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### ABSTRACT

During 1962-68, 1482 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.

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## INTRODUCTION

Measurements of CO<sub>2</sub> 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 1000 m, show that the irregular fluctuations in the CO<sub>2</sub> content of the air decrease with elevation and the seasonal variations therefore become 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 cruises over larger distances and at higher flight levels. A new analysis technique was developed to improve the accuracy and gas standard were established in cooperation with Scripps Institution of Oceanography, Univ. of California.

The results obtained during 1963 at 5000 m are in good agreement with data reported by Bolin and Keeling (1963) from flights at the 500 mb level during 1958-1961 over the Pacific, confirming a growth rate of 0.6 - 0.7 ppm/yr as calculated by Bolin and Keeling. The 1963 data also show how release and absorption of CO<sub>2</sub> at the earth's surface are reflected in the seasonal CO<sub>2</sub> variations at all tropospheric levels up to the tropopause. In contrast, no or only small variations were found in the lower stratosphere (Bischof and Bolin, 1966). This shows how the vertical exchange of CO<sub>2</sub> 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 to 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.

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Furthermore in cooperation with other institutions, such as Environmental Science Services Administration (ESSA) and Woods Hole Oceanographic Institution (WHOI) in the U.S., 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 1482 samples were collected during 1962-1968.

A data separation was made in order to obtain a mean annual CO<sub>2</sub> cycle for the troposphere as well as for the stratosphere, and the average rate of annual CO<sub>2</sub> increase for this period of time. The variability of data has also been studied. An extensive presentation of these studies is given in a separate article (Bolin and Bischof, 1970).

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

2 AIR SAMPLING AND ANALYSIS

2.1 Air sampling technique

In spite of the most varying kinds of aircraft used in this project, air samples were collected in the same type of 500 ml Pyrex glass flasks with two stopcocks and 14 mm standard taper joint connections, see figure 1. Samples, in general are collected by connecting the flasks to an air ventilation system, for example, using ram air from a Pitot tube. The air is drawn through the sample flask for some time, occasionally a sucking pump is connected to the outgoing stopcock, or a Ventury tube is used, in order to increase the air exchange in the sample flask. Usually, the flasks also are 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 ram air intake and turbo compressor for cabin air conditioning. Pressurised and heated ram air is brought to the cabin, while fresh air via a bypass is brought to the fresh air outlets at the passengers 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 and the results are 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 being evacuated before sampling show that a sampling time of 3 minutes is 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 (Figure 1). By avoiding high pressure technique 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 (1963).

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

In general, a somewhat modified infrared gas analyzer of type URAS, manufactured by Hartmann and Braun, Germany, was used, but also other types (IRGA I and II, by Grubb Parsson, London). 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 gastanks. Standard gas calibration is annually made against the Snijps standards. We thereby obtain our primary standards.

2.3 Description of the analysis procedure

Before entering the analyzer (A), all gases have to pass a water vapor trap (5). In principle, two different operations are made.

- a) Standard gas calibration, by flowing standard gas with wellknown CO<sub>2</sub> 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. recorder-scale factor, and to check the linearity of the calibration curve. Ten standard gas tanks are available, containing gas with CO<sub>2</sub> concentrations from 300 to 340 ppm. Standard gas is brought into the analyzer sample cell with a flow rate of

