent.
1	$2{\cdot}9 \times 10^{-4}$	$1{\cdot}6 \times 10^{-4}$	$1{\cdot}35 \times 10^{-4}$	118
2	$2{\cdot}3 \times 10^{-4}$	$1{\cdot}3 \times 10^{-4}$	$1{\cdot}35 \times 10^{-4}$	96
3	$2{\cdot}8 \times 10^{-4}$	$1{\cdot}4 \times 10^{-4}$	$1{\cdot}35 \times 10^{-4}$	104
4	$4{\cdot}0 \times 10^{-4}$	$1{\cdot}4 \times 10^{-4}$	$1{\cdot}35 \times 10^{-4}$	104
5	$2{\cdot}5 \times 10^{-4}$	$1{\cdot}4 \times 10^{-4}$	$1{\cdot}35 \times 10^{-4}$	104
6	$3{\cdot}8 \times 10^{-4}$	$1{\cdot}3 \times 10^{-4}$	$1{\cdot}35 \times 10^{-4}$	96
7	$2{\cdot}5 \times 10^{-4}$	$1{\cdot}4 \times 10^{-4}$	$1{\cdot}35 \times 10^{-4}$	104

As good recoveries of helium at this level from 1 litre of argon had been established, a third series of experiments was carried out with a very much lower level of helium. This time the helium-4 in the concentrated gas was measured with the modified mass spectrometer. It should be noted that the concentration apparatus was made of Pyrex glass and may therefore be slightly porous to natural helium. Blank values on the apparatus were equivalent to $0{\cdot}2$ to $0{\cdot}3 \times 10^{-6}$ ml of helium.

Synthetic samples were prepared by using 1 litre of helium-free argon and 0·65 ml of air, *i.e.*, $3{\cdot}5 \times 10^{-6}$ ml of helium-4. Results are given in Table III.

TABLE III

RECOVERIES OF HELIUM FROM 0·65 ml OF AIR IN 1 LITRE OF ARGON

Sample No.	Volume of helium, ml	Corrected for blank, ml	Volume of helium added, ml	Recovery, per cent.
1	$3{\cdot}8 \times 10^{-6}$	$3{\cdot}5 \times 10^{-6}$	$3{\cdot}5 \times 10^{-6}$	100
2	$3{\cdot}5 \times 10^{-6}$	$3{\cdot}2 \times 10^{-6}$	$3{\cdot}5 \times 10^{-6}$	92
3	$3{\cdot}9 \times 10^{-6}$	$3{\cdot}6 \times 10^{-6}$	$3{\cdot}5 \times 10^{-6}$	103
4	$7{\cdot}0 \times 10^{-6}$	$6{\cdot}7 \times 10^{-6}$	$3{\cdot}5 \times 10^{-6}$	191
5	$6{\cdot}1 \times 10^{-6}$	$5{\cdot}8 \times 10^{-6}$	$3{\cdot}5 \times 10^{-6}$	166
6	$3{\cdot}8 \times 10^{-6}$	$3{\cdot}5 \times 10^{-6}$	$3{\cdot}5 \times 10^{-6}$	100

The analysis showed that the hydrogen content of the concentrated gas was undesirably high, and in view of the resolution problem it was decided that it must be reduced to a minimal value. Experiments with helium-3 and varying amounts of hydrogen showed that a 10 per cent. increase in the mass-3 peak arising from H_3^+ (from the hydrogen) required more than 300 times as much hydrogen as helium.

Hydrogen is not removed by activated charcoal at −196° C; however, several chemical methods are available and experiments were carried out with palladised asbestos and "B.T.S. reagent" (finely divided copper made up into pellets with an organic binder), as supplied by B.A.S.F. of Germany. Both methods appeared to be equally effective in reducing the hydrogen content, but the B.T.S. reagent was chosen because the addition of oxygen gas to effect the removal of hydrogen was not necessary.

Blends, consisting of 1 litre of argon, 3·5 ml of air and 1 ml of hydrogen, were used for the experiments with the two reagents, and the results obtained are given in Table IV.

TABLE IV

RESIDUAL HYDROGEN FROM 1 ml OF HYDROGEN IN 1 LITRE OF ARGON

Reagent and Sample No.		Total volume of concentrated gas, ml	Volume of hydrogen, ml	Hydrogen removal, per cent.
Palladised asbestos	1	$9{\cdot}4 \times 10^{-4}$	$8{\cdot}1 \times 10^{-4}$	99·92
Palladised asbestos	2	$2{\cdot}1 \times 10^{-3}$	$1{\cdot}94 \times 10^{-3}$	99·81
Palladised asbestos	3	$1{\cdot}7 \times 10^{-3}$	$1{\cdot}62 \times 10^{-3}$	99·84
Palladised asbestos	4	$3{\cdot}7 \times 10^{-3}$	$3{\cdot}58 \times 10^{-3}$	99·64
B.T.S.	1	$1{\cdot}6 \times 10^{-3}$	$1{\cdot}51 \times 10^{-3}$	99·85
B.T.S.	2	$1{\cdot}9 \times 10^{-3}$	$1{\cdot}8 \times 10^{-3}$	99·82

The hydrogen remaining was then 2 to 3×10^{-3} ml, *i.e.*, the hydrogen removal was 99·7 to 99·8 per cent. effective. The hydrogen content of the concentrated gas has to be measured to make sure that it does not exceed 300 times the helium-3 content.

OUTLINE OF FINAL METHOD

Samples of blanket gas are taken from a sample point in 500-ml stainless-steel, lead-shielded sample vessels at 35 p.s.i., and are allowed to stand for a day to reduce the radioactivity; they are then analysed.

Between 500 and 1000 ml of gas are introduced into the helium-concentration apparatus (Fig. 3) and the volume is measured accurately. After passing the sample over the B.T.S. catalyst the argon is condensed in trap 1, the concentrated helium (and neon) is pumped into the interspace above the second Töpler pump and then into trap 2, where any remaining traces of condensable gases are removed. The Töpler pump is used to transfer the concentrated gas into the sample tube where a pressure - volume measurement is made.

The sample tube is then transferred to the double-inlet system of the MS2 mass spectrometer where the gas is expanded into the 50-ml reservoir. Measurements are made of the peaks at mass numbers 2, 3 and 4. To save the small amounts of gas from pumping steadily away via the leak valve to the mass spectrometer, the instrument controls are set to the desired mass number with monitor gas in the 2-litre reservoir. The leak valve to the 2-litre reservoir is closed and the leak valve to the 50-ml reservoir is opened for the sample peak height to be measured or recorded. The leak valve is then closed and the procedure repeated at the next mass number. A check is made on the time at which the leak valve was originally opened, T_0, the length of time for which it is open and the elapsed open-time at which each peak is measured; peak heights are then corrected for "pump-out" rates to give peak heights at T_0. The corrected peak height is then directly converted to the volume of helium-3 (or helium-4).

The mass spectrometer is calibrated immediately before or after each sample by introducing a known volume of an accurately prepared standard gas.

Results

Sampling from the Dounreay Fast Reactor gas circuit was instituted in late January, 1965. Helium levels encountered were much higher than had been envisaged, being 1 to 2×10^{-2} p.p.m. by volume of helium-3 and 20 to 50 p.p.m. by volume of helium-4. At these levels the size of sample taken was considerably reduced; 200 to 300 ml was usually quite sufficient. There was a considerable day-to-day variation of the helium-3 (and helium-4) content probably associated with sampling problems in a non-circulatory gas blanket system.

Reproducibility has been checked by regular samples from a synthetic blend of helium-3 in argon at approximately 3×10^{-3} p.p.m. by volume, and by taking several aliquots from one of the reactor gas samples.

Results on the synthetic blend are as follows—

helium-3 content: $0{\cdot}0030 \pm 0{\cdot}0001$ p.p.m. by volume.

Results on 3 aliquots from one reactor gas sample—

helium-3: $0{\cdot}8 \times 10^{-3}$ p.p.m. by volume, $0{\cdot}8 \times 10^{-3}$ p.p.m. by volume, $0{\cdot}8 \times 10^{-3}$ p.p.m. by volume;

helium-4: 31 p.p.m. by volume, 34 p.p.m. by volume, 34 p.p.m. by volume.

Discussion

A method has been devised for measuring very low levels of helium-3 in argon. The limit of the method as used with the Dounreay Fast Reactor argon samples is 2×10^{-5} p.p.m. by volume, but for less radioactive samples the method should be capable of coping with at least 5 litres of argon, *i.e.*, a limit of 4×10^{-6} p.p.m. by volume.

Other instrument modifications were considered, notably those by Cuthbert,[3] but were unnecessary in view of the helium levels encountered. Use of the Cuthbert modifications should lower the limit to 1×10^{-6} p.p.m. by volume.

Recovery of helium from the argon is good and is certainly better than 90 per cent. Reproducibility is good, better than 10 per cent.

The method has been proved in use over some 12 months.

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A Precise Coulometer

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This paper is a contribution to the application of coulometry to accurate analysis, and describes an apparatus which can be used for the accurate assay of "pure" sodium carbonate. An instrument has been built which measures coulombs with a probable error of ±25 p.p.m. as the product of a constant current and its time of flow. The current is maintained constant by an electric servo-system, and it is adjusted so that the voltage drop across a precise resistor is equal to the e.m.f. of a standard cell. Time is measured by a quartz-crystal clock. The resistor and cell are checked against local standards, which in turn have been calibrated against international standards by the National Physical Laboratory. The clock is checked against a broadcast frequency and the General Post Office Speaking Clock. Thus the quantity of electricity for a titration is referred ultimately to the fundamental standards of mass, length and time; the titre is independent of knowledge of the purity of any chemical substance.

COULOMETRIC titration as an analytical technique may be said to have originated with the work of Szebelledy and Somogyi[1] in 1938. Since then the subject has developed rapidly, and many papers and reviews have appeared; Swift, Furman, Lingane and Tutundzic have been responsible for most of the early work. The accuracy reported has been adequate for routine analyses, but has seldom been better than ±1000 p.p.m.*

Despite this, Tutundzic[2] suggested in 1958 that the coulomb should replace silver as the ultimate standard[3] for acidimetry. Tutundzic's proposal received considerable discussion, including some opposition.

The following year Taylor and Smith[4] reported the coulometric standardisation of acids and bases, including sodium carbonate, with the same order of precision as the best volumetric titrations. Their standard deviations ranged from 30 p.p.m. for potassium hydrogen phthalate to 100 p.p.m. for hydrochloric acid. They assayed sodium carbonate with a standard deviation of 70 p.p.m., but they controlled the current manually; the assay was not confirmed independently.

The present work seeks to overcome these two objections recognising that, if accuracy as good as, or better than, that by volumetric titration can be attained, it may lead to the recognition of the coulomb as a universal standard in volumetric analysis. Such a standard is independent of absolute knowledge of the purity of the chemical substances used as standards (knowledge that is difficult to obtain), and takes advantage of the high degree of precision that can be reached by electrical measurements.

The instrument must therefore be able to determine the number of coulombs taking part in a reaction with a coefficient of variation no greater than 100 p.p.m., this representing about the best that can be obtained in ordinary volumetric analysis. The efficiency of the electrode reaction must approach the theoretical very closely.

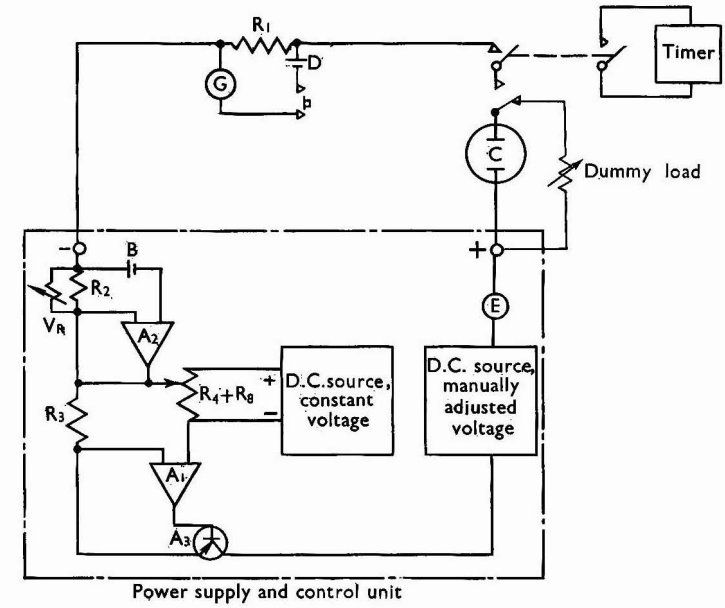
This paper describes the apparatus we have designed for the purpose. Experimental work on the coulometric titration of sodium carbonate, to be described later, provides evidence that the neutralisation of bases by electrically generated hydrogen ions can be carried out quantitatively. The entire process, the generation of hydrogen ions and measurement of current and time, is simpler and no less precise than reference of the sodium carbonate to silver, which is probably the best chemical method of assaying sodium carbonate.

APPARATUS

All the known types of coulometer, including the current - time integrating motor,[5] were considered. Others, such as the silver perchlorate method, might give similar precision but none was so directly related to the fundamental physical standards.

The instrument comprises (*i*) a precisely regulated constant-current source, whose output is monitored against a voltage standard, coupled with (*ii*) a means of measuring the time of flow of the current and (*iii*) a suitable cell wherein the reaction takes place. The cell is described elsewhere.[6] The remaining two main items will now be described.

* All errors and deviations are expressed in p.p.m. throughout the report. This applies to physical quantities such as voltage and current, as well as chemical quantities.



A_1 = Fast-acting current stabiliser
A_2 = Slow-acting trim amplifier
A_3 = Amplifier
B = Controlling reference cell
C = Coulometer cell
D = Working reference cell
E = Ammeter
G = Galvanometer
R_1, R_2, R_3, R_4 = Resistances
V_R = Manual current adjuster

Fig. 1. Coulometer block diagram

CURRENT SUPPLY (Fig. 1)—

This is a rectified a.c. supply, the voltage of which can be adjusted manually to be approximately correct, and is thereafter not disturbed. The current flowing in the cell circuit is controlled at the desired value by comparing the voltage drop across a precise 4-terminal resistor with the reference voltage, so that in maintaining constant voltage drop it also maintains constant current. This is achieved by varying the impedance of a group of control transistors influenced by two separate correcting amplifiers: (*a*) a fast-acting circuit which corrects for transient variations in the mains supply but does not have high long-term accuracy, (*b*) a slow-acting circuit which compensates circuit (*a*) for thermal and other drifts during the titration.

Interaction between the two control amplifiers is avoided by the considerable difference between their time constants.

Variations in the resistance of intermediate connecting leads and circuits are unimportant.

In addition to these automatic corrections a manual adjustment is provided in the form of an adjustable shunt across R_2. This enables the current to be brought to the exact value required. It is necessary not only to hold the current steady but also to measure it accurately. This is achieved by the use of a precise resistor connected in series with the titration cell. The value of the resistor is chosen so that, at the desired current, the voltage drop across it shall be equal to the e.m.f. of a Weston unsaturated cadmium - mercury cell. A galvanometer is used to detect any errors, and manual correction to circuit (*b*) above can then be made. In practice these adjustments are small and are only occasionally required during a titration. A 1-mm deflection of the galvanometer represents a current change of about 7 p.p.m. The current variations can thus be held by automatic means, aided by occasional manual adjustment, to 10 to 20 p.p.m. during a titration, and its value is known to within +20 p.p.m.

For currents of the order of 1 amp a resistor of 1 ohm is used for measurement purposes. Provision is made for the use of lower currents by replacing the 1-ohm standards by 10 or 100-ohm standards. This means that R_2 and R_3 must also be replaced with appropriate values at the same time.

CIRCUIT DESCRIPTION

The principles of circuit operation are as follows.

The current from the main d.c. source (Fig. 1) passes through the five regulator transistors connected in parallel, amplifier A_3, resistors R_3, R_2, and R_1 and the coulometer cell. R_1 is a very precise and stable resistor which is accurate within ± 12 p.p.m. of its stated value (1 ohm), and is used for current measurement as described above.

R_2 and R_3 are good quality wire-wound resistors, but have neither the stability nor the accuracy of R_1. They are used to provide the voltage-drop signals for the two stabiliser circuits (*a*) and (*b*).

FAST-ACTING STABILISER (*a*)—

The voltage developed across R_3 is compared with the voltage from potentiometer R_4. This is in turn supplied from a stabilised power unit. Any difference between the two voltages will appear as an error signal fed into amplifier A_1 and thence into the regulator transistors A_3. The transistors change their impedance and cause the current to return to its correct value. The control action, which takes place in a fraction of a millisecond, can thus hold the current steady in the face of most cell-impedance changes, mains-voltage variations and so on. The stabilised power unit supplying R_4 is unlikely to produce transient variations in voltage but will certainly drift. This is corrected along with other slow drifts by the following circuit.

SLOW-ACTING STABILISER (*b*)—

The voltage developed across R_2 is compared with a Mallory RM42R cell, and any error signal is fed into amplifier A_2 which terminates in a servo motor geared to the potentiometer R_4, and this re-sets the operating point of the fast-acting stabiliser. In practice two resistors, R_4 and R_8, are connected in series across the 50-volt stabilised supply. The slow-acting servo motor corrects the value of R_4, and R_8 is manually adjusted before the equipment is used so that R_4 starts from about the middle of its range.

R_4 and its fine adjustment resistor, R_8, are wound with precious-metal wire and use a precious-metal sliding contact, thus eliminating for all practical purposes the electrical noise from these components.

The amplifier is a typical chopper type using vacuum tubes with an input sensitivity of about 12 μV. The response time for full-scale travel is determined by the servo-motor gearing and is about 10 seconds.

The choice of the reference cell is governed by the requirements of low drift during a titration and the ability to deliver appreciable currents into the amplifier input.

The control transistors perform their function by absorbing the difference between the voltage that the titration cell requires, and the output voltage of the power supply. The difference, which must be kept positive, is set manually to a value that is always within the maker's rating.

By means of a switch the titration cell can be replaced by a resistor of approximately equal resistance. This enables the current to be set to the desired value before a titration is started. After 15 minutes the rate of drift is low enough for the equipment to be used. The cell is then switched back into circuit and the current is controlled almost immediately at the correct value.

PROTECTION—

Protection of the power supply unit against accidental short-circuits is particularly necessary with transistor circuits, and is provided internally by a high-speed electronic trip circuit. Both this and the working of the fast-acting stabiliser are described more fully in Appendix I.

TIME MEASUREMENT

In the early stages of development a 100-kilocycle per second quartz-crystal oscillator was used, followed by several frequency divider stages using vacuum tubes. For a variety of reasons this proved unreliable and was replaced by the present equipment which uses a 10-kilocycle per second quartz-oscillator, followed by a number of solid-state binary frequency dividers to a final frequency of 10 cycles per second. This registers time in units

of 0·1 second on a pair of electro-magnetic counters. The counters are run simultaneously as a check on each other. One counter can be pre-set to switch off at a selected number of counts.

The crystal is not temperature controlled as such effects are not significant over a range of 15° to 25° C. Checks on the time-keeping of this equipment against standard broadcast frequencies and the General Post Office Speaking Clock show the most significant error to be possibly one unit of 0·1 second at the end of the titration. In a normal period of 6000 seconds, this could be 15 p.p.m.

STANDARDS—

Current and time require to be measured accurately. Current is measured by observing the voltage developed across a resistor. Thus standards of voltage, resistance and time are required. No standards of time are kept by the Agricultural Division as there is ready access to certain broadcast frequencies and the General Post Office Speaking Clock.

RESISTANCE STANDARD—

The lowest resistance (1 ohm) comprises a network of ten 10-ohm resistors, connected in parallel to make a 1-ohm, 4-terminal resistor. The wire is double fibre-glass covered which, besides acting as an insulator, provides a soft bedding layer against differential expansion stresses. The initial stresses are removed by prolonged annealing. The wire material is a grade of manganin with a resistance with temperature curve as Fig. 2. This curve was compensated by the addition of a single-series element of copper to give an improved form with a variation over the range 17° to 32° C of 15 p.p.m.

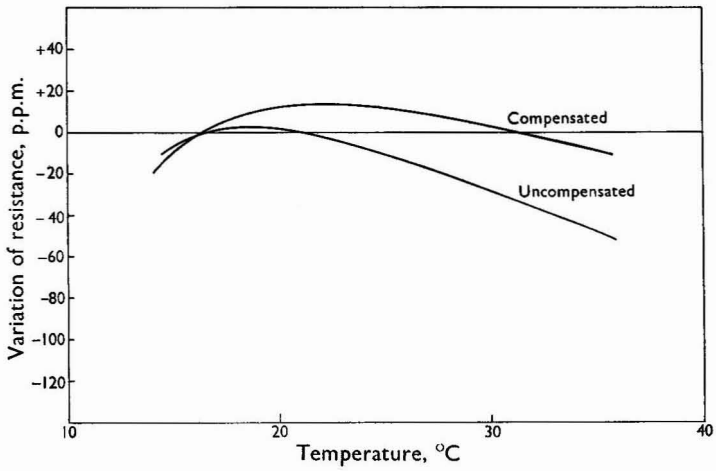


Fig. 2. Comparison of compensated and uncompensated resistors

The resistor, which is enclosed and oil filled, rises to an equilibrium temperature of 3° C above the oil temperature. This enables the final wire temperature to be compared with the resistance - temperature curve (Fig. 3) to ensure that no significant resistance change has occurred.

