

CO₂ Measurements With an Infrared Laser Spectrometer on Flask Samples Collected at Jungfrauoch High-Altitude Research Station (3500 Meters asl) and With Light Aircraft up to 8000 Meters Over Switzerland

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We discuss the use of an infrared laser spectrometer for CO₂ concentration analysis of flask samples. The precision of the system is 2.5%, or 0.75 ppm. A series of monthly measurements at the Jungfrauoch high-altitude research station, Switzerland (3500 m asl), is discussed together with vertical profiles up to 8000 m asl.

INTRODUCTION

Several years ago we started the construction of an infrared laser spectrometer (IRLS) [Lehmann, 1979; Zumbrunn, 1981] to analyze CO₂ on small samples, either air from small ice cubes or samples of ambient air. Since 1979 we have calibrated our analyzer with three CO₂-in-air standard gases (321.06 ppm, 342.03 ppm, and 384.99 ppm, based on 1974 manometric calibration (World Meteorological Organization provisional scale)), prepared at the Scripps Institution of Oceanography, La Jolla, California. All measurements reported here are based on these standards. The IRLS is designed for discrete sample measurements.

During the summer of 1980 we started a 1-year measuring program at the Jungfrauoch to investigate whether this location could serve as a baseline station for CO₂ measurements and to check the long-term stability of our detection system. Approximately one day each month we measured the diurnal time series by taking two samples every 2 hours.

Recently, we started a new program to measure vertical CO₂ concentration profiles up to 8000 m above sea level (asl). The sample collection was done from a small aircraft. The scope of this program is to evaluate the seasonal variations of the vertical CO₂ profile and to distinguish between local effects in space and time and large-scale seasonal variations.

Parallel to these air sampling programs we developed a new technique to determine the CO₂ concentration in the air bubbles of 1-cm³ ice samples [Zumbrunn *et al.*, 1982; Neftel *et al.*, 1982].

MEASURING SYSTEM

Figure 1 schematically represents our IRLS. A quasi-continuous tunable diode laser, cooled by a closed cycle cooler to 20 K, emits in the wave number range 2300 to 2380 cm⁻¹ in different modes with narrow bandwidth (10⁻⁵ cm⁻¹). The beam of light passes an optical system consisting of two focusing lenses, two optical cells in line with absorption path lengths $l_1 = 0.5$ cm and $l_2 = 15$ cm, respectively, and a monochromator before it strikes the PbSe detector. The light is chopped. The detector signal is amplified with the usual lock-in technique and displayed with an $x(t)$ plotter. The monochromator is used to select a specific mode and to suppress most of the light originating from spontaneous emission. To determine the small contribution on the signal from spontaneous emission still passing the monochromator at the peak center ν_0 , the short cell is filled with 1-torr pure CO₂. More than 99.9% of the light with the frequency ν_0 is absorbed. The remaining signal in the line center caused by spontaneous emission has to be subtracted from the measured quantities $I(\nu_0)$ and $I_0(\nu_0)$. This procedure avoids a high CO₂ exposure of the 15-cm sample cell, which would entail a memory effect.

The intensity I of the beam of light passing an absorption cell with length L , containing a gas with total pressure p and CO₂ concentration c , is attenuated following an exponential law:

$$I = I_0 \cdot \exp[-\alpha(\nu, p, T) \cdot c \cdot p \cdot L] \quad (1)$$

where

- $\alpha(\nu, p, T)$ absorption coefficient, cm⁻¹ atm⁻¹;
- ν wave number, cm⁻¹;
- T temperature, °K;
- I_0 beam intensity with zero absorption;
- p pressure, atm⁻¹;
- c CO₂ concentration, ppmv.

