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A system for high-quality CO_2 isotope analyses of air samples collected by the CARIBIC Airbus A340-600

S. Assonov[1]*, P. Taylor[1] and C. A. M. Brenninkmeijer[2]

[1]JRC–IRMM, Retieseweg 111, Geel 2440, Belgium
[2]MPI for Chemistry – Air Chemistry Division, Joh, Becherweg 27, Mainz 55128, Germany

In 2007, JRC-IRMM began a series of atmospheric CO_2 isotope measurements, with the focus on understanding instrumental effects, corrections as well as metrological aspects. The calibration approach at JRC-IRMM is based on use of a plain CO_2 sample (working reference CO_2) as a calibration carrier and CO_2-air mixtures (in high-pressure cylinders) to determine the method-related correction under actual analytical conditions (another calibration carrier, in the same form as the samples). Although this approach differs from that in other laboratories, it does give a direct link to the primary reference NBS-19-CO_2. It also helps to investigate the magnitude and nature for each of the instrumental corrections and allows for the quantification of the uncertainty introduced. Critical tests were focused on the instrumental corrections. It was confirmed that the use of non-symmetrical capillary crimping (an approach used here to deal with small samples) systematically modifies $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$, with a clear dependence on the amount of extracted CO_2. However, the calibration of CO_2-air mixtures required the use of the symmetrical dual-inlet mode. As a proof of our approach, we found that $\delta^{13}C(CO_2)$ on extracts from mixtures agreed (within 0.010‰) with values obtained from the 'mother' CO_2 used for the mixtures. It was further found that very low levels of hydrocarbons in the pumping systems and the isotope ratio mass spectrometry (IRMS) instrument itself were critical. The m/z 46 values (consequently the calculated $\delta^{18}O(CO_2)$ values) are affected by several other effects with traces of air co-trapped with frozen CO_2 being the most critical. A careful cryo-distillation of the extracted CO_2 is recommended. After extensive testing, optimisation, and routine automated use, the system was found to give precise data on air samples that can be traced with confidence to the primary standards. The typical total combined uncertainty in $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ on the VPDB-CO_2 scale, estimated on runs of CO_2-air mixtures, is ±0.040‰ and 0.060‰ (2-σ values). Inter-comparison with MPI-BGC resulted in a scale discrepancy of a similar magnitude. Although the reason(s) for this discrepancy still need to be understood, this basically confirms the approach of using specifically prepared CO_2-air mixtures as a calibration carrier, in order to achieve scale unification among laboratories. As important practical application and as a critical test, JRC-IRMM took part in the passenger aircraft-based global monitoring project CARIBIC (http://www.caribic-atmospheric.com). In this way, reliable CO_2 isotope data for the tropopause region and the free troposphere were obtained. From June 2007 to January 2009, approximately 500 CARIBIC air samples have been analysed. Some flights demonstrated a compact correlation of both $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ with respect to CO_2 concentration, demonstrating mixing of tropospheric and stratospheric air masses. These excellent correlations provide an independent, realistic data quality check. Copyright © 2009 John Wiley & Sons, Ltd.

The importance of CO_2 in the reductive-oxidative cycle on earth and its fundamental link with the biosphere are beyond dispute. The seasonal cycling of CO_2 reflects mainly biospheric activity, from periods when respiration dominates to periods of massive photosynthetic activity. During the Anthropocene, a significant fraction of global climate warming has been attributed to the superimposed increase of CO_2 which mankind is now attempting to abate. The global CO_2 cycle is extraordinarily complex and variable. While mankind's contribution to the total input of CO_2 into the atmosphere is the best known part of the budget, it has little impact compared with the large natural fluxes and their variability in space and time. The latter fluctuations relate to oceans, terrestrial ecosystems, and biomass-burning.

Various approaches have been used to tackle the problem of quantifying the balance of CO_2, including monitoring concentrations in a variety of ways – measuring fluxes, studying exchange processes (over the ocean and vegetation), $^{14}CO_2$ measurements, and also stable isotope measurements.[1–3]

Correspondence to: S. Assonov, JRC–IRMM, Retieseweg 111, Geel 2440, Belgium.
E-mail: assonov_sergey@yahoo.com

Isotope analyses of unpolluted air-CO_2 require accuracy as well as long-term consistency in scale, agreement among laboratories, and reliably precise calibration. This reliability particularly applies to longer-term projects, and to endeavours like CARIBIC,[4] where air representative of large air masses is sampled from the upper troposphere and the lower stratosphere. The relevant aspects have been addressed during WMO/IAEA Meetings of Experts on Carbon Dioxide Concentrations and Related Tracer Measurement Techniques, with recommendations to ''develop high-quality measurements of carbon cycle tracers that can be used to attribute natural fluxes to their controlling processes ($^{13}CO_2$, O_2/N_2, ^{18}OCO)''.[5] Inter-laboratory data compatibility targets for air-CO_2 isotope measurements are set at 0.01‰ for $\delta^{13}C(CO_2)$ and 0.05‰ for $\delta^{18}O(CO_2)$).[6] Adherence to these recommendations is an analytical challenge and much work is required on the use of reference materials (RMs). Brand and colleagues at the Stable Isotope Laboratory of the Max-Planck-Institute for Biogeochemistry (MPI-BGC, Jena, Germany) have performed extensive studies in this field.[7–11] That facility has been selected as the central calibration laboratory for air-CO_2 isotope measurements and it prepares and distributes JENA-reference air sets (JRAS) aimed at reaching inter-laboratory data compatibility targets.[12] Round-robin inter-comparison programmes have demonstrated that laboratories working with ambient air-CO_2 measurements attain better consistency in $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$) for air than that for pure CO_2 gases.[13,14] This implies that much work still needs to be done.

In 2007, the Institute for Reference Materials and Measurements of the Joint Research Centre of the European Commission (JRC-IRMM) began to carry out atmospheric CO_2 isotope measurements in collaboration with the Max-Planck Institute for Chemistry (Mainz, Germany) through the project CARIBIC. The project has involved air-CO_2 isotope analyses, both in terms of actual measurements of air samples in the monitoring project and in measurement methodologies, calibration issues, and data treatment. The JRC-IRMM has focused on error budget analyses, including all corrections involved (instrumental corrections, extraction-related correction and N_2O correction) and traceability to the level of the primary reference material NBS-19-CO_2.

The CARIBIC automated instrument container is installed monthly on a Lufthansa Airlines passenger aircraft for measurement flights from Frankfurt to long-range destinations (China, South and North America, India), at altitudes of 9 to 12 km. The use of commercial aircraft has been a powerful, cost-effective approach to study atmospheric composition (a wide range of compounds and species) and dynamics on a global scale. A consortium of 11 institutes from several EU countries operates CARIBIC.[15] In the automated container, real-time measurements of O_3, CO, NO, and aerosols, among others, are carried out. Moreover, air sampling for subsequent laboratory analyses of CO_2, N_2O, CH_4 and SF_6 and other trace compounds (non-methane hydrocarbons, oxygenated and chlorinated hydrocarbons) takes place. These extensively analysed air samples have been used for the isotope analyses discussed here.

CO_2 isotope measurements on air samples started at JRC-IRMM in June 2007. By January 2009 about 500 CARIBIC samples had been analysed, giving a reliable CO_2 isotope data set for the monitoring program. The present manuscript describes technical-analytical aspects and the calibration approach and briefly considers the error budget analyses; recommendations on the raw data treatment are given elsewhere.[16] Data of two flights are included, while interpretation of the whole data set will be published separately (in preparation).

