

Apparatus for the Analysis of Small Samples of Gas.

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THE simple apparatus here described has been evolved, primarily, for the analysis of samples of gas of about 1 c.c. Samples of this magnitude can be analysed with an accuracy of about 1 per cent.

Where larger samples for analysis are available (*i.e.* 15 c.c.), an accuracy of about 0.1 per cent. is obtainable with a minimum of manipulation.

INTRODUCTION.—In the analysis of samples of gas of about 1 c.c., causes of error become important, which would be quite negligible for larger samples. The chief of these are:—

- (1) Rubber connections, which may lead to (*a*) small air-locks at the joints, (*b*) small leaks when the rubber becomes old.
- (2) Physical solution of the constituent gases in each reagent, as distinct from the specific chemical absorption for which the reagent is used.
- (3) The limiting error of reading, which is proportionately greater for smaller samples.

The present apparatus has been designed to reduce such effects to a minimum:

- (1) Rubber connections have been abolished.
- (2) The volume of absorbent reagent has been diminished.
- (3) The sensitiveness of reading has been increased.

APPARATUS AND PROCEDURE.—A diagrammatic sketch of the apparatus is given in Fig. 1.

It consists essentially of two three-way taps, T_1T_2 , connected with the glass bulbs C and B, respectively, and joined together at their "one-way" ends.

The experimental procedure is as follows:

- (1) The gas sample is introduced into the bulb B from A. The way this is done depends on the vessel in which the sample is received. Where possible, it is convenient for this to be fitted with a capillary three-way tap, with the "common" end uppermost. This is joined to A by rubber tubing, and air driven out of the connection with mercury from the apparatus. If, however, as is frequently the case, the sample is contained in an inverted test-tube, it may be transferred to the apparatus by means of a capillary U-tube, one end of which is connected with A by rubber tubing, and the other end, which should be drawn out, inserted under the test-tube in a mercury-jar, after air has been driven out by means of mercury.

(2) The gas sample is transferred to C and measured. This is done by measuring the pressure at which the constant volume of bulb (or bulbs) is filled. The pressure is measured on a mercury manometer, M_1 . By running mercury beyond the tap T_1 , to a marked point F, C is sealed against any leak out of gas or leak in of air during the pressure measurement. It may be convenient, when the highest accuracy is not required, for this point F to be taken on the horizontal part of the tube, instead of on the vertical (water-jacketed) part, as shown in the diagram.

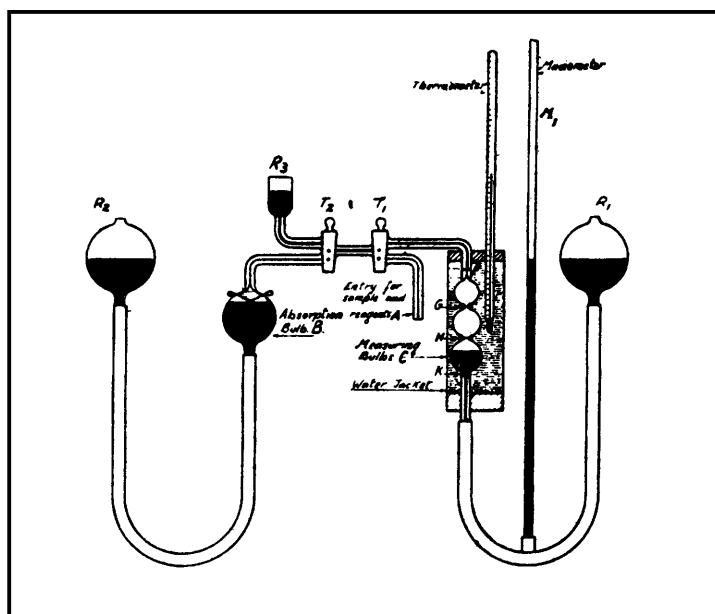


FIG. 1.

(3) A quantity of the appropriate absorbent, equal in volume to about half that of the gas sample, is introduced into B from A.

(4) The gas is transferred to B, where the absorption takes place.

(5) The gas is transferred back to C and again measured. Immediately the gas has passed T_2 the latter is reversed, and the gas followed up by mercury from R_3 to the mark F as before.

The measuring vessel C consists of three bulbs, one, two, or three of which can be used according to the magnitude of the gas sample. In this particular apparatus their volumes are 1, 3 and 6 c.c. respectively. Horizontal marks G, H, K are etched below each bulb. Gas samples, of magnitude ranging from about 0.25 to 15 c.c. (at N.T.P.) can be dealt with. A water jacket fitted with thermometer surrounds the measuring bulbs.