For a measurement, we tune the laser several times continuously over an absorption line of the ¹²C¹⁶O₂ molecule, e.g., the R(16) line of the 00^o-00^o1 fundamental vibration-rotation transition and determine the minimum intensity, corresponding to the maximum of the absorption coefficient of the selected line. For all measurements the same absorption line at the peak center ν_0 is used; the absorption coefficient $\alpha(\nu_0, p, T)$ then depends only on p and T . The absorption coefficient is calibrated as a function of pressure and temperature using the standard gases with known CO₂ concentrations.

The expression $\ln [I(\nu_0)/I_0(\nu_0)]$ is linear between 321 ppm and 385 ppm within the limits of error. The limiting factors for the precision are fluctuations of the temperature of the absorption cell, small fractionation processes during the filling procedure, and laser instabilities. Between two samples, one of the standard gases is always measured. In addition, we tune over the absorption line while the sample cell is evacuated to determine the laser intensity I_0 for zero absorption. The absorption coefficient used to determine the CO₂ concentration of the sample is obtained by linear interpolation between the values calculated from the standard gas measurements. In this

IR LASER SPECTROMETER

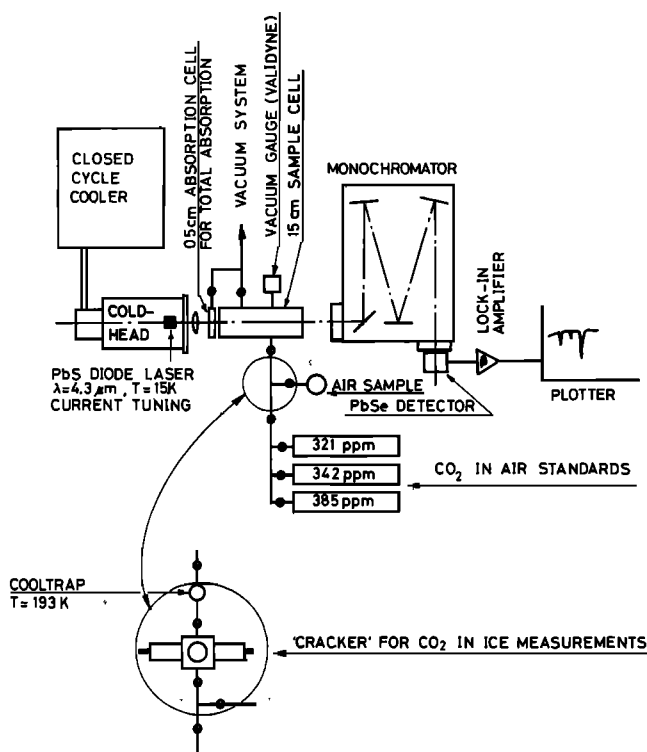


Fig. 1. Schematic representation of the IRLS.

way, variations of the ambient temperature are considered. Each sample is measured at least twice. The reproducibility of a sample measurement is 0.25%. With a temperature-stabilized cell it should be possible to improve the precision by about a factor of 2.

We are using clean 70-ml glass flasks, one end with greased stopcocks, as sample containers. Before each run the flasks are cleaned in an ultrasonic bath, and the stopcocks are greased with a thin film of degassed Apiezon N and afterward evacuated to a vacuum better than 10^{-2} torr. At the Jungfraujoch we always opened two flasks simultaneously against the wind without breathing. At the same time we registered different meteorological parameters, i.e., temperature, wind speed, and humidity. Normally, the samples were measured the next day. If this was not possible, we stored them in a dark room. We observed an increased CO₂ concentration in the flask, when they were exposed to light. Most probably the cause is CO₂ production by photolysis of the grease (C. D. Keeling, personal communication, 1982).

RESULTS

Jungfraujoch

Since May 1980 we measured nine series of samples, each series covering 24 hours. We could not find reproducible diurnal variations as typical features of industrial pollution or influences of biological activity on a regional scale. This is an indication that the Jungfraujoch could serve as a CO₂ baseline monitoring station. Figure 2 represents a typical diurnal time series. The small scatter is remarkable. A symbol on the right side of the figure indicates the mean CO₂ concentration of all air samples.

