Carbon Dioxide Measurements from Aircraft

By WALTER BISCHOF, *Institute of Meteorology, University of Stockholm, Sweden*[1]

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ABSTRACT

During 1962–68, 1 482 air samples were collected from aircraft, partly from jet airliners, at both tropospheric and stratospheric flight levels. The sampling and analysis technique is described and the accuracy of measurement discussed.

1. Introduction

Measurements of CO_2 concentrations in air samples collected from aircraft were begun in 1957 at the Institute of Meteorology in Stockholm as a complement to the Scandinavian ground station network. Data obtained during 1957–1961 from flight levels above 1 000 m. showed that the irregular fluctuations in the CO_2 content of the air decrease with elevation. The seasonal variations therefore are less obscured (Bischof, 1960, 1962). These variations and the annual mean were found to be close to those reported by Keeling (1960). Unfortunately, an attempt to calculate an annual increase for this period failed because of insufficient accuracy in the analysis method used at that time.

In 1962, a project was started to collect air samples from commercial jet aircraft on flights over longer distances and at higher flight levels. A new analysis technique was developed to improve the accuracy and gas standards were established in cooperation with Scripps Institution of Oceanography, Univ. of California.

The results obtained during 1963 at 5 000 m were in good agreement with data reported by Bolin & Keeling (1963) from flights at the 500 mb level during 1958–61 over the Pacific, confirming a rise in tropospheric CO_2 of 0.6–0.7 ppm/yr as calculated by Bolin & Keeling. The 1963 data also show how release and absorption of CO_2 at the earth's surface are reflected in the seasonal CO_2 variations at all tropospheric levels up to the tropopause. In contrast, no or only small variations were found in the lower stratosphere (Bischof & Bolin, 1966). This confirmed that the vertical exchange of CO_2 is damped by the tropopause, as already tentatively concluded by Bischof (1965) from data collected during flights between Copenhagen and Los Angeles in 1963.

Between 1962 and 1968, 837 samples were collected from flights with DC-8 aircraft mainly over Scandinavia, the North Atlantic, and the North American continent, but also on flights to Tokyo, Rio de Janeiro and Bombay.

Furthermore, in cooperation with other institutions, such as Environmental Science Services Administration (ESSA) and Woods Hole Oceanographic Institution (WHOI) in the USA, air samples were collected on flight expeditions over the Caribbean Sea, the east coast of North America, and the Indian Ocean. Samples have also been obtained from aircraft belonging to the Swedish Air Force and from small private planes. A total number of 1 482 samples were collected during 1962–68.

A data separation was made in order to obtain a mean annual CO_2 cycle for the troposphere as well as for the stratosphere, and the average rate of annual CO_2 increase for this period of time. The variability of the data has also been studied. An extensive presentation of these studies is given in a separate article (Bolin & Bischof, 1970).

In this article a description of the air collection and analysis technique is presented and the accuracy of the measurements is discussed.

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2. Air sampling and analysis

2.1. *Air sampling technique*

Although many kinds of aircraft were used in this project, air samples were always collected in the same type of 500 ml Pyrex glass flask having two stopcocks and 14 mm standard taper joint connections, see Fig. 1. In general samples were obtained by connecting the flasks to an air ventilation system, for example, using air from a Pitot tube. The air was drawn through the sample flask for some time, occasionally a sucking pump was connected to the outgoing stopcock, or a Ventury tube was used, in order to increase the air exchange in the sample flask. Usually, also the flask was evacuated before sampling, in order to ensure complete air exchange in the flask.

To collect air samples from a DC-8, a surprisingly easy way was found by connecting the flasks to the fresh air ventilation system in the cabin. Unlike other jet airliners, the DC-8 is equipped with a separate air intake and a turbo compressor for cabin air conditioning. Pressurised and heated air is brought to the cabin, while fresh air via a bypass is brought to the fresh air outlets at the passenger's seat. Tests were made to check the contamination risk by comparing the results from DC-8 flights during descent with results obtained from a Piper plane shortly afterwards. In addition, samples from different DC-8 aircraft and from different outlets on the same aircraft were compared. The results were found to be identical.

Wherever air samples are taken, the sampling time must be long enough to ensure a complete air exchange in the sample flask. Tests with flasks not evacuated before sampling show that a sampling time of 3 minutes was required when using an air flow of 0.6 l/min, which is equal to about three times the volume of the sample flask.

2.2. *Analysis equipment*

A special flask sample analysis equipment was developed at the Institute in Stockholm (Fig. 1). By avoiding high vacuum techniques and pressure regulation it has been possible to construct a portable equipment which is easy to operate. The accuracy of measurement was found to be about 0.2 ppm, i.e. about the same as reported by Keeling (1968) (cf. below).

