153. *An Accurate Method for the Determination of Carbon Dioxide in Gas Samples.*

By R. R. Baldwin.

A method has been developed for the accurate determination of the amount of carbon dioxide in gas samples. The procedure is to draw the gas from a sample bulb through a trap cooled in liquid air, at a slow rate controlled by a capillary restriction connected to a vacuum pump. When the sample has been completely removed, the trap containing the condensed carbon dioxide is transferred to another apparatus, where the carbon dioxide is vaporised and measured. The method is rapid and permits analyses to be carried out at the rate of one every 20 minutes. The accuracy attainable approaches 0·001% of the total gas at low carbon dioxide concentrations, and about 0·25% of the carbon dioxide at higher concentrations. The method is easy and convenient, and does not require the full attention of the operator. Errors in manipulation are easily detected and can be rectified without repetition of the analysis.

A frequent problem in the study of combustion processes is the determination of the carbon dioxide content of a gas stream. This may involve either a direct determination of the carbon dioxide formed from the combustion of the fuel, or a determination of unburnt products such as carbon monoxide, hydrocarbons, etc., by removing the carbon dioxide with an absorbent such as "Carbosorb" and oxidising these unburnt products to carbon dioxide by passage through a copper oxide furnace at 1000° before sampling. The range of carbon dioxide concentrations in such cases may be from 6% to 0·01% or lower. An earlier paper (Bamford and Baldwin, *J.*, 1942, 26) has discussed the limitations of the conventional absorption methods when applied to the determination of small quantities, and has outlined a vacuum analysis method, based on the separation and direct measurement of the constituents by fractional condensation and oxidation methods. For example, carbon dioxide is determined by circulating the gas through a trap cooled in liquid air in which this gas condenses; after removal of the uncondensed gases, the carbon dioxide is vaporised and measured.

Although that method is reliable and accurate enough to permit the detection of carbon dioxide concentrations as low as 0·003—0·005%, it has two disadvantages: first, the length of time required for analyses, which for a single carbon dioxide determination is at least one hour; secondly, the strain on the operator who is continually engaged in such operations as circulating the gas using a Töpler pump, removing the uncondensed gases with the Töpler pump, etc. The method now described is simple and reliable, and permits the analysis of samples at the rate of one every 20 minutes. The accuracy of the method is as stated above. Moreover, the method requires relatively little attention on the part of the operator. A further advantage is that any air leaks are easily detected and can usually be corrected without repetition of the analysis.

Experimental.

The principle of the method is essentially similar to the vacuum method already described, that is, the separation of the carbon dioxide by condensation in liquid air. Instead of taking a small sample of the gas from the sample bulb, measuring it by the pressure exerted in a known volume, and then circulating it several times with the aid of mercury reservoirs through a trap cooled in liquid air, the present method involves drawing at a controlled rate the whole gas sample, by means of a vacuum pump, from the bulb through a trap cooled in liquid air. When the bulb has been completely evacuated, the carbon dioxide which has been condensed is vaporised and measured very much as in the original vacuum method. The proportion by volume of carbon dioxide in the dry gas is then given by

$$CO_2 = 100\ pvT/Vt(P - w)\%$$

where p is the pressure of the carbon dioxide, measured in the volume v, P the pressure of gas in the sample bulb, V the volume of the sample bulb, T the absolute temperature of the gas when sampled, t the absolute temperature of the dioxide when measured, and w the saturated vapour pressure of water at $T°$ (it is reasonable to assume saturation in the case of gases sampled from a combustion process).

The apparatus used for the evacuation of the bulb is shown in Fig. 1, and the experimental procedure is as follows.

(i) The apparatus is assembled, and the bulb B connected to the apparatus by the ground-glass joint. The whole apparatus is then evacuated.

(ii) Liquid-air traps are placed on V_1 and V_2 (if it is used), and T_4 is closed; T_2 is opened so that the gas in the bulb expands into the trap V_1, and is allowed to remain for 2 minutes. This ensures that any carbon dioxide which does not condense during the initial rush of gas into the trap has an opportunity of diffusing back into the cold region.

