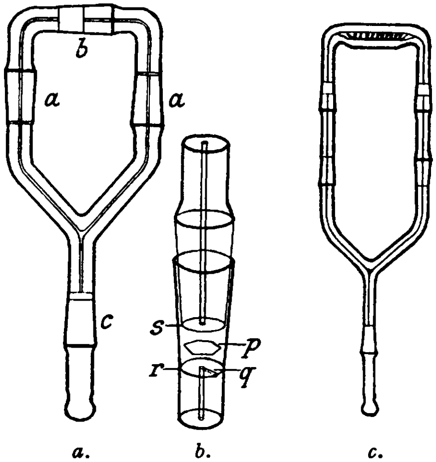
246. *A New Method for the Micro-analysis of Gases.*

By Robert Spence.

A constant-volume micro-gas analysis apparatus is described. The gas is circulated over a small quantity of solid reagent contained in a capillary loop fitted with micro-non-return valves. Absorption can be followed directly by observation of the pressure, and when absorption is complete, the gas is returned to the micro-burette, where its pressure is again determined. The analysis is rapid and accurate.

The accurate analysis of small quantities of gas is of great importance in biology, and the recent development of the study of gas reactions has afforded numerous examples demanding a reliable and convenient method of micro-gas analysis. Existing methods are reviewed by Farkas and Melville (" Experimental Methods in Gas Reactions," London, 1939) and by Hartridge (*J. Sci. Instr.*, 1939, **16**, 317). In the most modern apparatus (Blacet and Leighton, *Ind. Eng. Chem., Anal.*, 1931, **3**, 266, and see Sutton, *J. Sci. Instr.*, 1938, **15**, 133) analysis is carried out at constant pressure, the change in the volume of the gas at different stages in the analysis being measured by means of a graduated capillary tube. When the volume of the sample has been determined, the gas is forced into a small tube over mercury and solid reagents or liquids absorbed on fritted glass are introduced by means of a platinum loop. Under the best conditions 100 cu. mm. of gas can be analysed by this method with an accuracy of 0·1%. There are, however, a number of disadvantages inherent in the constant-pressure method which are to a considerable extent eliminated in the constant-volume method now to be described.

Fig. I.

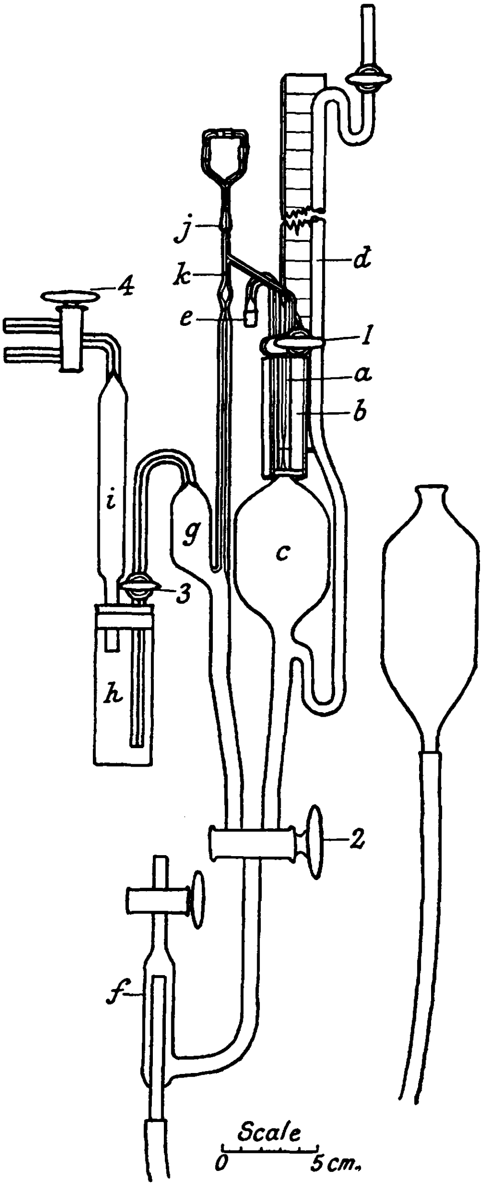


a. b. c.

The new apparatus consists essentially of a loop of capillary tubing round which the gas is caused to circulate, and in doing so it passes over small quantities of absorbent located at suitable points in the tube. The gas can be quickly withdrawn from this loop into a capillary burette, where its pressure is determined whilst a second loop containing different reagents is affixed.

