A Method to Make Standard CO_2 Samples for Infrared Gas Analysis and the Operation of an IRGA Analyser for Air Samples from the Scandinavian Network.

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Abstract

A method of making CO_2 standard gas mixtures varying between 1 and 400 ppm in concentration with an accuracy of ± 1 ppm is described. An accurately known volume of pure CO_2 gas is mixed with CO_2 free dry air in an evacuated vessel. A method to take samples from this vessel and to analyse the samples in an IRGA gas analyser is described. The use of the apparatus for the Scandinavian CO_2 network is described.

1. Description of the apparatus (Fig. 1).

The apparatus consists of a round bottomed, thick walled Pyrex glass flask (A) of about 20 liter volume, which can be evacuated safely. The volume of the flask is estimated by weighing with water. The flask is fitted with a rubber stopper (B), covered on the inside with a silicone lubricant. (Glass joint better.) Through the stopper are inserted four capiallry tubes (C_1, C_2, C_3 and C_4). The first capillary tube (C_1),

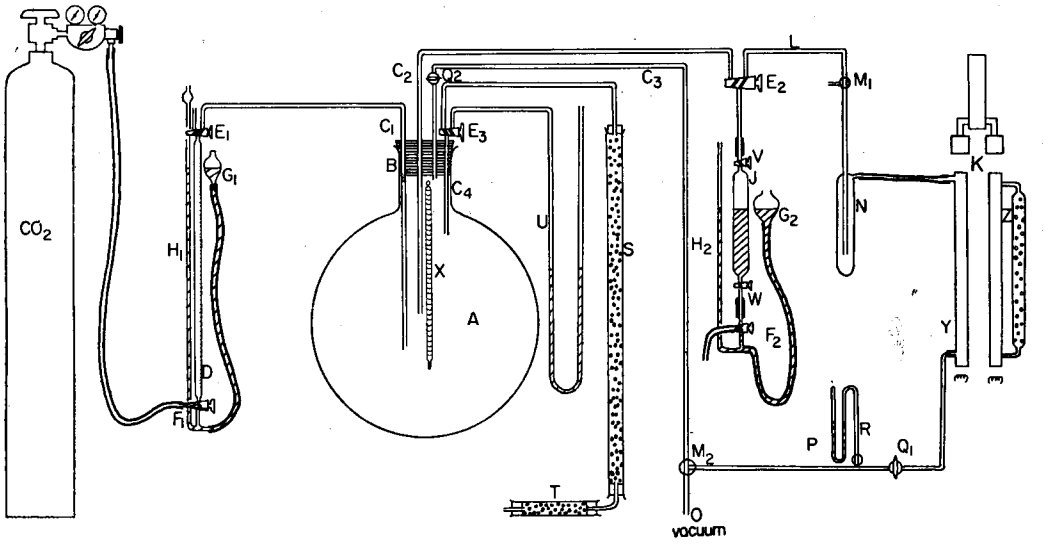

Fig. 1.

which has an inner diameter of 0,1 mm and 10 mm^3 volume, and reaches to the middle of the flask (A), is connected to the gas burette (D) through the two way stopcock (E_1). The burette (D) is graded in 100 parts of a ml and can be connected to the mercury bulb (G_1) or to the gas cylinder (I) through the three way stopcock (F_1). The CO_2 gas cylinders manufactured by Svenska Kolsyrefabriken, Stockholm, contain 99.5 % pure CO_2 and 0.5 % argon. The Hg bulb (G_1) is connected to the open niveau tube (H_1). The second capillary tube (C_2) is connected to the gas pipette (J) (volume 250 ml) through the two way stopcock (E_2) (similar to E_1). By turning (E_2), (J) can be connected to the gas analyser (K) through the tube (L). The gas pipette (J) is connected to the three way stopcock (F_2) (similar to F_1). The stopcocks of (J) are called (V) and (W). (J) can be connected to the mercury bulb (G_2) (similar to G_1), which is fitted with a level tube (H_2), or to the free air through (F_2). The tube (L) is fitted with a three way stopcock (M_1) wich makes it possible to let in air in different parts of the system. Between (L) and the analyser (K), an air dryer (N) is connected, containing Dehydrite (Magnesium Perchlorate) which does not absorb CO_2 The tube (Y) of the gas analyser (K) is connected with the glass tube (P), which is fitted with a Hg manometer (R) and a stopcock (Q_2). (P) is through the three way stopcock (M_2) connected to the vacuum pump (O). (M_2) can connect (O) with (K), with (A) through the capillary tube (C_3) which is fitted with the stopcock (Q_2) or with both. This makes it possible to evacuate the tube (Y) in the gas analyser (K) or the vessel (A) or the whole system. Through the fourth capillary tube (C_4) the vessel (A) can be connected with the Ascarite tube (S) fitted with the Calcium Chloride tube (T) or with the Hg manometer (U), using the two way stopcock (E_3) (similar to E_1).

