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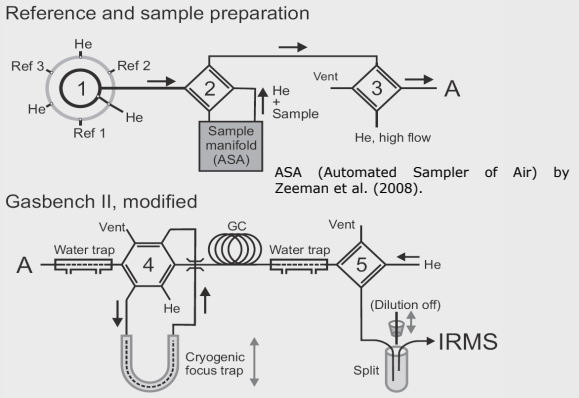
Measurement of $\delta^{13}C$ of atmospheric CO_2 on a routine basis

15th WMO/IAEA Meeting of Experts on Carbon Dioxide

Introduction:

The $\delta^{13}C$ value of CO_2 in canopy air provides information about physiological processes underlying biosphere-atmosphere net CO_2 exchange. Since CO_2 from "background air" and respiration processes have different $\delta^{13}C$ values, these CO_2 sources can be distinguished, and the coupling of terrestrial and atmospheric carbon fluxes can be addressed. The "Keeling Plot" approach (regression of the $\delta^{13}C$ of CO_2 to its inverse $[CO_2]$) can be used to determine the $\delta^{13}C$ value of ecosystem-respired CO_2 with the possibility to partition net CO_2 exchange into assimilation and respiration. This implies the precise and accurate determination of $\delta^{13}C$ in CO_2 in large numbers of air samples in order to assess temporal and spatial variability within an ecosystem.



ASA (Automated Sampler of Air) by Zeeman et al. (2008).

Figure 1: Flow diagramm of the laboratory setup. He (valve 1) is flushing sample air from the ASA (Theis et al. 2004) via valve 2 and 3 to the cryogenic focus trap of the Gasbench II (4). Simultaneously, He flows through the GC column and a diverting valve (5) to the IRMS.

Problem:

Linearity tests with gases with different CO_2 mixing ratios have shown a strong relationship between peak amplitude and corresponding δ-values.
Possible reasons:

- Signal-to-noise ratio
- Maximum linearity deviation of standard pulses tolerated by Finnigan MAT is 0.06 ‰/V
- Small memory-effect in the ASA tubing system ?

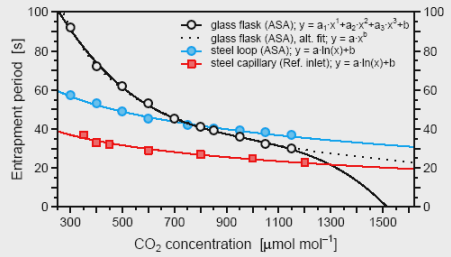


Figure 3: Empirical relations between sample CO_2 concentration and trapping time required peak amplitudes that are equal to the IRMS reference gas pulses.

Results:

- The overall precision of $\delta^{13}C$ measurements of CO_2 was determined to be <0.08 ‰ (σ) for samples with standards stored in glass flasks inside an ASA (n=33) and <0.06 ‰ (σ) for directly supplied standards (n=5), over the course of several measurement campaigns between February 2006 and March 2008.
- The $\delta^{13}C$-values of different mixing ratios of one identical source CO_2 (n=12) with synthetic air (from 300 to 1800 ppm) can be measured with a total precision of 0.04 ‰ (σ) using normalized peak amplitudes.

Laboratory setup:

- Sampling system ASA (Theis et al., 2004) modified
- Multiple reference gas inlets, sharing the flow path of the sample gas (Fig. 1, 1 + 2). Referencing after **I**dentical-**T**reatment principle (Werner and Brand, 2001) now possible
- Vents to purge the capillaries, release (over)-pressure (Fig. 1, 3 + 4)
- Modified Gasbench II with ConFlo III split allowing undiluted transfer of sample CO_2 to the IRMS
- Homebuilt cryogenic trap (Ni-wire in steel capillary)
- Automated $N_2(l)$ refill system for cold trap controlled by ISL scripts
- Software optimisation (automated adaption of trapping time)

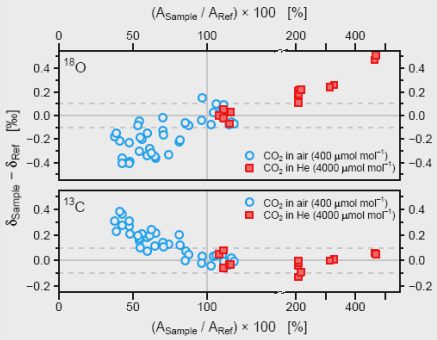


Figure 2: Linearity performance of $\delta^{13}C$ (and $\delta^{18}O$) analysis using the modified Gasbench, expressed as the deviation from the $\delta^{13}C$ (or $\delta^{18}O$) reference value vs. the relative IRMS chromatogram peak amplitude (A).

Solution:

Optimizing sample peak amplitudes close to the peak heights of the reference gas pulses by freezing the same amount of CO_2 for each sample, independent of $[CO_2]$. Implementing an ISL script which adapts trapping time relative to $[CO_2]$.

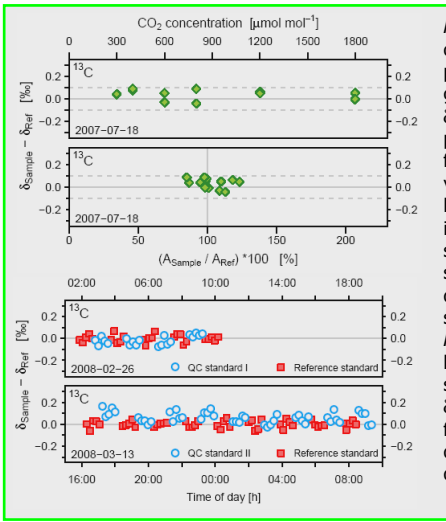


Figure 4a: Application of concentration-dependent variable cryogenic trapping time for $\delta^{13}C$ measurement. Top panel shows deviations from reference $\delta^{13}C$ value for different dilutions of the same CO_2 in air. Bottom panel shows deviation of sample peak amplitudes to corresponding standard pulses height.
Figure 4b: Deviation between measured sample and reference $\delta^{13}C$ for laboratory reference standard and 2 quality control standards.

Literature:
DE Theis et al. (2004): Rapid Comm. Mass Spectrom. 18, 2106ff
RA Werner, WA Brand (2001): Rapid Comm. Mass Spectrom. 15, 501ff
MJ Zeeman et al. (2008): Rapid Comm. Mass Spectrom. 22, 3883ff

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