The record of the Jungfraujoch was terminated July 1981. Later on we derived the CO₂ concentration from the elevation of the Jungfraujoch from the vertical profiles taken by air-planes. To relate our CO₂ measurements to the worldwide CO₂ data, in Figure 3 the Jungfraujoch data are compared with a CO₂ curve which is representative for a geographical latitude of 50°N. The functional dependence is given by

$$c(t) = A_0 + B_0(t - t_0) + A_1 \cos(\omega t) + B_1 \sin(\omega t) \\ + A_2 \cos(2\omega t) + B_2 \sin(2\omega t) + A_3 \cos(3\omega t) + B_3 \sin(3\omega t)$$

$$t_0 = 1977 \text{ yr} \quad \omega = 2\pi \text{ yr}^{-1}$$

$$A_0 = 333.18 \text{ ppm} \quad B_0 = 1.48 \text{ ppm yr}^{-1}$$

$$A_1 = 1.147 \text{ ppm} \quad B_1 = 4.80 \text{ ppm}$$

$$A_2 = 0.427 \text{ ppm} \quad B_2 = -2.39 \text{ ppm}$$

$$A_3 = 0.298 \text{ ppm} \quad B_3 = 0.393 \text{ ppm}$$

The coefficients $A_1, B_1, A_2, B_2, A_3, B_3$ were calculated by a least squares fit of the available data from Weathership P, which is located in the northern Pacific, on a similar latitude (145°W, 50°N) as the Jungfraujoch (8°E, 46°N) [Wong and Pettit, 1981; Bacastow et al., 1981]. The linear term B_0 was calculated from the Mauna Loa CO₂ record. The higher elevation of the Jungfraujoch leads to a reduced amplitude of about 1 ppm compared with those from the Weathership P [Bolin and Bischof, 1970; Pearman et al., this issue]. The values indicated by open circles are taken from the vertical profiles at the elevation of the Jungfraujoch. Our data follow generally the calculated CO₂ curve. Larger deviations can be seen in the time between October and January. Because we could not measure more than one day per month, it is impossible to decide whether these deviations reflect an effect of the alpine region or whether they reflect day-to-day fluctuations.

Light Airplane Measurements

By courtesy of the Swiss Military Department we have the opportunity to collect samples over central Switzerland on several flights with a Pilatus Porter aircraft. We have carried out 14 missions and collected about 30 samples on each flight between ground (500 m asl) and 8000 m asl. The flasks are filled with ambient air through a flexible teflon tube mounted on a wing of the airplane. No exhaust gases from the motor are observed. Simultaneous to the first two flights we measured diurnal time series at the Jungfraujoch. For comparison, values are indicated in Figure 3 and show a good agreement. Figure 4 shows the profiles taken until now. Because there are essentially no sources or sinks in the atmosphere, one expects that the vertical CO₂ gradient depends upon whether the ground acts as a net source or sink. The vertical CO₂ profiles reported by Bolin and Bischof [1970] demonstrate this clearly. It is surprising that our profiles still exhibit a CO₂ concentration increasing with altitude during winter time, when the ground acts as a source. Only the profile from March shows a decreasing CO₂ concentration above 3000 m asl.

Figure 5 shows for two different vertical intervals (3–5 km, 5–7 km asl) the amplitude of the seasonal variation of the measured profiles together with the data reported by Bolin and Bischof. The y axis represents the deviation from the mean annual values (the linear increase is subtracted). Comparing the data reported by Bolin and Bischof with our data, one has to consider that their data represent mean values of