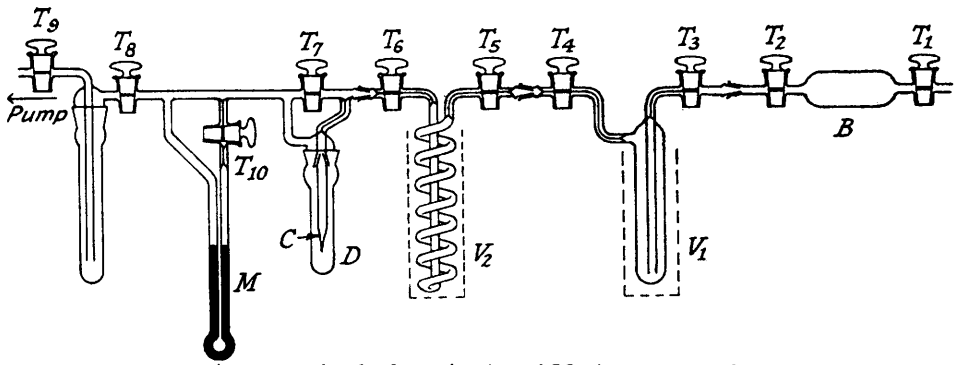
(iii) If trap V_2 is now used, tap T_6 is now closed and T_4, T_5 opened, whereupon the gas expands into V_2. A further period of 2 minutes is allowed for the same reason as given in (ii).

(iv) Tap T_7 is now closed and T_8 is opened so that the gas is drawn out by the vacuum pump through

the controlling capillary *C*. If trap V_2 is not used, then stage (iii) is omitted, and after T_7 has been closed, T_4 is opened. The pumping is continued for a period which depends on the pumping speed of the capillary, and in the final form of the apparatus is about 10 minutes.

(v) Owing to the fact that the pumping speed falls off as the pressure in the bulb is reduced, there is a limit to the useful time during which pumping can be controlled by the capillary. After this period,

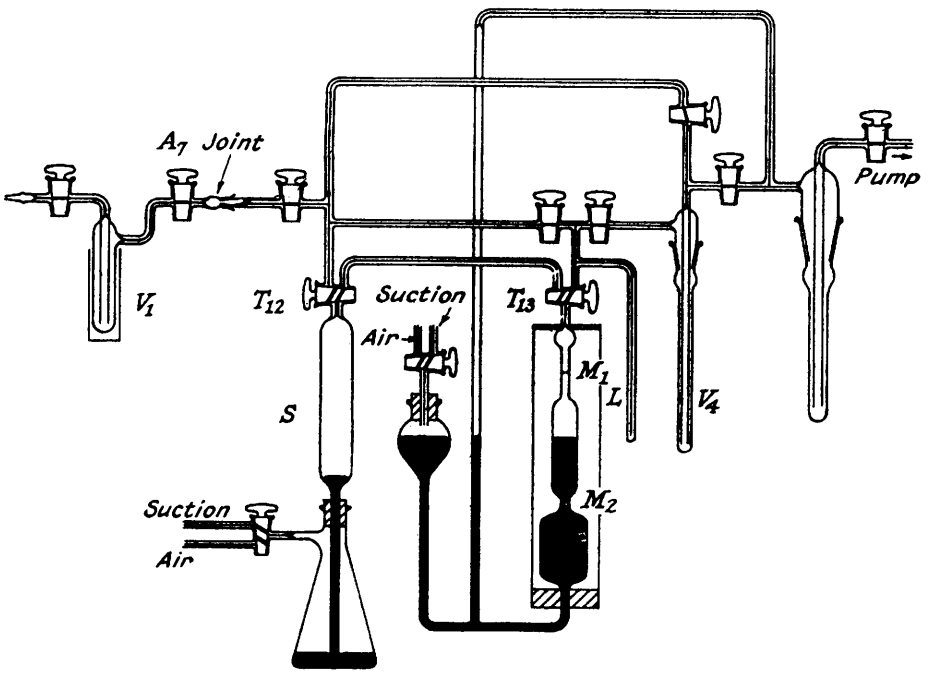
FIG. 1.



Apparatus for the determination of CO_2 *in a gas sample.*

normally 10 minutes, T_8 is closed and T_7 opened. The pressure recorded by the manometer *M* will normally be about 40 mm. of mercury or less, and in this case the pressure in the apparatus is gradually reduced to zero by opening the tap T_8 slightly. This operation should take about 2 minutes, care being taken to avoid too rapid evacuation of the residual gas. If the pressure should be above about 40 mm., pumping controlled by the capillary is continued until this pressure is reached. Once the experimental

FIG. 2.



Apparatus for measurement of CO_2.

procedure has been fixed, the value of this pressure on opening T_7 forms a useful check that no leak has occurred during the evacuation.

(vi) When the pressure has been reduced nearly to zero, tap T_8 is fully opened, and the apparatus evacuated for 1—2 minutes. All taps T_1—T_8 are then closed, and the bulb and traps dismantled.