The Reagent Loop.—Each absorbent or system of absorbents is contained in a loop of the type shown in Fig. 1*a*. The non-return valves *a*, *a* cause the gas to circulate round the loop when the mercury column in the side tube (see p. 1302) oscillates up and down. A small quantity of solid reagent is contained in the chamber *b*. The loop is made from Pyrex capillary tubing (about 0·25 mm. bore and 3 mm. diameter). Sockets for the ground joints *a*, *b*, and *c* are made by drawing out quill tubing and cutting the taper at a point where the diameter is slightly larger than that of the capillary. The socket and capillary are then carefully fused together by a very small flame, and the socket cut to a suitable length (about 0·7 cm.). A second piece of capillary is drawn to fit the socket, cut to about the correct length, and ground in with carborundum powder. In the case of reagent chambers, a space of about 3 mm. is left between the end faces of the cone and socket, whereas in the valves this space is reduced to about 0·2 mm. Moreover, before sealing the socket of the valve to the capillary tube, a small groove *q* (Fig. 1*b*) is pressed in the face of the latter when softened in a small flame and the face is then ground flat. A small chip of thin flexible glass, obtained by blowing a very thin bulb and flattening the wall in the flame, is inserted between the two ground faces of socket and cone. This allows free passage of gas in one direction *via* the groove *q* but prevents passage in the opposite direction. Picein wax is used as a sealing material for the valves and joints and when the loop is not in use a stopper is inserted in the end. The total volume of such a loop may be between 10 and 20 cu. mm.

FIG. 2.



The Measuring System, Töpler Pump, and Method of Analysis.—The construction of the remainder of the apparatus is apparent from Fig. 2. It consists essentially of two Töpler pumps, a micro-burette, and a mercury manometer, all supported on a wooden stand. In the particular instrument to be described, the side arms of the stopcock 1 have a bore of about 1·5 mm. The micro-burette *a* consists of about 4 cm. of this capillary immediately below the stopcock. For the sake of accuracy, the diameter is reduced to 0·5 mm. in the neighbourhood of the calibration mark. The temperature of the gas in the micro-burette is controlled by the water jacket *b*, made from the two microscope slides and two pieces of boxwood waxed together, and its pressure can be obtained from the mercury manometer *d* after the zero reading has been deducted.

An advantage of this type of apparatus is that gas may be withdrawn direct from a reaction system at low pressure by means of Töpler pump *c*, and to facilitate attachment to the system, the side arm *e* of stopcock 1 is fitted with a standard ground-joint cone. However, when it is desired to transfer a specimen of gas at atmospheric pressure to the micro-burette, the end of the above-mentioned side arm is immersed in a mercury trough near to the tube containing the specimen. It is then a simple matter to transfer the gas by means of a small pipette of the kind described by Sutton (*loc. cit.*). Before the gas is actually drawn into the micro-burette, it is advisable to remove all traces of adsorbed gas from the bulb *c* by raising and lowering the mercury several times and evacuating through the Töpler pump *g*. Adsorption is one of the main factors to be taken into consideration in micro-gas analysis, but in this case, as the pressure is always reduced to less than 1 mm. before compression into the micro-burette, the possible error from this cause during analysis is small. If the highest accuracy is required, bulb *c* and possibly the loop and stopcock 1 should be made from fused silica free from bloom (cf. Hartley, Henry, and Whytlaw-Gray, *Trans. Faraday Soc.*, 1939, **35**, 1452). The possibility of error from adsorption would then be entirely removed. The pressure lowering produced by allowing the mercury to fall to the bottom of bulb *c* is a routine step in the analysis which should always be carried out before a determination of the pressure of the gas in the micro-burette. This is specially important after collecting the specimen, because in some cases the walls of the bulb may become exposed to the gas at relatively high pressures, whereupon adsorption is considerable.