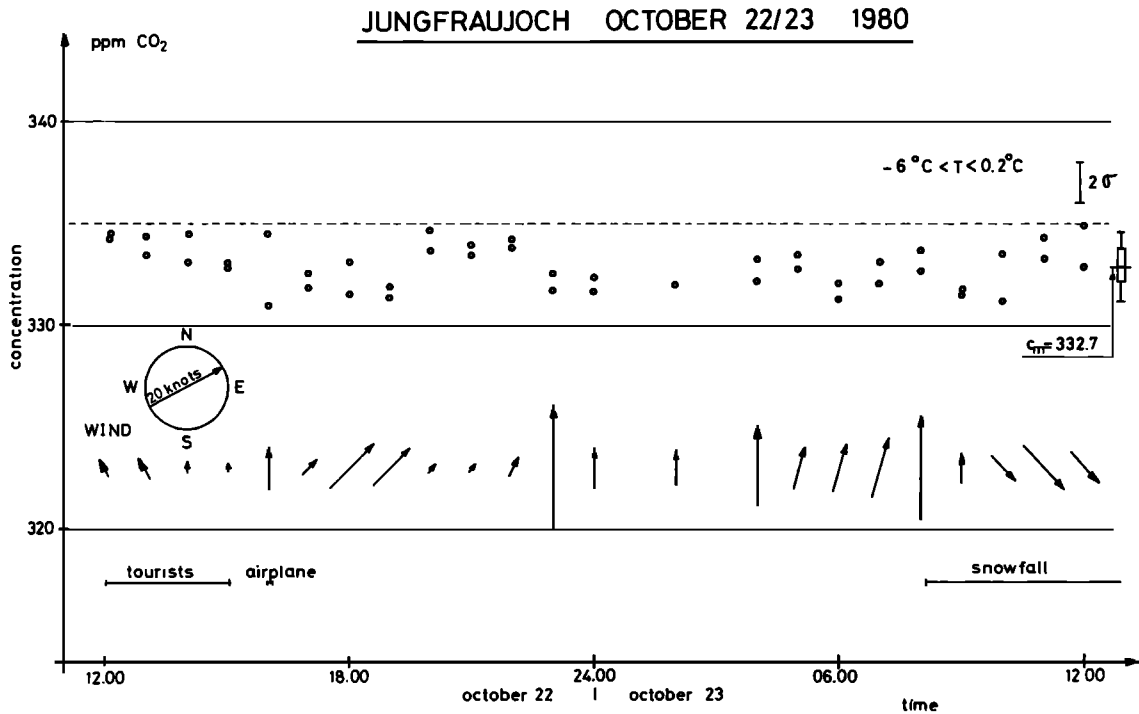


Fig. 2. Typical CO₂ diurnal variation at the Jungfraujoch. The symbol at the right side indicates the lowest, the median, and the highest values. The rectangle in between encloses the mean 50% of all measured values at October 22 and 23, 1980.

several years and were taken in higher latitude, mostly over the sea. With the data acquired so far, we cannot decide whether the deviations of our profiles from those reported by Bolin and Bischof reflect an effect of the alpine region, where our vertical profiles were taken, or whether they reflect only statistical fluctuations.

The CO₂ gradients in the lower troposphere exhibit more scatter. They directly reflect the anthropogenic and biospheric activities and the meteorological conditions near ground. The vertical temperature profile from January 13, 1982, shows a

typical inversion around 1200 m asl. At this level the vertical exchange of air is hindered, and therefore CO₂ is accumulated in the layers near the ground.

CONCLUSIONS

The IRLS proves to be a well-suited system for CO₂ analysis on small flask samples. The actual precision of a single measurement of the system is 0.25%. Though our measuring time covered only 3% of the total time during the observation period, the CO₂ data from the Jungfraujoch reveal the similar

