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Measuring δ^{13}C of atmospheric air with non-dispersive infrared spectroscopy

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The potential use of non-dispersive infrared spectroscopy for measuring δ^{13}C in air is demonstrated. This technique has already been successfully established for breath test analyses in medical diagnostics, where the CO_2 concentration ranges from 1 to 5 vol.% in the exhaled breath of vertebrates. For breath tests, the sensitivity and accuracy has been improved to reach a standard deviation of 0.2‰ (delta-value). Further adjustments were necessary to improve the sensitivity of the instrument at concentration levels typical of atmospheric air. The long-term stability is given by a standard deviation of 0.35‰ for CO_2 concentrations of about 400 ppm with signal averaging over 60 s.

1. Introduction

Measurements of the relative deviation of the ^{13}C/^{12}C isotope ratio in a sample from the same ratio in a reference material (usually denoted by δ^{13}C) are widely used in environmental and health studies, as they present a signature of the CO_2 origin (see *e.g.*, ref. [1]). CO_2 exchange is an important aspect of the biogeochemical cycles of carbon in, among others, forestry, agriculture, biodiversity studies, paleoclimatology (ice cores), and volcanic activity. CO_2 also contributes to the green house effect. Monitoring sources of CO_2 is important for studying the ecosystem balance, as well as for verification purposes, for example, related to the Kyoto protocol. In medicine, the incorporation of a ^{13}C label into a substrate that undergoes a metabolic cycle may reveal the presence or stage of a disease, or may be used to monitor a variety of bodily functions [2–5].

The major technique for measuring isotope ratios is mass spectroscopy, which has been steadily improved, and has seen many specialised applications over the course of its history in the past 100 years. Recently, other techniques have entered this field, including opto-galvanic

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[6] and other laser-based methods [7–10], as well as F-TIR [11] and NDIR spectroscopy. Wide interest in using such techniques has been expressed, whereas commercial solutions are still rare. For example, a commercial tuneable diode laser spectrometer (TDLS) from Campbell Scientific is used for ecological studies [12]. But complexity and use of cryogenics makes this system cumbersome for general, widespread field applications.

For many environmental applications, the accuracy needed to study the physiology of the ecosystem is $0.1\permil$ or better; for example, to discriminate photosynthetic and respiratory components, detect influences from atmospheric turbulence, and to study the relations between plant carbon and water.

An NDIR type instrument for measuring $\delta^{13}C$ was first used in 1996 for the diagnosis of *Helicobacter pylori* infections, and was soon also applied in hepatology, gastroenterology, and in dietary studies, as well as in studies of lactose deficiency and pancreas function [2–5]. These breath tests have the advantage of being non-invasive and easy to perform. As the instrument is portable, robust and stable, which is a prerequisite for measurements in a clinical setting and field measurements in general, the question arises if this technique could be equally useful for ecological and environmental research. To our knowledge, the NDIR technique has not been applied to environmental or ecological field research. In one study NDIR was used for $\delta^{13}C$-measurements, after chemical CO_2 extraction from plant or soil samples [13].

In this article, we describe the adaptation of a commercial breath analyser (Wagner Analysen Technik, model IRIS2^{TM}) to the direct measurement of the $^{13}CO_2/^{12}CO_2$ ratio in atmospheric air samples. The CO_2 mixing ratio in natural air is in the range of 350–500 ppm (by volume or number density), or two orders of magnitude lower than in typical exhaled breath (roughly 4 % or 40,000 ppm).

2. Materials and methods

The breath analyser of this investigation uses the URAS14 detection module from ABB Process Industries in Frankfurt/Main, Germany. This type of module is routinely manufactured for specific medical instrumentation [14], but was modified to improve its performance at low CO_2 mixing ratios. The one-channel analyser was stripped of its calibration cuvettes (used for concentration calibration in breath analysis), which increased the optical interaction length to 20 cm, an ABB design limit for the measurement chamber.

