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Instrumental tests and the calibration approach aimed isotope analyses of air CO₂ at JRC-IRMM

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1 Introduction

Isotope monitoring requires reliable and accurate data. For $\delta^{13}\text{C}(\text{CO}_2)$ and $\delta^{18}\text{O}(\text{CO}_2)$ measurements, the inter-laboratory compatibility targets are currently set at 0.010 and 0.050 ‰ respectively. Numerous activities are focused on consistent calibration, data treatment and corrections for all instrumental effects. Some instrumental effects relate to CO₂ cryogenic extraction from air. Thereafter each lab make their measurements linked to calibrated air cylinders and/or CO₂-air mixtures. The advantage of using calibration carrier in the same form as samples is to eliminate and/or cancel out such corrections.

However CO₂ isotope composition of mixtures in high-pressure cylinders may be modified by storage, impurities, pressure regulators, leaks etc. To solve the calibration problem(s), W.Brand (MPI-BGC, Jena, DE) started preparation and distribution of certified (CO₂+N₂O)-air mixtures; initially as inter-comparison material, with the goal to use these as calibration materials. Limited amount of the mixtures is somewhat disadvantage.

At IRMM, we needed to set-up a new lab and start high quality CO₂ isotope measurements in a short period of time. Thereafter we have based our calibration on plain CO₂ (working reference) and used CO₂-air mixtures as another calibration carrier, to test and correct for instrumental effects. We found that CO₂-dynamic mixing is really useful to test instrumental effects and optimize the system. The poster focuses on all the practical aspects and on the approach we used for a reliable calibration.

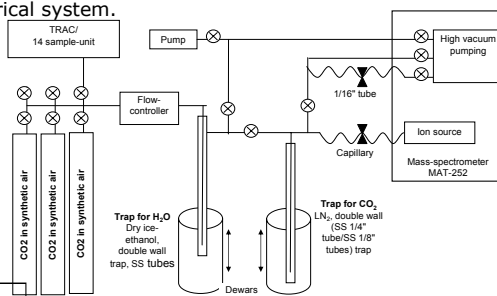
2 Extraction system:

The extraction system is based on that of W.Brand at MPI-BGC in Jena. It consists of cryogenic traps for freezing H₂O (-78°C, dry ice+ethanol) and CO₂ (-196°C, liquid N₂), a vacuum manifold with pneumatic valves and pumps. The system is compatible with the MAT-252 and runs in automated mode under ISODAT 2.0. Furthermore, its performance was investigated in great details, and there are no removable filters which need to be dried. One of important aspects – non-symmetrical geometry and capillary crimping on the sample and reference side of IRMS. CO₂-air mixtures (high pressure cylinders) running via the same extraction are assumed to be used as calibration carriers, also aimed to eliminate effects of the non-symmetrical system.

After numerous tests, the inner 1/8" gold tube in the CO₂ trap was replaced by an electropolished 1/8" SS tube (a little bended, to have thermal contact with the outer 1/4" tube, sand-blasted, washed in HNO₃ in ultrasonic bath etc.). Stainless steel is found (Werner et al., 2001) to give nearly the same trapping effects as gold. Our tests confirm this.

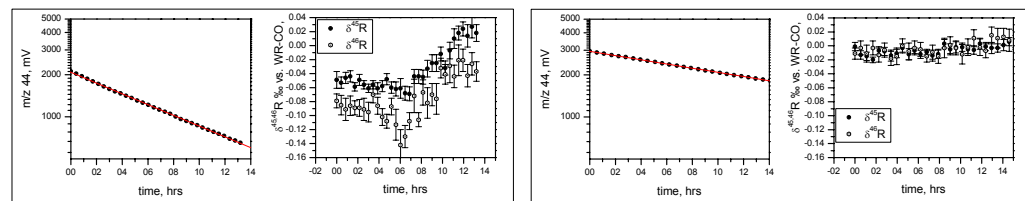
Our tests confirm this.

| Parameters | Optimized value |
|--|---|
| Air flow rate | 55 cc STP/min |
| Pressure inside the CO ₂ trap | ~160 mbar |
| Amount of CO ₂ extracted | 0.3 cc STP |
| Thawing procedure | Additional cryo-distillation step (re-freezing and pumping of air traces), final thawing of ~18 min |
| Number of change-overs | ≥ 20 |
| Integration time | 8 s |
| Idle time | 26 s |
| Total duration of a single run | ~90 min. |



Left: Parameters optimized for the CO₂ extraction system and analyses on MAT252 at JRC-IRMM.