CO_2 ISOTOPE ANALYSES BY MASS SPECTROMETRY

CO_2 isotopic analyses were performed by isotope ratio mass spectrometry (IRMS) on a MAT-252 instrument (Thermo-Finnigan, Bremen, Germany). Analyses on CO_2 extracted from air samples were typically performed in the dual-inlet (DI) mode which provides higher precision and accuracy than the continuous-flow (CF) mode.

The principle of the DI mode is a repeated sample-reference comparison under identical conditions. The three main CO_2 ion beam currents (m/z 44, 45 and 46) are measured and the ion signal intensity ratios $^{45}I/^{44}I$ and $^{46}I/^{44}I$ are calculated. Sample gas and working reference CO_2 (WR-CO_2) are introduced into the ion source via capillaries. The main ion currents at m/z 44 from the sample and WR-CO_2 are balanced and each measurement includes at least 10 changeovers. By calculating relative delta values ($\delta^i R_{sample} = (^i I/^{44}I_{sample}/^i I/^{44}I_{working\ ref.\ CO2} - 1)$ for each changeover, the $^{ti}I/^{44}I$ ratios of a sample are directly linked to that of the WR-CO_2. The average $\delta^i R$ and its standard error (internal precision) are then calculated using N changeovers.

Measured $\delta^i R$ ratios are corrected for known instrumental effects such as cross-contamination/scale shrinking due to ion source memory,[17,18] isotope effects due to cryogenic extraction (method-related correction) and N_2O isobaric interference. Each correction requires quantification by designated tests. $\delta^i R_{sample}$ values are scaled to the primary reference material NBS-19-CO_2, the anchor of the VPDB-CO_2 scale. As a last step, $\delta^{13}C$ and $\delta^{18}O$ values are calculated by applying the ^{17}O correction.[16]

Tests for the mass spectrometer performance

Tests of system stability, signal stability, pressure linearity, peak flatness and abundance sensitivity were performed regularly and these met specifications. To reduce the cross-contamination for CO_2, the ion source conditions were set as follows:

(i) ion source slits and lenses machined of tantalum were used.[18,19]

(ii) the pumping window of the ion source was fully open (high conductance).

(iii) the ion source was tuned (high linearity mode) under reduced emission current (0.875 mA instead of 1.50 mA).

Although steps (ii) and (iii) reduce sensitivity (2 times and 1.4 times, respectively), and thus increase the noise-to-signal ratio, they also reduce cross-contamination to almost zero.

The required signal integration time was tested by 'zero-enrichment' runs. Here, the raw data scatter mainly arises from instrumental fluctuations (emission, stability of amplifiers, and feedback resistors). Measurements using an 8 s integration time demonstrated the best internal reproducibility, namely 0.005‰ for $\delta^{45}R$ and 0.008‰ for $\delta^{46}R$ (1-σ, n = 10). Integration for 4 s gave still reasonable results, whereas measurements for 2 s gave a large scatter. Based on zero tests, an integration time of 8 s and a changeover number of $\geq$20 were selected.

Tests proving a symmetrical DI mode

Completely identical behaviour of two capillaries from the two bellows (a symmetrical DI mode) was not obvious. However, 'zero-enrichment' tests as well as the good agreement between $\delta^{13}C$ and $\delta^{18}O$ measurements of reference CO_2 gases with published values (see below, also Table 2) proved that the DI mode was symmetrical.

Cross-contamination

For CO_2, two types of memory effects in the MAT-252 ion source have been discussed:[19] a short-lived memory effect ($t_{1/2}$ of a few seconds) and a longer memory effect (when the ion source is not optimised, $t_{1/2}$ may be up to 10 min). These effects are of a different nature. The short-lived memory is probably due to the trapping of gas in hidden volumes and some gas adsorption. The longer-lived memory has been described[18] as including gas trapping in the form of chemisorption,

gettering (by newly formed reactive films, re-deposition of sputtered metal) and ion implantation. Both sputtering and implantation are prominent at high accelerating voltage, relevant to the MAT-252 operating at 10 kV (all other IRMS machines for light elements (C, N, O, S) operate at much lower voltages). Gas trapped in implanted and chemical forms cannot be released without re-processing through ion bombardment. To minimise the effects, Verkouteren *et al.*[18,19] proposed the use of ion source slits of tantalum (installed). They further advised ion source tuning under reduced emission current (applied) and a somewhat reduced accelerating voltage (not applied). The two last measures work more or less in the same way.

The magnitude of cross-contamination was evaluated by measuring two CO_2 gases with a large isotope difference using variable ion source flushing times ('idle time'). The idle time was first varied up to 300 s (maximum in the control software); after optimisation, only times of 26 s and 180 s were used for testing. We observed after the ion source cleaning and under stable conditions (23-04-2007, 7 months after cleaning) a scale contraction of 0.015‰ ($\Delta\delta^{45}R \approx -35.33‰$) and 0.020‰ ($\Delta\delta^{46}R \approx -21.71‰$) (Fig. 1).

The cross-contamination can be defined by the value η as follows:[17]

$$\eta = [\delta_{true} - \delta_{meas.}]/[\delta_{true} \cdot (2 + \delta_{meas.})] \qquad (1)$$

Values of $\eta_{45} = 2.0 \cdot 10^{-4}$ and $\eta_{46} = 4.6 \cdot 10^{-4}$ were determined on 23 April 2007 and these agree well with the values
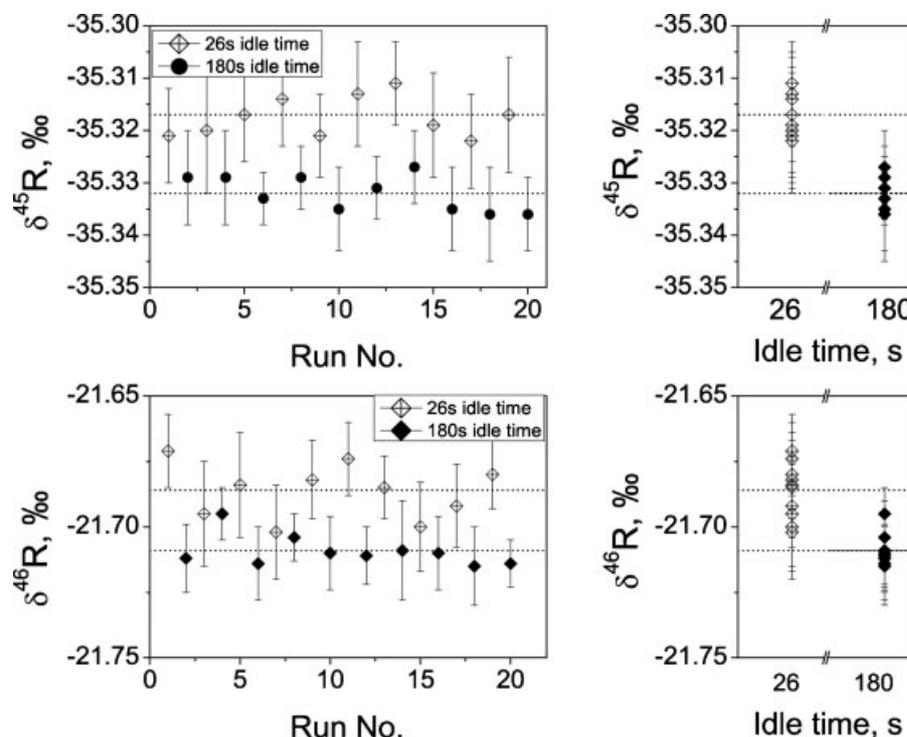

Figure 1. $\delta^{45}R$ and $\delta^{46}R$ values obtained with idle times of 26 s (○) and 180 s (●) in fully symmetrical DI mode (shown are 2-σ values, internal precision). The discrepancy of 0.015‰ and 0.020‰, respectively, is observed for the large isotope difference between two gases (-35.33 and $-21.71‰$ in $\delta^{45}R$ and $\delta^{46}R$, respectively). The corrections for air samples analysed vs. WR-CO_2 are ~0.001‰ and 0.007‰, respectively.