In figure 1, the schematic of the NDIR measurement is presented. A heated filament is used as broadband IR source, which alternatively illuminates the sample and reference chamber, according to the chopper position. Both detectors, which are sensitive with high isotopic specificity to either $^{13}CO_2$ or $^{12}CO_2$, are placed in a tandem configuration after the chamber. The concentrations of the detector gas fillings were optimised for low CO_2 concentrations, while minimising cross-sensitivity arising from the overlapping part in the CO_2 spectral range. A phase-sensitive detection technique is used to measure the differential signal of both channels, using board-level lock-in amplifiers. The electronic integration time constant was set to 60 s. Absorption losses in the sample chamber finally give rise to a heat signal registered by the photo-acoustic detectors as pressure changes. With this technique, pressure differences in the picoPascal range can be observed.

Depending on the pump speed, the sample volume (140 ml) can be replaced in 40 s to several minutes. The heater block is temperature-controlled and the temperature is monitored at the heater and detector unit. The whole measurement unit is contained inside an aluminium box, which also contains a pressure sensor. A built-in pressure correction function was disabled
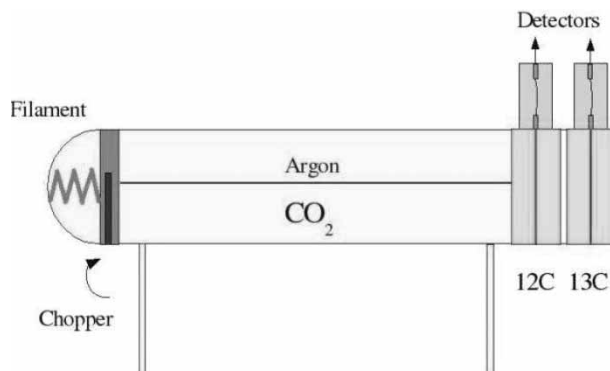
Figure 1. Schematic view of the NDIR set-up. Differential techniques are used in the measurement chamber (CO_2 path containing the sample and reference path filled with Argon) and detectors (each equipped with two compartments). Detector 1 ($^{12}CO_2$) is used as filter for Detector 2 ($^{13}CO_2$). All components are arranged along the optical axes. The whole measurement unit is mounted on a temperature controlled aluminium block. For details we refer to [5, 14].

using the ABB control software. The URAS14 module is placed into a case used for the IRIS-Doc8 medical instrument with eight inlet ports, and the IRIS-software was used for controlling the instrument and for data acquisition.

The measurement flow parameters were set as follows (total of ca. 90 s): The time in which the sample is pumped into the chamber was 20 s (inlet time), the time during which the sample is pumped in a closed loop for thermodynamic stabilisation was 10 s (waiting time) and the time between the 30 consecutive measurements was 2 s (interval). The 30 individual readings were averaged to obtain one isotope ratio determination. The inlet time of 20 s is roughly a factor of two, very short to completely replace the sample volume, but for the purpose of this measurement, namely to determine the stability of the instrument, this did not matter. Samples were introduced alternately through Port 1 ('unknown' sample) and Port 2 (reference gas).

Measurements were made at the Centre for Isotope Research of the University of Groningen. All data are taken over a period of several hours (usually overnight). Only the $^{12}CO_2$ and $^{13}CO_2$ concentration signals and pressure and temperature sensor data were output by the software. All automatic calibration procedures of the breath analyser were disabled.

3. Results and discussion

Data taken with an unmodified instrument for breath analysis (in this case a commercially available IRIS_II^{TM} from Wagner-Analysen-Technik), indicated that the standard deviation of the $\delta^{13}C$ measurement increased from 0.2 ‰ to 1 ‰ and higher, when the CO_2 concentration in the air sample was decreased from 1 % (volume) down to ambient air concentrations (0.04 %). Also, at CO_2 concentrations below 500 ppm, the measurements turned out to be increasingly non-reproducible.