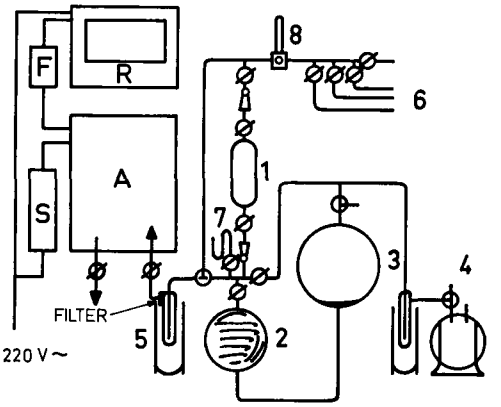

Fig. 1. Analysis equipment. *A*, Analyzer; *S*, voltage stabilizer; *R*, recorder; *F*, recorder filter; *1*, sample flask; *2*, 1 l Hg reservoir; *3*, 2 l Hg reservoir; *4*, vacuum pump; *5*, water vapour trap; *6*, standard gas connections; *7*, vacuum meter; *8*, flow meter and regulator.

Similar equipment has been installed at the Istituto Universitario Navale, Naples, Italy (Bischof & De Maio, 1964) and at ESSA, APCL, Boulder, Colo, USA. A detailed description is available (Bischof, 1970).

In general, a somewhat modified infrared gas analyzer of type URAS, manufactured by Hartmann and Braun, Germany, was used, but other types (IRGA I and II, by Grubb Parsson, London) also have been in service. Since 1966, an UNOR of MAIHAK, Hamburg, replaced the earlier analyzers. This instrument is now used also for continuous measurements on aircraft.

Standard gas was prepared by AGA, Stockholm, and stored in 50 l high pressure gas tanks. Standard gas calibration was made annually against the Scripps standards. We thereby obtained our primary standards.

2.3. *Description of the analysis procedure (see Fig. 1)*

Before entering the *analyzer* (*A*), all gases must pass a *water vapor trap* (*5*). Then two different operations are performed: (*a*) *Standard gas calibration*, by flowing standard gas with a known CO_2 concentration through the analyzer; (*b*) *Flask sample analysis*, by bringing sample air into the analyzer.

Standard calibration is made before starting any flask analysis to obtain a calibration factor, i.e. a recorder-scale factor, and to check the linearity of the calibration curve. Ten

standard gas tanks are available, containing gas with CO_2 concentrations from 300 to 340 ppm. Standard gas is brought into the analyzer sample cell with a flow rate of 0.3 l/min controlled by a *flow meter and regulator* (*8*). Calibration is made either with a constant flow rate or after flushing the cell with the resting air in the sample cell (static air analysis).

A complete calibration includes the use of at least three different standards, each one used ten times. A mean value is obtained and a comparison made with two of our primary standards. With the equipment in good condition, no deviation larger than ± 0.2 ppm is accepted. Otherwise the calibration has to be rechecked. Some of the errors are due to hysteresis and non-linearity in the membrane condensor. By following the procedure described above we ensure that these errors are less than ± 0.2 ppm.

In performing the *flask sample analysis* the flask is attached to the equipment by a 14 mm standard taper joint connection. The sample air is brought into the sample cell by using a mercury pump system containing two *mercury reservoirs* (*2*), (*3*), which are connected to a *vacuum pump* (*4*). The vacuum pump is also used to evacuate all remaining air in stopcocks and connection lines between the sample flask and the 1 l Hg reservoir. The vacuum is checked by a *vacuum meter* (*7*).

After evacuating the connection lines, the flask stopcock is opened and the sample air is brought into the 1 l Hg reservoir by pumping the mercury into the 2 l Hg reservoir, using the vacuum pump. In reverse order, the mercury is used to push the sample air from the 1 l reservoir into the analyzer and through the sample cell. To have complete gas exchange in the sample cell, about 150 ml of sample air at room pressure is required (static air analysis). The analysis result is noted on the *recorder* (*R*) and is compared with one of the standard gases. While preparing a new sample for analysis, a comparison between the standard just used and one of the other standards is performed. This procedure allows an analysis capacity of about ten samples per hour, including standard gas comparison for each sample. In order to check the analysis reliability flask samples containing standard gas usually are analysed at the beginning and occasionally also during routine analysis work.