$\eta_{45} = 1.9 \cdot 10^{-4}$ and $\eta_{46} = 4.3 \cdot 10^{-4}$ determined on 18 October 2008, showing that the effect was stable over time. (As the cross-contamination may depend on the CO_2 signal, tests should be done at the same signal as for actual samples.)

Our value of η_{45} is higher than that of $8.7 \cdot 10^{-5}$ estimated by Ghosh et al.[7] We stress that their method (tracing the decay of the m/z 44 signal after closing both changeover valves) gives a quick check only. This takes into account only a short-lived memory effect and does not appear to include the long-term effect as also demonstrated by their Fig. 8.[7] Gas trapped by chemisorption, gettering, and implantation[18] cannot be released without re-processing by incident ion beam/ion bombardment. In our opinion, their method[7] underestimates the magnitude of cross-contamination by at least a factor of 2. The novel approach to test and/or correct for cross-contamination is to scale data to the 2nd anchor (LSVEC) of the δ^{13}C-VPDB-CO_2 scale.[20] To apply it to CO_2-air analyses, one can analyse CO_2 characterised on the two point δ^{13}C-VPDB-CO_2 scale; available reference CO_2 gases are NIST RMs CO_2 8562-8564.[20]

Our tests demonstrated that the scale contraction is very small. The δ^{45}R difference between the actual air samples and WR-CO_2 is around 2.5‰; thus, the cross-contamination correction of 0.001‰ in δ^{45}R can be neglected. For δ^{46}R the correction would be around 0.007‰ which, being less than the uncertainty in δ^{46}R due to other effects, rendered the correction unnecessary (also avoiding an associated increase of uncertainty).

Residual background

The MAT-252 instrument had an elevated background of hydrocarbons (both the pumping system and the analyser) as evidenced by increased scatter for δ^{45}R (due to proton donation) and an increased signal on m/z 55 (typical for hydrocarbons). Thereafter, the pumping system was modified as follows.

(i) In July 2007, the pumping system was cleaned and all crucial parts (changeover valves, ion source housing, manifolds, cold traps) heated at $\sim 80°C$. Catalytic oil traps (URB-025, Pfeiffer, Aslar, Germany) were installed on the rotary fore-pumps.

(ii) In January 2008, an ion-getter pump (40 L/s, StarCell Varian Inc., Palo Alto, CA, USA) was installed at the waste side of the change-over valves, with a separating valve between the ion-getter pump and the turbo-pump. Thereafter, the vacuum in the waste line dropped to $\sim 6 \cdot 10^{-7}$ mbar with gas load (measured by the ion-getter pump current) and $\sim 2 \cdot 10^{-8}$ mbar without gas load.

(iii) In March 2008, a Pfeiffer oil-free pumping station was installed (TSH 071E pump backed-up by a diaphragm pump) to pump the bellows and the CO_2 extraction line.

(iv) In June 2008, the oil-based fore-pumps of the turbo-pumps were replaced by Varian scroll pumps SH-110 (vacuum of $1 \cdot 10^{-1}$ mbar) and IDP3 (vacuum of $1.7 \cdot 10^{-1}$ mbar).

From mid-2007 to the end of 2007, the signal on m/z 55 decreased from 12 mV (as registered on cup-45, CO_2 gas load on) to 0.5 mV. In 2008 the signal had stabilised at 0.3 mV.

THE CO_2 EXTRACTION LINE AND TESTS

Hardware

The extraction system is based on that of Brand and co-workers at MPI-BGC in Jena.[9] It consists of two cryogenic traps (Fig. 2) for freezing H_2O ($-78°C$, dry ice + ethanol) and CO_2 ($-196°C$, liquid N_2) in a vacuum manifold with pneumatic valves and pumps. The system is compatible with the MAT-252 and runs in automated mode under software control. There are no removable filters which require to be dried (e.g.,[21,22]).
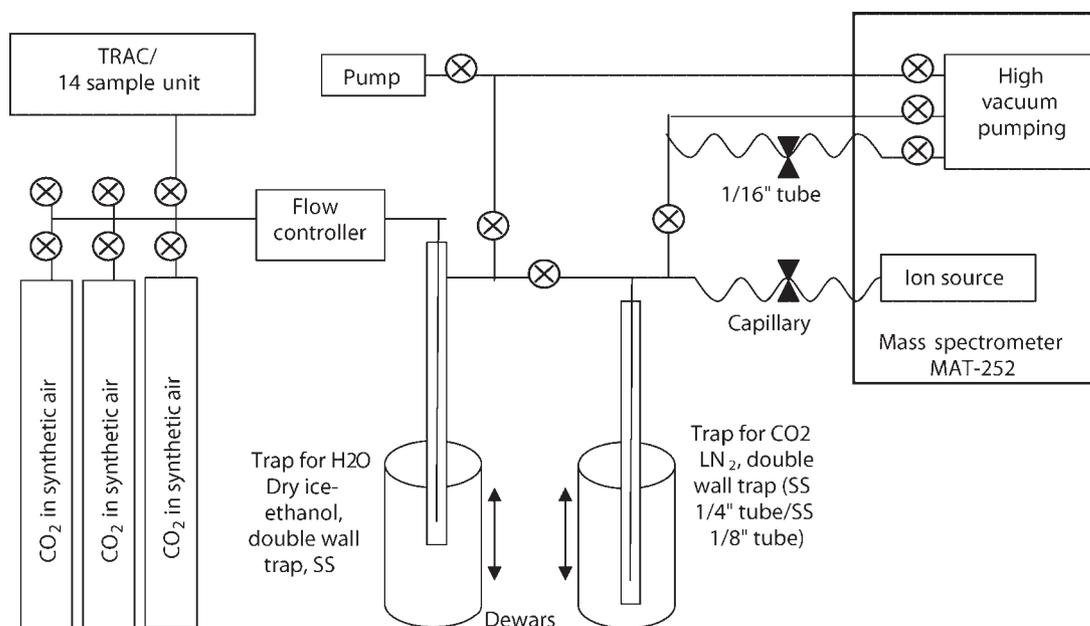

Figure 2. Schematic diagram of the CO_2 extraction line. The line is based on the system at MPI-BGC, Jena.[9]

The extraction line was custom-made (Masstech, Bremen, Germany) without final testing. After installation and preliminary tests, some valves were rearranged to minimise the trap volume and thus increase the CO_2 pressure; this minimises capillary-related effects. Two pneumatic valves (Swagelok®, part SS 4BK-1C; Swagelok, Solon, OH, USA), a mass-flow controller of 0–100 cc min^{-1} (MKS®; Andover, MA, USA), and a six-multi-port inlet (one of the multi-port inlets of the MAT-252) were also installed. The CO_2 trap is connected to the changeover valve via a capillary. As recommended,[9] only 316 stainless steel (SS) capillaries from VICI Valco (part no. T100C5D, tube kit 1/16 ''0.005''/ 0.12 mm; VICI Valco, Houston, TX, USA) are used[a].

After numerous tests, the inner 1/8″ gold tube in the CO_2 trap[9] was replaced by an electropolished 1/8″ SS tube (a little bent to make thermal contact with the outer 1/4″ tube, sandblasted, washed in HNO₃ in an ultrasonic bath, followed by multiple washes with Milli-Q water; Millipore, Billerica, MA, USA). As gold is extremely ductile, eliminating leaks in the system was rather difficult. We found that stainless steel gave nearly the same CO_2 trapping effects as gold.