During the period of the tests (about 15 months) the resistance value changed from 1·00032 to 1·00035 ohms.

VOLTAGE STANDARD—

An unsaturated Weston cadmium - mercury type cell is used (Muirhead D–942–C), which reduces the variations of e.m.f. due to temperature - electrolyte concentration changes found in the saturated type. The cell is enclosed and lagged to reduce temperature differentials between the limbs. The over-all variation of e.m.f. is about 2 μV per °C.

Because of the supposed inferior long-term stability of the unsaturated type of cell, the working cell has been compared frequently with the I.C.I. Agricultural Division standards (see below). The results show that the working cell varied by $\pm$10 p.p.m. over a period of 3 months.

REFERENCE STANDARDS—

Both voltage and resistance standards are maintained by I.C.I. Agricultural Division Standards Laboratory along with a 5-decade standard potentiometer. All these items carry National Physical Laboratory certificates, so the possible errors can be assessed as follows—

voltage: 5 p.p.m. ± errors in the value of the absolute volt,
resistance: within 1 or 2 p.p.m. ± errors in the value of the absolute ohm.

The possible errors of measurement of coulombs are as follows:

VOLTAGE ERRORS	PARTS PER MILLION
Uncertainty in the absolute volt	±10
National Physical Laboratory certification of standard	± 5
Divisional standard cell temperature—	
Lagged unthermostatted	±10
Later lagged and thermostatted	± 4
RESISTANCE ERRORS	
Uncertainty in the absolute ohm	±10
Maker's certification	± 1
Potentiometer discrimination	± 5
TIMING ERRORS (including errors due to the timing of intervals)	15

The probable over-all values for the initial and final arrangements are 25 and 24 p.p.m., respectively.

Standard deviations of 50 p.p.m. have been obtained by using the coulometer in work that will be reported later. These results include the errors due to manipulation, weighing and any deviations from stoicheiometric reactions at the electrodes.

DISCUSSION

ACCURACY AND STABILITY—

Within the limits of discrimination of the experimental measurements, no change in the working standards has been detected over a period of 3 months. Checking against the Divisional standards has become a precaution against random damage and unforeseen variations. Now that steady values are established, checking can be much less frequent.

RELIABILITY—

The working reference cell is protected by a variable high resistance as a sensitivity control. Its robust construction was shown by its return to its original e.m.f. within 24 hours, on the one occasion when the current drain from it exceeded the maker's maximum.

The working standard resistor is liberally rated, and its stability has been established, so that it gives no cause for anxiety.

The timer counters gave some trouble at first but this was cured by an increase in the duration of the driving impulses.

The remainder of the apparatus has functioned continuously without trouble.

The original purpose of the work was to produce a coulometer of improved accuracy in comparison with the current - time, and motor coulometers previously reported.[4,5] A bench instrument was made to demonstrate the working principles, and the results of titration (see following paper[6]) confirm that our estimated probable errors of the order of 25 p.p.m. are realistic.

Improved temperature control of the standards of resistance and voltage, and repeated calibrations at the National Physical Laboratory to establish their rates of drift, will reduce total possible electrical error to about 20 p.p.m. The error in time standardisation should always be negligible. With errors at this level, no further development is profitable until present work in various national laboratories to establish more accurately the values of the Faraday, the volt and the ohm has reduced their probable errors to below the present values.

CONCLUSIONS

The accuracy of the instrument, and its capability of being checked against internal and external standards, renders it suitable for the most precise work.

It is reliable and versatile enough for general purpose work.

We thank our colleagues, Messrs. J. J. E. Ness and J. Lindsley, who constructed and maintained the apparatus.

Appendix I

Description of regulated power supply[7,8] (Fig. 3)

The main 52-volt transformer secondary winding, connected to a "Variac," enables any voltage between 4 and 52 volts to be set manually. The a.c. is rectified and fed to the regulating transistors, TR_8 to TR_{13}, which are connected in parallel. Voltage rise on open circuit is minimised by resistors R_6 and R_7. The bases of TR_8 to TR_{13} are fed by the differential amplifier TR_1 and TR_2, followed by TR_3, TR_6 and TR_7, giving an over-all control factor of 2000. The input signal to this amplifier is the difference between the e.m.f. developed across R_3 and the nominally equal e.m.f. from the stabilised supply. This supply is stabilised in two stages by gas-discharge tubes and is thus largely free from short-term variations. The current flowing through the cell is by this means held constant against short-term fluctuations arising from mains-voltage variations or changes in cell impedance.

Protection against accidental overcurrent is provided by a trip circuit comprising TR_4, which monitors the e.m.f. across resistor R_5, and, if this is excessive, triggers the bi-stable TR_{14} and TR_{15} into its other state. This causes TR_5 to cut off, and with it TR_6 and TR_{13}, thus stopping the current flow before it can cause any damage. The change over of the bi-stable also releases relay RL_1 and opens the a.c. feed to the rectifier. The system is re-set by applying a temporary earth potential to the base of TR_{15}, which causes the bi-stable to revert to the normal condition of TR_{14} conducting and TR_{15} cut off.

The internal power supplies for the amplifiers and protection current are obtained, as shown, from additional secondary windings on the main transformer. These are conventional and do not merit comment.

The output of the unit is up to 2 amps, 50 volts.

Appendix II

List of components

R_1, R_2, R_3	= Precise 4-terminal resistors (see text)
R_4	= 500-ohm potentiometer, palladium - silver, with J & M alloy 625 wiper
R_5	= 0·076-ohm, 5-watt, wire-wound resistor
R_6, R_7	= 1000-ohm, 5-watt, wire-wound resistors
R_8	= 50,000-ohm potentiometer, molybdenum - palladium - gold, with J & M alloy 625 wiper
R_9	= 33-ohm, ½-watt resistor
R_{10}	= 15,000-ohm, ½-watt resistor
R_{11}	= 3900-ohm, ½-watt resistor
R_{12}	= 8200-ohm, ½-watt resistor
R_{13}	= 12,000-ohm, ½-watt resistor
R_{14}	= 18,000-ohm, ½-watt resistor
R_{15}	= 1000-ohm, ½-watt resistor
R_{16}	= 6800-ohm, ½-watt resistor
R_{17}	= 3900-ohm, ½-watt resistor
R_{18}	= 12,000-ohm, ½-watt resistor
R_{19}	= 1000-ohm, ½-watt resistor
R_{20}, R_{21}	= 10,000-ohm, ½-watt resistors
R_{22}, R_{23}	= 1500-ohm, ½-watt resistors
R_{24}	= 100-ohm, ½-watt resistor
R_{25}	= 3000-ohm, 3-watt wire-wound potentiometer
R_{26}	= 100-ohm, ½-watt resistor
R_{27}	= 33,000-ohm, 7½-watt resistor
R_{28}	= 8200-ohm, 1-watt resistor
R_{29}	= 5000-ohm, 3-watt wire-wound rheostat
R_{30}	= 22,000-ohm, ½-watt resistor
R_{31}	= 10,000-ohm, ½-watt resistor
R_{32}	= 47,000-ohm, ½-watt resistor
R_{33}, R_{34}, R_{35}, R_{36}, R_{37}, R_{38}	= 2-ohm, 5-watt resistors
C_1	= 250-μF capacitor, 50-volt working
C_2, C_3	= 8-μF capacitors, 450-volt working
C_4, C_5	= 47-pF capacitors, 150-volt working
C_6	= 2-μF capacitor, 12-volt working
C_7	= 250-μF capacitor, 50-volt working
C_8	= 5000-μF capacitor, 100-volt working
RL_1	= Over-load trip relay
TR_1, TR_2, TR_3, TR_6	= GET 874 transistors

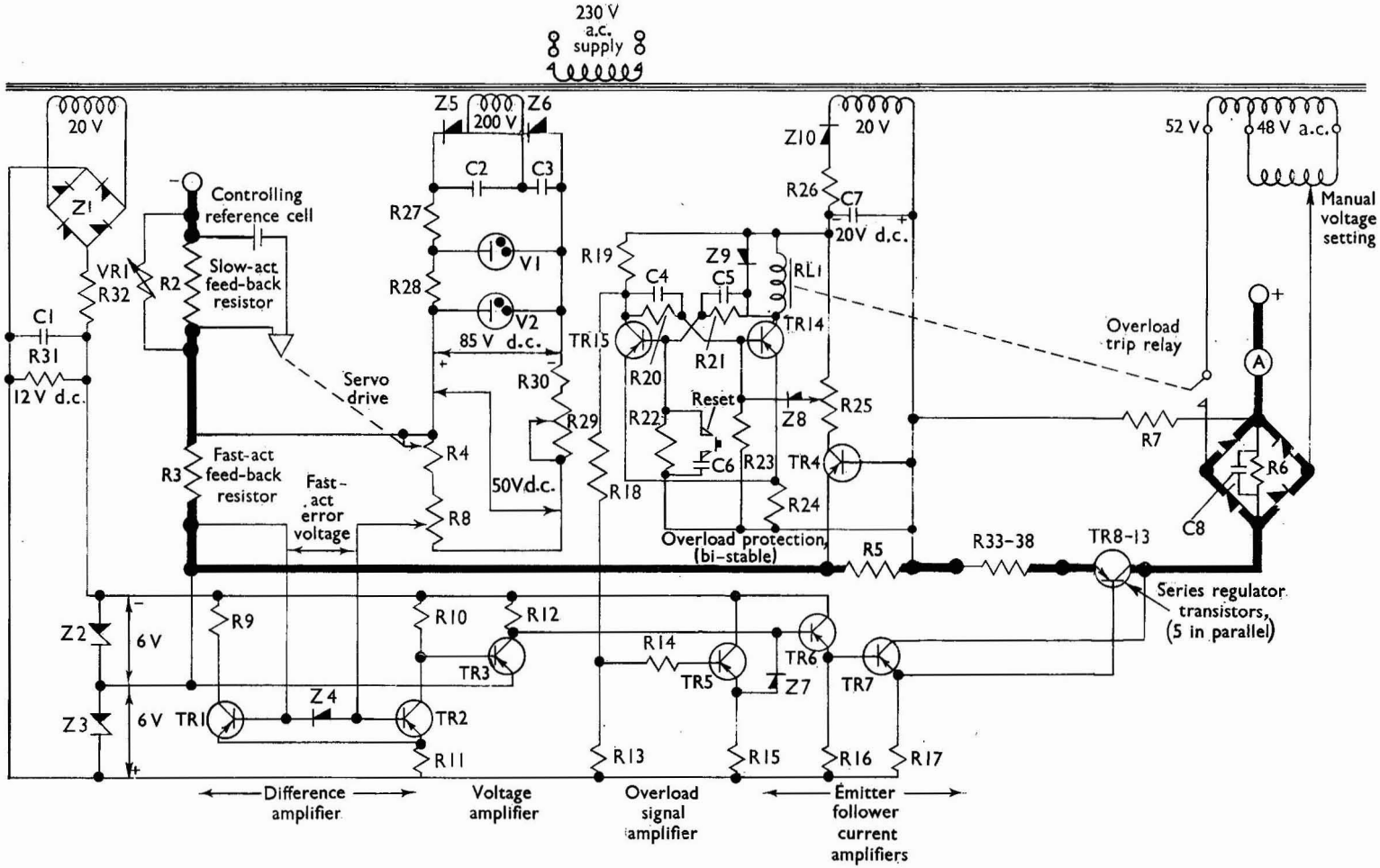


Fig. 3. Power supply and control unit

TR_4, TR_5, TR_{14}, TR_{15} = GET 102 transistors
TR_7, TR_8, TR_9, TR_{10}, TR_{11}, TR_{12}, TR_{13} = OC 36 transistors
V_1 = 150B2 valve
V_2 = 85A2 valve
V_R = 1000-ohm, 3-watt rheostat
T_1 = Main supply transformer, with earthed screen between primary and secondary windings
Input, 10–0–200–220–240 volts, 50 c/s.
Output, 200 volts, 30 mA;
20 volts, 0·5 amp;
20 volts, 100 mA;
0–48–52 volts, 2 amps.
Z_1 = Rectifier, 5D23
Z_2, Z_3 = Rectifiers, OAZ 204
Z_4 = Rectifier, GJ4M
Z_5, Z_6 = Rectifiers, 80 AS
Z_7, Z_8, Z_9, Z_{10} = Rectifiers, DDOOO
Z_{11} = Rectifier, 1B1B1N538

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Precise Coulometry: The Titration of Pure Sodium Carbonate

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A method is given for the precise and accurate titration of sodium carbonate with hydrogen ions generated by the coulometer described in the preceding paper. This coulometer maintains automatically a constant current for a measured length of time. The results are in good agreement with those obtained by titration with standard acid referred to pure silver as the ultimate standard, and support proposals to establish the coulomb as a standard in volumetric analysis. Factors are discussed that affect the accuracy and precision of analysis by controlled current coulometry.

Taylor and Smith[1] have shown that acids and alkalis can be analysed coulometrically with high precision by using a manually controlled low current, but apparently there was no independent assay of the compounds titrated. No earlier work is known to the authors in which high currents, macro amounts and automatically controlled currents were used. The instrument used in our investigations[2] measures time, and controls and accurately measures currents high enough to be used in macro-scale titrations. The construction of the coulometer and its mode of operation were described in the previous paper,[2] but it was realised that other factors such as cell design, weighing and transfer of the sample, and even the value of the Faraday would affect the over-all accuracy and precision obtainable in coulometric titrations. In this paper these factors are discussed for the titration of sodium carbonate, a precise and accurate method for which is given. The sodium carbonate used was laboratory working standard material that had been analysed in recent inter-laboratory trials by the Society for Analytical Chemistry,[3] and was of the purity (100 $\pm$ 0·2 per cent.) required by the Analytical Standards Sub-Committee of the Analytical Methods Committee for primary standards.

Experimental

Coulometer—

The coulometer[2] used in this work controls the current by maintaining a constant voltage across a precise standard resistor. The voltage drop across this resistor is compared with the e.m.f. of a standard cell, and the difference between them is shown on a sensitive galvanometer where a 1-mm deflection corresponds to a 7 p.p.m. error in current; little manual correction is necessary. Three current levels of 1 amp, 100 mA and 10 mA are provided. Each level can be adjusted on a dummy load approximately equal to the cell resistance before the current is switched on to the cell. Time is measured by a quartz-crystal clock that is checked against standard radio transmission. The probable error[2] in the quantity of electricity, *i.e.*, the product of current and its time of flow, is $\pm$25 p.p.m. Time is registered in units of 0·1 second by an electro-magnetic counter with cyclometer presentation of 5 digits. One counter can be pre-set to switch off at a given number of counts. Two independently driven counters are run in parallel; by comparing them, miscounts can be detected and erroneous experiments discarded.

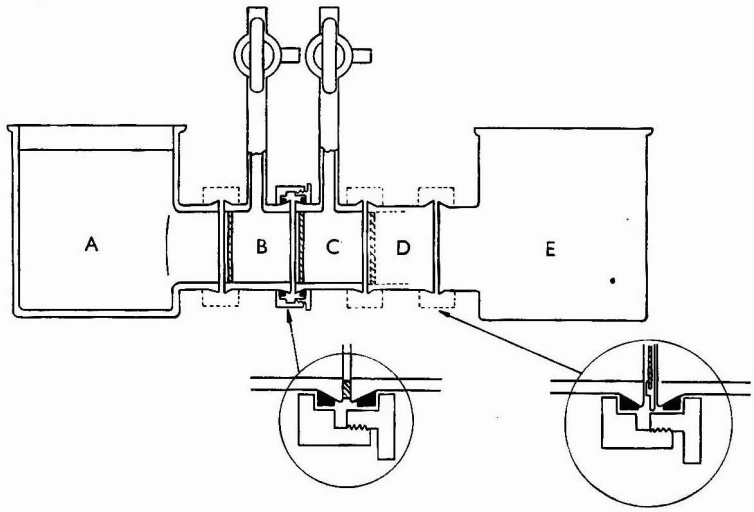
Summary of the method—

The working electrode at which hydrogen ions or hydroxyl ions are generated is of platinum. Sodium sulphate is used as the supporting electrolyte, and is boiled in the cell before the titration to remove carbon dioxide. Copper and cupric sulphate are used as auxiliary electrode and electrolyte. The sodium sulphate solution is pre-titrated by generating, at 10 mA, hydrogen ions and hydroxyl ions to traverse the inflection, finishing at a pH just lower than that of the point of inflection. The sample is added and titrated at 1 amp for a pre-set time that is approximately 0·2 per cent. longer than would be required if the sample were 100 per cent. pure. After boiling the solution again to expel carbon dioxide, it is cooled and back-titrated at 100 mA by generating hydroxyl ions until it is just alkaline. Hydrogen ions are then generated at 10 mA to give a known excess beyond the pH of inflection as in the pre-titration. The net anodic generation is used to calculate the purity of the sample.

In both the pre-titration and back-titration precautions are taken to ensure that no adsorption of hydrogen ions or hydroxyl ions has occurred, as shown by the reproducibility of repeated traverses of the point of inflection.

TITRATION CELL—

The cell used follows the design of Taylor and Smith,[1] and is modified to permit increased current, easier manipulation and easier replacement of the agar gel. Several designs in glass and Perspex were tried; the design eventually used, made of both borosilicate glass and Perspex, is illustrated in Fig. 1. Figures for weight loss, etc., are published in the Pyrex Bulletin No. 7, February, 1962. The rate of extraction of sodium was experimentally determined as 0·5 mg on boiling 300 ml of de-mineralised water in the cell for 30 minutes, and then allowing it to stand for 20 hours.



A = Titration compartment, B, C, D = De-mountable sections,
E = Auxiliary electrode compartment,
Parts marked in black are made from PTFE.

Fig. 1. Cell for acid - alkali titration

The glass titration compartment, A, containing M sodium sulphate is cylindrical with a diameter of 8·5 cm, and has a Fluon cap, the underside of which has a smooth domed shape to facilitate washing down. The lower edge of the rim is "feathered" (made thin and tapering) so that it produces a liquid-tight seal against the rim of the titration compartment. When the solution is boiled in the cell considerable differential expansion occurs, but the flexibility of the "feathered" edge accommodates this without overstressing the glass. To prevent the solid part of the cap from wedging itself into the taper aperture of the cell, because the feathered edge is flexible under load, the top edge of the cap is extended by a stainless-steel ring which rests on the rim of the glass (Fig. 2).

The cap contains apertures to hold—

(*a*) the generator electrode at which the titrant is produced. This is a piece of bright platinum foil, 7 cm by 4 cm, bent in an arc, approximately 4 cm in radius, outside the heater (*d*);
(*b*) a combined pH-reference electrode (Ingold type 401–S) for end-point indication. Being coaxial in form it is less affected by potential gradients in the electrolyte than a separate glass electrode and reference half-cell;
(*c*) a glass tube to inject nitrogen for removing carbon dioxide;
(*d*) a silica-sheathed heater;
(*e*) a resistance thermometer;
(*f*) a mercury-in-glass thermometer;
(*g*) a water condenser (when required), or a glass stopper (B34).

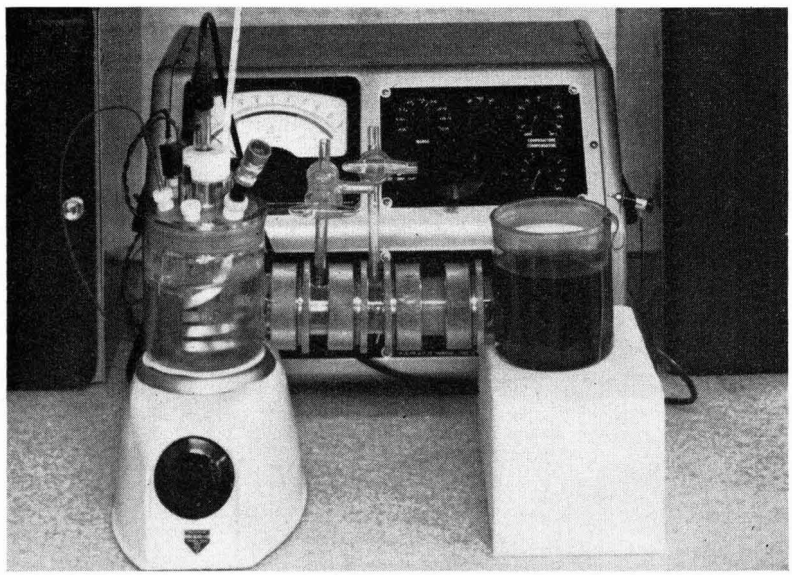


Fig. 2. Titration cell showing details of cell cap

[*To face page* 364

The heater is a multi-stranded helix of thin Nichrome wire, wound on a stout core wire insulated with Fibreglass braids. The core and heater are welded together at the inner end, and connected at the outer end to a metal-shrouded 2-pin plug with a bayonet safety catch. All the heating spiral is below liquid level; the rising portion of the sheath remains cool as it carries only connecting wires. Maximum heat dissipation is 13 watts per inch length, 150 watts total.