3 Some tests:



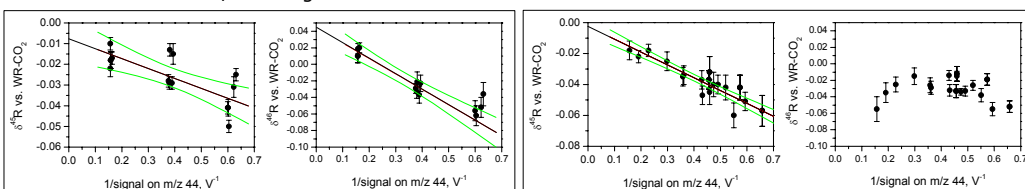
a). Symmetrical and non-symmetrical capillary crimping.

Left: Long-time zero test in the CO₂ trap with the non-symmetrical crimping. The volume was filled with pure WR-CO₂ and analyzed over 13 hours. Gradual isotope modifications started 3 hrs after filling. That means that isotope modifications (due to capillary, trap geometry etc) are stable over a single run (which lasts not longer than 1 hour) and thus the "method-related correction" can be determined on CO₂-air mixtures and applied for samples. (Errors are 2σ values based on 20 change-overs.)

Right: Long-time zero test, with symmetrical crimping. To have signals similar to the above test, more CO₂ was filled in the trap; other conditions are the same. The tests demonstrates that the use of a non-symmetrical system, with different capillary crimping and different geometry, introduces a systematic bias and thus data needs to be corrected. (Note, one cannot get an identical filling CO₂ in the ref-bellow and the CO₂ trap, thus resulting in a small offset vs. zero).

b). Dependence on the CO₂ amount (non-symmetrical crimping).

The dependence of relative $\delta^{45}\text{R}$ and $\delta^{46}\text{R}$ on the CO₂ amount extracted from the dynamic dilution mixture based on WR-CO₂ ("true" $\delta^{45}\text{R}$ and $\delta^{46}\text{R}$ are expected to be zero). $\delta^{45}\text{R}$ values of CO₂ extracted from the dynamic mixture demonstrate the amount-dependence, the intercept of the $\delta^{45}\text{R}$ trend line agrees with expected $\delta^{45}\text{R}=0$ (left and right panels below). However $\delta^{46}\text{R}$ values sometimes demonstrate a linear trend with a positive intercept (left, presumably effect of NO₂) and sometimes do not demonstrate a clear trend (right). This implies that several effects play a role for $\delta^{46}\text{R}$, namely modification by extraction (negative shift), NO₂ formed in the ion source (positive shift), contamination and/or background in MS.



4 Calibration approach:

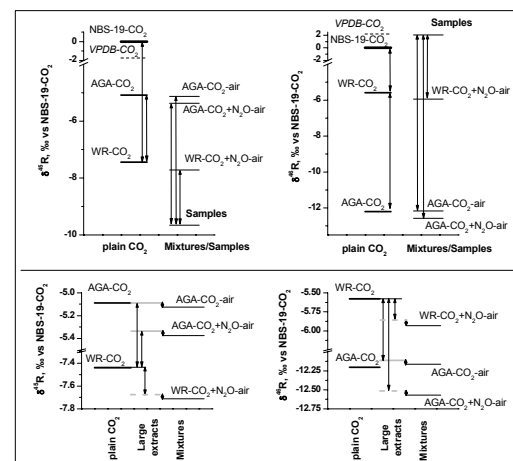
• WR-CO₂ works as the first calibration carrier, then several CO₂-air mixtures are used in order to determine the overall-correction (Mixtures serve additional calibration carriers). In this any deviation in the system performance can easily be recognised;
• CO₂-air mixtures (with and without N₂O) are based on "known CO₂". That helps to check the trueness of the N₂O correction and the overall correction and independently test each of effects included in the "overall-correction". That approach together with dynamic dilution (relative $\delta^{45}\text{R}$ and $\delta^{46}\text{R}$ are to be zero) also can help recognising any drift.