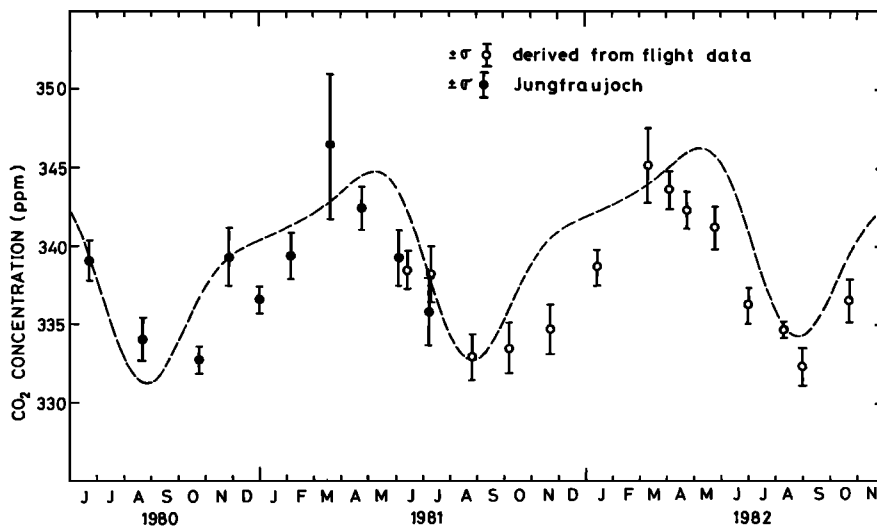


Fig. 3. Comparison of the measured CO₂ data at the Jungfraujoch and the CO₂ data corresponding to the elevation of 3500 m asl from the vertical profiles with a CO₂ curve derived from the WeatherShip P and the Mauna Loa CO₂ record. The open circles represent the values derived from the measured vertical profiles.