ISODAT 2.0 software (ThermoFinnigan) is used to control the pneumatic valves, pneumatic lifts for the Dewars, and the 16-position VICI-Valco® valve inside the sampling container (a step-forward actuation). The MKS mass-flow controller is set manually. Liquid N₂ and dry ice are filled manually. The line works in an automated mode, performing ~16 runs in 24 h (reference mixtures and/or samples).

The CARIBIC sampling units (TRACs) each contain 14 air flasks. The inlets and outlets of the 2.7 L flasks volume are all connected to the ports of two VICI-Valco® 16-position valves. Two positions at each Valco valve are free and connected via tubing (which basically replaces a flask position). In flight, before sampling, each flask is flushed with ambient air for 5 min and subsequently filled with sample air to ~3 bar; sampling lasts ~1 min, covering ~20 km flight distance. As ambient air at altitudes of 9 to 12 km is dry, no drying agents have been used. Details on the CARIBIC project and the sampling procedure are given elsewhere.[15] Six TRAC units are rotated among up to five laboratories in five countries.

For measurement, the outlet of a TRAC unit is connected to the inlet of the extraction line, with one of the laboratory 'CO₂-air' mixtures connected to the TRAC inlet. On selecting a flushing line in the TRAC, the 'CO₂-air' mixture is directed to the extraction system; this verifies the performance and absence of contamination in the TRAC connection lines. Other laboratory 'CO₂-air' mixtures are connected directly to other inlets of the extraction line.

Tests

Obtaining high-quality isotope data on ambient air CO_2 is a challenge as several small, sometimes subtle effects may cause deviations.[9] The main tests carried out were:

1. *Verification of complete CO_2 extraction.* An air flow at 55 cc min^{-1} and a pressure in the trap of ~160 mbar (regulated by crimping a 1/16″ tube to the respective

pump) were found to correspond to ~100% CO_2 extraction. When the first and the second trap were connected in series and both were immersed in liquid N₂, no CO_2 was detected in the second trap. The two traps have identical dimensions and therefore have the same 100% efficiency. ~0.3 cc STP CO_2 is found to give a stable performance. The extraction (380 ppm CO_2) lasts 900 s.

2. *Isotope modifications of pure CO_2 by the trap.* Repeated freeze/thaw cycles were carried out of pure WR-CO₂ expanded in the CO_2 trap. No effect on $\delta^{45}R$ was observed but a small drift of $\delta^{46}R$ occurred (Fig. 3). The drift in $\delta^{46}R$ is probably due to known $\delta^{18}O(CO_2)$ effects on a metal surface[9] and/or accumulated air traces which give a m/z 46 ion from NO₂ in the ion source.[9,23] The test proves an absence of undesirable effects by the trap itself on pure CO_2.

3. *Cleanliness of the vacuum system.* Initially, a large scatter of $\delta^{45}R$ and $\delta^{46}R$ on the same CO₂-air mixture was observed over a single day (data before Mid-July 2007 in Fig. 4(a)). As the isotope integrity of the WR-CO₂ is beyond doubt, the contamination was assumed to be related to the CO_2 extraction process, e.g., contamination accumulated during freezing, pumping of frozen CO_2, and other steps. After cleaning the pumping system in mid-July 2007 and installing the ion pump in January 2008 (see above), the $\delta^{45}R$ and $\delta^{46}R$ scatter was significantly reduced (Fig. 4(a)).

4. *Verification of $\delta^{18}O(CO_2)$ equilibration.* To obtain reliable $\delta^{18}O(CO_2)$ data, CO_2 needs to be equilibrated on the metal surface for ~20 min before analysis.[9] The effect was tested by a sequence of 12 extraction runs performed
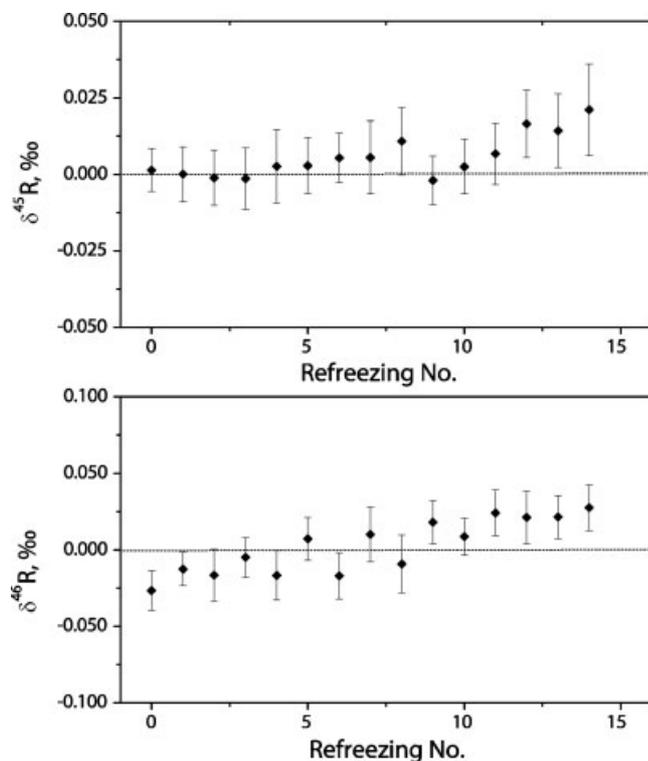