Measurement of carbon dioxide. (vii) The trap V_1, immersed in liquid air, is then transferred to the measuring apparatus shown in Fig. 2, connected by the ground-glass joint, and the whole apparatus

evacuated for about 5 minutes. It is essential that a good vacuum be obtained, otherwise the distillation of the carbon dioxide from the trap V_1 to the limb L becomes slow, if not impossible. If necessary, the vacuum can be checked by using the Töpler arm S as a crude McLeod gauge. Alternatively, the measuring vessel itself can be used by lowering the mercury to the mark M_2 with the tap T_{13} open, then closing T_{13} and reading the manometer when the mercury is brought to the level M_1. As the ratio of the volumes defined by M_2 and M_1 is about 15 : 1, a pressure of about 0·01 mm. can be detected in this way.

(viii) When the vacuum is satisfactory, liquid air is placed round the limb L, and the carbon dioxide condensed in the trap V_1, vaporised by replacing the liquid-air trap with a carbon dioxide–acetone bath at −80°. About 5 minutes are necessary for the distillation of the carbon dioxide, and if towards the end of the period the pressure in the apparatus is undetectable (less than 0·01 mm.), distillation may be considered complete.

In some cases, it proves impossible to obtain a satisfactory distillation, and on testing the vacuum an appreciable pressure is observed. This is almost always due to the presence of air, and the only remedy is to circulate this residual gas through the trap V_4 cooled in liquid air, as in the earlier vacuum method. After circulating about three times, any uncondensed gas is then pumped away through V_4 with the vacuum pump. The carbon dioxide condensed in V_4 is distilled to the limb L in the usual way. It is clear that, owing to the very low concentration of carbon dioxide in air (0·03%), any additional amount introduced by this procedure is negligible unless the leak is very serious.

(ix) When the distillation is complete, the carbon dioxide–acetone bath at −80° is placed on the limb L, and the pressure of the vaporised dioxide measured. If the amount of carbon dioxide is small, the small volume defined by the mark M_1 is used. If the pressure developed in this volume exceeds 300 mm., it is advisable either to measure the carbon dioxide in stages, storing the excess in the Töpler arm S, or to use the much larger volume defined by the mark M_2. The volume defined by M_1 may be made about 6 c.c., in which case, with a bulb volume of 100—150 c.c., 0·3 mm. on the mercury manometer corresponds to 0·002%. A small correction, easily determined by separate experiments, must be applied to the carbon dioxide pressure to allow for the temperature of the cold limb L being −80°, and not room temperature.

Summarising the experimental procedure, it will be seen that about 20 minutes are required for the evacuation of the bulb, and another 20 minutes for the measurement of the carbon dioxide condensed in the trap. Although an individual determination requires 40 minutes, therefore, it is possible, by having two traps, to average one determination every 20 minutes.

Results.—Tests were first carried out to ascertain whether the method was capable of removing small traces of carbon dioxide from a gas sample quite efficiently. It was thought that under these conditions it might be necessary for the gas to remain in contact with the liquid-air trap for a long time to ensure that it cooled to the temperature at which the partial pressure of carbon dioxide was sufficiently small to guarantee efficient condensation. This would necessitate the pumping speed being too low for the method to be of any practical value. Accordingly, tests were first carried out with air, which affords a convenient and very reproducible source of a gas containing a small amount of carbon dioxide. Tests were carried out at various pumping speeds, obtained by varying the capillary C, and two alternative types of trap were tried. One, referred to as (*a*) in Table I and shown in Fig. 3, was the normal type of trap used in vacuum work, while the second (*b*) was a spiral made from 4-mm. inside-diameter tubing. The results are shown in Table I; the pumping speed figures refer to the average rate at which pressure fell initially.

TABLE I.

Capillary pumping speed, mm./sec.	Time for evacuation, mins.	Trap.	CO_2, %.	Accuracy.
1·1	60	(*a*)	0·036	±0·001
		(*b*)	0·035	
4	15	(*a*)	0·036	±0·001
		(*b*)	0·035	
15	6	(*a*)	0·037	±0·001
		(*b*)	0·033	
35	3	(*a*)	0·036	±0·001
		(*b*)	0·030	
[Vacuum analysis apparatus (*loc. cit.*)]	—	—	0·036 0·034	±0·003

It will be seen that with trap (*a*) the results are self consistent and agree with the vacuum method within the experimental error, even at the very highest pumping speed. It is clear that the spiral (*b*) is less efficient at high speeds, owing probably to the fact that, on account of its smaller volume, the gas spends much less time in it.