A glass compartment, E, similar to A, contains the auxiliary generator electrode (copper sheet measuring 9 cm by 6 cm) and M cupric sulphate. The two compartments are connected by a tube 3·6 cm in diameter, consisting of three de-mountable components B, C and D, held in position by screwed stainless-steel couplings. B and C are made of glass and are filled, by suction, with sodium sulphate from A. They contain medium-grade (No. 3 porosity) sintered-glass discs to decrease the diffusion of sodium carbonate from the titration compartment A, and inlets, connected to a nitrogen supply, to blow back the solution into A. D is made of Perspex and contains a fine (No. 4 porosity) sinter cemented in with Tensol Cement No. 7, and a gel of 3 per cent. of agar in 0·5 M sodium sulphate, to prevent liquid diffusion. A No. 4 sinter is also held in a gasket between D and E.

WEIGHING AND TRANSFER OF SAMPLE—

The normal method of transfer from a glass weighing-bottle was attempted, but the capacity of the titration vessel did not allow a sufficient volume of wash water to be used. The finely powdered carbonate readily dispersed into the air when handled, probably aided by static electrification in the dry weighing-bottle. To overcome these difficulties a weighing capsule was designed in polythene, and was gold-coated all over to eliminate static effects (Fig. 3). The lid is a fairly tight fit so that it is possible to lift the capsule and contents by

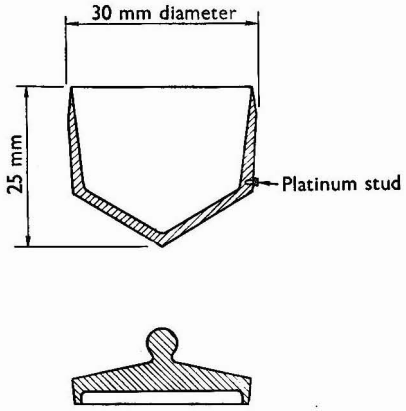


Fig. 3. Weighing capsule

the knob on the lid. Samples are inserted by grasping the knob with ratchet forceps, lowering the capsule until it is completely immersed in the electrolyte, and pushing the bottom away from the lid by pressing on the platinum stud with a spatula. The forceps and spatula are then rinsed with the minimum amount of water and removed. The capsule *plus* sample is sufficiently heavy to settle to the bottom of the cell until most of the sample has dispersed; the capsule then rises clear of the electrodes and stirrer, but remains submerged, tilted on its side by the weight of the platinum stud so that the last traces of sample can dissolve. The capsule and top remain in the solution throughout the titration.

pH MEASUREMENT—

A Pye "Dynacap" pH meter is used to indicate the variation of pH with millicoulombs generated in the pre-titration and back-titration; the output of the pH meter is recorded on a Honeywell-Brown strip-chart recorder with a chart speed of 40 inches per hour. In order to check that the titration efficiency was 100 per cent. at the beginning and end of

the titration, the point of inflection was traversed three times, switching off the current at a chosen (but not critical) pH. The reproducibility of the number of coulombs required to titrate the solution from this pH to the point of inflection shows that one can ignore the possibility of the diffusion of impurities. To allow for the response time of the pH electrode only times of generation in the same direction are compared.

REAGENTS—

Sodium sulphate—Prepare an approximately M solution of sodium sulphate (analytical-reagent grade) in de-mineralised water.

Cupric sulphate—Prepare an approximately M solution of cupric sulphate (general-purpose grade).

DETAILED PROCEDURE

SAMPLE PREPARATION—

Dry the sodium carbonate sample to constant weight at 270° C, ±10° C in a platinum dish, frequently stirring with a platinum rod. Cool the sample in a desiccator and quickly add a catch-weight of approximately 3 g to the capsule. Insert the lid firmly and re-weigh.

AGAR GEL—

Mix sufficient agar powder with de-mineralised water to give a 6 per cent. w/v solution, and boil. Add an equal volume of boiling neutral M sodium sulphate and mix thoroughly to give a final 3 per cent. w/v gel. Pour into a warm, dry gel compartment, and when the surface of the gel is firm (after approximately 20 minutes) cover with distilled water by using a tangential jet. Store in boiled-out 0·5 M sodium sulphate solution adjusted to pH 7 and protected from carbon dioxide.

PREPARATION AND ASSEMBLY OF CELL—

Remove any grease from the platinum electrode with chromic - sulphuric acid, rinse and finally immerse the electrode in aqua regia for a few seconds. Then rinse thoroughly. Clean the copper electrode with emery cloth. The deposition of copper is of no interest, but simply ensures that neither hydroxyl ions nor hydrogen ions are produced at this electrode. Clean the components of the glass cell thoroughly and finally boil in de-mineralised water. Grease the ground-glass faces with a silicone grease free from alkali-metal esters, and assemble the cell as indicated in Fig. 1, with A on a magnetic stirrer. Insert a plastic coated stirring rod. Partly fill A with M sodium sulphate solution, and fill compartments B and C completely with M sodium sulphate solution by suction from A. This expels air, containing carbon dioxide, from B and C, keeps the gel moist, and allows the solution level in A to be adjusted so that the cell contains the minimum volume necessary for titration, thus reducing the risk of loss by splashing. E must also be filled above the level of the side-arm with sodium sulphate solution of at least 0·5 M concentration so that the gel is kept moist and its conductivity is not reduced by loss of ions due to diffusion. If cupric sulphate is in contact with the gel, some transfer of cupric ions may occur, so the sodium sulphate solution in E is not replaced by cupric sulphate solution until immediately before the titration.

Insert a water-cooled condenser in the main aperture in the cap, switch the heater on full to boil the solution in A, and remove carbon dioxide. Blow back the solution from B and C, taking care to use a sufficiently low nitrogen pressure (corresponding to a flow of 2 litres per hour) to avoid rupturing the gel. Boil for 10 minutes, switch off the heater and cool the solution by bubbling through it a fast flow of "white spot" nitrogen, which is passed through a soda - asbestos column to remove carbon dioxide. The cooling rate can be increased by blowing air on to the side of A.

PRE-TITRATION—

In order to pre-titrate the solution, remove the condenser when the solution temperature has dropped below 75° C and insert the combined pH-reference electrode which can tolerate this temperature. Switch the pH meter to the 6 to 8 pH range, reduce the nitrogen flow, and fill B and C by suction to a depth of a few millimetres, which is sufficient to carry 100 mA but constitutes a negligible volume (3 per cent.) of untitrated solution. Titration of this volume at a pH between 6·5 and 7·5 to the equivalence point would require less than 1 second

at 10 mA, *i.e.*, 2 p.p.m. of the total titre. Siphon the 0·5 M sodium sulphate solution from E, replace with M cupric sulphate solution and insert the copper electrode. Connect the electrodes to the output sockets of the coulometer. Adjust the current to 10 mA on dummy load. Switch off, re-set the counter to zero, switch on the recorder chart drive and the current to the cell generating hydroxyl ions. Two hands are required. The recorder pen is not jolted on switching, but the slight effect of the generator field on the reading of the pH electrode gives a small marker (0·05 pH unit). Mark the start of the pre-titration on the recorder chart. Titrate at 10 mA to pH 7·4, or until sufficient of the curve is recorded to allow determination of the point of inflection (Fig. 4). Note on the chart the point at which the current was switched off and the number of seconds counted. Ten p.p.m. of the total titre is equivalent to ± 5 seconds. Location to this precision permits an error of $\pm 0{\cdot}1$ pH units. Re-set the counters to zero, reverse the current and repeat the pre-titration until the number of millicoulombs between the cut-off pH and the point of inflection in the direction of generation of acid is reproducible. Finish the pre-titration on the acid side.

ADDITION OF SAMPLE—

Remove the combined pH electrode, rinse and store in distilled water. Fill B and C by suction from A before adding the sample, so that the sinters and intervening electrolyte minimise the risk of diffusion of carbonate into the gel. Switch off the stirrer to make manipulation of the sample capsule in the solution easier. Turn off the nitrogen supply and lower the capsule, held in ratchet forceps by the knob on the lid, under the liquid surface to prevent dispersion of the sample into the air when the capsule is opened. Push the capsule away from the lid by pressure on the platinum stud, using a glass rod or spatula. Release the lid, rinse the forceps and rod or spatula with de-mineralised water before removal so as to wash into the cell any traces of sample which may adhere to them. Insert the stopper in the cell cap and re-start the stirrer.

TITRATION—

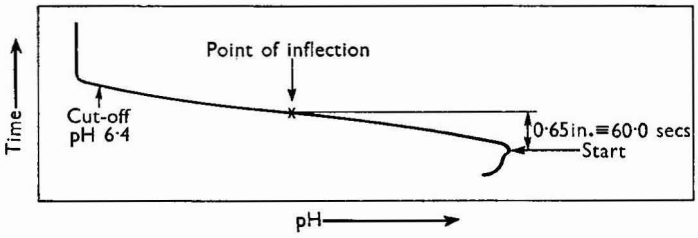
Adjust the current to 1 amp on the dummy load. Switch off the current. The resistance of the cell is approximately 30 ohms. The temperature reaches 40° to 50° C, but the gel will not suffer unless 70° C is exceeded. Re-set the counters to zero and pre-set the main counter for a time 10 seconds in excess of that required if the sample were 100 per cent. pure. Switch to hydrogen ion generation in the cell. Adjust the current if necessary every 2 minutes for the first 15 minutes, and then every 15 minutes until the end of the titration when the current will be switched off automatically.

BACK-TITRATION—

Switch the heater full on to boil the solution and expel carbon dioxide. Blow back the solution from B and C so that any carbonate which has diffused into these compartments will be neutralised and the carbon dioxide expelled. Wash down the underside of the cell top and stopper with de-mineralised water and replace the stopper with a water condenser. Boil for 10 minutes, switch off the heater, and cool by bubbling purified nitrogen through the solution. Fill B and C to a depth of a few millimetres. Adjust the current to 100 mA on the dummy load. Switch off the current and re-set the counters to zero. Switch on the current to generate hydroxyl ions in the cell to a pH of approximately 7·4. Switch off and note the time. Fill and empty B and C until less than 0·03 pH change occurs (usually not more than three flushes are required) to ensure that no hydrogen ions or hydroxyl ions can be held in the sinters. Re-fill to a depth of a few millimetres. Adjust the current to 10 mA on the dummy load and repeat the procedure for pre-titration.

CALCULATION—

Calculate, from the chart speed and chart distance, the number of seconds of excess hydrogen ion generation after the last point of inflection in the pre-titration. In the same way, calculate the total number of seconds of hydrogen ion and hydroxyl ion generation at 10 mA before the last point of inflection in the back-titration (Fig. 4). Multiply each current, in amps, by the time passed, in seconds, to give coulombs. Subtract the total number of coulombs of hydroxyl ions generated from the total number of coulombs of hydrogen



Generation time (in seconds) at 10mA

Traverse number	H^+	OH^-
1	76·0 (from starting pH)	
2	—	103·0
3	102·0	—
4	—	102·0
5	52·0 (to point of inflection)	—
Total	230·0	205·0

Net time of H^+ generation 25·0 seconds

(Note: A 3 second error in back-titration is approximately 10 p.p.m. for a 3-g sample)

Fig. 4. A typical record of back-titration. Chart speed 40 inches per hour

ions generated; any lags in electrode response to changing pH in the pre-titration and back-titration will cancel out. Divide by the Faraday and the weight of sample, and multiply by the equivalent weight and by 100 to give the percentage purity, *e.g.*,

Standard cell voltage	1·01943 volts
Resistor (nominal 1 ohm for 1 amp)	1·01806 ohms
Current (nominal 1 amp)	1·00135 amps
Weight of sodium carbonate *in vacuo*	2·99688 g
Equivalent weight of sodium carbonate	52·9945
Gram equivalent of sodium carbonate in sample	0·0565508
Value of the Faraday	96,489 absolute coulombs per g equivalent
Number of coulombs required for 100 per cent. purity	5456·52
Switch off main current at	$\frac{5456{\cdot}52}{1{\cdot}00135} + 10 = 5459$ seconds

Hydrogen ion generation—

Current, in amps	Time, in seconds	Coulombs
1·00135	5459·0	5466·37
0·01	33·0	0·33

Hydroxyl ion generation—

0·1	102·0	10·2
0·01	25·0	0·25

Total coulombs used = 5466·70 − 10·45 = 5456·25 coulombs

$$\text{Percentage purity} = \frac{5456{\cdot}25}{5456{\cdot}52} \times 100 = 99{\cdot}995 \text{ per cent.}$$

Atomic weights are based on $^{12}C = 12$ scale.

Results

An estimate of the diffusion of sodium carbonate into the agar gel was obtained by performing the pre-titration to pH 7, then adding 3 g of sodium carbonate to the solution in A and leaving it there for 1·5 hours instead of titrating it. The pH of the solutions from compartments B and C was then measured, and the solutions titrated with 0·01 N sulphuric acid to pH 7 (see Table I). Diffusion into compartment C was negligible, and as C was separated from the gel by a No. 4 porosity sinter, loss of carbonate into the gel was assumed to be nil.

Table I

Diffusion of sodium carbonate into compartments B and C

Compartment	pH	Volume (in ml) of 0·01N reagent required to bring pH to 7
B	10·0	6·0
C	6·5	0·1

In order to assess the diffusion of cupric ions, compartments A, B and C were filled with sodium sulphate solution, compartment E was filled with cupric sulphate solution and they were left for 16 hours. No visible contamination was detected; the cupric-ion content of the solution from B and C was determined colorimetrically and polarographically and found to be 0·036 mg, thus showing that a transfer of cupric ion would give an error of only 20 p.p.m. if a titration had been performed. As the gel is never left in contact with the cupric sulphate during actual titrations for more than 7 hours, the error due to copper diffusion would be much less than 20 p.p.m. Diffusion of hydrogen ions from the cupric sulphate solution into compartment C was found to be nil.

To test the reproducibility of the instrument, 25-ml aliquots of an approximately 120 g per litre solution of analytical reagent grade sodium carbonate were titrated. These were weighed into the titration cell from a glass weight burette.[4] The balance was calibrated by using it to weigh National Physical Laboratory certified weights. The results are given in Table II. The atomic weights used were those agreed by the International Union of Pure and Applied Chemistry[5] in 1962, based on $^{12}C = 12$, giving 52·9945 for the equivalent weight of sodium carbonate.

TABLE II

DETERMINATION OF REPRODUCIBILITY WITH A STANDARD SOLUTION OF SODIUM CARBONATE (SAMPLE 1)

Weight of sodium carbonate solution added, in grams	Weight of sodium carbonate *in vacuo*, in grams	Coulombs required	Sodium carbonate found, in grams	Percentage purity
26·6718	3·14215	5717·88	3·14042	99·945
25·9257	3·05425	5558·26	3·05275	99·951
25·4713	3·00072	5460·19	2·99889	99·939
26·8610	3·16444	5758·59	3·16278	99·948
27·4556	3·23449	5885·55	3·23251	99·939
30·5787	3·60242	6555·32	3·60037	99·943
26·5084	3·12290	5683·09	3·12131	99·949
			Mean	99·945

Catch-weights of approximately 3 g of carefully dried sodium carbonate of a different make (sample 2) were weighed in gold-coated polythene capsules which were subsequently transferred to the titration cell. Results of the determination of purity are given in Table III.

TABLE III

PURITY OF SODIUM CARBONATE (SAMPLE 2)

Weight of sodium carbonate *in vacuo*, in grams	Coulombs required	Weight of sodium carbonate found, in grams	Percentage purity
3·0232	5504·16	3·02304	99·995
3·0067	5474·27	3·00662	99·997
3·0052	5471·44	3·00502	99·994
3·0077	5475·32	3·00720	99·983
3·0034	5468·16	3·00327	99·996
3·0099	5480·02	3·00978	99·996
3·0073	5475·15	3·00711	99·994
		Mean	99·994

Combined standard deviation (Tables I and II) 0·005.

Sample 2 is kept as a laboratory working standard and has been assayed independently by weight titration with hydrochloric acid standardised against silver. The mean value and the standard deviation of eighteen results obtained over 2 years were, respectively, 99·993 per cent. purity and 0·003, with extreme figures for purity of 100·000 and 99·990. The mean values obtained by the weight titration and coulometric assay differ by only 10 p.p.m.

Eight samples of sodium carbonate from the second source were weighed into polythene capsules and titrated. The operator knew the weight only to ± 2 mg (660 p.p.m. in 3 g), and the excess acid was calculated from the upper limit of the weights. Table IV compares the sodium carbonate found with the sodium carbonate added, *i.e.*, the weight *in vacuo* corrected for the percentage purity found by the weight titration method. Sodium sulphate

from a different manufacturer was used for the last four determinations. The solution was initially much more alkaline (pH >8 instead of between 6 and 7), but it was not realised until the titration was in progress that this solution had been used to make the gel. Diffusion of alkali from the gel made with this solution probably accounts for the high result of 190 p.p.m.; the solution was neutralised before being used for gels for the subsequent titrations.

TABLE IV

TEST OF REPRODUCIBILITY ON UNKNOWN WEIGHTS

Sodium carbonate added, in grams	Sodium carbonate found, in grams	Difference, in p.p.m.
3·00533	3·00560	+90
2·99783	2·99773	−30
3·00362	3·00379	+60
3·00131	3·00143	+40
3·00552	3·00609	+190
3·00508	3·00488	−70
3·00789	3·00764	−80
3·00167	3·00137	−100

In titrating sodium carbonate from the same source (sample 2), different quantities of excess hydrogen ions were generated in order to test the effect of varying the excess. The results are given in Table V, and also indicate the efficiency of generating hydrogen ions when no sodium carbonate is present to react with them, and of generating hydroxyl ions at one-tenth the current density used during the main part of the titration of sodium carbonate.

TABLE V

EFFECT OF VARYING THE EXCESS HYDROGEN IONS GENERATED

Excess coulombs	Percentage of main titration	Weight (in grams) of sodium carbonate— added	found	Percentage purity
10	0·2	3·00051	3·00039	99·996
20	0·4	3·00704	3·00698	99·998
50	1·0	3·00172	3·00145	99·991

As the mean of the results given in Table III is 99·994 and the standard deviation is 0·005 it can be seen that, unless errors compensate, within this range—

(*i*) the quantity of excess hydrogen ions generated is not critical,

(*ii*) the efficiency does not decrease when no titratable substance is present,

(*iii*) the titration efficiency is at least 99 per cent. with hydroxyl ions generated at one-tenth the current density of that used in the main part of the titration of sodium carbonate, shown by the generation of 10,000 p.p.m. of hydroxyl ions which resulted in less than 100 p.p.m. error.

SUMMARY OF POSSIBLE ERRORS—

Errors in the weight of samples handled in capsules were initially ±0·1 mg, but this value was later reduced to ±0·05 mg by the use of a more sensitive balance. These correspond to 30 and 15 p.p.m., respectively, in 3 g. The equivalence point can be determined to ±10 p.p.m. The errors associated with the determinations of atomic weight are those assigned by I.U.P.A.C. in 1962.[5]

A summary of the estimated possible errors is given below—

Atomic weight of sodium		± 2·5	p.p.m.
Atomic weight of carbon		± 4	p.p.m.
Atomic weight of oxygen		± 6	p.p.m.
Weight of samples in capsules		±30	p.p.m. (initially)
Weight of samples in capsules		±15	p.p.m. (finally, see Tables IV and V)
Determination of the equivalence point		±10	p.p.m.
Value of the Faraday		±33	p.p.m.
Timer		± 3	p.p.m.
Time (to nearest 0·1 second) at 1 amp		±10	p.p.m.
Standard cell voltage—			
Uncertainty in the absolute volt	probably	±10	p.p.m.
National Physical Laboratory certification		± 5	p.p.m.
Temperature		±10	p.p.m. (initially)
Temperature		± 4	p.p.m. (finally, see Tables IV and V)

Precise resistor—

Uncertainty in the absolute ohm	probably	±10 p.p.m.
Makers' certification	probably	± 1 p.p.m.
Instrument discrimination		± 5 p.p.m.

Discussion

The determinations in Tables III, IV and V were consecutive, though obtained over several weeks. The results in Tables II and III show that it is possible to achieve a standard deviation of 50 p.p.m. in the coulometric titration of sodium carbonate that is slightly less precise than that obtained by reference to silver. If there is any bias, values for the purity given by this method are likely to be high, due to contamination of the hydrochloric acid by other chlorides before analysis. Errors in the coulometric method are likely to be caused by low generation efficiency and will, therefore, also give high apparent purities. Nevertheless, the agreement to 10 p.p.m. of the means by the two methods suggests that the errors are comparable.

The coulometric analogue of the normal volumetric practice of adding excess acid, boiling out carbon dioxide and back-titrating with dilute alkali was followed, because it was found tedious to remove the carbon dioxide by passing nitrogen through the solution.[1] Because this method gave satisfactory results, no check was made of the effect of changing parameters other than the excess of hydrogen ions generated. It is thought unlikely that highly critical conditions were selected by chance. Nevertheless, further investigation to define more closely the optimum conditions might succeed in reducing the errors still further and simplifying the actual titration.