Figure 3. The effects of several freeze/thaw cycles of WR-CO₂ admitted to the cold trap on $\delta^{45}R$. Shown are 1-σ values. 0 and 7 correspond to runs without refreezing. The horizontal line shows the expected values for this (original) CO_2. Given are 2-σ values based on 20 changeovers (internal precision).
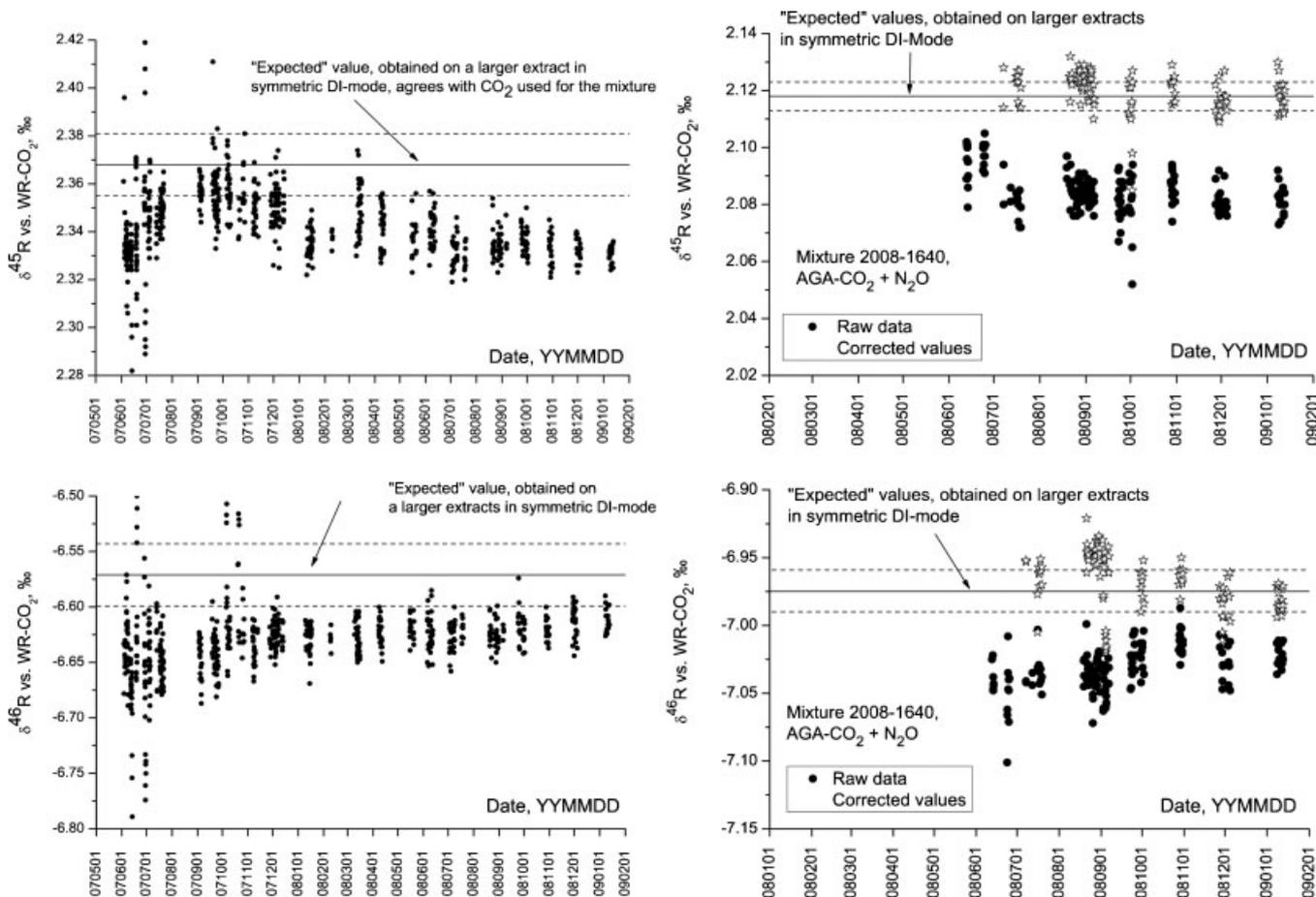
Figure 4. (a, left) Data on two (twin) AGA-CO_2-air mixtures (without N_2O) prepared in MPI-C, Mainz, April 2007 (10-L cylinders, Scott-Marrin Inc., filled to ~85 bar). The two cylinders have the same $\delta^{13}C(CO_2)$ and constant offset of 0.106‰ in $\delta^{18}O(CO_2)$. (The data of the second/twin mixture are corrected for this offset so that data of two mixtures can be plotted together.) From the scatter, typical 1-σ values are estimated as about 0.01‰ for $\delta^{13}C(CO_2)$ and 0.015‰ for $\delta^{18}O(CO_2)$ (first guess estimation). (b, right) Mixture 2008-1640 made by Air Liquide, Belgium (50-L aluminium cylinder, ~150 bar), based on the aliquot of AGA-CO_2 in synthetic air doped with N_2O. Shown are raw data and the corrected values (the 'method-related' correction based on runs on AGA-CO_2-air mixtures). Some outliers from the expected values may be due to insufficient preconditioning of the pressure regulators and connecting lines. From the scatter, typical 1-σ estimated are similar to those in (a).

using a '$CO_2 + N_2O$-air' mixture with a large isotope difference relative to the WR-CO_2. Each run consisted of a 'short' analysis (initial extraction, thawing for ~5 min, analysis), followed by an additional freezing of the remaining CO_2, pumping of non-condensable gases, thawing + equilibration for 20 min and re-analysing the remaining CO_2. No effect was observed for $\delta^{45}R$ ($\delta^{13}C$). The $\delta^{46}R$ ($\delta^{18}O$) values obtained on initial extracts had a positive bias which disappeared after longer equilibration (Supplementary Figure S1, see Supporting Information). The additional cryo-distillation (freezing + pumping non-condensable gases) also helps to purify the extracted CO_2 from traces of air which corrupt the $\delta^{46}R$ measurement due to NO_2 production in the ion source.[9,23] Thereafter, an additional cryo-distillation step and 20 min of equilibration were used.

5. *Evaluation of asymmetrical capillary crimping.* To obtain a strong signal from a limited amount of extracted CO_2 while having isotopically unaltered WR-CO_2 over a long sequence, Werner *et al.*[9] advised mismatched capillary crimping. The crimping on the CO_2 trap is about three times less than the crimping on the WR-CO_2 side. As the

mismatch may result in isotope fractionation of CO_2 from the trap, the effect must be well reproduced. The trap was filled with pure WR-CO_2 and analysed over 13 h ('zero-enrichment' test for non-symmetrical system). At the beginning, a negative bias was observed (Fig. 5, upper panel), with the bias for $\delta^{46}R$ being larger than for $\delta^{45}R$, that is fractionation due to non-symmetrical crimping. Isotope modifications started after ~3 h when the signal intensity drops to ~70%, with the $\delta^{45}R$ and $\delta^{46}R$ bias slowly drifting in a positive direction. A test with symmetrical crimping demonstrated practically zero isotope modifications (Fig. 5, lower panel, see also test 10). As the duration of a single run (thawing + measurement) is less that 1 h, the test is satisfactory.

