The influence of the carrier gas on the infrared gas analysis of atmospheric CO_2

By WALTER BISCHOF, *Department of Meteorology, Arrhenius-laboratory, S-104 05 Stockholm 50, Sweden*

(Manuscript received January 31, 1974)

ABSTRACT

Experiments made with different types of infrared gasanalyzers (URAS 1, UNOR 2, UNOR 5B) show considerable deviation in the result when using various mixing ratios of N_2 and O_2 as a "carrier gas" for CO_2.
Tellus 135

1. Introduction

In the long-term project for monitoring atmospheric CO_2, standard gases containing CO_2 in air have been used for calibration since the beginning of the project in 1957 (Bischof, 1970). The primary standards have since 1963 been frequently compared with standards used at Scripps Institution in order to obtain comparable values in our sampling programmes. Scripps standards, however, consist of CO_2/N_2 mixtures. Standard gases used in other similar projects containing both CO_2 in air and in N_2 have occasionally been calibrated at our institute. Re-calibrations with Scripps standards showed, however, considerable deviation in the result. It is shown that this discrepancy to a considerable degree is due to the different types of gas-analyzer which are used, and more importantly to the fact that different carrier gases have been used in the standards.

2. Experiments

In order to investigate the influence of different types of gas-analyzers and of various "carrier gases" for CO_2, gasmixtures of constant CO_2 content but varying N_2/O_2 ratios were prepared and analyzed by using special equipments developed for the experiment. The constant CO_2 concentration thus obtained in a sample flask is connected to the equipment for flask sample analysis. In this way a reproducibility of the analysis of about 0.4 ppm can be obtained for an individual sample.

Three types of analyzers were investigated: URAS 1, UNOR 2 and UNOR 5B (which is a somewhat modified instrument specially manufactured to provide a portable analyzer). The analysis accuracy is about 0.2 ppm, in general the comparison cell of each analyzer was filled with a CO_2/air mixture, but experiments were made also using CO_2 in N_2O_2 mixtures, see below. Altogether, 266 mixtures were prepared and analysed during 1972–73. Most of the experiments were repeated several times to calculate average values.

3. Results

In Fig. 1, the average analysis index, i.e. the departure of an analyzed sample from a given reference gas, is plotted as a function of the R-ratios $O_2/(O_2+N_2)$ in the sample ($R=1$ corresponds to 100% O_2), the comparison cell being filled with CO_2/air. The reference gas used here contains 321.4 ppm CO_2 in air, expressed in relation to Scripps standard calibration values.

The result clearly shows how sensitive the

[1] Contribution No. 280.

This paper is essentially the content of the Report AC-26, September 1973, of the Institute of Meteorology, University of Stockholm.

This work has been supported by the Swedish Science Research Council under Contract No. 0223-051.

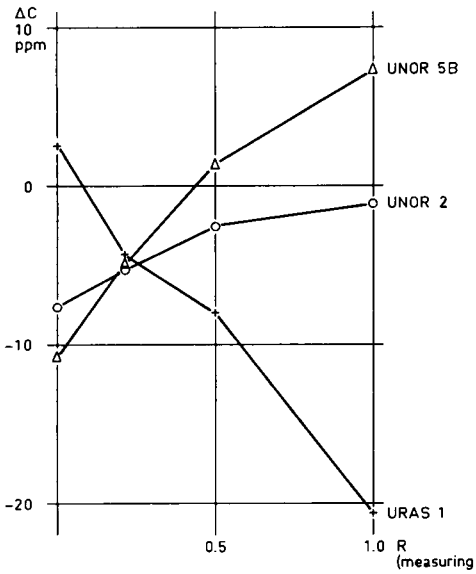

Fig. 1. Analysis index ΔC as a function of the ratio R, $O_2/(N_2+O_2)$, of the carrier gases in the *measuring cell*. Thus $R=1$ corresponds to 100 % O_2. The analysis index ΔC is the departure of an analysis from a constant comparison gas (321.4 ppm CO_2 in air).