When the loop containing the required absorbent has been attached at *j* and the mercury level has been adjusted to a point below the Töpler bulb *g*, it is connected to a water pump or vacuum line *via* stopcocks 3 and 4 and the phosphoric oxide tube *i*. Then, by turning stopcock 2, it is possible to evacuate thoroughly by means of Töpler *g*. It is necessary to turn stopcock 3 at each stroke of the pump in order to control the flow of mercury, but as only a few strokes are required, evacuation is easy and rapid. A constriction in the tube below the point *k* prevents an accidental rush of mercury into the loop, where it would interfere with the operation of the valves. It also allows of an easy adjustment of the meniscus to *k*. When this has been done, stopcock 2 is turned, and the pressure in *a* is diminished by lowering the mercury. The micro-burette can now be connected to the loop *via* the two-way stopcock 1, and the gas circulated by raising and lowering the mercury level in the short piece of 1·5 mm. tubing immediately above the stopcock. A conveniently placed mark on this capillary enables the operator to follow the absorption on the manometer without having to return the gas to the micro-burette. When absorption is complete the mercury is lowered to the bottom of bulb *c*, care being taken not to leave any droplets in the capillary and, after about ½ min., stopcock 1 is closed. The mercury is now adjusted to the mark in *a* and the new pressure is determined. This pressure, however, has to be multiplied by the ratio of the total volume of the loop, capillary, and bulb *c* to that of the bulb and micro-burette only, in order to obtain the actual amount of gas absorbed by the reagent. The correction normally amounts to about 0·1%. It is advisable to determine the volume of bulb *c* during the construction of the apparatus. That of the micro-burette is obtained by introducing a little dry air from the Töpler pump side, the normal inlet tube and stopcock bore having previously been filled with mercury. Mercury from a tared crucible is now allowed to enter *via* the inlet tube, and the position of the air bubble adjusted until the meniscus is level with the calibration mark on the micro-burette. The volume is calculated from the loss in weight of the tared crucible of mercury. If, after an absorption, the mercury level is adjusted to the mark on the micro-burette, the pressure of the gas contained in the loop, capillary tubing, and micro-burette can be determined and by comparing this with the pressure exerted by the gas when confined in the micro-burette alone, the volume of the loop and capillary above the stopcock is readily obtained.

The gas having been transferred to the micro-burette, the loop is filled with dry air by first connecting trap *h* to the atmosphere *via* stopcock 4 and allowing most of the mercury to return to the Töpler pump. Before air is actually admitted, however, the mercury level must be adjusted well below *g* so as to prevent any mercury being driven into the loop. The loop may now be removed and closed with a small stopper and a second loop can be attached if required. When absorption is rapid, the whole cycle need not occupy more than 5 minutes.

Determination of Oxygen by Absorption on Copper.—A piece of fine copper wire, made into a spiral by wrapping over a thin piece of steel wire, was inserted in a short length of 1·5 mm. capillary tubing which was provided with ground joints for attachment to the lower half of the loop, as shown in Fig. 1*c*. The wire was first activated by repeated oxidation by oxygen and reduction by a drop of methyl alcohol. The section of tubing containing the wire was then wrapped with a single layer of asbestos paper, and over this, 12 turns of nichrome wire (0·005 inch diameter) at the rate of 6 turns per cm. Finally, the wire was covered with two layers of asbestos paper. The tube was brought to a suitable temperature when connected with a resistance of about 320 ohms in series with the 210-volt A.C. mains. After thorough evacuation of the loop by the Töpler pump, the sample of dry, carbon dioxide-free air was circulated and, with freshly activated copper, absorption was complete in about 4 minutes. Prolonged heating of the copper causes an increase in the absorption time.

Percentage of Oxygen in Dry, Carbon Dioxide-free Air; v = 0·06 *c.c.*

	P, mm.	*T*.	$P_{corr.}$.	Mm. absorbed.	%.
Initial value	762·5	19·1°	762·5	—	—
Final value	603·0	18·7	604·8	157·7	20·68
Initial value	790·0	16·5	790·0	—	—
Final value	626·0	17·2	625·4	164·6	20·84

The values given under $P_{corr.}$ are corrected to the initial temperature and for the volume of the loop.

Determination of Oxygen by Combustion of Yellow Phosphorus.—Although the copper method works extremely well, the process of activation is a complication. In many cases, therefore, the yellow phosphorus method (Blacet and Leighton, *loc. cit.*) is more convenient, if slightly less accurate. As the lower limit of oxygen pressure in the combustion of phosphorus vapour is inversely proportional to the square of the diameter of the vessel, it is advisable to increase the size of the reagent chamber to 5 mm. diameter and 5 mm. in length in order to ensure adequate removal of oxygen. Otherwise the loop is exactly as shown in Fig. 1. If the chip of yellow phosphorus is fused during the evacuation process, absorption is rapid and the whole analysis can be completed in 5 minutes.