After some adaptations to the atmospheric concentration range (vide supra), the NDIR instrument was tested again. To determine the instrument's stability, we chose to supply the same CO_2-in-air mixture to each of two inlet ports. The $\delta^{13}C$ value measured was the relative deviation of the $^{13}C/^{12}C$ ratio of the sample at Port 1 from the same ratio of the reference gas at Port 2. Figure 2 shows the concentration readings for the $^{13}CO_2$ detector (left y-axis, open circles and triangles) and for the $^{12}CO_2$ detector (right y-axis, full circles and triangles) over a time-period of 5 h. Data from Port 1 and Port 2 are indicated by circles and triangles, respectively.
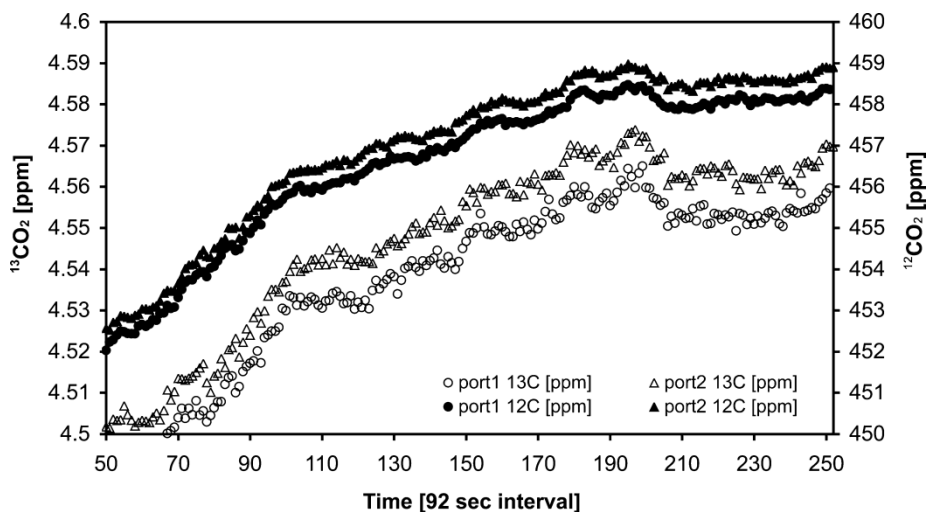
Figure 2. Raw data for $^{13}CO_2$ (left axis) and $^{12}CO_2$ (right axis) concentrations, measured at two different ports supplied with the same gas (air).

As drifts and oscillations are present for both ports, they clearly correlate to a very high degree. This is shown in figure 3, which illustrates the $\delta^{13}C$ value (of sample at Port 1 with respect to the reference material at Port 2, as mentioned before) for the same measurement series of figure 2. As expected for identical gas samples at Ports 1 and 2, the mean is close to zero. The standard deviation for 200 data points is 0.35‰ (for a 1-min signal averaging and over a 5-h time interval). This characteristic can be taken as a measure of the long-term stability of the instrument.

To reveal the characteristics of each detector separately, we calculated relative deviations based on the ratios $^{13}C_{Port\,1}/^{13}C_{Port\,2}$ and $^{12}C_{Port\,1}/^{12}C_{Port\,2}$, instead of the $^{13}C/^{12}C$ ratio. In figure 4, the open triangles represent the $^{13}CO_2$ and the closed circles represent the $^{12}CO_2$
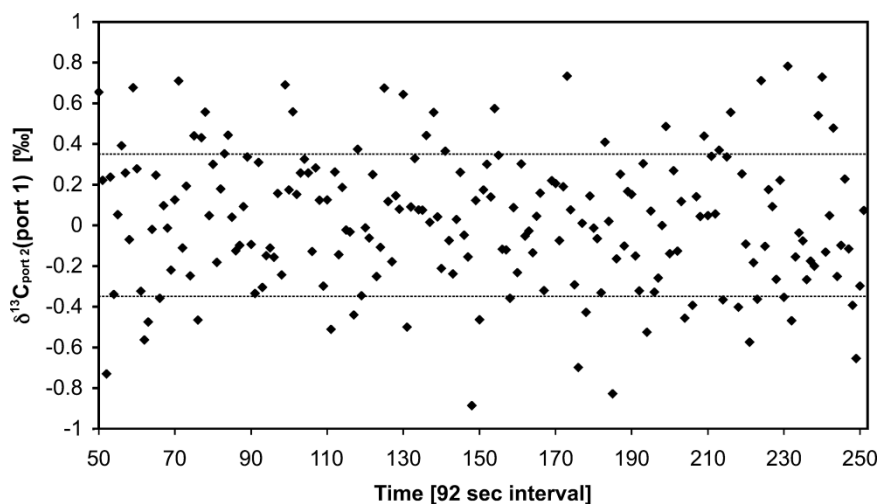