5 CO₂-air mixtures (with and without) N₂O based on "known CO₂".

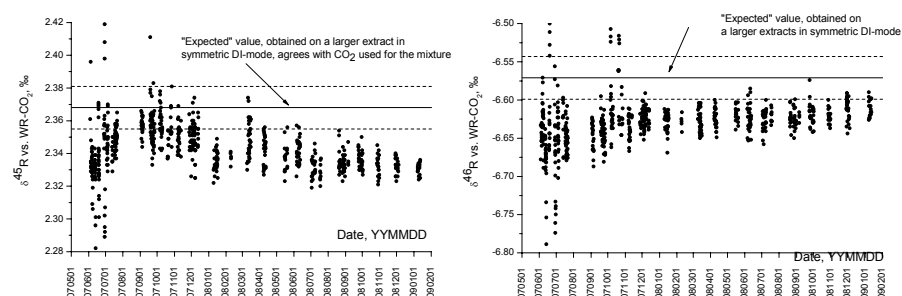
• True delta values for mixtures are determined on large extracts transferred to symmetrical bellow system (zero-enrichment was demonstrated). The values agreed with the values of plain/"mother" CO₂ gases.
• The fact that mixtures agree with the "mother" CO₂ gases, helped us to check and control the N₂O correction as well as the trueness of the overall correction. Several distances may be measured, these are shown on the figure as arrows.

Upper panel: the measurement scheme on plain CO₂ gases and on air samples. Here the calibration link between plain CO₂ and CO₂-air mixtures is missing.

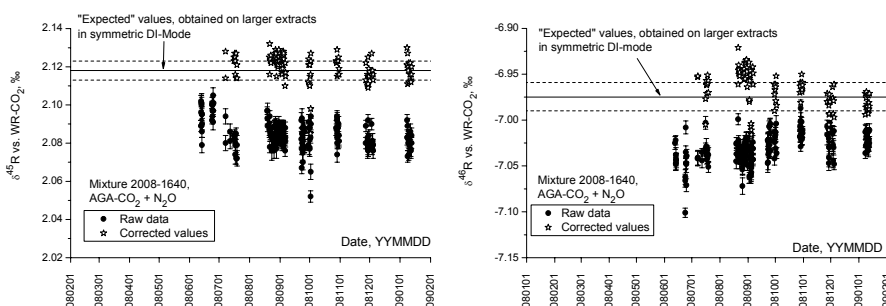
Lower panel: realisation of this link. Large extracts from the mixtures analysed in symmetrical DI-mode gave "true" values (agreed with values of "mother" CO₂). The distance (small arrows) between actual values obtained on a mixture and corresponding "large extracts" gives the correction magnitude. Other distances have been measured as well, proving our calibration approach.



6 Performance tests.



Raw data obtained on two (twin) AGA-CO₂-air mixtures (without N₂O) prepared in MPI-C, Mainz. The mixtures were used to obtain the overall correction. From the scatter, typical 1σ are estimated as about 0.01 ‰ for $\delta^{13}\text{C}(\text{CO}_2)$ and 0.015 ‰ for $\delta^{18}\text{O}(\text{CO}_2)$ (first guess estimation).



The mixture 2008-1640 (Air Liquide, Belgium), based on the aliquot of AGA-CO₂ in synthetic air doped with N₂O. Shown are raw data and the corrected values (the "overall" method-related correction is based on runs on AGA-CO₂-air mixtures). Some outliers from the expected values may be to insufficient preconditioning of the pressure regulators and connecting lines. (Shown are 1σ values.) Estimated 1σ values are similar as those on the Figure above.

Summary:

- The extraction line was found to modify $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of analyzed CO₂ and a dependence on the CO₂ amount was observed. Among the most crucial effects were (i) a non-symmetrical crimping of capillaries; (ii) $\delta^{46}\text{R}$ increase due to air traces; (iii) initial problems with traces of oil vapor, which can be addressed by use of scroll pumps to back-up turbo pumps;
- The calibration approach at JRC-IRMM is based on the use of WR-CO₂ as a calibration carrier (calibrated vs. NBS-19-CO₂) and CO₂-air mixtures (another calibration carrier, calibrated vs. WR-CO₂) as the means to determine an overall "method-related" correction. The approach, together with use of a symmetrical DI mode for calibration periods, permitted us to decouple and determine magnitude of each instrumental effect separately. The approach at JRC-IRMM may be considered as a complimentary one to the principle to use CO₂-air mixtures solely as a calibration carrier as recommended by WMO/GAW.
- CO₂-air mixtures based on "known" CO₂ with and without N₂O were tested, in order to independently quantify/prove the overall "method-related" correction as well as N₂O-correction. $\delta^{13}\text{C}(\text{CO}_2)$ on extracts from mixtures agree within 0.010 ‰ with values obtained from the "mother" CO₂ used for the mixtures.
- Based on the data scatter observed for CO₂-air mixtures and simplified error balance, total combined uncertainty in $\delta^{13}\text{C}(\text{CO}_2)$ and $\delta^{18}\text{O}(\text{CO}_2)$ on the VPDB-CO₂ scale was estimated as ± 0.040 ‰ and 0.060 ‰ (2-σ values).