Cell design—

After the determinations in Table III were completed, considerable difficulty was experienced with leakage, particularly from the joint between A and B. The screwed stainless-steel coupling was finally replaced by "Tufnol" flanges (Fig. 5), so providing an exposed

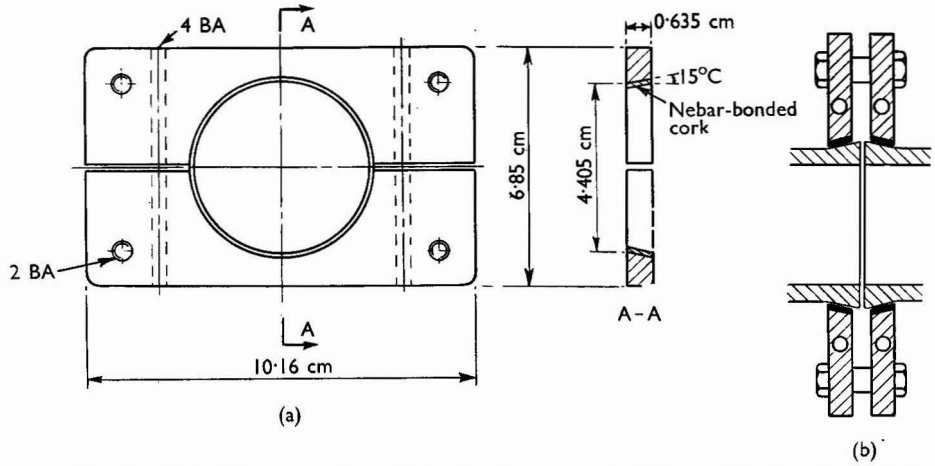


Fig. 5. Tufnol flanges. Fig. 5 (*a*) : the flanges are held in position by silver steel rods with 2BA and 4BA threads. They are fitted by sliding into the holes and screwing the nuts tight. Fig. 5 (*b*) : method of fixing the flanges (centre section)

glass-to-glass joint so that any leakage could be detected. Cell design is still a major problem involving a compromise between ease of cleaning and replacement, low electrical resistance and precautions to avoid loss of sample. The cell and electrode design were chosen purely for the practical reasons already mentioned, and since satisfactory results were obtained these conditions were not varied.

Choice of auxiliary electrode system—

It is important to suppress the generation at the auxiliary electrode of ions which can migrate and take part in either the chemical or electrode reaction in the titration compartment. Taylor and Smith[1] accomplished this in titrating acids by using the oxidation of silver

to silver chloride as an auxiliary system. Insufficient details of their sodium carbonate analysis are given, but a silver cathode was apparently used, possibly after deposition of silver chloride so that the reduction involved only the liberation of chloride ions. A silver - silver chloride electrode with potassium chloride was therefore tried, but it was found difficult and tedious to deposit sufficient quantities of silver chloride in an even coating. During electrolysis hydroxyl ions were produced, and chloride ions migrated to the anode where they were oxidised, so giving incorrect results. No significant improvement resulted on replacing the potassium chloride solution with sodium sulphate.

In deciding on an alternative auxiliary system the following points were considered—

(*a*) electrode potential,
(*b*) pH of the solution,
(*c*) preference for a salt of sulphuric acid,
(*d*) a simple method of detecting diffusion through the gel.

Copper and cupric sulphate were chosen as fulfilling most of these conditions. The Cu^{2+}/Cu potential is low under the given conditions, and the deposition of copper, preferentially to the reduction of water, is well-known. It gives an acid solution, and although the pH is as low as 3·2 for M cupric sulphate, hydrogen ions and cupric ions are attracted to the copper cathode during most of the titration. The strong blue colour of the hydrated cupric ion also gives immediate indication of penetration into the agar gel.

SUPPORTING ELECTROLYTE—

It is essential that the electrolysis of impurities in the sodium sulphate does not cause errors, particularly as the concentration of sodium sulphate is ten times that of sodium carbonate at the beginning of the titration. The maximum impurity which may react during electrolysis, according to the makers' specification, is 0·002 per cent. as reducing substances; chloride, heavy metals and ammonium ions may be present up to 0·001 per cent., and iron up to 0·0005 per cent. In 300 ml of M sodium sulphate solution, in comparison with 3 g of sodium carbonate, these become 280 p.p.m., 140 p.p.m. and 70 p.p.m., respectively.

In the authors' experience chloride can be oxidised irreversibly, even in alkaline media. However, any irreversible reaction would take place during the pre-titration. Errors due to reversible oxidation or reduction should not appear, as the pre-titration and back-titration finish in oxidising conditions. Therefore, impurities in the sodium sulphate should not affect the accuracy of the titration, whether they are reversibly or irreversibly oxidised.

For the last four determinations in Table IV, sodium sulphate from a different manufacturer had to be used. Although this latter sodium sulphate was within specification, the initial pH was 8·1 instead of between 6·0 and 7·4, and the equivalence pH was 7·3 instead of approximately 7. Some precautions were taken, such as neutralising the solution before making up the gel. Care must obviously be taken to avoid absorption into the gel of any alkali (or acid), which may diffuse out and cause errors.

THE VALUE OF THE FARADAY—

For accurate coulometric titrations the value of the Faraday must be known accurately. Remy[6] has summarised the determinations to date, re-calculated these on the basis of the isotope $^{12}C = 12$, and considered critically the reliability of the results. The mean of these, excluding the one which he considers seriously in error, is 96,489 absolute coulombs per g equivalent. A statistical examination of the errors which each observer gives for his determination indicates that the 95 per cent. confidence limits for the mean are ± 3 absolute coulombs per g equivalent.

THE COULOMB AS A STANDARD IN VOLUMETRIC ANALYSIS—

This has already been suggested[7] and would be useful because many of the present standard substances used in volumetric analysis continue to be the subject of much critical examination. The Society for Analytical Chemistry has, so far, recommended to the International Union of Pure and Applied Chemistry only sodium carbonate as being of sufficient purity ($100 \pm 0{\cdot}02$ per cent.) for use as a primary standard, and this has not yet been accepted. The definition of the coulomb, on the other hand, is already agreed internationally and, as is well known, it can be measured without great difficulty against the fundamental standards of mass, length and time. Most inorganic reactions involve electrons, and if a

reaction can be made to proceed with 100 per cent. over-all efficiency by generation of ions at an electrode, and the completion of the reaction and the number of coulombs used can be accurately determined, then the coulomb may be used as a standard for volumetric analysis. These conditions have been satisfied for the titration of sodium carbonate with the technique described and electrical apparatus which is easily operated and stable. It is planned to investigate the titration of other primary standard compounds, including those that may be recommended for oxidation - reduction and precipitation reactions.

Conclusion

The results show that the coulometric titration of sodium carbonate can be almost as precise as titration with hydrochloric acid standardised against silver. The mean values of the coulometric and volumetric results for the purity of samples agree to within 10 p.p.m.

Compared with the established method, which starts from silver and takes at least 5 days, the coulometric method is rapid, taking less than 1 day. It is therefore an attractive alternative to the present procedure.

If investigation of coulometric titrations of other acids and alkalis, and of reactions involving oxidation and reduction shows the same accuracy and precision, this should establish the coulomb as the ultimate titrimetric standard.

We thank Mr. R. M. Pearson for the initial suggestion on which this work was based, and for his continued help and advice. Mr. J. Lindsley and Mr. A. W. Remmer carried out most of the experimental work, and Mr. H. N. Redman prepared and weighed the samples.

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Iodimetric Determination of Organo-aluminium Compounds

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The alkyl groups in various types of organo-aluminium compounds have been shown to react with iodine in hydrocarbon solution, and the stoicheiometry has been determined of the reactions occurring between iodine and trialkylaluminium, dialkylaluminium chloride and dialkylaluminium alkoxide compounds.

Based on these reactions a reasonably rapid and accurate iodimetric method has been devised for the determination of low concentrations of organo-aluminium compounds in various hydrocarbon solvents. The method is applicable to the analysis of the hydrocarbon solutions of organo-aluminium catalysts used for the polymerisation of ethylene and propene. Good agreement is obtained between the iodimetric procedure and by a procedure based on conductiometric titration with a standard solution of isoquinoline for trialkylaluminium compounds and dialkylaluminium chlorides. The iodimetric procedure is also applicable to dialkylaluminium alkoxide compounds, which cannot be determined by isoquinoline titration.

Dilute hydrocarbon solutions of various types of organo-aluminium compounds are used as co-catalysts with Group IV and VI halides, in processes for the polymerisation of ethylene and propene to polyolefin polymers. Three of the principal types of organo-aluminium catalysts that are used in these processes are AlR_3, $AlR_2(OR')$ and AlR_2Cl (where R and R′ are C_1 to C_4 alkyl groups). A rapid and simple method was required for determining these types of catalysts in the hydrocarbon solutions used for ethylene and propene polymerisation, in amounts down to 10 millimoles per litre.

Various methods, based on gasometric principles, have been described for determining methyl to butyl alkyl groups, and hydride groups in organo-aluminium compounds: Bonitz[1] and Ziegler[2] used the reaction between the organo-aluminium sample and 2-ethylhexanol, and determined the amounts of alkane and hydrogen gases produced by mass-spectrometric analysis—

$$>AlC_nH_{2n+1} + ROH = >Al(OR) + C_nH_{2n+2}$$

$$>AlH + ROH = >Al(OR) + H_2$$

Crompton and Reid[3] and Dijkstra and Dahmen[4] used the reaction between organo-aluminium compounds and hexanol, followed by water, and lauric acid, respectively, and analysed the resulting mixture of liberated alkane and hydrogen gases by gas chromatography. Neumann[5] developed a gasometric method for determining aluminium-bound hydride groups, based on a reaction with *N*-methylaniline at low temperatures—

$$>AlH + CH_3\text{–}NHC_6H_5 = >AlN\begin{matrix}CH_3\\C_6H_5\end{matrix} + H_2$$

Methods of analysis based on these principles, although capable of giving excellent information on the composition of the sample, were too lengthy and complex for routine control testing of plant streams.

Bonitz[1] described a method based on a conductiometric or potentiometric titration with isoquinoline for determining organo-aluminium compounds. He described the colourless 1 to 1 complexes formed between isoquinoline and dialkylaluminium hydrides and trialkylaluminium compounds, and the strongly red coloured 2 to 1 complex formed between isoquinoline and dialkylaluminium hydrides. These complexes were further studied by Neumann.[5] Farina *et al.*[6] and Nebbia and Pagani[7] have reported modified potentiometric-titration procedures for determining organo-aluminium compounds.

Mitchen[8] extended the studies of the red coloured 2 to 1 complex formed between isoquinoline and dialkylaluminium hydrides and, based on his observations, devised a method for the simultaneous spectrophotometric determination of trialkylaluminium compounds and dialkylaluminium hydrides in mixtures. Wadelin[9] utilised this colour-forming reaction to devise a photometric-titration method for determining the total isoquinoline-reactable organo-aluminium compounds.

Razuvaev and Graevskii[10] and Hagen and Leslie[11] have devised methods involving the use of visual indicators for titrating organo-aluminium compounds with standard solutions of bases and ethers.

Methods based on a conductiometric[1,5] or potentiometric[1,5,6,7] titration with organic bases, or the spectrophotometric method described, in which these reagents are used[8,9] are excellent for determining trialkyl-aluminium compounds and dialkyl aluminium chlorides (in both, only low concentrations of aluminium-bound hydride groups are assumed to be present). They cannot, however, be applied to the determination of dialkylaluminium alkoxide compounds, which do not co-ordinate with bases. In addition, these methods did not have the required sensitivity. Similarly, visual-indicator titration procedures[10,11] could not be applied to the determination of dialkylaluminium alkoxide compounds as no reaction occurs between these compounds and organic bases or ethers.

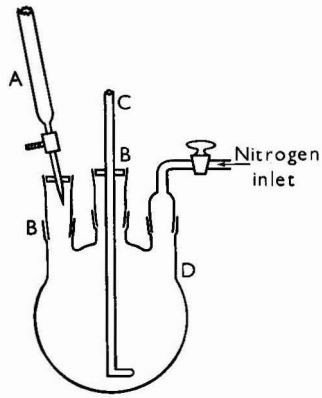
Bartkiewicz and Robinson[12] have shown that a hexane solution of triethylaluminium consumes iodine according to the following equation, and have used this reaction for determining the reducing capacity of triethyl aluminium—

$$Al(C_2H_5)_3 + 3I_2 = AlI_3 + 3C_2H_5I$$

It seemed that this reaction might offer the basis for a sensitive and rapid method for the analysis of organo-aluminium compounds. Based on this observation, the method discussed below has been developed for the determination of trialkylaluminium compounds and other types of organo-aluminium compounds in hydrocarbon solutions.

Experimental

The preliminary iodination experiments were carried out with a 5 per cent. solution of diethylaluminium chloride in anhydrous toluene. Several volumes of this solution were transferred by pipette into dry, nitrogen-purged reaction flasks (see Fig. 1) by using the technique described by Crompton.[13] A fixed volume (50 ml) of iodine reagent (0·4 N) was then added to each solution, and the mixture was left for 5 minutes to allow the reaction to proceed.



A = Burette with polyethylene stopcock
B = B24-to-B24 adaptors with Gaco seal
C = Glass stirrer
D = 250-ml, 3-neck (B24) flask

Fig. 1. Apparatus for determining the iodine number

Aqueous acetic acid was then added to each reaction mixture. The excess of iodine remaining was determined by titration with sodium thiosulphate solution and the amount of iodine consumed by the various sample volumes was calculated.

A plot of iodine consumption against the volume of diethylaluminium chloride solution taken (Fig. 2, Procedure A) shows that the iodine consumption is not proportional to the volume of sample taken, and that the line drawn through the experimental points intersects the sample-volume axis at a positive value, indicating that low iodine consumptions are being obtained in these determinations. This suggested that the iodine reagent contained a small amount of an impurity that reacted rapidly with the alkyl groups in diethylaluminium chloride.

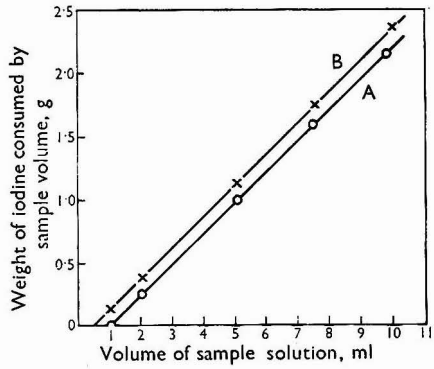


Fig. 2. Iodine consumption of dilute diethylaluminium chloride solutions: graph A, 50 ml of iodine reagent added to sample; graph B, sample added to 50 ml of iodine reagent

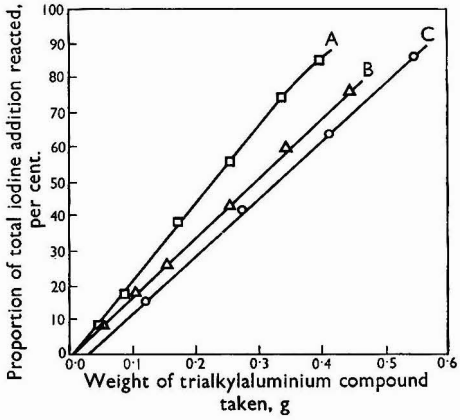


Fig. 3. Influence of excess of iodine and reaction time on the iodine consumption: graph A, triethylaluminium; graph B, tripropylaluminium; graph C, diethylaluminium chloride

It can be seen in Fig. 2 (Procedure B) that higher iodine consumptions are obtained when the order of mixing the diethylaluminium chloride solution and iodine is reversed, *i.e.*, when the iodine is transferred by pipette into the reaction flask first. These conditions are, presumably, less favourable for the occurrence of the side reaction. However, the presence of the impurity still affects the determination of iodine consumption to some extent. The effect of the impurity was overcome by using a "double titration" procedure, described below.

The iodine consumptions, I_1 g and I_2 g, of two different volumes, V_1 ml and V_2 ml, of the sample solution are determined. The same volume of iodine reagent is used in each determination. The correct iodine consumption of $V_1 - V_2$ ml of sample solution is, therefore, equal to $I_1 - I_2$ g of iodine.

Several iodine-number determinations (grams of iodine consumed per 100 grams of sample) were carried out on a solution of diethylaluminium chloride by the "double titration" procedure, and these results are compared, in Table I, with the results obtained by the "single titration" procedure. The "double titration" results are consistently higher and do not vary appreciably with the amount of sample taken for analysis.

TABLE I

DIETHYLALUMINIUM CHLORIDE (5 PER CENT. IN TOLUENE): EFFECT OF DISSOLVED IMPURITY IN THE IODINE REAGENT

Sample volume taken, ml	Iodine number, g of iodine consumed per 100 g of sample	
	Uncorrected ("single titration")	Corrected ("double titration")
2·5	22·7	28·6
3·0	—	28·5
5·0	26·2	28·1
7·5	26·7	28·4

The effect of excess of iodine on the iodine-number determination was examined. Varying volumes of dilute solutions of triethylaluminium, diethylaluminium chloride and tripropylaluminium were added to a fixed volume (50 ml) of the iodine reagent and the

reaction was allowed to proceed for 10 minutes. It can be seen from Fig. 3 that when iodine consumption is plotted against sample size the iodine consumption is not affected, unless more than 80 per cent. of the iodine present is consumed in the reaction. These experiments were then repeated with dilute solutions of diethylaluminium ethoxide and dipropylaluminium isopropoxide. Fig. 4 shows that the iodine consumption of this less reactive type of organo-aluminium compound is more dependent upon the molar excess of iodine present. With a 10-minute reaction period the iodine consumption is affected if more than 50 to 60 per cent. of the iodine is consumed. Extension of the reaction time to 20 minutes, however, circumvents this effect. Complete iodination of all the types of organo-aluminium compounds examined is obtained in 20 minutes, even in the presence of only a 20 to 30 per cent. excess of iodine reagent.

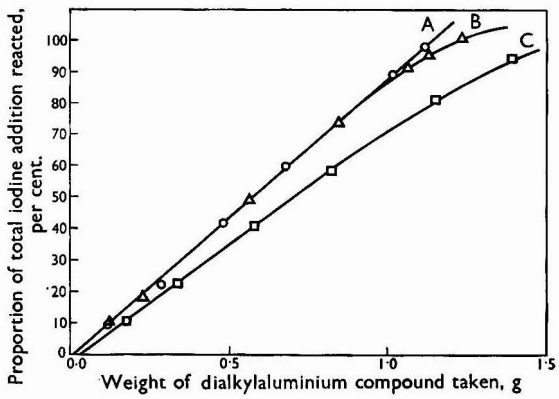


Fig. 4. Influence of excess of iodine and reaction time on the iodine consumption: graph A, diethylaluminium ethoxide, 20 minutes' reaction; graph B, diethylaluminium ethoxide, 10 minutes' reaction; graph C, dipropylaluminium propoxide, 5 minutes' reaction

In the experiments described so far, dilute aqueous acetic acid (2 N) has been added to the mixture of iodine reagent and sample before back-titrating the excess iodine with standard sodium thiosulphate solution. It was observed, however, that considerably higher iodine consumptions occurred for dialkylaluminium alkoxides if distilled water only was added at this stage. No explanation was found for this effect. It did not occur with trialkyl-aluminium and dialkylaluminium chloride compounds, and seemed to be connected in some way with the presence of alkoxide groups in the molecule. It was decided to use aqueous acetic acid in the final analytical procedure.

STOICHEIOMETRY OF THE IODINATION OF ORGANO-ALUMINIUM COMPOUNDS—

The stoicheiometry of the reactions that occur during the iodination of iso-octane solutions of the purest available specimens of various organo-aluminium compounds was then examined. Ethyl, propyl, butyl, hydride and alkoxide groups in these samples were determined by the procedure described by Crompton and Reid.[3,13] Alkyl groups higher than butyl were determined by a procedure in which a cold toluene solution of the organo-aluminium compound was decomposed at −60° C by the addition of a dilute solution of glacial acetic acid in toluene. Aqueous sodium hydroxide was then added to the solution. Liquid paraffins, produced by the hydrolysis of the higher alkyl groups, were then determined in the separated toluene phase by gas chromatography.

In Table II are shown the values of the determined iodine consumptions of iso-octane solutions of various organo-aluminium compounds. Each alkyl group in trialkylaluminium compounds consumes one mole of iodine. These results confirm the conclusions reached by Bartkiewicz and Robinson.[12] Similarly, each alkyl group in diethylaluminium chloride consumes one mole of iodine. The reaction between iodine and dialkylaluminium alkoxides follows a different course, however, as only 1·25 moles of iodine are consumed per mole of this type of compound, *i.e.*, 0·625 moles of iodine are consumed per alkyl group.

