6. *A Method for the Accurate Analysis of Gaseous Mixtures.*

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A method of gas analysis is described which is free from the main sources of error inherent in standard methods, and gives results reliable to 0·03% or better. The method depends on pressure measurements after separation of constituents by cooling or chemical oxidation changes, no confining liquid or absorbents being used. The apparatus has considerable flexibility, being suitable for the precise analysis of many kinds of gaseous mixtures.

SEVERAL inherent sources of error render ordinary methods of gas analysis unsuitable for adaptation to precision measurements on mixtures containing a number of constituents. The use of liquid absorbents is necessarily accompanied by uncertainty, it is practically impossible to apply complete corrections for the physical solubility of the various gases in the reagents, and components estimated towards the end of the analysis may be in considerable error through losses incurred during repeated contacts with liquids. These difficulties cannot be entirely overcome by the use of solid absorbents. Further troubles are encountered when moist mercury menisci have to be used, on account of the difficulty of keeping the volume of liquid and also the shape of the meniscus the same. In addition, the principle of measurement by contraction is in itself unsatisfactory, especially if only small percentages of the gas are present. All these difficulties are, of course, enhanced if only a small quantity of the initial gas is available.

The authors' experience has been that analyses reproducible to 0·1—0·2% for the main constituents of the mixture can be obtained with a standard Bone and Wheeler apparatus, but the absolute accuracy is generally much less than this. The presence or absence of constituents in concentrations of 0·1—0·2% is always in some doubt. The present apparatus was designed particularly for the analysis of mixtures containing about 80% of inert gas, the errors for the individual constituents being less than 0·03%. The method may, however, be applied equally successfully to other mixtures.

EXPERIMENTAL.

Apparatus and Method.—The method of analysis consists in the successive quantitative conversion of the components into carbon dioxide and/or water, which are measured separately. Dependence on contraction measurements is thus avoided, although the latter may be used as checks if desired. The measurement of carbon dioxide and water is effected by determining the pressure they exert in one of two standard volumes, which in the present apparatus have a ratio of about 7 : 1. This enables either large or small amounts of gas to be measured accurately.

The apparatus is shown in the diagram. The two measuring bulbs B_1 and B_2 are immersed in a thermostat and may be put into communication with a thermostated Bourdon gauge B of the Foord type (*J. Sci. Instr.*, 1934, **11**, 126) or a Toepler pump T. The Bourdon gauge can be read to within 0·05 mm. of mercury. The volumes of the bulbs used depend on the amount of gas available. In the present apparatus they are about 80 c.c. and 10 c.c. respectively, but there is no reason why they should not be considerably reduced. The Toepler pump serves to evacuate the gas from the bulbs and enables it to be passed either round the circuit DL_1PL_2, comprising two liquid-air traps and a tube containing a platinum spiral P, or round the alternative circuit DL_1QL_2 which includes a quartz tube Q containing copper oxide. Both the platinum spiral and the quartz tube may be heated electrically. To reduce the dead space, capillary tubing of 1 mm. internal diameter is used wherever possible. The jacket J of the Bourdon gauge is connected to a wide mercury manometer G, which serves to measure the initial pressure of the gas. The accurate adjustment of the pressure
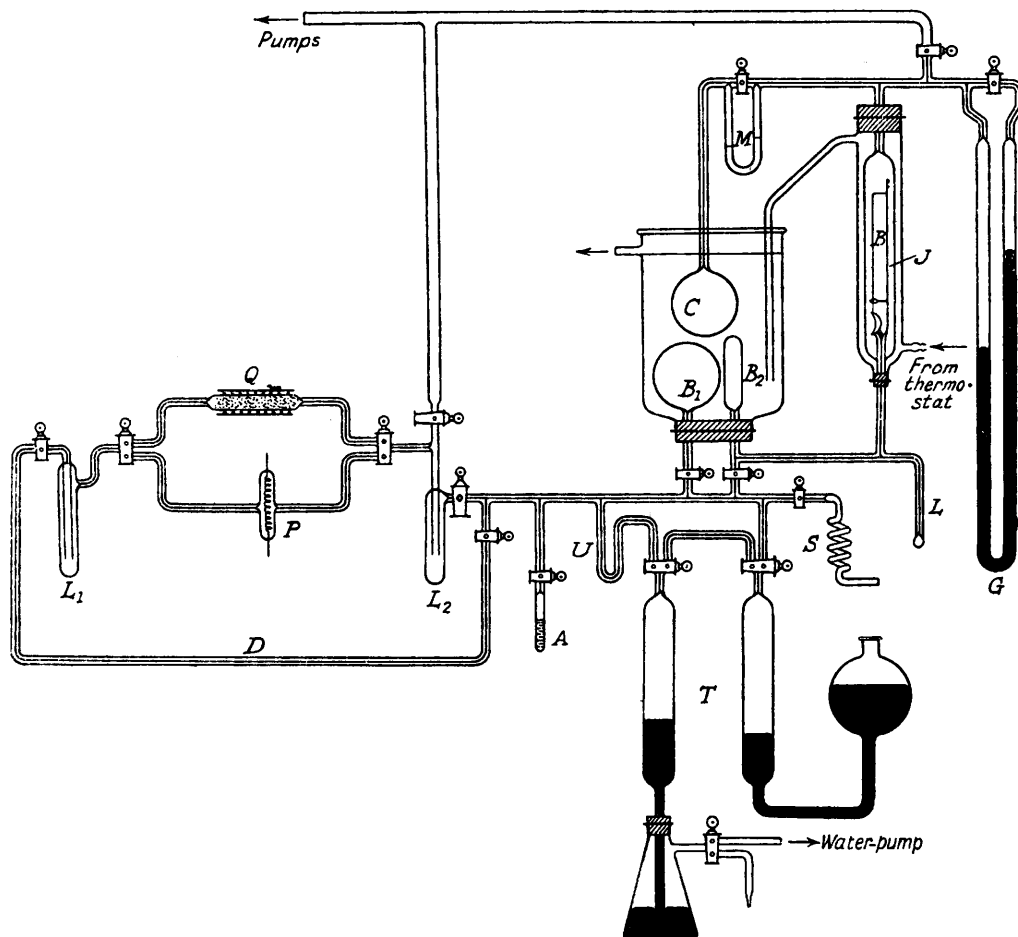
in the jacket, which is necessary for contraction measurements, is accomplished by using a constant-pressure bulb C, which may be put into communication with the jacket through a small manometer M, containing low-vapour-pressure oil. The pressure in the jacket may in this manner be reproduced to within 0·02 mm. of mercury. The bulb C is immersed in the same thermostat as B_1 and B_2: this eliminates errors due to temperature fluctuations in the thermostat, which would otherwise have to be controlled to within 0·01° to obtain a reliable measurement of the contraction. The whole apparatus may be evacuated by a three-stage mercury diffusion pump backed by a Hyvac pump.