Figure 3. Relative isotope ratios ('delta-values'): Port 1 with respect to Port 2. In other words: Instead using the PDB-ratio value in the δ-calculation, the $^{13}C/^{12}C$ values of the measurement series from Port 2 are used. The resulting δ-value is indicative of the instrument stability (mean is 0.008‰ and standard deviation is 0.35‰ over a 5-h time span).
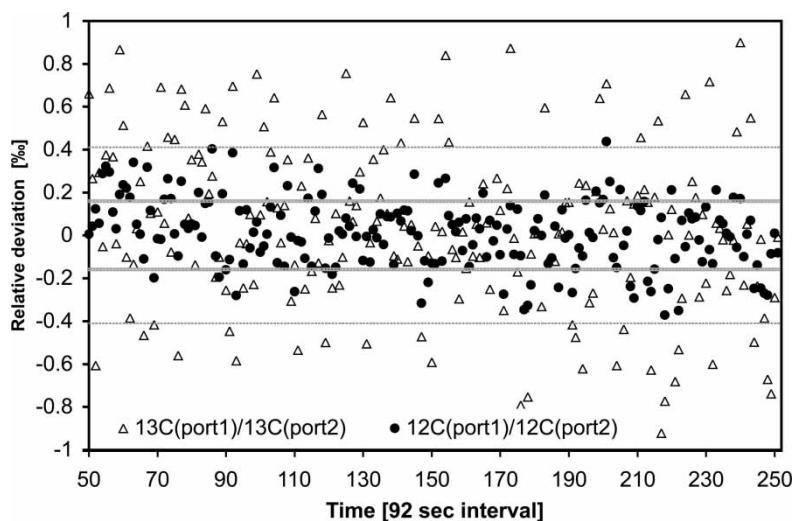
Figure 4. Delta-like values for each detector are calculated: $(^{13}CO_{2\ Port\ 1}/^{13}CO_{2\ Port\ 2}-1)$ and $(^{13}CO_{2\ Port\ 1}/^{13}CO_{2\ Port\ 2}-1)$, to reveal the stability of the detectors separately. As expected, the standard deviations, indicated by the broken horizontal lines in the figure, are larger for $^{13}CO_2$ (0.41‰) than for $^{12}CO_2$ (0.16‰).

detector behaviour, respectively. As expected the $^{12}CO_2$ signal has a better stability (standard deviation of 0.16‰) compared with the $^{13}CO_2$ signal (standard deviation of 0.41‰).

Averaging over a period of 15–30 min would further improve the variation in the data and leads to a standard error (standard deviation of the mean from a given time interval) of close to 0.1‰. Thus, the achievable precision, given the instrumental stability together with an averaging over 15–30 minutes would already be sufficient for a variety of applications in ecological and environmental research.

Further investigations with gas samples of different isotopic make-up and calibration with respect to standard materials are needed. These, as well as real-life field studies in an atmospheric monitoring station, will be carried out after first implementing another set of instrument improvements, including an improved gas handling. In addition, the software will be modified to suit the needs of environmental researchers. We believe that it is fully realistic to expect a standard deviation of 0.2‰ or better with a 1-min measuring time.

4. Conclusion

We conclude that we have successfully demonstrated the potential of the NDIR technique for $\delta^{13}C$ measurements on natural atmospheric air samples, without any sample pre-treatment or pre-concentration, with only a slightly modified version of a commercially available $^{13}CO_2/^{12}CO_2$ breath analyser. For atmospheric concentrations, the long-term stability of the instrument reaches 0.35‰ (standard deviation). The instrument is robust, does not require cryogenics, can be operated over long time-periods without operator intervention, and is relatively cheap. Together with an improved performance at low CO_2 concentrations, along the lines described in this article, such an instrument will have a profound impact on the field of atmospheric monitoring and ecological studies through its ability to measure long time series, *in situ*, and with a relatively high temporal coverage.

Acknowledgements

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