Having confirmed that small traces of carbon dioxide could be removed efficiently, tests were next made to see if larger percentages could be completely condensed. Owing to the difficulty of making up samples containing 3—4% of carbon dioxide, reproducible to 0·002%, it was considered advisable to test these samples by determining the amount of the dioxide escaping the trap, using another trap placed in series with the main trap. The results of these tests are summarised in Table II, and the following points emerge:

(i) Tests 2—7, using the spiral trap (*b*) to measure the amount of dioxide escaping the first trap, show that satisfactory results are obtained up to about 5 mm./sec. pumping speed.

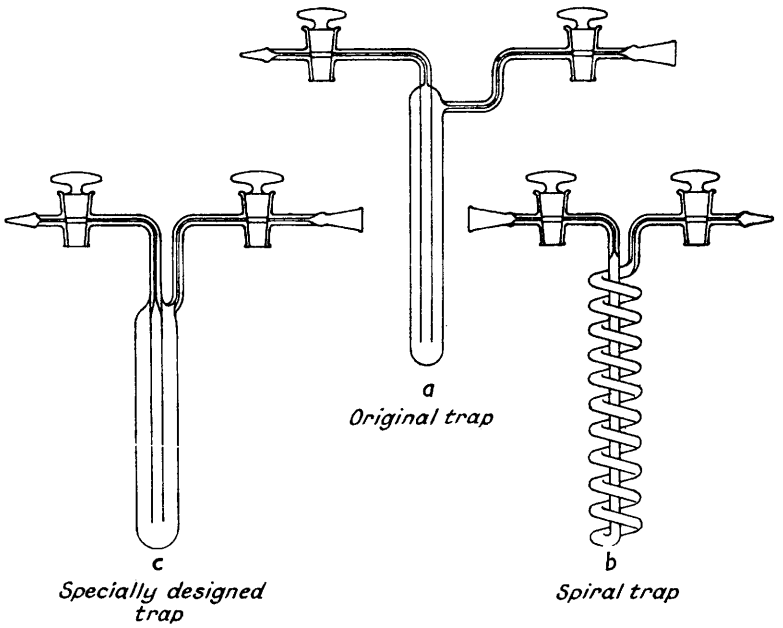
(ii) Test 1 shows that the use of two traps of type (*a*) in series gives excessively high losses, even though the pumping speed is very low. This is attributed to the large volume of this type of trap resulting in a sudden rush of gas through the trap V_1 when taps T_4 and T_5 are opened. It is possible that this sudden rush also occurs, but to a smaller extent, when the spiral is used as the second trap, and that

the small loss of carbon dioxide shown at the lower pumping speeds (up to 6 mm./sec.) may arise through this cause. In this case the actual losses when the method is used in the normal way without a second trap may be smaller than those given in the table.

TABLE II.

Test No.	Capillary pumping speed, mm./sec.	First trap.	Second trap.	CO_2 content of second trap, %.
1	1·0	(*a*)	(*a*)	0·046
2	1·0	(*a*)	(*b*)	0·004
3	3·5	(*a*)	(*b*)	0·004
4	5·0	(*a*)	(*b*)	0·003
5	6·0	(*a*)	(*b*)	0·009
6	12·0	(*a*)	(*b*)	0·022
7	30·0	(*a*)	(*b*)	0·064
8	3·5	(*c*)	(*b*)	0·015
9	3·5	(*c*)	(*b*)	0·022

FIG. 3.



(iii) The only alternative possibility for the loss of carbon dioxide shown even at the lowest flow rates seems to be that, as the whole of the trap (*a*) cannot be immersed in the liquid air, some dioxide escapes condensation during stage (ii) of the experimental procedure. To test this, the specially designed trap (*c*), which could be completely immersed in the liquid air, was used in tests 8 and 9. This gave unusually high losses, and the only explanation for this appears to be that, whilst with the normal type of trap the carbon dioxide condenses on the wall, with type (*c*) the rapid chilling produces a mist of carbon dioxide particles, some of which are carried away too quickly by the gas flow.

When using a single trap of type (*a*) with a pumping speed of about 5 mm./sec., it is clear that the loss of carbon dioxide is almost negligible, and this speed has been adopted in using the apparatus for routine work.

Preliminary tests suggest that the method can also be adapted to enable carbon monoxide to be estimated by drawing the carbon dioxide-free gas through a copper oxide furnace at about 400°, and then condensing the carbon dioxide formed in a liquid-air trap. These tests, however, are not yet complete.

I wish to express my thanks to the " Shell " Refining and Marketing Company Limited for permission to publish this paper.

UNIVERSITY COLLEGE, HULL. [*Received, August 6th,* 1948.]