6. *Evaluation of the memory effect.* By analysing CO_2-air mixtures of contrasting isotopic composition in a sandwich-like sequence (Fig. 6), with duplicated extractions from each mixture, the absence of a memory effect was proven. The discrepancy in $\delta^{45}R$ and $\delta^{46}R$ between duplicates (Fig. 6) is close to zero. An obvious $\delta^{46}R$-outlier of the first run and a small positive trend in the $\delta^{45}R$-
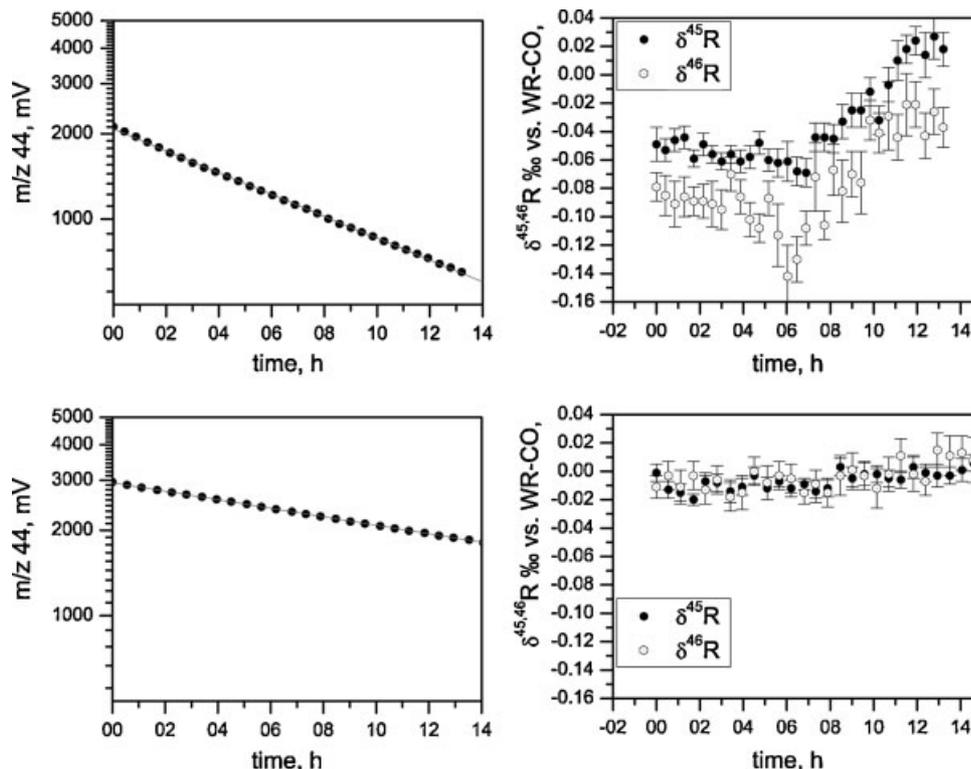
Figure 5. Upper panel: Long-term zero test in the CO$_2$ trap with the non-symmetrical capillary crimping. The trap volume was filled with pure WR-CO$_2$. Observed is an exponential intensity decrease and isotope modifications starting 3 h after zero time, when the intensity drops to $\sim$70% of the initial value. Error bars are 2-σ values. Lower panel: Long-term zero test in the CO$_2$ trap, with symmetrical capillary crimping. To have signals similar to that in the upper panel, much more CO$_2$ needs to be in the trap. Other conditions are the same.
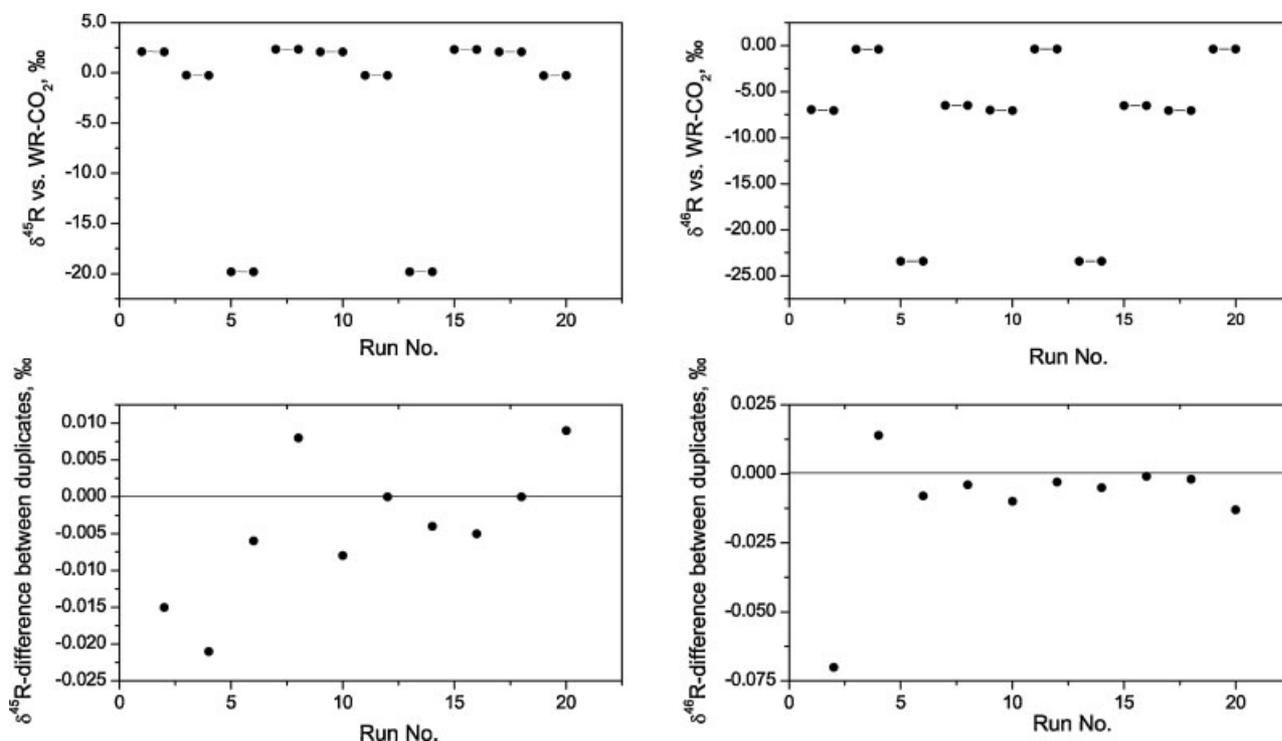

Figure 6. Test to investigate the memory effect in the CO$_2$ trap using runs of isotopically contrasting CO$_2$-air mixtures. Extractions from each mixture were made in duplicate. The discrepancy between duplicates (lower panels) is close to zero, confirming a negligible memory in the CO$_2$ trap. Obvious deviation in δ^{46}R-discrepancy on the first run (outlier) and the small positive trend in the δ^{45}R-discrepancy are probably due to some drift in vacuum/instrumental conditions (the data are not drift-corrected). (Test performed after cleaning the system and oil-free pump installation.)

discrepancies were observed, perhaps due to a drift in vacuum conditions and/or insufficient preconditioning before the first run (data are not drift-corrected). A typical sequence of samples started only when runs on a CO_2-air mixture were reproducible, and samples were sandwiched with CO_2-air mixtures. When drift on the CO_2-air mixture is observed (example in Supplementary Figure S2, see Supporting Information), the sample results are drift-corrected.

7. *Investigation of the nature of effects included in the 'method-related' correction.* A CO_2-air mixture was analysed with the CO_2 amount taken as a variable (extraction time varied). Several sequences were performed on different days and under various vacuum conditions. By plotting $\delta^{45}R$ and $\delta^{46}R$ vs. the inverse of the CO_2 amount (signal on m/z 44), a tight correlation was observed (Supplementary Figure S3, see Supporting Information), with scatter increasing at lower levels of CO_2. The amount-dependence for $\delta^{45}R$ was found to be reproducible and also observed at reduced air flow rates (typical rate at 55 cc/min, tested at 30, 40 and 45 cc/min). As previously described,[9] an exponential decrease of changes with increasing CO_2 amount occurred, probably due to a capillary mismatch. In addition, some changes due to incomplete CO_2 extraction cannot be excluded. If these were the only effects, the $\delta^{46}R$-changes would be about twice as much as the $\delta^{45}R$-changes. Although this difference was observed for pure CO_2 (Fig. 5, upper panel), it was not always observed for CO_2 extracted from gas mixtures (Supplementary Figure S3, see Supporting Information). We explain that as $\delta^{46}R$ increase due to traces of air.

8. *Assessment of the 'expected' or 'true' $\delta^{45}R$-$\delta^{46}R$ values independently using dynamic dilution.* The CO_2 flow from a 15 L SS tank via a crimped capillary was diluted by nitrogen gas (grade ALPHAGAZ 2, Air Liquide, Liege, Belgium; with $CO_2 < 0.1$ ppm) and directed into the extraction line inlet. The reference bellow was filled from this tank so that the 'expected' $\delta^{45}R$ and $\delta^{46}R$ values are zero. The amount-dependence was always observed for $\delta^{45}R$, with a zero intercept of the trend (Supplementary Figure S4, see Supporting Information). The data for $\delta^{46}R$ demonstrated no clear trend, although on some days the trend line was curved. This discrepancy emphasises the complexity for $\delta^{46}R$: in addition to the capillary mismatch and possible modifications due to incomplete CO_2 extraction (both $\delta^{45}R$ and $\delta^{46}R$ were modified systematically to negative values; with increased CO_2 amount the modification decreases), $\delta^{18}O(CO_2)$ equilibration on a metal surface and NO_2 production from air traces in the ion source must be considered.[9] The magnitude of the two latter effects may depend on the amount of CO_2 in a complex way. The amount of traces of air co-trapped with CO_2 is not necessarily proportional to the amount of CO_2. That may explain the curved trend for $\delta^{46}R$ (Supplementary Figure S4, see Supporting Information).