The absorption bulb B is fitted with platinum electrodes and spark gap, or a platinum spiral, or both. The volume of B is about 25 c.c.

The connecting glass tubes are made of capillary tubing of 1 mm. bore.

The manometer is attached to a silver-backed glass scale, 1 metre in length, graduated in mm. This need not be placed inconveniently close to the rest of the apparatus, but may be mounted on a neighbouring wall or other suitable place.

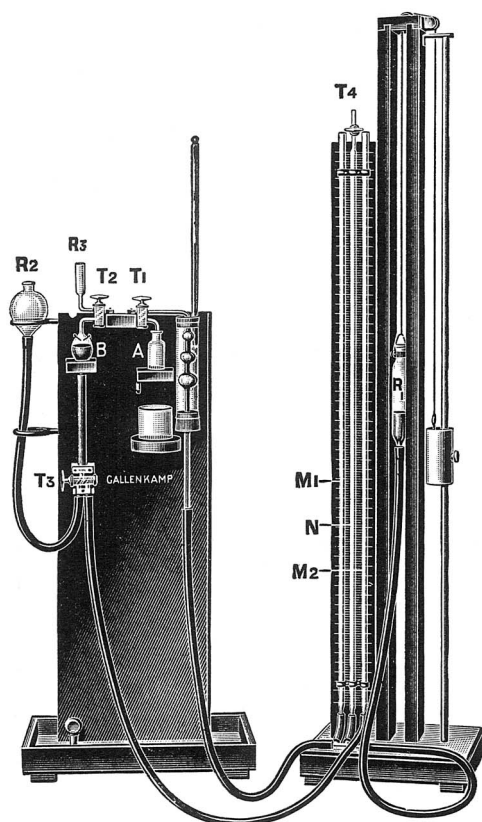


FIG. 2.

The central glass part of the apparatus, with its wooden stand, may then be gently shaken in order to agitate the absorbent solution. Very slight movement gives adequate agitation of the liquid. Reading is very easy and parallax is avoided.

There are none of the difficulties of levelling that are found with the constant-pressure types of apparatus. Manipulation is simple and rapid. A gas of 6 constituents (say CO_2 , O_2 , CO , CH_4 , H_2 , N_2) can be analysed within half an hour.

The size of that part of the apparatus in which the gases are manipulated is quite small, *i.e.* $9'' \times 9'' \times 1''$. It is simple and strong. The amounts of mercury and of reagents are small. The complete apparatus is shown in Fig. 2.

REDUCTION OF ANALYSES.—Let K be the reading on the manometer when the measuring bulbs are filled at atmospheric pressure. This is determined once and for all by connecting them with the atmosphere, through T_1 and T_2 , with R_3 empty, and bringing the mercury to the appropriate mark. (If at any time it is feared that the level of the bulbs relative to the scale can have changed, this can be checked by the same procedure). K is not necessarily level with the mark on the bulb, as the bore of the tube at the mark may not be the same as that of the manometer. By determining K as above, however, capillarity effects are eliminated, provided the bore of the manometer tube is uniform.

Let A be the reading on the manometer at the beginning of the analysis,

Then P , the pressure in the bulbs,

$$= B + A - K, \text{ where } B \text{ is the barometric pressure.}$$

The bulbs are washed out with water between analyses; hence the gas is always saturated with water vapour. The partial pressure of the gas under analysis is then:—

$$B + A - K - W,$$

where W is the vapour pressure of water at the temperature indicated by the thermometer in the water-jacket.

If V be the volume of the bulbs, then the volume of a sample at N.P. is:—

$$V \times \frac{B + A - K - W}{76}$$

If the manometer reading after absorption of, say, CO_2 be A' , the volume of gas at N.P. now is:—

$$V \times \frac{B + A' - K - W}{76}$$

The volume of CO_2 absorbed is, then:—

$$\frac{V(A - A')}{76}$$

The percentage of CO_2 is:—

$$\frac{A - A'}{B + A - K - W} \times 100.$$

The quantity $(B + A - K - W)$, representing the original pressure of the gas sample, is determined once for each analysis. The percentage of each constituent is directly proportional to a difference of readings on the manometer.

BAROMETER ATTACHMENT.—Analysis requires a knowledge of the barometric pressure. A barometer may be incorporated in the apparatus as follows (see Fig. 2). By the side of the manometer, M_1 , is placed a second tube, N , of the same bore, and connected at its lower end with M_1 and R_1 . The upper end is fitted with a capillary tap, T_4 . If R_1 is raised so as to drive mercury past T_4 , the latter closed, and then R_1 lowered to some position lower than T_4 by more than the barometric height, the space below T_4 will be a Torricellian vacuum, and the barometric pressure will be equal to the difference in the heights of mercury in this tube and in M_1 . A barometer reading can be so taken at any time during an analysis. If a drying tube is attached to T_4 , and the latter occasionally left open, the space above the mercury is kept free of water vapour. Normally, the reservoir

is sufficiently high for the barometer tube to be completely filled with mercury. If a leak past T_4 is suspected, R_1 can be raised at any time, and the mercury taken past the tap immediately before reading.