2. Mixing of Standard gas

The Hg bulb (G_1) is lowered so that the Hg level is on the height of (F_1) with the connection between (D) and (G_1) open. No air is allowed to stay below the stopcock (F_1). The rubber tubing which connects the gas cylinder (I) with (D) is removed from (F_1) and (F_1) is turned to connect (D) with the free air. A glass vessel is kept under the tip of (F_1) and by help of a rubber bulb some air is blown through (D) in order to remove Hg in the stopcocks. The rubber bulb is connected to the free end of the stopcock (E_1). Then the bulb is removed, (E_1) is still kept open to the free air, (I) is connected to (F_1) and CO_2 gas is blown through (D) during several minutes. Then the gas stream is stopped and (E_1) is closed. (F_1) is turned so that (D) is in connection with (G_1) and (G_1) is raised until the Hg level in (H_1) reaches the zero mark on the burette (D). Then (E_1) is opened some seconds in order to let the CO_2 in (D) reach room pressure. The levels of (H_1) and (D) are adjusted to exactly the same height and the exact reading of the level in (D) is taken. The burette is kept in room temperature for one hour and the level is adjusted to room pressure, and the reading is checked. During this time the vessel (A) is evacuated to vacuum (less than 1 mm Hg) through the capillary tube (C_3) with the stopcock (Q_3) open and the stopcock (M_2) connected both to (C_3) and (P). The stopcock (Q_1) is closed during this operation. The vacuum can be controlled on the manometer (R). The stopcocks (E_1), (E_2) and (E_3) have of course to be kept closed. After about 15 minutes the flask (A) is evacuated and the stopcock (Q_2) is closed and the pump stopped. Then CO_2 from (D) is introduced in (A) by careful opening of (E_1) so that (D) is connected to (C_1). When the Hg level in (D) rises, the bulb (G_1) is raised simultaneously in order to control the volume in (D). When the level in (D) reaches the desired value or better when it is a little below it, the stopcock (E_1) is closed and the level in (D) is adjusted to room pressure by adjusting (G_1) and comparing to the level in (H_1).

By careful operations of (E_1) the introduced amount of CO_2 can be adjusted to exactly the desired volume. After this operation the stopcock (E_3) is opened in order to let in CO_2 free air through the absorption tube (S). A drying tube is connected to (S) in order to protect the Ascarite from moisture. The flask (A) is filled with air in about half an hour. The pressure is then checked with the manometer (U) by turning (E_3) to connect (A) to (U). The temperature in (A) is then checked on the thermometer (X). The flask (A) now contains a known amount of CO_2 in a known volume at known temperature and room pressure. The pressure is read off on an ordinary barometer.

3. Analysis of standardsamples with the IRGA

The Hg bulb (G_2) is raised so high that with (F_2) in connection to (J), Hg enters into the gas pipette (J). *The stopcock (W) in the pipette (J) is closed* and the stopcock (V) is opened. (E_2) is turned to connect (J) with the tube (L), (M_1) is turned to connect (L) with (N), (Q_1) is opened, (M_2) is kept as before and the system is evacuated with the vacuum pump (O). The vacuum is checked on (R). Then (E_2) is turned to connection with (A). (J) is now filled with standard sample. (W) is opened and (G_2) is lowered until the Hg level reaches (W). The stopcock (Q_1) is then closed and the pump is stopped. (E_2) is turned to connect with (L) and by raising (G_2) the sample is brought into the tube of the IRGA analyser (K). The level in (J) is adjusted to 760 mm pressure by comparing to the level in (H_2) using the difference between room pressure (from barometer) and 760 on a mm scale behind the tubes. The temperature in the IRGA is checked (in our apparatus it is constant at 32° C in a thermostated room). The reading on the voltmeter is noted. A second sample is taken from (A) as described above. The first sample gives often a somewhat high reading due to CO_2 in the capillary tube (C_2) which has not mixed with the air. It is therefore important to have a very small capillary diameter in (C_2) and to take several samples from (A).