TABLE II

STOICHEIOMETRY OF THE IODINATION OF THE ORGANO-ALUMINIUM COMPOUND

Sample description	Composition of sample, w/w per cent.		Iodine consumption, moles of iodine consumed per mole of organo-aluminium compound
Triethylaluminium	$Al(C_2H_5)_3$	88·8	2·97
	$Al(C_2H_5)_2(C_4H_9)$	5·3	
	$Al(C_2H_5)_2H$	1·1	
	$Al(C_2H_5)_2(OC_2H_5)$	4·3	
Tripropylaluminium	$Al(C_3H_7)_3$	90·5	3·09
	$Al(C_6H_{13})_3$	1·7	
	$Al(C_3H_7)_2H$	1·4	
	$Al(C_3H_7)_2(OC_3H_7)$	2·2	
Diethylaluminium chloride	$Al(C_2H_5)_2Cl$	93·0	2·00
	$Al(C_2H_5)(C_4H_9)Cl$	4·0	
	$Al(C_2H_5)(OC_2H_5)Cl$	3·0	
Dipropylaluminium isopropoxide	$Al(C_3H_7)_2(OC_3H_7)$	92·7	1·25
	$Al(C_6H_{13})_2(OC_3H_7)$	5·3	

REPRODUCIBILITY OF THE PROCEDURE—

The reproducibility of the method for the determination of the iodine consumption was determined by statistical analysis. Iodine-consumption determinations were made with 6 different sample volumes of dilute solutions of 3 typical organo-aluminium compounds. The mean iodine number of samples, its standard error and its 95 per cent. confidence limits are shown in Table III. It can be seen that, for the 3 organo-aluminium compounds examined, the standard errors of the iodine-number determinations are acceptably low.

TABLE III

REPRODUCIBILITY OF IODINE-NUMBER DETERMINATIONS

Sample description	Number of determinations	Mean iodine number, g of iodine consumed per 100 g of sample	Standard error	95 per cent. confidence limits
Triethylaluminium	6	613·8	2·6	613·8 ± 7·3
Diethylaluminium ethoxide	6	158·6	1·9	158·6 ± 5·3
	6	156·5	1·1	156·5 ± 3·1
Dibutylaluminium ethoxide	6	42·9	0·3	42·9 ± 0·9

METHOD

APPARATUS—

Dilution flasks—These are 100-ml stoppered Pyrex-glass calibrated flasks with nitrogen inlet side-arm and stopcock above the graduation mark.

Safety pipettes—These are "Exelo"-type plunger pipettes of 1, 2, 5, 10 and 25-ml capacity.

T-pieces; glass, 3 inches.

Graduated cylinder, 50 ml.

Burette, 50 ml—This is preferably fitted with an E-MIL polythene stopcock (obtainable from H. J. Elliott Limited, Treforest Industrial Estate, Pontypridd, Glamorgan).

Reaction flask, 250 ml—This is a B24, three-neck flask with glass stirrer and nitrogen and burette inlets (see Fig. 1).

REAGENTS—

Iso-octane—Dry iso-octane by standing it over 50 g of molecular sieve, type 4A (obtainable from British Drug Houses Ltd.) for 2 weeks. Swirl the bottle daily.

Nitrogen—Dry by passing through a molecular-sieve packed tower, oxygen content less than 25 p.p.m.

Iodine reagent (0·4 N)—To 2·5 litres of toluene in a dry bottle add 130 g of analytical-reagent grade iodine and shake the contents to dissolve the iodine. Add to the solution 50 g of freshly heated (at 120° C) 4A molecular sieves, stopper the flask, and leave it for several days, occasionally swirling it.

Sodium thiosulphate (0·25 N) *aqueous, standardised.*

Acetic acid (4 N) *aqueous*—Dilute 250 ml of glacial acetic acid to 1 litre with distilled water.

SAMPLING—

If the sample contains more than 20 per cent. of organo-aluminium compound it is necessary to dilute the solution with iso-octane in the following way.

Transfer by pipette 20 ml of dry iso-octane into a dry 100-ml calibrated flask with a nitrogen inlet side-arm, and purge the solvent with nitrogen for 30 seconds. Connect a nitrogen line to the side-arm of the calibrated flask, open the stopcock and apply a gentle nitrogen purge. Transfer sufficient of the sample into the calibrated flask, by means of a safety pipette, to give a concentration of approximately 20 per cent. of the organo-aluminium compound in the diluted solution. Purge the exterior of the tip of the safety pipette with dry nitrogen during the transfer, as described by Crompton.[13]

Make up the volume to 100 ml with dry iso-octane, stopper the flask and mix the contents thoroughly.

PROCEDURE—

With a pipette fitted with a rubber suction bulb, transfer 50 ml of the same batch of iodine reagent into two dry 250-ml reaction flasks. Apply a gentle purge of nitrogen to displace the air from the flasks. Switch on the stirrers and adjust the speed to approximately 1 revolution per second. Transfer a different volume of the sample solution into each flask by means of a safety pipette. Observe the precautions described above to prevent decomposition of the sample during transfer. Stopper the reaction flasks immediately after the sample delivery. Maintain the gentle nitrogen purge during the subsequent reaction.

Suitable pairs of sample volumes required for the analysis of a 200 millimole per litre solution, of various types of organo-aluminium compounds, are shown in Table VIII. Correspondingly larger or smaller volumes should be taken if necessary.

TABLE VIII

OPTIMUM PAIRS OF SAMPLE VOLUMES REQUIRED FOR THE ANALYSIS OF A 200 MILLIMOLES PER LITRE SOLUTION OF VARIOUS TYPES OF ORGANO-ALUMINIUM COMPOUNDS

Type of organo-aluminium compound analysed	Sample volumes required* "A" ml	"B" ml
Trialkylaluminium compounds	6	12
Dialkylaluminium chlorides	9	18
Dialkylaluminium alkoxides	12·5	25

* The following relationships are used to calculate the sample volumes required:—

1 mole of trialkylaluminium compound ≡ 6 × 126·9 g of iodine
1 mole of dialkylaluminium chloride ≡ 4 × 126·9 g of iodine
1 mole of dialkylaluminium alkoxide ≡ 2·5 × 126·9 g of iodine

Let the reaction proceed for 20 minutes, then remove the nitrogen supply and introduce 40 ml of 2 N acetic acid into each reaction flask. Increase the stirrer speed until the aqueous and toluene phases are thoroughly mixed and then titrate the solution with 0·25 N sodium thiosulphate solution. Continue the titration until the solution becomes pale brown in colour. Commence drop-wise titration and stop the stirrer between each addition of titrant. Continue the titration until the pink colour completely disappears from the toluene phase and the toluene becomes pale yellow.

CALCULATIONS—

Iodine consumption (g of iodine consumed per litre of sample)

$$= \frac{(T_1 - T_2) \times f \times 126{\cdot}9 \times 1000}{(V_2 - V_1) \times 1000}$$

Trialkylaluminium compounds (millimoles of trialkylaluminium compound per litre of sample)

$$= \frac{(T_1 - T_2) \times f \times 1000}{(V_2 - V_1) \times 6}$$

Dialkylaluminium chlorides (millimoles of dialkylaluminium chloride per litre of sample)

$$= \frac{(T_1 - T_2) \times f \times 1000}{(V_2 - V_1) \times 4}$$

Dialkylaluminium alkoxides (millimoles of dialkylaluminium alkoxide per litre of sample)

$$= \frac{(T_1 - T_2) \times f \times 1000}{(V_2 - V_1) \times 2{\cdot}5}$$

Where V_1 = Volume of sample solution taken (smaller volume), ml.
V_2 = Volume of sample solution taken (larger volume), ml.
T_1 = Back-titration of sodium thiosulphate obtained with smaller sample volume, ml.
T_2 = Back-titration of sodium thiosulphate obtained with larger sample volume, ml.
f = Normality of sodium thiosulphate solution.

DISCUSSION OF RESULTS

ANALYSIS OF DILUTE HYDROCARBON SOLUTIONS OF TRIALKYLALUMINIUM COMPOUNDS—

The catalyst contents of dilute hydrocarbon solutions of various trialkylaluminium compounds was determined iodimetrically, by the conductiometric titration with isoquinoline and by the determination of aluminium. It can be seen in Table IV that reasonably good agreement is obtained between the iodimetric and the isoquinoline methods of analysis. The iodimetric method can be applied to solutions containing as little as 20 millimoles per litre of catalyst.

TABLE IV

DILUTE TRIALKYLALUMINIUM SAMPLES

Sample description	Trialkylaluminium content, millimoles per litre: Based on aluminium determination	Based on isoquinoline consumption	Based on iodine consumption
Triethylaluminium in iso-octane	715	687	684, 673
Triethylaluminium in iso-octane	1353	1314	1305
Tripropylaluminium in iso-octane	314	294	309
Tripropylaluminium in iso-octane	105	—*	104
Tripropylaluminium in iso-octane	62·8	—*	61·3
Tripropylaluminium in iso-octane	20·1	—*	19·6

* Isoquinoline method is not applicable because of the low electrical conductivity of the test solution.

Commercial trialkylaluminium usually contains a small amount of dialkylaluminium alkoxide as an impurity, which is produced by oxygen contamination during the manufacture. An isoquinoline titration determines only the "active" trialkylaluminium content of the sample; aluminium determinations include both "active" trialkylaluminium and "inactive" dialkylaluminium alkoxide. Higher results are therefore expected, and indeed found, in the latter method of analysis. The presence of small amounts of dialkylaluminium alkoxide in trialkylaluminium compounds causes little interference in the iodimetric method. Thus, the determined iodine number of a solution known to contain 180 millimoles of trialkylaluminium compound per litre and 20 millimoles of dialkylaluminium alkoxide per litre (*i.e.*, total organo-aluminium content of sample contains 10 per cent. of the alkoxide derivative), indicates a trialkylaluminium content of 187 millimoles per litre, which is about 4 per cent. higher than the added amount.

ANALYSIS OF DILUTE HYDROCARBON SOLUTIONS OF DIALKYLALUMINIUM CHLORIDES—

It can be seen from Table V that good agreement is obtained between the iodimetric and the isoquinoline methods of analysis. Diethylaluminium chloride usually contains a maximum total of 5 per cent. of ethylaluminium chloro-ethoxide and triethylaluminium or ethylaluminium dichloride as impurity. The presence of these contaminants at this level of concentration does not interfere appreciably in the iodimetric determination of diethylaluminium chloride.

TABLE V

DILUTE DIETHYLALUMINIUM CHLORIDE SAMPLES

Diethylaluminium chloride content, millimoles per litre		
Based on aluminium determination	Based on isoquinoline consumption	Based on iodine consumption
218	198	197
192	172	177, 179

ANALYSIS OF DILUTE HYDROCARBON SOLUTIONS OF DIALKYLALUMINIUM ALKOXIDES—

Depending upon the method of manufacture used, dialkylaluminium alkoxide catalysts might contain small amounts of either trialkylaluminium or alkylaluminium dialkoxide as impurity. The dialkylaluminium alkoxide content of several dilute hydrocarbon solutions was determined iodimetrically. These values are compared in Table VI with results obtained by aluminium determinations. Good agreement was obtained between the two methods when the total organo-aluminium content of the test solution contained less than 5 per cent. of the previously mentioned impurities (sample A). As expected, poorer agreement was obtained for a solution of dipropylaluminium isopropoxide which contained an appreciable amount of propylaluminium di-isopropoxide as impurity (sample B). Commercial preparations of dialkylaluminium alkoxides usually contain less than 5 per cent. of their total organo-aluminium content in the form of alkylaluminium dialkoxide or trialkylaluminium impurity and no serious interference from these impurities is therefore to be anticipated.

TABLE VI

DILUTE DIALKYLALUMINIUM ALKOXIDE SAMPLES

Sample description	Calculated as dialkylaluminium alkoxide, millimoles per litre: Based on aluminium determination	Based on iodimetric determination	Differences, per cent.
Sample A: $AlR_2(OR)$ containing less than 5 per cent. of AlR_3 or $AlR(OR)_2$ impurity Diethylaluminium ethoxide in iso-octane ..	795	795	Nil
Sample B: $AlR_2(OR)$ containing 25 per cent. of $AlR(OR)_2$ impurity Dipropylaluminium isopropoxide in iso-octane	272 273	238	−12·5

The iodimetric method of analysis also presents a method for detecting whether a change in the composition of stocks of hydrocarbon solutions of organo-aluminium compounds has occurred during storage. This could arise from the contamination of the material with extraneous oxygen and/or water, thus leading to a reduction in the iodine number because of alkyl group decomposition as follows—

$$2 > AlR + O_2 \text{ - - - } 2 > Al(OR)$$

$$> AlR + H_2O \text{ - - - } > Al(OH) + RH$$

Regular iodimetric determinations present a method, therefore, of detecting whether contamination of the organo-aluminium compound occurs to any extent during storage. Such information could not be obtained from aluminium determinations alone, as these remain virtually unchanged even when the sample has become heavily contaminated.

APPLICATION OF THE IODIMETRIC METHOD TO HIGHER MOLECULAR WEIGHT ORGANO-ALUMINIUM COMPOUNDS—

The iodimetric method was applied to a solution of impure trihexadecylaluminium in toluene. The usual stoicheiometry was assumed in the reaction of the components of this sample with iodine. It is seen in Table VII that reasonable agreement is obtained between the expected and the found iodine consumptions of this substance.

TABLE VII

APPLICATION OF THE IODIMETRIC METHOD TO TRIHEXADECYLALUMINIUM

Composition of sample, w/w per cent.		Iodine consumption, g of iodine per 100 g of sample	
		Expected	Found
$Al(C_{16}H_{33})_3$	47·8		
$Al(C_{32}H_{65})_3$	4·0		
$Al(C_{16}H_{33})_2(OC_{16}H_{33})$	4·5	55·7	54·0
$C_{16}H_{32}$	9·2		
$C_{32}H_{64}$	1·6		
Toluene	32·0		
Total	99·1		

The author thanks the Directors of Shell Chemical Company Limited for permission to publish this paper.

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A Flame-photometric Method for Determining Traces of Calcium in Lithium Chloride

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The determination of calcium in solutions of lithium chloride (1·5 per cent. w/v) containing up to 2 μg per ml of calcium, and up to 1 μg per ml of aluminium has been investigated. The use of different organic solvents has been studied, and the sensitivity of the determination has been increased 3-fold by the use of an aqueous methanol - butanol mixture. It has been shown that the only serious interference effect, that arising from the presence of the aluminium content, can be prevented by the addition of *trans*-1,2-diaminocyclohexane-*NNN'N'*-tetra-acetic acid (CDTA). Recoveries from synthetic samples showed no appreciable bias, and replicate results indicated a satisfactory precision, and a sensitivity of about 0·02 μg per ml.

The use of alcohols and ketones to increase the sensitivity of flame-photometric methods is discussed by Dean,[1] who indicates that for calcium a 2-fold or 3-fold enhancement of the emission is possible. The organic solvents most commonly used[2,3,4] include acetone, ethyl methyl ketone, methanol, ethanol, propanol, butanol and acetic acid. In view of the low concentrations of calcium expected to be found in the lithium chloride (between 0·001 and 0·012 per cent.) it was decided to investigate the use of organic solvents in increasing the calcium emission.

The samples of lithium chloride, as received, may contain up to 0·006 per cent. of aluminium (determined spectrographically), as well as small amounts of phosphorus, sulphur and iron, all of which are known[1] to interfere with the calcium emission. It was, therefore, proposed to investigate the influence of aluminium and other possible sources of interference, and also methods of eliminating these effects. These include the use of releasing agents,[5,6] *e.g.*, lanthanum and Group II elements, as well as complexing agents such as 8-hydroxyquinoline and EDTA.[8] It was also proposed to consider the use of *trans*-1,2-diaminocyclohexane-*NNN'N'*-tetra-acetic acid (CDTA) for eliminating interference effects. This reagent is reported[9] to form more stable complexes with cations than does EDTA. Other methods, *e.g.*, prior removal of the source of interference, or addition of excess of the interfering element were not considered, as the former would considerably complicate the analysis and the latter would result in some loss of sensitivity.

Experimental

Reagents—

De-ionised water was used in all experiments.

Lithium chloride—Further purify analytical-reagent grade quality by passing a 12 per cent. aqueous solution of lithium chloride through an ion-exchange column containing Dowex A1 ion-exchange resin. The resin had previously been converted to the lithium salt by using 2 N lithium hydroxide solution. Dilute the solution obtained as required, or evaporate to dryness for the experimental work.

Methanol—Refine to meet the British Standard Specification 506:1958 and re-distil.

Calcium—Prepare a standard solution (1000 μg per ml) from analytical-reagent grade calcium carbonate neutralised with re-distilled 6 N hydrochloric acid. Dilute the solution according to requirements.

Aluminium—Prepare a standard solution (1000 μg per ml) from analytical-reagent grade aluminium dissolved in re-distilled hydrochloric acid.

All other reagents used were of analytical-reagent grade quality.

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APPARATUS—

Unicam SP900 flame spectrophotometer—The instrument was modified slightly so that a Beckman oxy-hydrogen burner can be used in place of the normal burner, and fitted with a concave mirror behind the flame. This mirror effectively doubled the response to the calcium emission.

Beckman oxy-hydrogen burner—Care was taken never to allow the burner to run without a liquid feed.

Bristol Dynamaster Recorder, (0 to 10 mV).

Agla 0·5-ml syringe pipette.

Polythene laboratory ware, e.g., bottles, beakers, measuring cylinders.

OPERATING CONDITIONS—

The operating conditions used during the experiment were as follows—

Hydrogen pressure 3·2 p.s.i., flow-rate 3·0 litres per minute.
Oxygen pressure 14 p.s.i., flow-rate 1·8 litres per minute.
Flame position: burner position adjusted to give maximum response to calcium emission.
Instrument Gain 3.
Slit width 0·1 mm. Any greater slit width resulted in interference from the adjacent lithium peak.
Spectrum scanned from 415 mμ to 428 mμ, the peak height being measured at 422 mμ by taking the mean distance from the peak maximum to the trough on either side.

WASHING PROCEDURE—

Light the burner and allow it to run for 5 minutes with water passing through it before each series of analyses. Pass water through the burner for 1 minute between each sample and for 5 minutes at the conclusion of a series. Do not switch off the burner at any time, and never allow it to run dry. Preliminary experiments indicated that deviations from this procedure could result in decreased reproducibility.

THE USE OF ORGANIC SOLVENTS—

Experiments were carried out with 1·5 per cent. solutions of lithium chloride containing calcium, and with different amounts of each of the following solvents relative to the aqueous solution; acetone, ethyl methyl ketone, methanol, ethanol, propanol, butanol and acetic acid. The most effective of these solvents in enhancing the calcium emission appeared to be methanol and butanol. The relationship between the percentage enhancement of the intensity of the calcium line and the percentage of methanol and butanol in the solution is shown in Fig. 1.

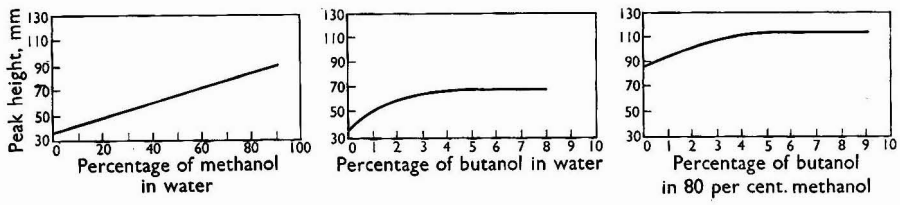

Fig. 1. Effects of the solvent on the calcium emission

The lithium chloride and the calcium content were kept constant. The relationship between the enhancement of the calcium emission and the butanol content of a solution containing 80 per cent. of methanol and 20 per cent. of water is also shown in Fig. 1. From these results it was decided to use as solvent in all subsequent work a mixture of 80 per cent. of methanol, 6 per cent. of butanol and 14 per cent. of water. This solvent increased the calcium emission 3-fold as compared with the calcium emission from a purely aqueous solution. It was considered advisable to restrict the methanol content to 80 per cent. to avoid solubility and solvent-preparation difficulties. The lithium chloride content of the solutions was restricted to 1·5 per cent., as the use of more concentrated solutions tended to result in blockage of the burner.

INTERFERENCE EFFECTS—

Lithium chloride—The depression of the calcium emission by the lithium chloride content (1·5 per cent.) of the solutions was found to be 10 per cent. This was regarded as a constant factor, as the lithium chloride content was to be fixed at 1·5 per cent.

Sodium—No significant effect was found on the calcium emission in amounts up to 12·5 μg per ml (the highest anticipated sodium content).

Phosphorus (*as sodium phosphate*)—No effect was found on the calcium emission in amounts up to 0·25 μg per ml.

Sulphur (*as sodium sulphate*)—No effect was found on the calcium emission in amounts up to 0·25 μg per ml.

Iron (*as iron*(III) *chloride*)—No effect was found on the calcium emission in amounts up to 10 μg per ml.

Aluminium—The percentage depression of the calcium emission caused by varying amounts of aluminium in the 1·5 per cent. lithium chloride solutions containing 0·25 μg per ml of calcium is shown in Table I. At the highest expected aluminium level (1·0 μg per ml) a 32 per cent. depression was observed.