USE OF PRESSURE GAUGE.—It may sometimes be convenient and more speedy, when high accuracy is not required, to read the pressure of the gas on a dial instead of on a mercury manometer. For a portable apparatus this would present considerable advantages.

An atmospheric gauge, has been used in conjunction with the mercury manometer. The gauge was used filled with alcohol, and the level of the mercury and alcohol interface kept constant within very small limits by making its area large, *i.e.* about 50 sq. cm. This was done by causing it to occur in the middle of a large bulb.*

An analysis was carried out, in which readings were taken both on the manometer and on the pressure gauge, and the results from the two sets of readings calculated independently. The figures agreed within 1 per cent. For many purposes, sufficient accuracy could be obtained with the gauge alone.

AUXILIARY MANOMETER.—It is sometimes desirable, particularly in the case of absorptions that take several minutes for completion, to be able to observe the progress of the reaction without having to transfer the gas to and from the measuring bulbs.

For this purpose, an auxiliary manometer M_2 is connected with the absorption bulb B through a three-way tap, T_3 , which, in its normal position, connects B with the reservoir R_2 . If, after gas has been introduced into B, this tap is reversed, it connects B with M_2 and cuts off R_2 . The progress of absorption of gas in the (approximately) constant volume above the absorbing solution in B can then be followed on the manometer M_2 .

PRECAUTIONS IN USE.—As with all types of apparatus, reagents must not be allowed to enter the measuring-bulbs, as their presence in any appreciable quantity may lower the aqueous vapour-pressure in the bulbs.

The portion of capillary tubing between the taps T_1 and T_2 becomes wetted with reagents; it is possible to wash this out between absorptions, by running water from R_3 to A. This is found, however, to be in general unnecessary, since any gas which might thus come in contact with the reagent has already been in contact with the same reagent.

After exploding for hydrogen and methane (and also before a fresh analysis), the absorption bulb should be washed free of alkali. This is conveniently done by washing out once with weak sulphuric acid and then with water, introduced at "A" in the same way as the absorbent reagents, the gas being retained meanwhile in the measuring bulbs. It is advisable at the same time to wash out the measuring bulbs with water, in case any minute traces of alkali had entered them. The washing may be done without loss of gas or admission of air, by drawing a small quantity of water into bulb B, and transferring it to the measuring bulbs in the presence of the gas sample. (If acid has not been washed out of B, some will be carried into the measuring bulbs and may react with traces of carbonates, producing carbon dioxide, affecting the methane figure.) This procedure eliminates

* This would be unnecessary with an all-steel gauge, which could be filled with mercury.

the necessity of a separate washing of the gas with water after absorption of carbon monoxide with ammoniacal cuprous chloride.

For suggestions and useful discussions, I am indebted to Mr. T. Carlton Sutton, M.Sc., with whose approval the apparatus has been developed.

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DISCUSSION.

The PRESIDENT remarked that Mr. Ambler had now taken from the gas analyst the possibility of saying that the sample was too small for analysis. He wished to express his very great appreciation of this paper, particularly of the trouble Mr. Ambler had taken in bringing the apparatus itself to the meeting.

Mr. T. C. SUTTON said that he had been closely concerned with the development of this instrument; such constructive ideas as he had been able to put forward had already been incorporated in it, and he would not detail them here; he had specially welcomed it, since the results of even rapid analyses made with it were accurate, and he could no longer be told that there was "insufficient sample." An analysis to one part in 500 could be made very quickly, and he thought that this, coupled with the fact that this was a simple apparatus which could be kept clean easily, was an important advance in gas analysis. He would like to point out that here was an instrument which, while being as good as any other for the analysis of large samples of gas, could be used without alteration as a sensitive and accurate instrument for micro-analysis. If required, the instrument could be made portable, and so could be taken to mine-heads, etc., when it was necessary to analyse gases on the spot.

Mr. G. N. HUNTLEY said that about 25 years ago he had devised an apparatus which had some resemblance to this one, and it had been described by Travers.

Mr. AMBLER, replying to Mr. Huntley, said that an instrument such as this embodied a number of separate principles; originality was not claimed for each separate part. The present form of the apparatus was the result of extensive adaptations and alterations that had been found useful in his daily work.