By making several standard mixtures with different concentrations of CO_2, a standard curve can be drawn. Fig. 2 shows a standard curve made with our apparatus. It is a linear, when a suitable range is selected. Ordinary air samples can then be analyzed in the IRGA using the same kinds of gas pipettes as (J). In the sampling procedure a small overpressure is given to the samples as described by FONSELIUS and KOROLEFF (1955). The system is evacuated to the stopcock (V), the overpressure is released through (F_2) by opening (W) and then the Hg bulb is raised after turning (F_2). (V) is opened and the sample is introduced as described above.

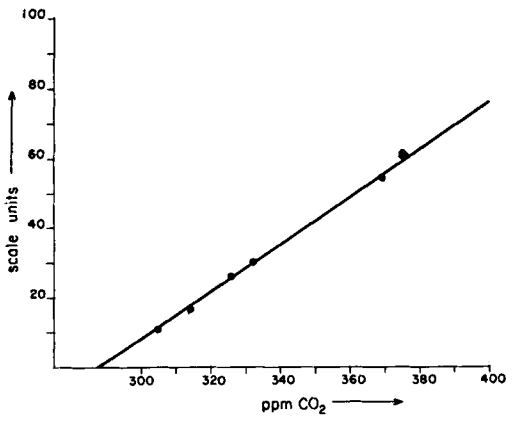

Fig. 2.

4. The IRGA gas analyser

The IRGA gas analyser model SB 1 with fluorite windows manufactured by Sir Howard Grubb Parsons & Co LTD, Walkergate, Newcastle upon Tyne 6, England, has been found to be very suitable for our purposes. A Philips L. F. Amplifier-voltmeter GM 6017/02 has been used as indicator. The gas analyser will not be described in details here, a good instruction is delivered from the manufacturer. However some instructions have to be included. The construction of the analyser is schematically shown in the figure. (Y) is the sample tube which can be evacuated to vacuum and (Z) is the standard tube containing CO_2 free air. The analyser is used on the highest sensitivity and the zero reading on the voltmeter is adjusted with a standard gas containing 275 ppm CO_2. The analyser is then calibrated using different standard mixtures as described above. Every day the analyser is checked with a standard gas and adjusted to give the right reading by using the balance shutter. Several checkings with the standard gas are made during a day's operation of the apparatus.

Our equipment is now used for the routine analyses from the Scandinavian network of CO_2 sampling stations described by FONSELIUS and KOROLEFF (loc cit). It may be pointed that the IRGA gives results compared to dry air, while the earlier technique (FONSELIUS and KORLEFF loc cit) gives the results compared to air saturated with water vapor at about 20° C. A correction to dry air is easily made when the temperature in situ and in the laboratory during the analysis is known. The accuracy of the infrared technique is somewhat better (around ± 1 ppm) than in the chemical method (± 3 ppm) and around 40—50 analysis can be run in one working day. The use of the equipment requires however more training and experience. In order to test the accuracy of the method two test series of 8 samples were analyzed.

The test was made in the following way. An air pump was connected to a T-tube to which were attached two series of 4 gas pipettes connected to each other by small pieces of rubber tubing. An air stream was sucked through the gas pipettes during 1 hour on the roof of the Institute building. The pump was stopped and the stopcocks of the gas pipettes were closed. The samples were analyzed for their CO_2 concentration. As shown in table 1 the difference between the samples in each series was about $\pm$ 1 ppm.

Table 1.

Series 1		Series 2	
a	b	a	b
318 ppm	317 ppm	315 ppm	317 ppm
318 »	319 »	315 »	315 »
318 »	319 »	317 »	316 »
319 »	318 »	317 »	317 »

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REFERENCE

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