9. *Verification of the symmetry of the bellows system.* The above tests (all done with asymmetrical capillary crimping) implied that asymmetrical crimping and the limited amount of CO_2 in the trap volume were responsible for $\delta^{45}R$-$\delta^{46}R$ changes. The crimping of capillaries at the left and right bellows was kept identical. A zero-enrichment test (the same CO_2 filled left and right) resulted in zero within the uncertainty, proving the bellows system to be symmetrical.

10. *Investigation of system asymmetries as a cause for $\delta^{45}R$-$\delta^{46}R$ modifications.* A series of experiments was performed with identical crimping (within $\pm5\%$) of all three capillaries (the CO_2 trap, two bellows). The decrease of flow from the CO_2 trap was compensated for by using larger amounts of CO_2 (1.5 cc STP instead of 0.3 cc in a typical run). First, a long-running zero test (WR-CO_2 filled in the CO_2 trap) in the identical crimping mode demonstrated a limited signal decrease (Fig. 5, lower panel). The offset and change in $\delta^{45}R$-$\delta^{46}R$ from the beginning until 14 h were negligible. Having performed an extraction from a gas mixture, the CO_2 was analysed when it was in the CO_2 trap. Next, the CO_2 was cryogenically transferred to the left bellow and analysed in fully symmetrical DI mode (proved by zero-tests as well as the agreement of the $\delta^{13}C$ and $\delta^{18}O$ values measured on reference CO_2 gases with published values, see below, also Table 2). The $\delta^{45}R$ values obtained from the gas in the CO_2 trap with symmetrical capillary crimping agreed within the uncertainty with the values obtained in the bellows-DI mode and agreed with the $\delta^{45}R$ value of the stock CO_2 used for the mixtures (more details are in the calibration section). The $\delta^{46}R$ obtained for the gas in the CO_2 trap was found to be slightly higher and demonstrated more scatter than the $\delta^{46}R$ obtained on the same gas cryogenically transferred to the bellow. ($\delta^{46}R$ of the stock CO_2 used for mixtures is not relevant – mixture preparation might have modified $\delta^{18}O(CO_2)$.) The test, repeated several times on two mixtures, proved that use of a non-symmetrical system is the major reason for $\delta^{45}R$-$\delta^{46}R$ modifications.

Conclusions of the tests

The above tests demonstrated that under optimised parameters (Table 1) the system had a stable performance and that isotope modifications of extracted CO_2 were small and well reproducible. These modifications depend on the CO_2 amount and on the non-symmetrical capillary crimping. (More optimisation may be done by selecting

Table 1. Parameters optimised for the CO_2 extraction system and analyses on the MAT-252

Parameters	Optimised 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 changeovers	≥20
Integration time	8 s
Idle time	26 s
Total duration of a single run	~90 min

capillary length, diameter, etc.) Given that the CO_2 amount on mixtures and samples is well balanced and isotope differences [air-CO_2 mixture vs. WR-CO_2] and [air samples vs. WR-CO_2] are similar, the overall 'method-related' correction can be determined on CO_2-air mixtures and applied to samples.

The scatter of $\delta^{45}R$ and $\delta^{46}R$ observed on the CO_2-air mixture over a single measurement sequence (Supplementary Figure S2, see Supporting Information) can be used to evaluate the typical analytical error of a single analysis (extraction and mass spectrometer performance). When CO_2-air mixtures demonstrate a drift in $\delta^{46}R$ over a single sequence (on some days, probably due to vacuum conditions), a fitting line for $\delta^{46}R$ data of mixtures may be used to apply the drift-correction for data of air samples (samples are sandwiched with CO_2-air mixtures). The $\delta^{45}R$ and $\delta^{46}R$ average values obtained for a CO_2-air mixture over a single analytical sequence (or a trend for $\delta^{46}R$) can be used to determine the 'method-related' correction.

When extracting variable amounts of CO_2 from a CO_2-air mixture (flow rate fixed, extraction time variable), the intercept of the $\delta^{45}R$ trend with the inverse of CO_2 amount may be considered as the first estimate of 'true' $\delta^{45}R$ of the mixture. The intercept of the $\delta^{46}R$ trend gives an overestimate of the 'true' $\delta^{46}R$, and sometimes no clear trend for $\delta^{46}R$ vs. the inverse of CO_2 amount is observed. The true $\delta^{45}R$ and $\delta^{46}R$ of a mixture may be determined by extracting larger amounts of CO_2 followed by cryogenic transfer to the bellow and analysis in symmetrical DI mode (the symmetry needs to be proven). The absence of leaks, vacuum cleanliness, and oil-free pumping are important factors that become more critical when performing calibration runs.

CALIBRATION APPROACH

The CO_2 monitoring community uses two approaches for calibration. In the historical approach, pure WR-CO_2 is used as a calibration carrier on the VPDB-CO_2 scale. All determinations (sample CO_2 and the 'method-related' correction) are performed vs. a WR-CO_2. An advantage is that the WR-CO_2 can be calibrated directly (using NBS-19-CO_2 and possibly NIST RMs CO_2). This calibration is straightforward. Critical requirements are (i) WR-CO_2 storage and re-filling must guarantee its isotopic integrity, and (ii) determinations of 'method-related' and N_2O corrections are essential. These determinations may be complicated and not very transparent. The 'method-related' correction can be determined by extracting large amounts of CO_2 from a mixture and assuming that this procedure minimises undesirable extraction-related effects.[21,22]

The second approach is based on use of reference air cylinder(s) as a calibration carrier. A set of large cylinders with ambient air has been calibrated at CSIRO, Australia;[24] also in use at INSTAAR.[21,22] However, the calibration itself is rather cumbersome. Later, large cylinders with CO_2-synthetic air mixtures were calibrated at MPI-BGC, Jena.[9] Initially, mixtures at MPI-BGC were linked to the CSIRO scale and only later calibrated by using reference CO_2-air mixtures prepared from isotopically characterised CO_2.[7] Thus, the reference material is in the same form as a sample

which is a realisation of the Identical Treatment (IT) principle.[9,10] The sample and the reference material are analysed using the same instrument and the same method, and applying the same corrections including that for N_2O. The advantage is that calibration propagation is less sensitive to the 'trueness' of all corrections. This approach can also be used for systems suffering from systematic isotope modifications of extracted CO_2, including non-symmetrical systems.

In the second approach, the WR-CO_2 acts as a medium that links samples to laboratory CO_2-air mixtures. Thus, neither accurate calibration of WR-CO_2 nor its long-term isotopic integrity is required. The approach includes the following steps:[7]

(i) Reference '$CO_2 + N_2O$-air' mixtures are prepared from carbonate-based CO_2 which was analysed vs. NBS-19-CO_2. These mixtures are characterised by $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ and by CO_2 and N_2O concentrations. Given that mixing at MPI-BGC has been shown to be free of contamination and isotope modifications,[7] the mixtures serve as secondary RMs (NBS-19-CO_2 is the primary).

(ii) Laboratory '$CO_2 + N_2O$-air' mixtures (high-pressure cylinders) are calibrated vs. reference '$CO_2 + N_2O$-air' mixture(s), using the same method and instrument. This step eliminates the need to determine and apply a 'method-related' correction. '$CO_2 + N_2O$-air' mixtures in large cylinders are thus tertiary (third level) RMs. The most difficult problem is to prove zero drift of these mixtures; that can be done after long-term operation.

(iii) Air samples are analysed in a sequence with laboratory '$CO_2 + N_2O$-air' mixture(s).