The two standard volumes comprise (1) the bulbs B_1 and B_2 and the spoon of the Bourdon gauge, called the " large " volume in the sequel, and (2) B_2 and the spoon, called the " small " volume.

To illustrate the method of analysis the procedure with a typical gas specimen is described.

(a) *Measurement of Initial Pressure.*—The gas is admitted to the evacuated system through the spiral S cooled in a solid carbon dioxide–ether mixture, to remove water vapour and other substances of low volatility. Any condensate obtained may be examined as described under (f) below. The initial gas is admitted to the

large volume so as to give a suitable reading of the Bourdon gauge when the standard pressure is applied to the jacket. This pressure may be 300—500 mm., and it is measured to one part in 2000 parts by the mercury gauge. The sum of the Bourdon reading and the standard pressure gives the initial pressure. After measurement, the gas is transferred to the Toepler pump.

(b) *Carbon Dioxide and Hydrocarbons other than Methane.*—(i) *Carbon dioxide if present alone.* The traps L_1 and L_2 are cooled in liquid air, and the gas in T is passed slowly round the circuit DL_1PL_2 for about 10 minutes, thus condensing out the carbon dioxide. The permanent gas is evacuated into the Toepler, and the condensate in the traps distilled to the small limb L by cooling the latter in liquid air. The bulbs are then isolated from the rest of the apparatus, and L warmed to $-78°$. The carbon dioxide vaporised is measured in the suitable standard volume by means of the Bourdon gauge *. The gas is then rejected. If it is desired to measure the contraction accompanying the removal of the carbon dioxide, the residual gas in T is transferred to the large volume and measured with the Bourdon gauge, the standard pressure being used.