TABLE I

DEPRESSION OF THE CALCIUM PEAK HEIGHT IN THE PRESENCE OF ALUMINIUM

Aluminium content, μg per ml	Depression of the calcium peak height, per cent.
0·05	0
0·125	0
0·25	−15
1·0	−32
1·25	−40
2·5	−60

ELIMINATION OF THE ALUMINIUM INTERFERENCE EFFECT—

The use of several reagents suggested in the literature for the elimination of the aluminium-interference effect on the determination of calcium was investigated. Table II shows the depression of the calcium emission of 0·5 μg per ml of calcium in the presence of 1 μg per ml of aluminium and the recommended amount of the particular reagent used.

TABLE II

EFFECT OF VARIOUS REAGENTS ON THE ALUMINIUM SUPPRESSION OF THE CALCIUM EMISSION

Reagent	Depression, per cent.	Comments
Lanthanum	−16	
Magnesium	−21	
Strontium	−22	
8-Hydroxyquinoline	−6	High background contribution
EDTA	—	Insoluble
None	−32	

The releasing agents, lanthanum, magnesium and strontium, did not appear to be completely successful in eliminating the interference effect of aluminium. The effect of 8-hydroxyquinoline had not been corrected for its calcium content, and the depression recorded could, therefore, be unrealistic. Also, there was a high background contribution from the reagent, and the 422-mμ calcium line appeared on the steep slope of the background and was difficult to measure. The use of CDTA was prevented because of the insolubility of the reagent and its salts in the solvent used for the flame-photometric determination.

As an effective anti-suppression agent had not been suggested by the results of these experiments, it was decided to investigate the use of CDTA. This reagent is reported to form more stable complexes than EDTA and its salts were found to be more soluble in organic solvents than those of EDTA.

USE OF CDTA—

Solutions were made up containing 0·1 M CDTA (as the lithium salt) and 1·5 per cent. of lithium chloride in methanol (80 per cent.), butanol (6 per cent.) and water (14 per cent.). These were made up in the following way.

A solution, *A*, was made up containing 17·4 g of lithium chloride dissolved in a mixture of 930 ml of methanol and 70 ml of butanol. A further solution, *B*, was prepared, containing

247 g of CDTA and 68·6 g of lithium hydroxide and made up to 1 litre with water. A 21·5-ml volume of solution *A* was combined with 3·5 ml of solution *B*.

Calcium and aluminium were added to each 25 ml of these solutions so that each contained 1 μg per ml of calcium and varying amounts of aluminium (0 to 2·5 μg per ml).

When measuring the intensity of the calcium line at 422 mμ it was necessary to allow for the contribution of the calcium impurity content of the 0·1 M lithium CDTA. This was determined in a separate experiment by a normal standard-addition procedure, and was found to be 0·60 μg per ml. Each calcium peak height (of solutions containing 1·0 μg per ml of calcium and 0·1 M CDTA) was, therefore, multiplied by a factor 1·0/1·6 to give the corrected calcium content of the solution. These experiments were repeated for solutions containing 0·05 and 0·01 M CDTA as the lithium salt. In each experiment the calcium emission (corrected) was compared with the calcium emission of a similar solution containing 1·0 μg per ml of calcium but no aluminium or CDTA, and the percentage depression caused by the aluminium was calculated.

The relationship between the percentage depression of the calcium emission (corrected for the calcium content of the lithium salt of the CDTA) and the amount of aluminium present is shown in Fig. 2 for solutions containing 0·1, 0·05 and 0·01 M CDTA and no CDTA. It can be seen that a 0·05 M CDTA solution is effective in eliminating the interference of up to 1·0 μg per ml of aluminium, the depression of 3 per cent. being tolerable.

The depression, found by using a 0·1 M solution of CDTA, was less than that found with a 0·05 M CDTA solution, but the improvement was not good enough to compensate for the disadvantage of the doubled calcium-impurity content.

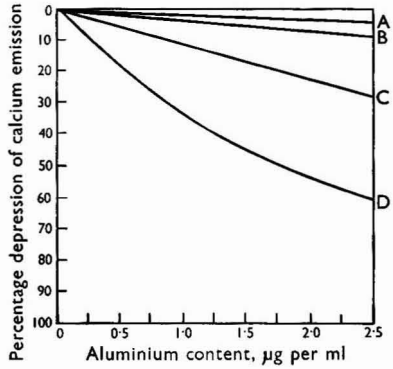

Fig. 2. Effect of CDTA on the depression of the calcium emission: curve A, a 0·1 M solution of CDTA; curve B, a 0·05 M solution of CDTA; curve C, a 0·01 M solution of CDTA; curve D, a solution containing no CDTA

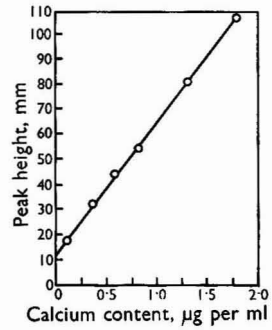

Fig. 3. Calibration graph for calcium in the presence of CDTA

A calibration graph was prepared (Fig. 3) with solutions containing 0·05 M CDTA (as the lithium salt) and 1·5 per cent. of lithium chloride in the methanol (80 per cent.), butanol (6 per cent.) and water (14 per cent.) solvent. Each solution contained known amounts of calcium (up to 2 μg per ml) and no aluminium. This calibration graph was a straight line and was used in the analysis of synthetic sample solutions containing varying known amounts of aluminium, but which were otherwise similar to the solutions used in the preparation of the calibration graph. The recoveries obtained are recorded in Table III. The contribution of the calcium-impurity content of the 0·05 M CDTA solution is the same for both the sample solutions and the solutions used for calibration, and therefore was ignored.

Replicate results were obtained at the 0·125 μg per ml level and the 1·875 μg per ml level. The standard deviations were 0·012 μg per ml (10 determinations) and 0·115 μg per ml (10 determinations), respectively. The limit of detection (based on the 2σ value) was approximately 0·02 μg per ml.

TABLE III

CALCIUM RECOVERIES FROM SOLUTIONS CONTAINING ALUMINIUM AND CDTA

Aluminium content, μg per ml	Known calcium content, μg per ml	Calcium recovered, μg per ml	Percentage recovery
0	0·125	0·12	96
0·25	0·375	0·39	104
0·50	0·625	0·64	102
1·0	0·875	0·84	96
1·0	1·125	1·06	94
1·0	1·625	1·60	98
0·25	1·875	1·90	102
1·0	2·125	2·058	97
		Mean recovery	99 per cent.

CONCLUSIONS

Traces of calcium can be determined flame photometrically by using a Unicam SP900 and a Beckman oxy-hydrogen burner in solutions of lithium chloride (1·5 per cent.) containing aluminium (up to 1 μg per ml). The sensitivity of the determination can be increased 3-fold by using a mixed methanol - butanol - water solvent, and the interference of aluminium can be prevented by the use of diaminocyclohexane tetra-acetic acid. At the 2-μg per ml level the standard deviation is 0·115 μg per ml and at the 0·125 level the standard deviation is 0·012 μg per ml, indicating a limit of detection (2σ) of 0·02 μg per ml.

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The Colorimetric Determination of Hydroxamic Acids

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N-Hydroxycarbamates, mono-hydroxyureas and di-hydroxyureas in tissue extracts have been determined by diazotising sulphanilamide with the nitrite produced on oxidation and coupling with *N*-1-naphthylethylenediamine. Mixtures of hydroxylamine and hydroxamic acids were determined (*a*), by selective oxidation at pH 3·5 and pH 8·0, and (*b*), after separation of the components by thin-layer chromatography.

Some hydroxamic acids, including the *N*-hydroxycarbamates, mono-hydroxyureas and di-hydroxyureas have carcinogenic,[1] anti-tumour,[2] anti-viral[3] and anti-bacterial[4] properties. They also induce chromosomal aberrations,[5,6] and inhibit thymidine incorporation into DNA of HeLa monolayers.[7] Hydroxamic acids of the type A–CONHOH, where A is aryl, alkyl or aralkyl, are commonly determined as ferric hydroxamates. The method is of limited sensitivity,[8,9] and is unsuitable for the determination of *N*-hydroxycarbamates[10] and hydroxyurea[11] because of the instability and low optical densities of the ferric complexes. Benzohydroxamic and acetohydroxamic acids have been determined by diazotisation and coupling after oxidation to nitrite by iodine in acetic acid.[9] Hydroxamic acids,[12] after acid hydrolysis to give hydroxylamine and hydroxylamine[13] itself, have been similarly determined. These methods have a lower limit of sensitivity of about 0·5 μg of hydroxamic acid per ml of final solution, and hydroxylamine interferes.[8] A less sensitive method,[10] that can be applied in the presence of hydroxylamine makes use of the pentacyanoferroate complexes of hydroxamic acids, but arylhydroxylamines and nitroso-aryls interfere.[14] In the present method, hydroxamic acids are determined at final concentrations of 10^{-6} to 2×10^{-5} M in water or tissue fluids, even in the presence of hydroxylamine.

Method

Apparatus—

Spectrophotometer—Optical densities were measured on a Unicam SP500 instrument.

Reagents—

Potassium chloride - hydrochloric acid buffer, 0·1 M—A mixture of 0·1 M aqueous solutions of potassium chloride and hydrochloric acid.

Potassium hydrogen phthalate buffer, 0·1 M—A mixture of 0·1 M aqueous solutions of potassium hydrogen phthalate and hydrochloric acid.

Acetate buffer, 0·1 M—A mixture of 0·1 M aqueous solutions of sodium acetate and acetic acid.

Phosphate buffer, 0·1 M—A mixture of 0·1 M aqueous solutions of sodium dihydrogen orthophosphate and disodium hydrogen orthophosphate.

Borate buffer, 0·1 M—A mixture of 0·1 M aqueous solutions of boric acid and sodium hydroxide.

Iodine—A 0·1 N aqueous solution.

Sodium thiosulphate—A 0·1 N aqueous solution.

Sulphanilamide—A solution of 1 g sulphanilamide in 100 ml of 2 N hydrochloric acid.

N-1-*Naphthylethylenediamine hydrochloride*—A solution of 0·05 g of the hydrochloride in 100 ml of water.

Trichloroacetic acid—An aqueous solution of 36 g of the acid in 100 ml of solution.

Thin-layer chromatography—

Glass plates were coated with films of silica gel G of 0·30-mm thickness, and the chromatograms were developed in (*a*), a mixture of 3 volumes of acetone and 7 volumes of light petroleum (b.p. 40° to 60° C), or (*b*), a mixture of 3 volumes of ethanol and 7 volumes of propanol. Hydroxylamine was detected on chromatograms with (*i*), ammoniacal aqueous

2 per cent. silver nitrate. Hydroxamic acids were detected with (*i*), (*ii*), 1 per cent. aqueous w/v sodium amminoprusside containing 0·1 per cent. w/v of magnesium chloride hexahydrate, (*iii*), 1 per cent. w/v ferric chloride in aqueous 50 per cent. ethanol, or (*iv*), 0·01 N iodine in phosphate buffer, pH 8·0, followed by sulphanilamide and *N*-1-naphthylethylenediamine hydrochloride, in the order given. All the compounds reduced reagent (*i*) and gave mauve spots with reagent (*iv*); the hydroxamic acids gave red to purple spots with reagent (*ii*) and purple-to-blue spots with reagent (*iii*). The R_F values of the following compounds in solvents (*a*) and (*b*), respectively, are given in parentheses: hydroxylamine hydrochloride (0, 0·21), methyl *N*-hydroxycarbamate (0·18, 0·65), ethyl *N*-hydroxycarbamate (hydroxyurethane) (0·23, 0·79), *n*-propyl *N*-hydroxycarbamate (0·37, 0·81), *n*-butyl *N*-hydroxycarbamate (0·41, 0·86), benzohydroxamic acid (0·22, 0·86), hydroxyurea (0, 0·59), dihydroxyurea (0, 0·71) and *N*-phenyl-*N'*-hydroxyurea (0·28, 0·87).

MATERIALS—

Phenylhydroxylamine,[15] hydroxyurea,[16] *N,N'*-dihydroxyurea,[17] the alkyl *N*-hydroxycarbamates[10] and other hydroxamic acids[18] were prepared as described. *N*-Methylhydroxylamine[19] was prepared by reducing nitromethane with zinc dust and ammonium chloride.

PROCEDURES—

1. *Determination in water*—The hydroxamic acid was dissolved in 0·5 ml of water (in triplicates); the solutions were treated with the following reagents in the order given and mixed after each addition: 0·5 ml of phosphate buffer (pH 8·0), 0·1 ml of iodine, 0·1 ml of sodium thiosulphate, 1·9 ml of sulphanilamide and 1·9 ml of *N*-1-naphthylethylenediamine hydrochloride. After 30 minutes, the optical density of the solution was measured in a 1-cm cell at 540 mμ against a reagent blank. The optical density was unchanged after 6 hours at 23° C. Hydroxylamine and dihydroxyurea were also determined by substituting 0·5 ml of acetate buffer (pH 3·5 and 4·5, respectively), for the phosphate buffer in the above procedure.

2. *Determination in an aqueous suspension of rat liver microsomes or in whole rat liver homogenate*—The suspension of microsomes was prepared as described.[20] The homogenate was prepared by homogenising 40 g of fresh rat liver in pH 7·4 phosphate buffer in a Potter & Elvehjem (1936)-type homogeniser with a Teflon pestle, and diluting to 200 ml with the same buffer. The hydroxamic acid was dissolved in 1 ml of water (in triplicates), mixed with 3 ml of the suspension of microsomes or homogenate, treated with 1 ml of trichloroacetic acid

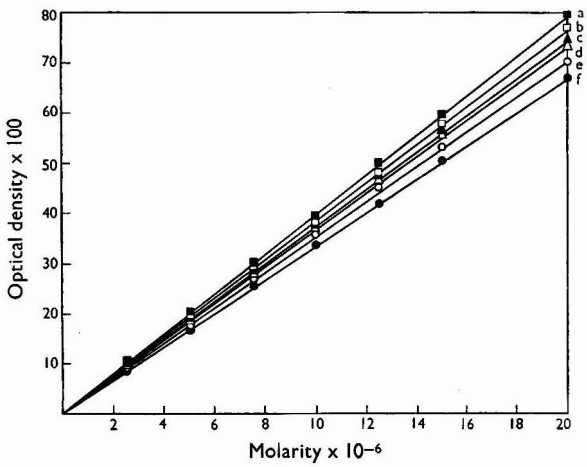

Fig. 1. The optical density of hydroxylamine and some of its derivatives at varying concentrations, as determined by procedure 1: graph ■, hydroxylamine (oxidised at pH 3.5); graph □, *N,N'*-dihydroxyurea; graph ▲, hydroxylamine; graph △, hydroxyurea; graph ○, *N*-hydroxyurethane; graph ●, benzohydroxamic acid. Graphs □ to ●, compounds oxidised at pH 8.0

(reagent 10), mixed, and spun by centrifuge to give a clear supernatant liquid. A 0·5-ml portion of this liquid was treated with 0·3 ml of 0·5 N aqueous sodium hydroxide at 0° C. It was then treated with the following reagents in the order given, and mixed after each addition: 0·5 ml of pH 8·0 phosphate buffer, 0·1 ml of iodine, 0·1 ml of sodium thiosulphate, 2 ml of sulphanilamide and 1·5 ml of *N*-1-naphthylethylenediamine hydrochloride. The optical density was measured, as in procedure 1, against a blank made up similarly from 1 ml of water and 3 ml of the suspension of microsomes or homogenate.

3 (*a*). *Determination in the presence of hydroxylamine: aqueous solutions of hydroxamic acid containing approximately the same or lower molar concentrations of hydroxylamine*—A 0·5 ml portion of the solution (in triplicates) was treated with 0·5 ml of pH 3·5 acetate buffer; the following reagents were added in the order given and mixed after each addition: iodine, sodium thiosulphate, sulphanilamide and *N*-1-naphthylethylenediamine as in procedure 1. The optical density was measured, as in procedure 1, against a reagent blank, and the concentration ($\alpha \times 10^{-6}$ M) of hydroxylamine in the final solution determined by reference to a standard calibration curve (see Fig. 1) obtained in a similar way for varying concentrations of hydroxylamine. Another 0·5-ml portion of the solution (in triplicates) was determined as in procedure 1. The contribution, A, of the hydroxamic acid to this optical density, B, was equal to $B - C$, in which B is the optical density measured at pH 8·0 and C the optical density of $\alpha \times 10^{-6}$ M hydroxylamine as determined by reference to the standard optical density - concentration curve for hydroxylamine at pH 8·0 (see Fig. 1). The concentration of hydroxamic acid was determined by reference of A to the standard optical density - concentration curve for the hydroxamic acid at pH 8·0. This method was inapplicable to the determination of a mixture of dihydroxyurea and hydroxylamine, as the former, when oxidised at pH 3·5, gave about 75 per cent. of the colour given by the same solution oxidised at pH 8·0 (see Fig. 2). For this mixture, procedure 3 (*b*), below, was applied.

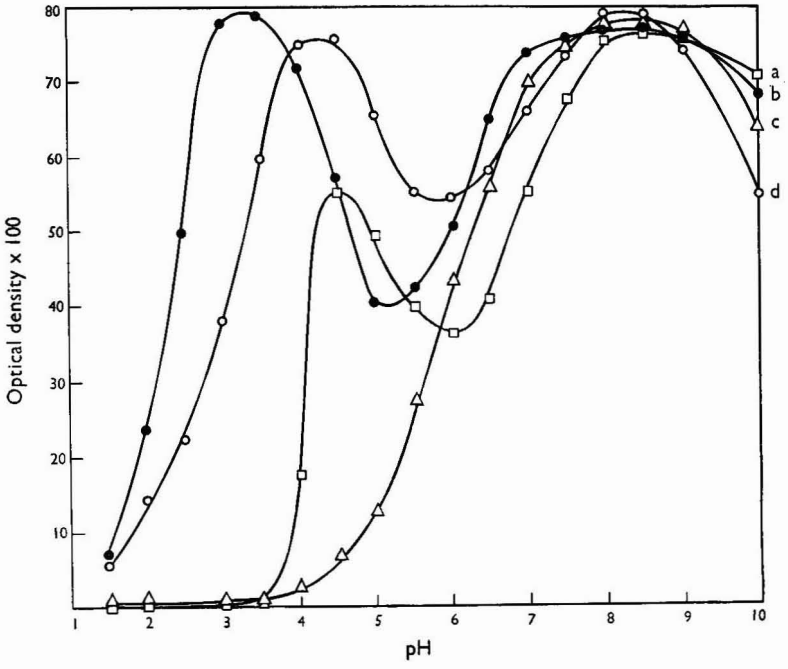

Fig. 2. Effect of the variation of the pH of the oxidation medium on the optical density of the final solution during the determination of hydroxylamine and some of its derivatives by procedure 1: curve □, *N*-hydroxyurethane; curve ●, hydroxylamine; curve △, hydroxyurea; curve ○, *N,N'*-dihydroxyurea

3 (*b*). *Determination in the presence of hydroxylamine: aqueous solutions of hydroxamic acid containing a higher molar concentration of hydroxylamine or a mixture of dihydroxyurea and hydroxylamine*—Because the accuracy of the determinations by procedure 3 (*a*) was found to

decrease as the value of the ratio A/B decreased, the components of the mixture in a measured volume were separated as described in the Section thin-layer chromatography. Samples of the known components were also run alongside the mixture and detected as described, to aid in the location of the components on the developed chromatograms. Each component was scraped off the chromatogram, eluted with water and the concentration determined as in procedure 1.

Results

Effect of pH on the oxidation of hydroxylamine and hydroxamic acids with iodine—

The pH values were maintained during the oxidation stage with the following buffer solutions: potassium chloride - hydrochloric acid for pH 1·5 to pH 2·0; potassium hydrogen phthalate for pH 2·5 to pH 3·0; acetate buffer for pH 3·5 to pH 5·0; phosphate buffer for pH 5·5 to pH 8·0 and borate buffer for pH 8·5 to pH 10·0. The following compounds were oxidised: methyl and ethyl *N*-hydroxycarbamates, hydroxyurea, dihydroxyurea and hydroxylamine. A 0·5-ml sample of a 2×10^{-4} M aqueous solution of the test compound (in triplicates) was treated with 1 ml of a 0·01 N solution of iodine in the appropriate buffer, mixed, treated with 0·1 ml of sodium thiosulphate, 2 ml of sulphanilamide and 1·4 ml of *N*-1-naphthylethylenediamine, and mixed immediately after each addition. This was found to be especially important after the addition of sodium thiosulphate, otherwise cloudy solutions were obtained. The optical density was measured as in procedure 1. The results obtained are plotted in Fig. 2, except those for methyl *N*-hydroxycarbamate which gave a curve identical with that shown for the ethyl homologue; they show that whereas there were only small differences in the oxidation by iodine of hydroxylamine and the hydroxamic acids studied at pH's above 7, significant differences occurred at lower pH values. At pH 3·5, hydroxylamine and dihydroxyurea were oxidised whereas hydroxycarbamates and hydroxyurea were unaffected.