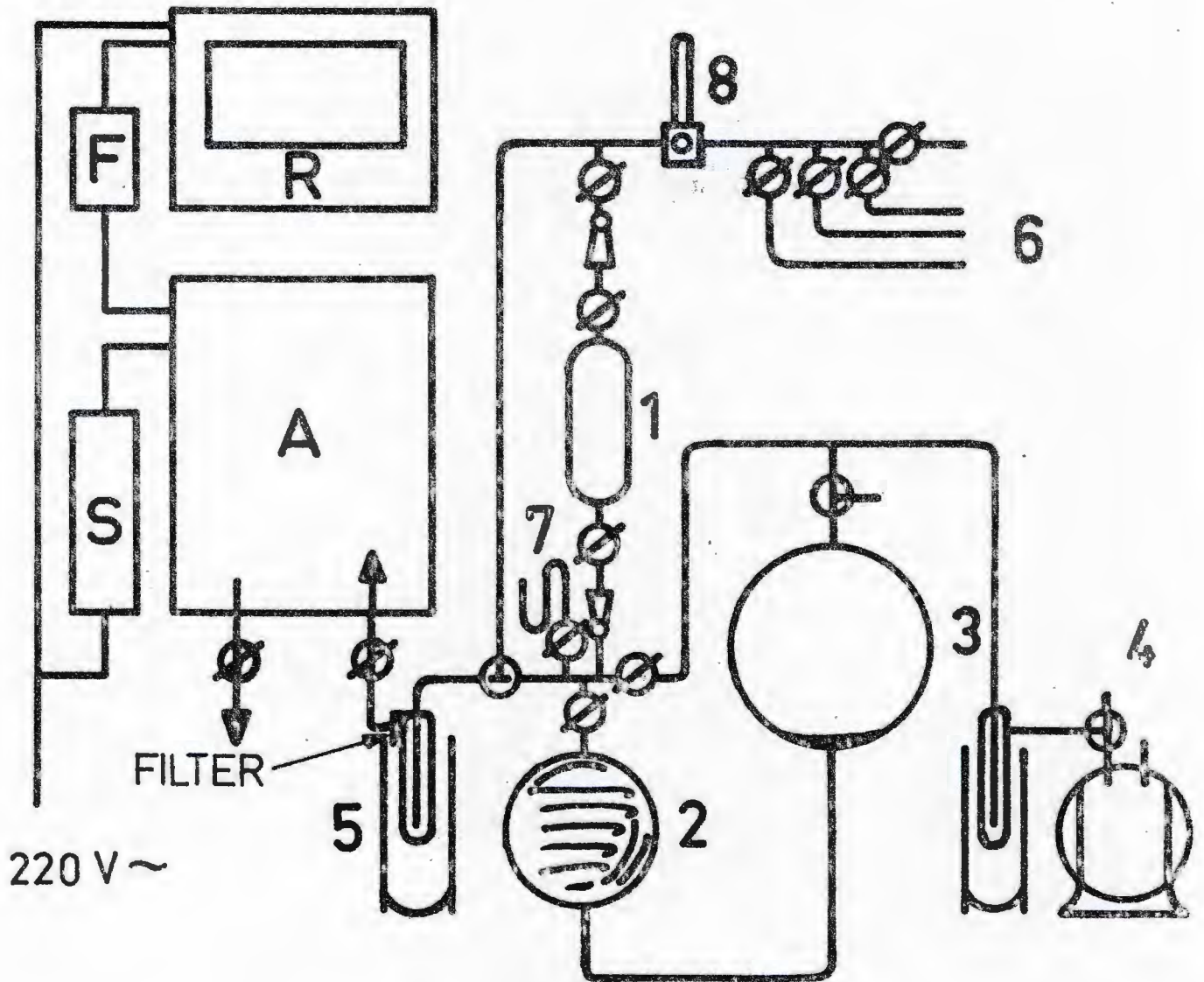


Fig. 1. Analysis equipment.

- |   |                    |   |                          |
|---|--------------------|---|--------------------------|
| A | Analyzer           | 1 | Sample flask             |
| S | Voltage stabilizer | 2 | 1 l Hg reservoir         |
| R | Recorder           | 3 | 2 l Hg reservoir         |
| F | Recorder filter    | 4 | Vacuum pump              |
|   |                    | 5 | Water vapor trap         |
|   |                    | 6 | Standard gas connections |
|   |                    | 7 | Vacuum meter             |
|   |                    | 8 | Flow meter and regulator |



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 air resting in the sample cell (static air analysis).

A complete calibration includes the use of at least three different standards, each one referred to 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  $\pm 0,2$  ppm are accepted. Otherwise the calibration has to be rechecked. Part of the errors are due to hysteresis and non-linearity in the membrane condenser characteristics. By the procedure we ensure that these errors are less than  $\pm 0,2$  ppm.

In performing the flask sample analysis the flask is connected 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 sample air at room pressure is required (static air analysis). The analysis result is obtained 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.

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In order to check the analysis reliability, flask samples containing standard gas usually are analyzed at the beginning and also occasionally during routine analysis work.

3 ACCURACY OF THE MEASUREMENTS

Investigations were made to check the reproducibility of the analyses, i.e. 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 is found by flowing standard gases of well-known concentrations through the sample cell as described in 2.1. A maximum deviation of  $\pm 0,2$  ppm between individual measurements and a standard deviation of  $\pm 0,1$  ppm is found, which is equal to the accuracy of the recorder. Part of these errors are due to the hysteresis of the membrane condensator and lack of linearity of the calibration. The results are summarized in Table 1.