(ii) *Carbon dioxide present with hydrocarbons.* The condensate in this case will contain, in addition to carbon, dioxide, hydrocarbons, and these, being volatile at $-78°$, will be measured with the dioxide. If ethylene is present, there is also the possibility that the whole of this compound will not remain condensed during evacuation with the Toepler pump, since its vapour pressure at $-196°$ is about 0·003 mm. To ensure that no appreciable quantity of olefin remains in the permanent gas, the latter is passed a few times through the capillary tube U immersed in liquid nitrogen, by means of the Toepler pump. By one or two operations of the latter, U can then be evacuated. After this treatment the pressure of ethylene in the residue cannot be greater than about 0·006 mm., which is not appreciable. The condensates in the traps and capillary are united, distilled into L, and measured. The hydrocarbon in the mixture is then oxidised by distilling the latter backwards and forwards through the copper oxide furnace at about 700° for about 10 minutes, the traps L_1 and L_2 being used for this purpose. The whole is then recondensed in L, and the carbon dioxide vaporised by warming to $-78°$. It is then measured and abandoned. The water formed during oxidation is next estimated by allowing the limb to warm to room temperature, care being taken that the whole of the liquid is vaporised. Tests have shown that a complete separation of carbon dioxide and water is obtained in this way, and that the presence of water does not interfere at all with the measurement of the carbon dioxide. If the nature of the hydrocarbon present is known, the figures obtained permit it to be estimated. If unknown hydrocarbons are present, and identification is necessary, the analysis cannot be carried out so accurately. The best procedure would appear to be the condensation of the mixture of carbon dioxide and hydrocarbon in the soda-lime tube A, after which the hydrocarbon is taken back to L and measured. It is then identified by combustion over copper oxide as described above. To check the results so obtained it is desirable to repeat the estimation, combusting the whole of the condensate without previous separation of carbon dioxide.

(c) *Oxygen.* This may be accurately determined by combustion with carbon monoxide and/or hydrogen over the platinum spiral. If the gas contains carbon monoxide and hydrogen in excess of the oxygen, the combustion is carried out by circulating the residual gas from (b) over the spiral maintained at a very dull red heat, the traps being cooled in liquid air. The carbon dioxide and water formed are measured as described in (b) (ii), and determination of the contraction [as in (a)] is used as a check. The oxygen content is given by $\frac{1}{2}(CO_2 + H_2O)$ and $\frac{1}{3}$ (contraction). If there is an excess of oxygen initially, a known pressure of carbon monoxide may be added.

(d) *Carbon monoxide and hydrogen.* These gases are quantitatively oxidised by copper oxide at 300°. The residual gas from (c) is circulated over the oxide for about 20 mins., with L_1 and L_2 in liquid air. After evacuation of the remaining gas, the products are measured as usual, together with the contraction if desired.

(e) *Methane.* The oxidation of methane to carbon dioxide and water by copper oxide at about 900° was found to be quite satisfactory. Circulation of the gas through the furnace for about 20 mins. ensures complete oxidation. The products and contraction are measured in the usual way.

(f) *Examination of the condensate in the spiral at $-78°$.* The exact treatment of the condensate must, of course, depend on the constituents present. The carbon content may be determined by distilling the substance through the copper oxide furnace at 700° a few times and measuring the carbon dioxide formed. If the condensate is a single compound, *e.g.*, water, it may be distilled to L at once and measured.

The methods described above have been thoroughly tested on various mixtures of known composition. Some figures are given below, together with those for a typical duplicate analysis of a gas specimen, in order to illustrate the order of accuracy obtainable.

Constituent.	Percentages by volume.				Constituent.	Percentages by volume.			
	Synthetic mixture.		Gas sample, duplicate analyses.			Synthetic mixture.		Gas sample, duplicate analyses.	
	Used.	Found.				Used.	Found.		
CO_2	6·58	6·61	9·23	9·21	H_2	2·72	2·70	3·59	3·61
C_5H_{12} ...	—	—	0·04	0·04	CH_4	0·51	0·51	0·07	0·06
O_2	0·25	0·24	0·20	0·21	N_2	85·74	85·71	78·83	78·83
CO	4·20	4·23	8·05	8·04					

* If the small volume is used, a correction should be applied for the change in the ratio of the apparent volumes of the bulbs due to the cooling of L to $-78°$.

The method may readily be extended to the analysis of mixtures of gases other than those mentioned above, the details depending on the nature of the problem. The following additional examples of the use of the apparatus may be mentioned. Small percentages of carbonaceous gas in an inert atmosphere may be easily estimated to 0·005% ; *e.g.*, the carbon dioxide content of samples of atmospheric air has been determined as 0·03%, in agreement with the accepted figure. Various methods for the estimation of oxygen have been developed, giving the oxygen content of the air as 20·94 $\pm$ 0·04%.

In order to shorten the time required for an analysis, it would be advantageous to use one limb of the Toepler pump as the thermostated large volume, as this would dispense with the rather slow process of evacuating the bulbs with this pump. However, the apparatus has been described as originally used, in the hope that it may provide a basis for the solution of problems of gas analysis confronting other workers.