Percentage of Oxygen in Dry, Carbon Dioxide-free Air; $v = 0{\cdot}06$ *c.c.*

	P, mm.	*T.*	$P_{corr.}$	Mm. absorbed.	%.
Initial value	726·0	17·8°	726·0	—	—
Final value	575·0	17·3	576·8	149·2	20·55
Initial value	712·0	17·2	712·0	—	—
Final value	565·0	17·1	565·8	146·2	20·53
Initial value	722·0	16·3	722·0	—	—
Final value	573·0	16·3	573·6	148·2	20·53

Unsaturated hydrocarbons and higher paraffins, if present in the gas, also become involved in the oxidation process (cf. Tausz and Görlacher, *Z. anorg. Chem.*, 1930, **190**, 95; Melville, *Trans. Faraday Soc.*, 1932, **28**, 1) and should therefore be previously removed. This can be done by circulating the gas through a loop, part of which is immersed in liquid air.

Oxygen can also be quantitatively removed by passage over reduced copper supported on kieselguhr at 200° (Meyer and Ronge, *Angew. Chem.*, 1939, **52**, 637). It is hoped to describe experiments with this reagent in a later communication.

Determination of Carbon Dioxide.—Carbon dioxide can be determined by means of a loop containing chips of solid potassium hydroxide which have become moistened by a few minutes' exposure to the atmosphere. The loop shown in Fig. 1*a* will allow of a number of determinations in the case of gases containing only a small percentage of carbon dioxide, such as coal gas; for instance, two successive determinations on the same sample of coal gas gave 2·47 and 2·46% of carbon dioxide. When the gas contains a higher proportion of carbon dioxide, it is advisable to use a rather bigger reagent chamber so as to avoid frequent replenishment of the alkali.

Determination of Hydrogen, Carbon Monoxide, Methane, and Ethane.—Hydrogen and carbon monoxide are oxidised over a copper oxide-coated spiral at 270°, a loop of the type shown in Fig. 1*c* being used. It is convenient to charge the reagent chambers with phosphoric oxide so as to observe the absorption of hydrogen directly. This is quite rapid, but the gases should be circulated for at least 15 minutes to ensure complete oxidation of the carbon monoxide (Gooderham, *J. Soc. Chem. Ind.*, 1938, **57**, 388). The carbon monoxide figure is obtained by subsequent absorption of the carbon dioxide. When hydrogen is absent, the reagent chambers of the copper oxide loop can be charged with moistened potassium hydroxide so as to obtain the carbon monoxide value in a single operation.

Methane and ethane may be sparked with excess of oxygen in a loop containing a bulb (0·5 cm. diameter) fitted with two platinum electrodes and two reagent chambers charged with phosphoric oxide. However, it is better to avoid complicating the operations by addition of oxygen by using Arneil's copper oxide–iron oxide catalyst (*J. Soc. Chem. Ind.*, 1934, **53**, 89T). The pure oxides are mixed together in the ratio 99 CuO : 1 Fe_2O_3 by weight and 20% of finely ground kaolin is added. The mixture is made into a paste with water and allowed to dry. Small pieces of the hardened paste are introduced into a loop of the type illustrated in Fig. 1*c*, the upper section of which is made of quartz. The temperature of the catalyst is raised to about 600° by an electric heater, and the oxide mixture is thoroughly evacuated at this temperature. If the reagent chambers are charged with phosphoric oxide in order to absorb the water vapour formed in the combustion, any increase in pressure will be equivalent to the ethane, whilst methane can be determined from the total amount of carbon dioxide produced by subtracting an amount equivalent to twice the ethane. Once the loop has been prepared, the method presents no difficulties, as combustion is complete in a few minutes and the catalyst can easily be reoxidised by circulating air.

If the loop dimensions given in this paper are doubled, the loops will be more robust and easier to fill, and the degree of accuracy will not be greatly impaired. Furthermore, a given charge in the reagent chambers will suffice for an increased number of analyses. It is hoped to give analytical data for synthetic mixtures of known composition at a later date.

The author wishes to thank the Chemical Society for a grant.

The University, Leeds.

[*Received, July 26th*, 1940.]