Effect of variation of time of oxidation—

A 0·5-ml sample of a 2×10^{-4} M aqueous solution of hydroxyurea, *N*-hydroxyurethane or benzohydroxamic acid was treated with phosphate buffer and iodine reagents as in procedure 1, mixed, and allowed to stand for varying time intervals before the remainder of procedure 1 was followed. The results (see Fig. 3) indicated that the optical densities of the final solutions remained unchanged when the compounds were oxidised for 1 to 20 minutes.

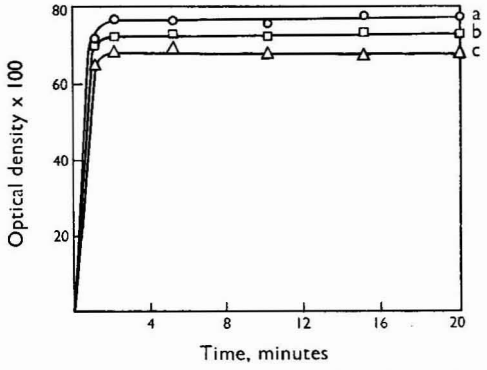

Fig. 3. Effect of the variation of the time of oxidation on the optical density of the final solution during the determination of hydroxyurea (curve ○), *N*-hydroxyurethane (curve □) and benzohydroxamic acid (curve △)

Determination in water or in suspensions of rat-liver microsomes or in rat-liver homogenate—

Hydroxylammonium chloride or the hydroxamic acid was dissolved in 0·5 ml of water and determined as in procedure 1. The results (see Fig. 1) show that Beer's law was obeyed within the concentration range of 10^{-6} M to 2×10^{-5} M in the final solutions. Solutions of hydroxylamine, *N*-hydroxyurethane, hydroxyurea and benzohydroxamic acid in 1 ml of water were treated with 3 ml of an aqueous suspension of rat-liver microsomes, or rat-liver

homogenate, and determined as in procedure 2. The results (molar extinction coefficients are given in Table II) showed small deviations from those obtained in the determination of the same compounds in water. Standard deviations in triplicate determinations varied between $\pm 0{\cdot}02$ and $\pm 0{\cdot}08$.

DETERMINATION IN THE PRESENCE OF HYDROXYLAMINE—

Equal volumes of a 4×10^{-3} M aqueous solution of *N*-hydroxyurethane and a 6×10^{-3} M aqueous solution of hydroxylammonium chloride were mixed, and a 0·1-ml sample applied as a streak along the origin of a glass plate coated with silica gel G; this was then air-dried and developed in solvent (*a*). Areas corresponding to each component were scraped off the chromatograms, eluted with 2 ml of water, and the component in 0·5-ml samples of the eluate determined as in procedure 3 (*b*). A mixture of equal volumes of a 4×10^{-3} M aqueous solution of hydroxyurea and a 6×10^{-3} M aqueous solution of hydroxylammoniom chloride, or of 4×10^{-3} M aqueous solutions of dihydroxyurea and hydroxylammonium chloride, was similarly examined after the chromatograms were developed in solvent system (*b*). Mixtures of equal volumes of a 2×10^{-4} M aqueous solution of *N*-hydroxyurethane and a 2×10^{-4} M aqueous solution of hydroxylammonium chloride, or similar mixtures of hydroxylammonium chloride and hydroxyurea, were determined according to procedure 3 (*a*). The results (see Table I) show that the components of mixtures of each of the three hydroxamic acids with hydroxylammonium chloride were separately determined by the procedures described. Standard deviations in triplicate determinations in these experiments varied between $\pm 0{\cdot}05$ and $\pm 0{\cdot}11$.

TABLE I

DETERMINATION OF HYDROXYLAMINE - HYDROXAMIC ACID MIXTURES IN WATER

Mixture (final concentration)	Optical density × 100 at pH 3·5 Theoretical*	pH 3·5 Found†	pH 8·0 Theoretical‡	pH 8·0 Found†	Percentage recovery: Hydroxylamine	Percentage recovery: Hydroxamic acid
A. *N*-hydroxyurethane (10^{-5} M) *plus*						
(*i*) Hydroxylamine ($1{\cdot}5 \times 10^{-5}$ M)§	60	57	36	35	95	97
(*ii*) Hydroxylamine (10^{-5} M)‖	40	37	74	70	92	57
(*iii*) Hydroxylamine (5×10^{-6} M)‖ ..	20	19	55	55	95	103
B. Hydroxyurea (10^{-5} M) *plus*						
(*i*) Hydroxylamine ($1{\cdot}5 \times 10^{-5}$ M)§ ..	60	61	38	35	101	92
(*ii*) Hydroxylamine (10^{-5} M)‖	40	39	76	75	98	100
(*iii*) Hydroxylamine (5×10^{-6} M)‖ ..	20	21	57	53	105	87
C. *N*,*N*′-dihydroxyurea (10^{-5} M) *plus* hydroxylamine (10^{-5} M)§	40	40	39	34	100	87

* Determined by reference to concentration - optical density curve for hydroxylamine at pH 3·5 (see Fig. 1.

† Mean of three determinations.

‡ A (*i*), B (*i*) and C were determined by reference to the concentration - optical density curve for the hydroxamic acid at pH 8·0; others were determined by summation of the two appropriate values by reference to the concentration - optical density curves for hydroxylamine and the hydroxamic acid at pH 8·0 (see Fig. 1).

§ Determined according to procedure 3 (*b*).

‖ Determined according to procedure 3 (*a*).

INTERFERING SUBSTANCES AND THE GENERAL APPLICABILITY OF PROCEDURES 1 AND 2 TO THE DETERMINATION OF HYDROXAMIC ACIDS—

A 0·5-ml sample (in triplicates) of 2×10^{-4} M aqueous solutions of each of the compounds listed in Table II was determined according to procedure 1 so that the final concentration of each compound was 2×10^{-5} M. Sodium nitrite was determined similarly, except that the reagents iodine and sodium thiosulphate were replaced with 0·2 ml of water. Hydroxylamine, *N*-hydroxyurethane, hydroxyurea and benzohydroxamic acid were also determined according to procedure 2. The results indicate that only those compounds capable of yielding nitrite under the oxidative conditions used, gave a positive reaction.

TABLE II

MOLAR EXTINCTION COEFFICIENTS (ϵ) OF HYDROXYLAMINE AND RELATED COMPOUNDS DETERMINED ACCORDING TO PROCEDURES 1 AND 2

Formula of compound determined	Molar extinction coefficient × 10^{-3} in Water*	Liver microsomes†	Liver homogenate†
NH_2OH	38, 40‡	36	35
$CH_3O.CONHOH$	35	—	—
$C_2H_5O.CONHOH$	36	35	35
$C_3H_7O.CONHOH$	38	—	—
$C_4H_9O.CONHOH$	37	—	—
$H_2N.CONHOH$	38	36	36
$C_6H_5.NH.CONHOH$	34	—	—
$H.CONHOH$	32	—	—
$C_6H_5CONHOH$	34	34	33
$CO(NHOH)_2$	39, 38§	—	—
$(-CONHOH)_2$	35	—	—
$[-C(=NH)NHOH]_2$	55	—	—
$CH_3CO.N(C_6H_5)OH$	0	—	—
$C_6H_{13}NO_6$‖	0	—	—
CH_3NHOH	0	—	—
H_2NOCH_3	0	—	—
C_6H_5NHOH	0	—	—
$C_2H_5OCO.NHOCO_2C_2H_5$	0	—	—
$NaNO_2$	50	—	—

* Determined according to procedure 1 at pH 8·0 unless otherwise indicated.
† Determined according to procedure 2.
‡ Determined according to procedure 1 at pH 3·5.
§ Determined according to procedure 1 at pH 4·5.
‖ Mannose oxime.
– Not determined.

DISCUSSION

Many hydroxamic acids show important biological effects[1 to 7]; they form precipitates or coloured complexes with a variety of inorganic cations, and some are used as analytical reagents.[21,22] The iron, copper, cobalt and nickel chelates are coloured.[22] Hydroxamic acids are formed, *in vivo*, as biological intermediates in the metabolism of some amino-aryls or acetamido-aryls,[23,24] and some have been isolated from microbial fermentations.[25] The oxidation of hydroxamic acids by several oxidising agents in aqueous and non-aqueous media yielded a variety of products, apparently by a free-radical mechanism.[18] Compounds of the type A.CONHOH, where A was aryl, alkyl, aralkyl, amino or alkoxy, have been oxidised by iodine in aqueous bicarbonate solutions to yield condensation products mainly of the type A.CONHO.CO.A.[18] The present work shows that the nitrite was also formed, *i.e.*,

$$2\ \text{A.CO.NHOH} + [\text{O}] \rightarrow \text{A.CO.NHO.CO.A} + \text{ONO}^- + \text{other products}$$

where [O] was the oxidising agent. It is unlikely that hydroxylamine was produced at any stage of the reaction as hydroxamic acids, except *N,N'*-dihydroxyurea, were not oxidised under some acidic conditions (see Fig. 2) under which hydroxylamine was rapidly oxidised. Since 1 mole of hydroxamic acid produced between 68 and 70 per cent. of the colour produced by 1 mole of nitrite under the same conditions (see Table II), the above relationship is qualitative.

Hydroxylamine was rapidly oxidised by iodine in acid and alkali, while the hydroxamic acids were more readily oxidised in alkali. This marked influence of the pH of the reaction medium may be related to the difference in the oxidation potentials of the neutral, cationic and anionic species, *e.g.*, $-CO.NHOH$, $-CO.\overset{+}{N}H_2OH$ and $-CO.NH\overset{-}{O}$, and to the energy requirements for the removal of a hydrogen atom to give free radicals of the type observed by electron spin resonance studies.[26] These pH effects have been utilised to develop a method (procedure 3 (*a*)) for the determination of hydroxamic acids in the presence of small amounts of hydroxylamine.

The procedures described were applicable to the determination of those compounds that gave a nitrite when oxidised by iodine. Substituted hydroxylamines in which the nitrogen

or oxygen atom was attached to a saturated carbon atom, or to an aromatic ring, *e.g.*, the *N*-aryl, *O*-aryl or alkylhydroxylamines, failed to give the reaction (see Table II). *N*-Aryl-hydroxamic acids, on oxidation with lead tetra-acetate, gave the corresponding nitroso-aryls.[27] Procedure 3 (*b*) indicated that a mixture of hydroxamic acids may be determined after separation of the components by the chromatographic procedures described.

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SHORT PAPERS

Plant Mineral Analysis by X-ray Fluorescence Spectrometry

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THE speed and versatility of X-ray fluorescence spectrometry is well established,[1] and many papers have been published describing the application of this technique to the elemental analysis of a wide range of materials.[2] As a result of improvements effected in instrument performance over the last few years, considerable attention has been directed to the analysis of trace quantities of metals in media of low average atomic number. The use of this method in plant analysis is therefore a natural development, as mineral elements in plants are normally present in trace quantities. Several workers[3 to 13] have described the use of the method in the quantitative analysis of plant materials for a limited number of elements.

The purpose of this paper is to report on a recent programme of work in which the analysis of plant materials by X-ray fluorescence spectrometry has been extended beyond that so far reported, for both number and concentration levels of the elements. Mention is also made of the preparation of synthetic standards by using impregnated cellulose as a carrier.

Experimental

Apparatus—

The work was carried out on a standard Philips PW1540 X-ray spectrometer utilising a 1-kilowatt constant-potential generator. The equipment was modified by fitting an ultra-thin window to the gas-flow proportional counter.

One of the limiting factors in the X-ray analysis of longer wavelengths is that counter efficiency is low owing to absorption of a large part of the relatively low-energy radiation by the counter window. This window normally consists of a 6-μ sheet of poly(ethylene terephthalate) coated with a thin layer of aluminium. The purpose of the aluminium is to establish a homogeneous field around the anode of the counter; this, in turn, ensures the degree of energy resolution required for the successful application of pulse height selection. Recent successful attempts to extend the range of X-ray spectrometry into the soft X-ray and vacuum ultraviolet region[14] have resulted in the development of ultra-thin flow counter windows, and in this work two such windows were used, one consisting of a 4-μ poly(ethylene terephthalate) sheet and the other of a 1-μ polypropylene sheet. With neither was a conductive coating used, as the disadvantage of a slight loss (about 15 per cent.) of the counter resolution was far outweighed by the increase in window transmission. The polypropylene window was used only for sodium as its long-term stability had not been established, although this particular window was, in fact, used for several days without showing signs of rupture.

Procedure—

A range of plant materials consisting mainly of grasses was dried and milled to pass through a 0·5-mm sieve. The samples were then made into pellets at a pressure of $5 \pm 0{\cdot}5$ tons per sq. inch with sufficient sample to give a disc about 30 mm in diameter and 5 mm thick. It is important that the thickness of the sample be in excess of the critical depth with respect to the shortest wavelength to be measured, which in this work was zinc K_α, 1·437 Å. On the assumption that the sample pellet density was unity, the critical depth was calculated as 2·9 mm, after allowing for the 35° take-off angle of the spectrometer. Equipment conditions were established to give the largest value of (peak counting rate of analysis wavelength)$^{\frac{1}{2}}$ — (background counting rate)$^{\frac{1}{2}}$, which is the optimum requirement for X-ray spectroscopic procedures.[15] A list of the selected operating conditions is given in Table I.

TABLE I

OPERATING CONDITIONS

Element	X-ray tube	Crystal	Detector
Sodium	Chromium	Gypsum	Flow proportional* *plus* pulse height selection
Magnesium ..	Chromium	Ammonium dihydrogen phosphate	Flow proportional *plus* pulse height selection
Aluminium, phosphorus, potassium ..	Chromium	Penta-erythritol	Flow proportional *plus* pulse height selection
Calcium, titanium	Chromium	Lithium fluoride	Flow proportional
Manganese, iron ..	Gold	Lithium fluoride	Flow proportional
Nickel, copper, zinc	Gold	Lithium fluoride	Scintillation

* Flow proportional counter fitted with 1-μ polypropylene window. All measurements were made under total vacuum conditions.

Intensity measurements were made on a range of elements between sodium and zinc, by a ratio technique. In general, a sufficient number of counts was taken to give a coefficient of variation within 1 per cent. entailing analysis times of between 4 and 200 seconds. Calibration curves were constructed by plotting count rates against element concentration. The slope, m, of such a calibration curve is a useful parameter as it represents the sensitivity for a particular element expressed in terms of counts per second per cent. The lower limit of detection was taken as the concentration giving a count rate equal to three times the standard deviation, σ, of the background count rate.[16] Since total counts, N, equals counting rate, R, multiplied by time, T, and $\sigma = N^{\frac{1}{2}}$; 3σ of $R_b = 3(N_b)^{\frac{1}{2}}/T_b$, where T_b is the analysis time. Hence the lower limit of detection of counts due to the analytical wavelength is $3(R_b/T_b)^{\frac{1}{2}}$, or expressed in terms of concentration lower limit of detection $= 3(R_b/T_b)^{\frac{1}{2}}/m$.

TABLE II

COUNTING RATES AND DETECTION LIMITS†

Element	m, counts per second for 1 per cent. concentration	R_b counts per second	T_b seconds	Detection limit, per cent.
Sodium	16·5	17	200	0·053
Magnesium	36	10	100	0·026
Aluminium	480	3	100	0·0011
Phosphorus	520	6	20	0·0031
Potassium	5400	50	4	0·0020
Calcium	35,000	100	4	0·0004
Titanium	57,000	90	10	0·0002
Manganese	20,000	90	20	0·0002
Iron	43,000	90	20	0·0001
Nickel	138,000	800	10	0·0002
Copper	60,000	900	10	0·0005
Zinc	100,000	900	10	0·0003

† Limit of detection taken as $3(R_b/T_b)^{\frac{1}{2}}/m$, where m equals counts per second for 1 per cent. concentration, R_b the background counting rate and T_b the counting time of the background.

RESULTS AND DISCUSSION

Table II lists the counting rates and the calculated detection limits. In addition to the twelve elements listed, significant responses were obtained from silicon, chlorine and titanium, but lack of analytical results prevented an assessment of detection limits being made. However, fairly accurate predictions can be made by interpolation of the results obtained for elements of similar atomic number, as the correlation between detection limits and atomic number follows a smooth curve with predictable adjustments for variations in the absorption coefficient of the matrix.[17]

The correlation found between measured intensity and concentration of an element was usually linear, as would be predicted for such a low average atomic number matrix. When the concentration of an element reached a relatively high level (*e.g.*, potassium at 1 per cent.), the correlation followed a smooth curve in which the slope decreased with increase of concentration of the

measured element. This self-absorption effect is fairly common in X-ray spectroscopy, and is always found when the mass-absorption coefficient of the measured element for its own radiation is significantly greater than that of the matrix. It was also found necessary to correct the calcium curve for potassium concentration, and this was achieved with a simple linear correction factor. In addition, the slope factor for magnesium showed variations of up to 20 per cent. depending upon the absorption coefficient of the matrix. It is to be hoped that the second of these matrix effects can be compensated for, by use of an incoherently scattered tube line.

PREPARATION OF SYNTHETIC STANDARDS—

Finally, an assessment was made of the feasibility of preparing synthetic standards by adding "doped" cellulose to plant material. Preliminary measurements indicated that (1 + 1) dilution of a typical plant sample with cellulose made no significant difference to the slope factors of elements between calcium (atomic number 20) and zinc (atomic number 30). A range of chromium standards was prepared by mixing equal weights of plant material with cellulose that had been impregnated with known amounts of chromium. Impregnation was carried out by adding known volumes of a standard solution of chromic chloride to weighed samples of cellulose, and drying overnight at 110° C. A calibration graph was constructed covering the range 0 to 0·1 per cent. chromium, and was found to be linear with a slope factor of 21,600 counts per second for 1 per cent. concentration of the element. This figure compares very favourably with the predicted value from neighbouring atomic numbers (*e.g.*, manganese gives 18,000 counts per second for 1 per cent. concentration of the element under identical conditions). The technique can also be applied to elements of lower atomic number than calcium, provided that the sample-to-cellulose ratio is increased. This is necessary as, owing to the shorter path length of these radiations, addition of large amounts of diluent significantly lowers the slope factors. We have found, however, that by increasing the sample-to-cellulose ratio to 10 to 1, the reduction in the slope factor for magnesium is only of the order of 1 per cent.

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The Determination of Total Available Oxygen in Di-tertiary Butyl Peroxide

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THE procedure described by Vaughan and Rust[1] for the analysis of di-t-butyl peroxide, based on the reaction with hydriodic acid in glacial acetic acid solution at 60° C, is not entirely satisfactory, as the calculation of results depends upon the use of an empirical factor. Mair and Graupner[2] have recently published details of a method that involves boiling the sample with a mixture of hydrochloric acid, acetic acid and sodium iodide under reflux. This is somewhat cumbersome in non-routine use and suffers from a relatively high blank.

To achieve complete reaction of di-t-butyl peroxide with iodide it is necessary to maintain a high reaction temperature, a high hydrogen ion concentration and a high iodide concentration. The latter requirement serves not only to increase the rate of reaction but also to maintain the equilibrium of the reaction—

$$I_2 + I^- \rightleftharpoons I_3^-$$

as far to the right as possible, and thus to minimise any possible loss of iodine from the system. The high hydrogen ion concentration is necessary as the reaction is almost certainly catalysed by the presence of acid. A free-radical mechanism is discounted because the thermal decomposition of di-t-butyl peroxide in a solvent is slow even at 110° C.[3] The presence of a mineral acid is necessary to obtain a sufficiently high hydrogen ion concentration. As Mair and Graupner[2] have observed, conditions must also be maintained as anhydrous as possible.

A relatively simple method was devised to satisfy these requirements and also to avoid errors arising from the loss of the volatile sample before iodine liberation could take place. The latter was achieved by weighing the sample into a gelatin capsule before analysis.

Method

Apparatus—

Gelatin capsules—Size No. 3 gelatin capsules, as supplied by Parke, Davis & Co.

Reaction flasks—50-ml calibrated flasks fitted with ground-glass stoppers held in place by springs.

Water-bath—A water-bath thermostatically controlled at 80° ± 1° C.

Reagents—

All reagents should be of recognised analytical-reagent grade.

Acetic acid (glacial), nitrogen saturated—Heat acetic acid (glacial) under reflux for 30 minutes. Cool the acid while bubbling nitrogen through the solution for 15 minutes.

Sodium iodide.

Hydrochloric acid, concentrated, sp.gr. 1·18.

Sodium thiosulphate solution, 0·1 N.

Starch solution, 0·5 per cent. w/v, freshly prepared.

De-mineralised water saturated with nitrogen—Boil de-mineralised water for 10 minutes. Cool the liquid while bubbling nitrogen through the water for 15 minutes.

Procedure—

Flush a reaction flask with nitrogen for 30 seconds. Introduce into the flask 3·0 g of sodium iodide, 20·0 ml of acetic acid and 2·0 ml of hydrochloric acid as rapidly as possible, replacing the stopper between additions. Flush the flask again with nitrogen for 30 seconds and stopper firmly. Weigh about 0·2 g of sample into a gelatin capsule. Fit the self-sealing cap tightly. Place the capsule in the flask and fix the stopper in position with small springs. Place the flask in the water-bath at 80° C for 15 minutes, swirling it frequently. After 15 minutes cool the flask and wash the contents into a 600-ml beaker with about 150 ml of de-mineralised water, saturated with nitrogen. Titrate the solution with 0·1 N sodium thiosulphate solution, adding starch as the indicator when the end-point is approached. Prepare a reagent blank in exactly the same way. (This should not exceed 0·4 ml of the 0·1 N sodium thiosulphate solution. If this value is exceeded it is probable that the sodium iodide used is impure.)