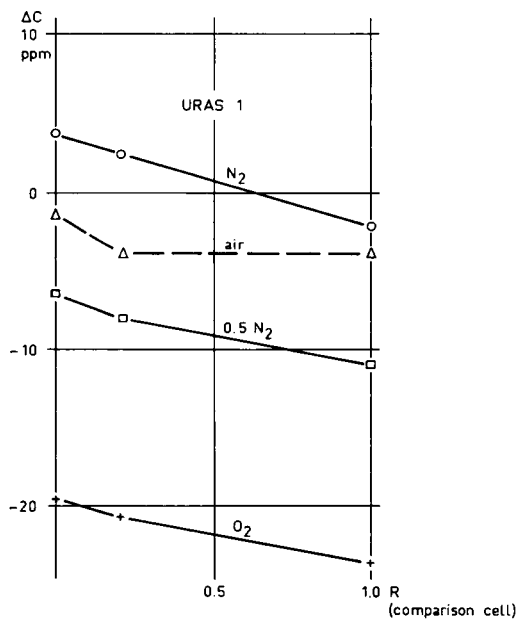

Fig. 2. Analysis index ΔC as a function of the ratio R in the *comparison cell*, plotted for various ratios R for the measuring gas, URAS 1.

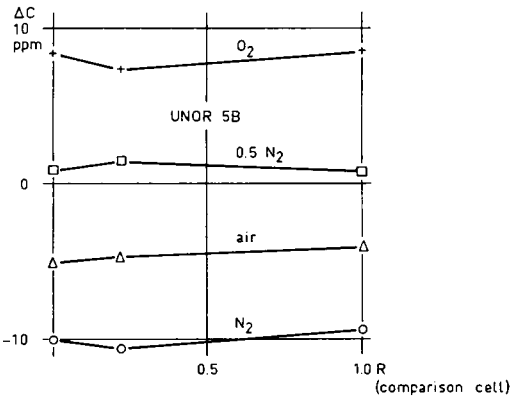

Fig. 3. Same as Fig. 2, but for the UNOR 5B.

infrared gasanalysis is with regard to the N_2/O_2 ratio of the carrier gas. It is likely that this is the result of varying absorbtion line broadening due to different foreign gas in the infrared analyzer.

Because of some differences in the analyser design, the response appears to be different for each analyzer type. However, for a N_2/O_2 ratio equal to that of atmospheric air, i.e. for $R=0.21$, nearby identical results are obtained for all three analyzers.

By repeating the experiment with different R-ratios for the comparison cell, it is furthermore found that the two types of UNOR are not much affected thereby, but the URAS is quite dependent on the value of this ratio in the comparison cell. This is shown in Figs. 2 and 3, where the deviation of the analysis index is plotted as a function of R for the carrier gas.

4. Discussion

From the result reported it is clear that the intercomparison of standards and samples as well may be complicated by the fact that different types of analyzers and gasmixtures are used within different projects. Presuming that all standards belonging to different projects are calibrated with reference to the very same primary standard system (for example Scripps standards) comparable analysis result of air samples are still obtained, as long as the analyzers of each project in turn are calibrated against a relative concentration value. Therefore, the atmospheric CO_2 data obtained from

a period of more than 10 years sampling activity (Bolin & Bischof, 1970; Bischof, 1973) are fully comparable with the Scripps data. However, the analysis and comparison system would become less complicated, if all projects were using the same kind of carrier gases.

Concluding remarks

Meanwhile, the influence of carrier gases has been investigated also by Pearman & Garratt (1974) who found similar results.

REFERENCES

Bischof, W. 1970. CO_2 measurements from aircraft. *Tellus 22*, 545–549.

Bischof, W. 1973. CO_2 concentrations in the upper troposphere and lower stratosphere. Part 3. *Tellus 25*, 305–308.

Bolin, B. & Bischof, W. 1970. Variations of the CO_2 content of the atmosphere within the northern hemisphere. *Tellus 22*, 431–442.

Pearman, G. I. & Garratt, J. R. 1974. Errors in atmospheric CO_2 concentration measurements made at monitoring stations. *Tellus 27*, 62–66, 1975.

ВЛИЯНИЕ НЕСУЩЕГО ГАЗА НА ИНФРАКРАСНЫЙ АНАЛИЗ АТМОСФЕРНОГО CO_2

Эксперименты, проделанные с различными типами инфракрасных газоанализаторов (URAS 1, UNOR 2, UNOR 5B), указывают на значительные различия в результатах измерений, если используются различные отношения смеси N_2 и O_2 в качестве несущего газа для CO_2.