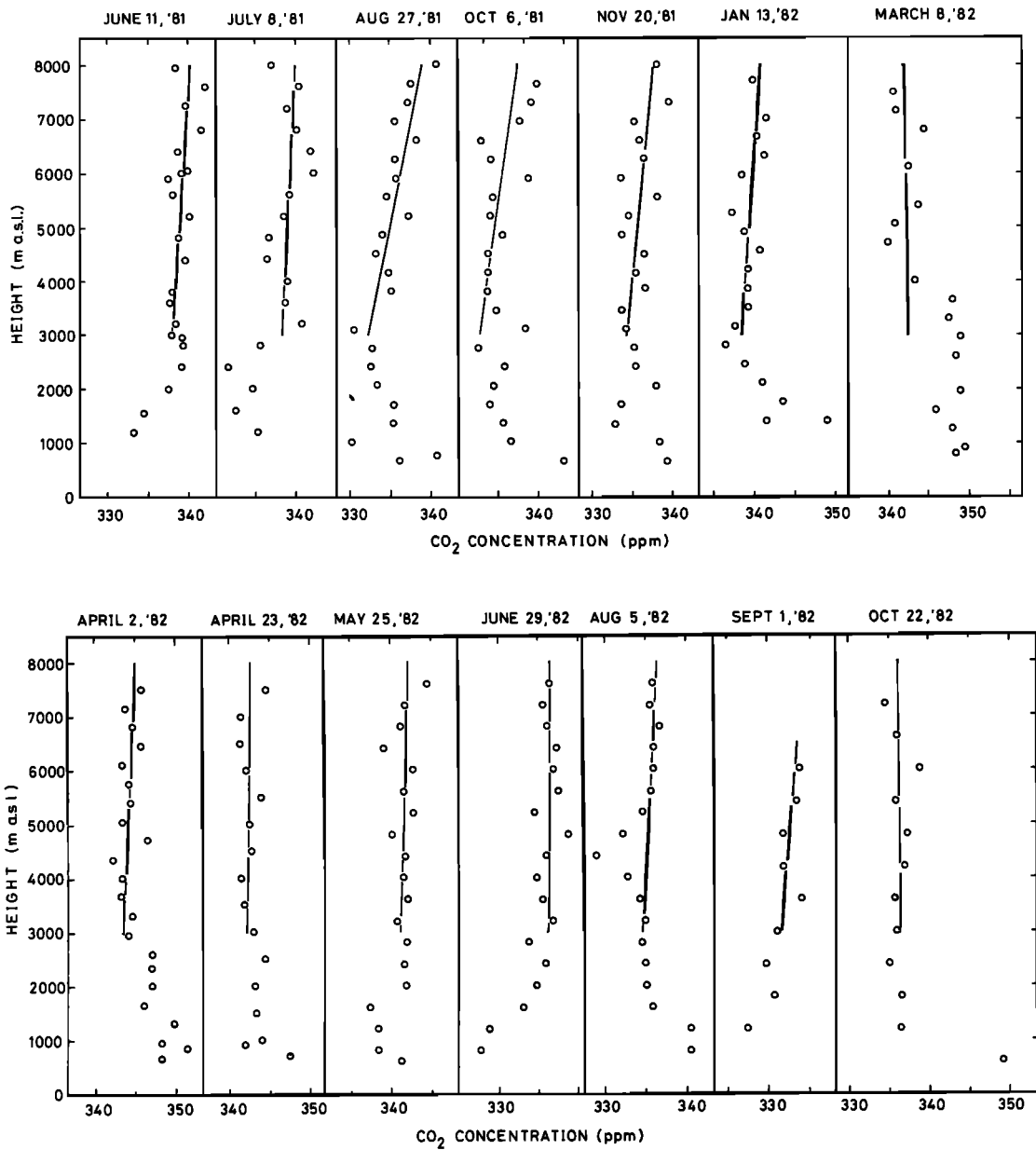


Fig. 4. Individual vertical CO₂ profiles.

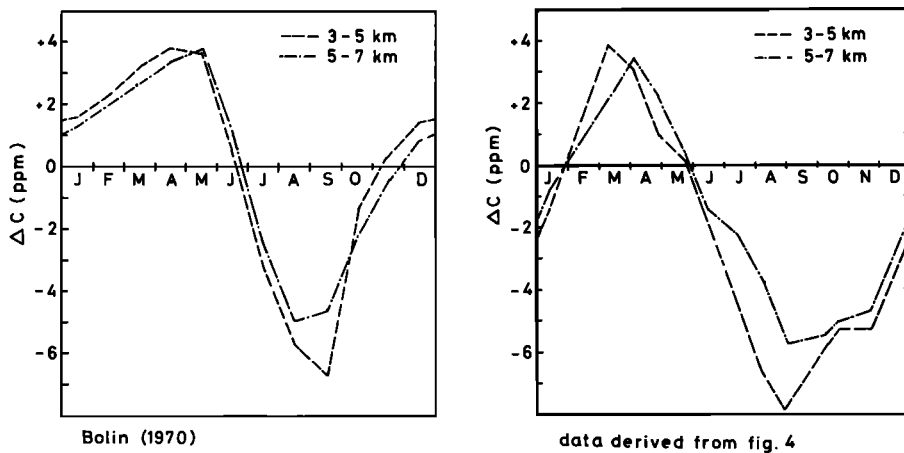


Fig. 5. Comparison of the measured vertical CO₂ profiles with the data reported by Bolin and Bischof. Indicated is the seasonal dependence of the deviation on the linear increase of the CO₂ in two different vertical intervals.

seasonal variation as the Weathership P data. There is no evidence against using the Jungfraujoch as a baseline station; it meets the requirements for such a station given by the WMO [Pearman, 1980]. To determine the background CO₂ concentration, a continuous monitoring station with higher precision is necessary.

The 14 successful flights showed CO₂ profiles with different CO₂ gradients near ground and above 3000 m asl. Local effects influence the CO₂ concentrations at lower elevations.

The present set of data does not allow a detailed interpretation in terms of atmospheric mixing.

Acknowledgments. We would like to thank B. Alder from the Armament Technology and Procurement Group (Swiss Military Authorities) for the opportunity of arranging the test flights and H. Oeschger, M. Heimann, and U. Siegenthaler for their valuable support. We are grateful to C. D. Keeling for providing us the three CO₂-in-air standard gases and for useful advice. This work was supported by the Swiss National Science Foundation and the University of Bern.

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(Received April 21, 1982;
revised February 9, 1983;
accepted February 14, 1983.)