Discussion

The method described above can be used to determine the total available oxygen content. The di-t-butyl peroxide content may be calculated after subtracting the available oxygen content arising from other impurities. These impurities are thought to be mainly hydroperoxide in character, although not necessarily t-butyl hydroperoxide. Their total may be determined by a suitable room-temperature available-oxygen procedure. An iron(III)-catalysed method in which saturated sodium iodide and glacial acetic acid[4] are used has been found to be reliable for this purpose.

Some samples analysed by the method described were also examined by gas - liquid chromatography, and a determination made of the total impurity content. A 1-metre, ¼-inch external diameter, stainless-steel column, packed with 20 per cent. w/w di-isodecyl phthalate on firebrick, was used at 75° C on a Perkin - Elmer Fractometer 451 with a flame-ionisation detector. A Gas

Chromatography Ltd. integrator IE 165 was also used. The total impurity content was determined by using the relationship of the integrated peak areas to that obtained from a known concentration of t-butyl hydroperoxide. This is an empirical approach, but is felt to be justified at the low levels concerned.

Results

The results given in Table I indicate that an essentially 100 per cent. reaction of the di-t-butyl peroxide is occurring under the conditions of the method. The standard deviation of the determination of total available oxygen content was 0·03.

Table I

Analyses of di-t-butyl peroxide samples

Sample number	Total available oxygen, per cent. w/w	Available oxygen content due to hydro-peroxide, per cent. w/w	Di-t-butyl peroxide content, per cent. w/w	Total impurity content, per cent. w/w, determined by gas - liquid chromatography
1	10·79	0·01	98·5	1·3
2	10·81	0·06	98·2	1·2
3	11·01	0·11	99·5	1·6
4	10·89	0·12	98·4	1·3
5	11·09	0·44	97·3	3·0
6	11·11	0·42	97·6	2·6
7	10·91	0·41	96·0	2·4

The author thanks Mr. I. M. Muten for the gas chromatography results, Messrs. N. J. Chalkley and W. H. Redmayne for assistance and guidance and the Laporte Industries Limited, General Chemicals Division for permission to publish this paper.

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Modification of a Simple and Rapid Titrimetric Method for Determining Carbon in Iron and Steel

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Since publishing our paper in the October issue of *The Analyst*, in which we described a method for determining carbon in iron and steel by the non-aqueous titration of the carbon dioxide evolved during the combustion of the sample in oxygen, we have modified the design of the apparatus and certain of the analytical conditions. This has resulted in a considerable improvement with regard to the speed of analysis and the flexibility of the method. Under these new conditions it is possible to determine carbon in the range of 0 to 0·2 per cent. in less than 2 minutes, and up to 0·63 per cent. of carbon can be determined before it is necessary to replenish the absorption solution.

Modification to apparatus—

The distance between the combustion furnace and the absorption cell has been kept as short as possible. The magnesium perchlorate used to remove moisture from the combustion gases has been omitted, thereby making it possible for a smaller prolong to be substituted to contain the manganese dioxide used for removing the sulphur gases. Whenever possible, flexible polythene tubing has been replaced with glass tubing, connections either being made with polythene or PTFE-lined neoprene sleeves. The issuing waste gases are passed through activated carbon to remove any toxic fumes that may be present.

Modification of analysis conditions—

Increasing the temperature and flow-rate, together with an increase in the amount of monoethanolamine and indicator in the absorbent solution, has resulted in a marked improvement in the

TABLE I

COMPARISON OF ANALYSIS TIMES

B.C.S.	Time	Percentage of carbon, Certificate value	Found
264	1 minute 36 seconds	0·037	0·038
237/1	2 minutes 5 seconds	0·105	0·105
270	1 minute 48 seconds	0·22	0·216
270	1 minute 40 seconds	0·22	0·216
295	2 minutes 20 seconds	0·265	0·269
291	3 minutes 15 seconds	0·47	0·47
159/2	3 minutes 5 seconds	0·54	0·54
293	3 minutes 10 seconds	0·63	0·635

speed of analysis. Comparative times are shown in Table I. It can be seen that the analysis time is dependent upon the level of carbon in the sample. This is a consequence of the time taken to empty, and if necessary re-fill, the 10-ml micro burette during the course of the titration. Addition of the extra mono-ethanolamine has improved the absorption capacity of the formdimethylamide solution, and it is now possible to absorb the equivalent of 0·63 per cent. of carbon in a standard 20-ml aliquot of this solution without any danger of losing carbon dioxide.

It is apparent from this work that the dilution effect referred to in our original paper appertained to the mono-ethanolamine constituent and not the formdimethylamide as originally thought. With these modified conditions, we no longer find it necessary to titrate the solution as the carbon dioxide is being evolved, and we have confirmed that quantitative yields can be obtained, even with the oxygen flowing for periods up to 5 minutes after all the carbon dioxide has been evolved. This feature makes the technique more flexible as the operator can, if necessary, perform other functions as the analysis proceeds. It is, however, essential to titrate the carbon dioxide as the combustion gases are evolved to obtain rapid results, such as those quoted in Table I.

MODIFIED ANALYTICAL CONDITIONS

Furnace temperature	=	1300° C
Sample weight	=	1 g
Flux	=	Lead strip (7 cm × ½ cm)
Oxygen flow-rate		Input = 2 litres per minute
		Throughput = 450 ml per minute
Titrant	=	0·02 N tetra-n-butyl ammonium hydroxide
Volume of absorption solution	=	20 ml
Composition of absorption solution	=	Formdimethylamide, mono-ethanolamine and thymolphthalein indicator (150 to 5 to 2)

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A Simple Method of Preserving Thin-layer Chromatograms

BY H. A. FONER

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THIN-LAYER chromatograms may be preserved by fixing them directly on the glass plates. This method is both cumbersome and expensive and, therefore, several methods of removing and preserving the adsorbent films have been described.

Barrollier[1] coated the adsorbent layer with a solution of collodion containing plasticiser, and peeled off the plastic film formed. Unfortunately, however, collodion films are tacky and tend to curl. A more widely used technique is to spray the chromatogram with an aqueous dispersion of poly(vinyl chloride) or poly(vinyl propionate).[2] The plastic impregnated layer is floated off in water, and subsequently strengthened by spraying more plastic on to the reverse side. An aqueous dispersion of poly(vinyl propionate) (Neatan) is available commercially.

The method proposed in this paper makes use of a commercially available aerosol spray.* This material consists of poly(vinyl chloride) polymers and a plasticiser dissolved in organic solvents, with a fluorinated hydrocarbon propellent. The transparent plastic film produced by this spray is tough, pliable and does not yellow with age. The aerosol form of the package makes the spray convenient to use, and the resulting film is both stronger and dries more rapidly than the water-based dispersions. The material is particularly suited for preserving cellulose chromatograms, giving a strong pliable film when sprayed from one side of the thin layer only. The method may be used on 20 × 20-cm plates.

In addition to the usual method of spraying the finished chromatogram, it is sometimes possible to pre-coat the chromatographic plate with poly(vinyl chloride) to give an even stronger film that is more easily removed.

Method

Normal chromatographic plates—

Outline with plastic adhesive tape, or with a pencil, the portion of the chromatogram that it is required to preserve. Spray three separate times with the vinyl spray, allowing the solvent to evaporate between each application. The plastic should be applied each time until the film appears just saturated. It is good practice to turn the plate through 90° before each application and to let the solvent evaporate with the plate in a horizontal position.

Cut through the outline on the plate with a sharp blade and scrape off the unwanted portion of the film. Immerse the chromatogram in cold water to which a wetting agent has been added. After a few minutes peel off the plastic film containing the adsorbent; this process may be facilitated by easing the film off the plate with a flexible blunt blade. If necessary, after drying, spray the reverse side of the film to give it added strength.

Poly(vinyl chloride) coated chromatographic plates—

This modification is suitable if the developing solvents and the chromogenic reagents do not react with the plastic film and if the plate is not heated above 110° to 120° C. A strong, easily removable film is formed. R_F values and development times do not appear to be affected by the presence of the poly(vinyl chloride) film.

Spray a clean glass plate with 3 separate thin layers of poly(vinyl chloride), allowing the plate to dry in a horizontal position between applications. Turn the plate through 90° before each spraying. Coat the plate with adsorbent and carry out the chromatographic analysis as usual. Coat the chromatogram with poly(vinyl chloride) and strip it from its glass plate as described previously.

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* Clear vinyl aerosol spray available from Fisons Scientific Apparatus Ltd., Bishops Meadow Road, Loughborough, England.

The Detection of Cashew-nut Shell Liquid by Thin-layer Chromatography

By T. W. Hammonds

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Comparison of mechanical and hand decortication procedures requires the detection of cashew-nut shell liquid on the surface of cashew kernels as a measure of efficiency. Paper chromatography of kernel extracts using methanol as the mobile phase, and detecting separated components by irradiation with ultraviolet light, is relatively insensitive (S. C. Bevan and S. Thorburn, private communication). Pereira *et al.*[1] have detected cashew-nut shell liquid in ethereal kernel extracts using both diazotised *p*-nitraniline and sulphanilic acid, although at low levels glyceride contamination of the extract results in a significant decrease in sensitivity.

Using a modification of the solvent system described by Bakshi *et al.*,[2] thin-layer chromatography of kernel extracts prepared with an acetone - water mixture (85 + 15), which minimises glyceride contamination, facilitates the detection of sub-microgram amounts of cashew-nut shell liquid present on the surface of the kernels.

Experimental

Shaking 20 g of cashew kernels with 50 ml of the acetone - water mixture (85 + 15) for 5 minutes results in the extraction of cashew-nut shell liquid residues without dissolving a significant amount of fat. Removal of the cashew-nut shell liquid from this aqueous extract was effected by adding a further 10 ml of water and partitioning with petroleum spirit (b.p. 40° to 60° C). The resulting extract was dried with anhydrous sodium sulphate and the solvent removed *in vacuo*.

The residue was dissolved in cyclohexane, and suitable amounts were loaded on to 300-μ chromatoplates of silica gel and developed over a 10-cm solvent path length with an ethyl acetate - toluene (10 + 90) solvent system.

The components were made visible by spraying first with a solution of diazotised *p*-nitraniline, and then with 20 per cent. w/v aqueous sodium carbonate.[3]

By this procedure the separation of the major component, anacardic acid (yellow spot R_F 0·13) and the minor components cardol (yellow spot R_F 0·42) and anacardol (orange spot R_F 0·55), was achieved, leaving polymerised material at the base-line.

Semi-quantitative determination by diluting the cyclohexane solution obtained until the spot due to anacardic acid just disappears is possible. Assuming the anacardic acid concentration in undecarboxylated cashew-nut shell liquid is 90 per cent.,[4] under these conditions approximately 0·07 μg of anacardic acid is just detectable, and may be used as the basis for the calculation of the approximate cashew-nut shell liquid content of a given sample.

Procedure—

(*a*) *Extraction of cashew-nut shell liquid*—Shake 20 g of cashew kernels with 50 ml of an acetone - water mixture (85 + 15) for 5 minutes in a 250-ml extraction flask.

Filter the extract through a Whatman No. 41 filter-paper, into a 250-ml separating funnel, washing the flask with portions of solvent and adding to the filtrate.

Add 10 ml of water and 25 ml of petroleum spirit (b.p. 40° to 60° C) and shake them together. Separate the aqueous phase and repeat the extraction with a further two 10-ml volumes of petroleum spirit (b.p. 40° to 60° C). Add a few sodium chloride crystals if emulsification occurs.

Combine the petroleum extracts and filter through anhydrous sodium sulphate, washing the filter-paper and sodium sulphate with two 10-ml volumes of petroleum.

Combine the extracts in a flask and remove the petroleum *in vacuo* in a 25-ml round-bottomed flask.

(*b*) *Preparation of thin-layer chromatoplates*—Dissolve the residue from (*a*) in 1·0 ml of cyclohexane and load suitable volumes (*e.g.*, 5, 10 and 20 μl) on to a line 1·5 cm from the edge of a 10 × 20-cm chromatoplate, previously coated with a 300-μ layer of Kieselgel G Merck dried for 1 hour at 100° C.

(*c*) *Thin-layer chromatography of the extract*—Develop the chromatoplate over a 10-cm solvent path length with an ethyl acetate - toluene (10 + 90) solvent system. Dry the developed chromatoplate under an infrared lamp for 1 minute.

(*d*) *Location of separated components on the chromatoplates*—Spray first with diazotised *p*-nitraniline reagent (prepared by mixing 25 ml of 0·3 per cent. *p*-nitraniline in hydrochloric acid (80 per cent. w/v) with 1·5 ml of 5 per cent. w/v aqueous sodium nitrite) and then with 20 per cent. w/v aqueous sodium carbonate, and observe the presence or absence of anacardic acid (yellow spot R_F 0·13).

Discussion

With this method, from 2 to 4 p.p.m. of cashew-nut shell liquid have been detected on commercial cashew kernels, and on cashew kernels produced by various experimental processes, 10 to 30 p.p.m. cashew-nut shell liquid were found. Although the surface washing procedure described does not result in total recovery of cashew-nut shell liquid owing to its fat-solubility and a consequent tendency to penetrate into the kernel, the method is a useful guide for the comparative determination of cashew-nut shell liquid on cashew kernels.

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Book Reviews

ELECTROCHEMICAL ANALYSIS: STUDIES OF ACIDS, BASES AND SALTS BY E.M.F., CONDUCTANCE, OPTICAL AND KINETIC METHODS. July 1964 to June 1965. Edited by ROGER G. BATES. Pp. xiv + 100. Washington D.C.: U.S. Government Printing Office. 1965. Price 60 cents.

This is the first of a series of annual summaries or progress reports that the N.B.S. proposes to issue in the form of the Technical Note. It is proposed to issue such summaries for all the Sections of the Analytical Chemistry Division, and the present issue deals with the Electrochemical Analysis Section headed by Dr. Bates. At present the Section is organised into seven groups, each of which contributes to the Report. To quote from the Preface, "It is the purpose of this report not only to review the individual projects of the Section but to convey as well, an impression of the interrelationships of the separate activities as they fuse into a single Section programme. The first goal could be achieved in a most satisfactory way by collecting together the published—or soon to be published—work of the staff as listed at the end of this document. The second aim, however, is more elusive. It can only be met by an integrated summary of the total Section effort, where accomplishment can be viewed against the backdrop of the mission, facilities, and personnel of the organisational unit." The second aim is well and succinctly fulfilled, and such information about a laboratory of such importance and influence is both welcome and valuable.

In addition to the account of facilities, equipment and personnel, there are reviews of the design of automated instrumentation for e.m.f. measurements, measurement of acidity, indicators as reference bases for acid - base studies in inert solvents, solvent effects on acid - base processes of analytical interest, aqueous solutions of mixed salts, behaviour of sodium-responsive glass electrodes, conductometric determination of traces of water, reference materials for dielectric measurements and kinetic methods of analysis.

This document will be of interest to all those engaged in work of a similar nature and to those who make use of the results and end-products of this laboratory.

E. BISHOP

NUCLEAR TECHNIQUES IN ANALYTICAL CHEMISTRY. By ALFRED J. MOSES. Pp. viii + 142. Oxford, London, Edinburgh, New York, Paris and Frankfurt: Pergamon Press. 1964. Price 45s.

The first two chapters (37 pages) of this monograph are essentially introductory and deal with safe handling of radioactivity and with nuclear instrumentation, including radiation sources. Four further chapters (52 pages) cover measurement of natural radioactivity and activation analysis, including activation by positive ions and γ-radiation, as well as neutron activation; this section, probably the most useful part of the book, contains by way of illustration experimental details of some 30 analytical methods, drawn from published work of other authors. The final four brief chapters (21 pages) cover radiation scattering, isotope dilution and tracer techniques, radiometric measurements and exchange reactions, and miscellaneous techniques including radiochemical-dating methods. Appendices, which include thermal neutron and fast-neutron activation data, and an index complete the book.

The declared purpose of this monograph is "to acquaint the analytical chemist with nuclear techniques." It would seem that "acquaint" is the operative word. If an analyst wishes to gain a superficial appreciation of what can be done with nuclear techniques, this book may fulfil his requirements. On the other hand, if he is seeking a practical manual with detailed experimental information to guide his first faltering footsteps into the strange world of radiochemistry, this is not the book for him.

H. J. CLULEY

WAVE MECHANICS FOR CHEMISTS. By C. W. N. CUMPER, M.A., Ph.D., F.R.I.C. Pp. x + 382. London: Heinemann Educational Books Ltd. 1966. Price 50s.

The analytical chemist must, of necessity, be, if not master of all disciplines, at least master of the fundamental principles of all disciplines so far as he possibly can. There can be little of more general fundamental importance than the behaviour of electrons in atoms and molecules. The analytical chemist desirous of possessing himself of the very powerful weapon of understanding afforded by the wave-mechanical approach will find in this book a competent and readable treatment without too much complex mathematics.

E. BISHOP

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Edited by WILLIAM HORWITZ. Tenth Edition. Pp. xx + 957. Washington D.C.: The Association of Official Analytical Chemists. 1965. Price $22.50 in the U.S.A.; $23.00 elsewhere.

This collection of standard methods is well known to analysts connected with food, drugs and agriculture. Others may not be aware that its scope is far wider than the title suggests, because in the U.S.A. the work of the official agricultural chemists covers about the same field as the public analysts and the official agricultural analysts in Great Britain. Hence this volume deals with fertilisers; herbicides; pesticides; mineral constituents of plants; beverages of all kinds; food; animal feeding stuffs; metals, other elements, preservatives and "residues," *i.e.*, of insecticides, in foods; oils, fats and waxes; drugs, including antibiotics and vitamins; cosmetics, and some minor commodities. It ends with 103 pages of numerical tables.

All the A.O.A.C. methods are the product of collaborative trials and modification in members' laboratories. After satisfying a specialised panel, they are published as "official—first action," and only after 5 years of satisfactory use are they raised to the status of "official—final action." Therefore, there will always be enough results for a proper statistical examination. This is often published in the Journal (of the Association) and can include an assessment of the standard deviation of a result, but regrettably the book never gives any indication of accuracy or precision. "Select bibliographies" are often included in the methods, usually to papers in the Journal, and this is far more than most standardising bodies condescend to do, so the required statistic could be found, but why can it not be stated at the end of each method?

No organisation can give equal attention to all fields of work, and the Preface stated that "the fastest growing area of interest is in pesticides, in formulations and in foods, and drugs in feeds." The only "multiple detection method" for pesticides is by paper chromatography. It is stated that "the paper-chromatographic method is technically obsolete, but the preparative portions are sound and form the basis for gas and thin-layer chromatographic methods which have not been studied collaboratively by the A.O.A.C. in time for this edition." These quotations sum up the difficulty of all comprehensive standardising organisations; it is impossible for all the sections to be up to date. The A.O.A.C. methods for trace elements, certain additives to feeding stuffs and fertilisers are more comprehensive, but not better, than the British equivalents, and few British agronomists would agree with the concept and determination of "available" nitrogen in certain fertiliser materials. Many sections reflect the great progress in chemical analysis in recent years; one may cite the uses of ultraviolet and infrared spectrophotometry in pesticide analysis, the great and increasing uses of all kinds of chromatography, thin-layer chromatography for the examination of mixed flavouring additives to foods, gas chromatography for fatty acids and sterols, a radioactive-tracer method for γ hexachlorocyclohexane (γ benzene hexachloride) to mention but a few. On the other hand, many traditional methods have been retained; some, for example the methods for methanol and fusel oils in alcoholic drinks, look almost quaint and should be replaced by gas chromatography. The pyknometer used in this section is more cumbersome and no more accurate than Lipkin's or Hennion's, both well established in the petroleum industry. (Perhaps no citizen of a country in which Syke's hydrometer and "proof spirit" are still legally the last word should comment adversely on *any* other country's methods of dealing with alcoholic liquors.)

But quite apart from examples like this, there are some inexplicable gaps. Perhaps the strangest is that no use at all is made of the polarograph, yet with apparatus of moderate sensitivity and medium cost, the difficulties of determining numerous trace metals, *e.g.*, tin, lead, zinc, thallium, cadmium, would be greatly diminished. The polarograph has also important applications to organic analysis, for example in determining certain chlorinated insecticides. Hardly any use is made of spectrography. There is, in this edition, a brief section on spectrographic methods, but it is too short to be of much use. The same may be said of the chapter on microchemical methods. Ten pages will not teach even the elements of the technique, and a microchemist will learn nothing from them. The chapter on standard solutions is not worthy of the rest of the book. However, when all the adverse comments have been made (and every individualistic analyst can find a few more), it must still be said that this compilation is virtually essential to analysts working in the fields that it covers, and a wonderful testimony to the zeal and hard work of the members of the Association of Official Agricultural Chemists.

H. N. WILSON