Table 1  
Analyzer calibration

deviation from average	$\pm 0$	0,1	0,2	0,3 ppm	
number of cases	63	39	5	0	107
percent of total	59	36	5	0	100
standard deviation:	0,08 ppm				

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

in Stockholm and at Scripps Institution respectively.  
The result is shown in Figure 2.

3.3.2 Double analysis.

On a DC-8 flight, both 1/2<sup>l</sup> and 2<sup>l</sup> flasks were used and analyzed in Stockholm. Due to the larger volume, double analysis could be made of the 21 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.

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	
number of cases	15	29	17	9	0	70
percent of total	21	42	24	13	0	100
standard deviation:	0,04 ppm					

3.4 Storing time

Samples were consistently analyzed within a few days after collection because it had been found (by analyzing standard gas samples) that a contamination risk exists after a few weeks which 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.

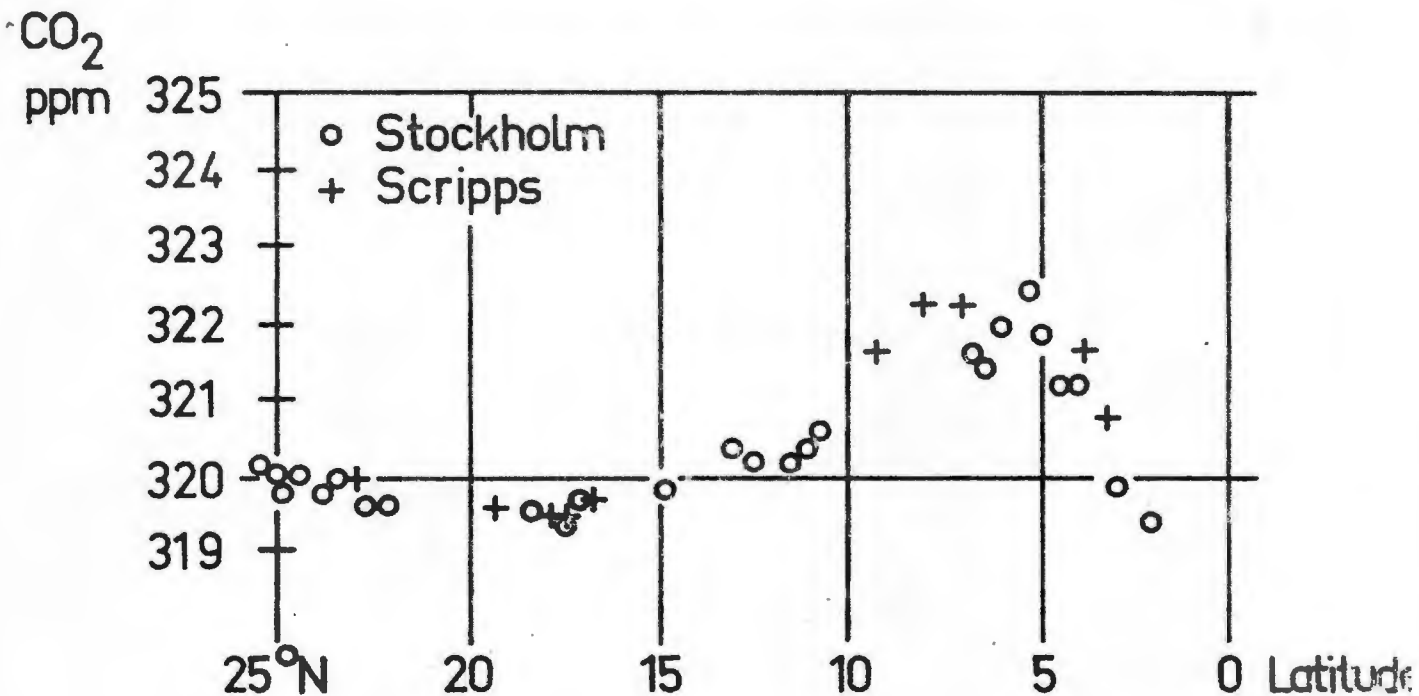


Fig. 2. Comparison between flask samples analyzed in Stockholm and at Scripps Institution respectively. (RFP flight (ESSA) of April 27-29, 1966, over the Caribbean Sea and south of Panama, the samples were collected at 1.600 m.)

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