Table 1. *Analyzer calibration*

Deviaiton from average	±0	0.1	0.2	0.3 ppm	
No. of cases	63	39	5	0	107
% of total	59	36	5	0	100
S.D.	0,08 ppm				

3. Accuracy of the measurements

Investigations were made to check the reproducibility of the analyses, i.e. to determine the sum of possible errors caused by the infrared gas analyzer itself and the rest of the analysis equipment, respectively.

3.1. *Check of analyzer calibration*

An analyzer characteristic was found by flowing standard gases of known concentrations through the sample cell as described in 2.1. A maximum deviation of ± 0.2 ppm between individual measurements and a standard deviation of ± 0.1 ppm was found, which is equal to the accuracy of the recorder. Part of this error was due to the hysteresis of the membrane condensor and lack of linearity of the calibration. The results are summarized in Table 1.

By analysing samples of standard gas filled in flasks, we can assess the reproducibility of the measurements. From Table 2 it can be seen that almost the same accuracy is attained in this way.

Since standard gas is very dry, this test is, however, not adequate to judge the accuracy of the analysis of samples from an atmosphere which is moist. It can be shown by bringing a few water droplets into the sample flask, that water vapour disturbs the measurements considerably. The quality of the analyses, therefore, is very much dependent on the efficiency of the water vapour trap. In other words, it is

Table 2. *Analysis of standard gas filled in flasks*

Deviation from average	0	0.1	0.2	0.3 ppm	
No. of cases	3	6	1	1	11
% of total	27	55	9	9	100
S. D.	0.14 ppm				

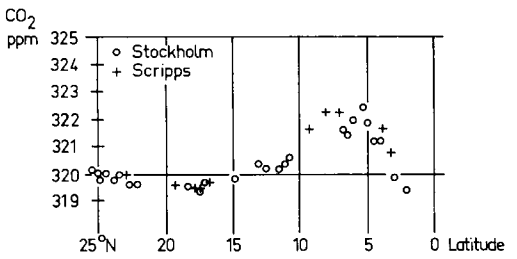

Fig. 2. Comparison between flask samples analysed in Stockholm and at Scripps Institution respectively. (RFF flight (ESSA) of April 27–29, 1966, over the Caribbean Sea and south of Panama, the samples were collected at 1.600 m.)

not enough to freeze out the water, because ice crystals may pass into the sample cell and evaporate. To avoid this, a water vapour trap has been given a special shape as shown in Fig. 1. In practice, samples received from DC-8 flights are, however, very dry.

3.2. *Field work*

Laboratory conditions still may be too idealized to judge the accuracy of the measurement. Therefore flask samples were taken during a period with high atmosphere moisture. Sample air was pumped through the sample flask and to the analyzer. A check of the flask analysis compared with results obtained by having air flowing directly into the analyzer showed that moist air flask analysis can be made with an accuracy better than ± 0.2 ppm.

3.3. *Comparison of data*

3.3.1 Flight samples

On a flight on December 14, 1962, two samples were obtained in 1 l flasks and analysed at Scripps Institution and in Stockholm respectively. The result was: Stockholm, 314.48 ppm; Scripps, 314.20 and 314.58 ppm. During a RFF (ESSA) flight over the Caribbean Sea, a number of samples were collected in our 1/2 l flasks and also in 2 l high vacuum flasks belonging to Scripps Institution. Analyses were made in Stockholm and at Scripps Institution. The result is shown in Fig. 2.

Table 3. *Double analysis from 21 sample flasks*

Deviation from average	0	0.01–0.05	0.06–0.10	0.11–0.15	0.15 ppm	
No. of cases	15	29	17	9	0	70
% of total	21	42	24	13	0	100
S.D.	0.04					

3.3.2 Double analysis

On a DC-8 flight, both 1/2 l and 2 l flasks were used and analysed in Stockholm. Due to the larger volume, double analysis could be made of the 2 l samples. From the result shown in Table 3 it can be seen that no deviation larger than 0.15 ppm occurred and that 87% of all deviations were found within a 0.1 ppm range.

3.4 *Storing time*

Samples were consistently analysed within a few days of collection because it had been found (by analysing standard gas samples) that a contamination risk exists after a few weeks. The risk is different for different flasks. This is probably due to diffusion through stopcocks in the presence of an external excess pressure and concentration difference between sample and room air, and depends of course also on the quality of the individual flask.

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САМОЛЕТНЫЕ ИЗМЕРЕНИЯ КОНЦЕНТРАЦИИ УГЛЕКИСЛОГО ГАЗА

В период 1962–68 гг. было взято 1 482 воздушных проб, частично с реактивных самолетов, как в тропосфере, так и в стратосфере. Описывается методика забора проб и их анализа, а также точность измерений.