Because the IT principle is applied at all steps, the uncertainties related to all corrections (method-related and N_2O correction, and even partly the ^{17}O correction) contribute less to the final results than in the first calibration approach. This approach provides a practical way to reach inter-laboratory data consistency targets (see introduction). MPI-BGC will serve as the central calibration laboratory by preparing and distributing '$CO_2 + N_2O$-air' reference mixtures,[12] aimed towards scale consistency.

We have recognised that setting up the second calibration approach requires more time. Large amounts of 'CO_2-air' mixture(s) in high-pressure cylinders must be available, with stability and isotopic integrity proven over years. (Selecting the right types of cylinders with the right treatment including removal of moisture prior to filling and the regulators are among the most critical aspects.) Proving stability (quantifying a drift) is achieved by careful inter-comparison of cylinders over years[9,24] (see also performance charts available from the intenet[25]).

Due to the time-consuming steps related to the second approach, we have started our analyses using the first calibration approach (plain CO_2 as calibration carrier, used to calibrate air-CO_2 mixtures) combined with important elements of the second approach. The latter means using air-CO_2 mixtures to determine the actual value of the method-related correction under actual analytical conditions – basically as another calibration carrier. By doing this, the samples are actually linked to air-CO_2 mixtures. In addition

to its practicality, this combination helps to evaluate each correction magnitude separately and permits detailed error budget analyses. Having accumulated enough data and calibrated air-CO_2 mixtures via reference JRAS sets recommended by WMO/GAW,[12] one can switch to the second approach and recalculate the data.

PRACTICAL ASPECTS: MEASUREMENTS, CALIBRATION, DETERMINATION OF 'METHOD-RELATED' CORRECTION, USE OF REFERENCE MATERIALS

Analytical sequence

From June 2007 to January 2009, each analytical sequence has been as follows:

(i) At least three runs of an 'AGA-CO_2'-air mixture connected to one of the inlet ports
(ii) A run on a twin AGA-CO_2-air mixture connected via the TRAC flushing line (see above) to another inlet. In this way, absence of contamination is verified.
(iii) Three to five runs on CARIBIC air are sandwiched with the 'AGA-CO_2-air' mixture (the same as in step (i)).
(iv) At the end, 'AGA-CO_2-air' is measured at least twice.
(v) With more CO_2-air mixtures becoming available during 2008, each sequence also included some runs of these mixtures, each connected to its own inlet port.

As each sequence includes at least 6 to 8 measurements on the same 'AGA-CO_2'-air mixture, these data form the basis for determining the 'method-related' correction on the WR-CO_2 scale and, if any, a drift in the $\delta^{45}R$ and $\delta^{46}R$-difference between the CO_2-air mixture and WR-CO_2 (example in Supplementary Figure S2, see Supporting Information). After installation of the oil-free pumping for the CO_2 extraction line and the scroll fore-vacuum pumps (see above), no drift in $\delta^{45}R$ and only a limited drift in $\delta^{46}R$ were observed during up to 36 h.

Working reference CO_2

Presently, all data are linked to the WR-CO_2, making its calibration and isotopic integrity highly critical. High-purity CO_2 (Air Liquide, Belgium) was selected as WR-CO_2 ($\delta^{13}C = -5.823 \pm 0.026$‰ and $\delta^{18}O = -7.761 \pm 0.046$‰, 2-$\sigma$ values); its isotope composition is close to that of ambient air CO_2 ($\delta^{13}C \approx -8.5$‰ and $\delta^{18}O \approx 0$‰). At 3.5 bar an aliquot of this pure CO_2 was filled to a high-purity 15 L Silco steel tank (Restek®, Bellefonte, PA, USA) attached to the reference bellow via a valved manifold. This enables very reproducible

re-filling of WR-CO_2. (As a security measure, the same 15 L SS tank was filled with the gas in an identical manner.)

The $\delta^{13}C$ differences between sample CO_2 and WR-CO_2 or between CO_2-air mixtures and WR-CO_2 are rather small (about 2.5‰) so that the cross-contamination correction is negligible under current conditions (0.001‰, see above). The difference in $\delta^{18}O$ is about 8‰, making the correction only 0.007‰.

Reference materials used

The WR-CO_2 in the 15 L tank was initially calibrated vs. the primary reference NBS-19-CO_2 at MPI-BGC (tank transported to Jena). Later the calibration was repeated at IRMM by using NBS-19-CO_2 prepared at MPI-BGC. The two calibrations agree well with the difference in $\delta^{45}R$ being 0.005‰ and in $\delta^{46}R$, 0.008‰; the average $\delta^{45}R_{WR-CO2/NBS-19-CO2} = 7.498 \pm 0.008$‰ and $\delta^{46}R_{WR-CO2/NBS-19-CO2} = 5.615 \pm 0.016$‰ (1-$\sigma$). The calibration was also proven by analysing NIST RMs and NARCIS-1 and NARCIS-2 CO_2 (Table 2). A $\delta^{13}C$ agreement (with a discrepancy of < 0.02‰) was observed for all gases except for very light CO_2. For $\delta^{18}O$ a good agreement was observed for NIST RMs CO_2, with a discrepancy of about 0.10‰ for NARCIS-1 CO_2. This may be due to limited number (2 ampoules) of NARCIS-1 ampoules analysed; we note, however, that its final calibration still needs to be established.

Next, a direct inter-comparison with MPI-BGC was performed as follows:

- two reference air sets (2 + 2 glass flasks, carbonate CO_2 mixed with N_2O + synthetic air) prepared[7,11] and characterised at MPI-BGC were analysed at IRMM;
- 2 + 2 glass flasks were filled with two CO_2-N_2O-air mixtures in use at IRMM and then analysed first at IRMM and then at MPI-BGC, with a time interval of 2 weeks;
- 13 CARIBIC air samples were first analysed at IRMM and then at MPI-BGC, with a time interval of 2 months.

Although the number of inter-comparisons is limited, the difference between the IRMM and MPI-BGC scales observed for $\delta^{13}C(CO_2)$ on CO_2-N_2O-air mixtures agrees with that observed on actual samples (Fig. 7, upper and lower panels), the difference about 0.04‰. However, the difference in $\delta^{18}O(CO_2)$ of about 0.07‰ for mixtures is found to be smaller for actual samples; the latter being about 0.01‰. The reason for that may be twofold: (i) with time the $\delta^{18}O(CO_2)$ obtained after storage may be shifted to negative values and (ii) the different connectors and connecting tubes used for glass flasks and sampling TRACs may play a role.

Table 2. Test for the calibration: NIST RMs and NARCIS-1 and -2 CO_2 gases. Given are standard combined uncertainties (2-σ, type A uncertainty)

Gas/	Obtained $\delta^{13}C^*$, ‰	Published[14,20,26,27] $\delta^{13}C^*$, ‰	Obtained $\delta^{18}O$, ‰	Published[14,26,27] $\delta^{18}O$, ‰
NIST RM 8562	-3.74 ± 0.03	-3.72 ± 0.08	-18.62 ± 0.03	-18.56 ± 0.06
NIST RM 8564	-10.46 ± 0.03	-10.45 ± 0.08	-10.09 ± 0.04	-10.06 ± 0.05
NIST RM 8563	-41.55 ± 0.03	-41.59 ± 0.08	-33.75 ± 0.05	-33.76 ± 0.07
NARCIS-1	-8.57 ± 0.03	-8.55 ± 0.03	-0.77 ± 0.04	-0.68 ± 0.13
NARCIS-2	1.91 ± 0.03	1.92 ± 0.02	-2.66 ± 0.03	-2.64 ± 0.03

*The values are calculated with the data set of Assonov and Brenninkmeijer[28] except the values published for NARCIS-1. These were calculated with the data set of Allison et al.[29]
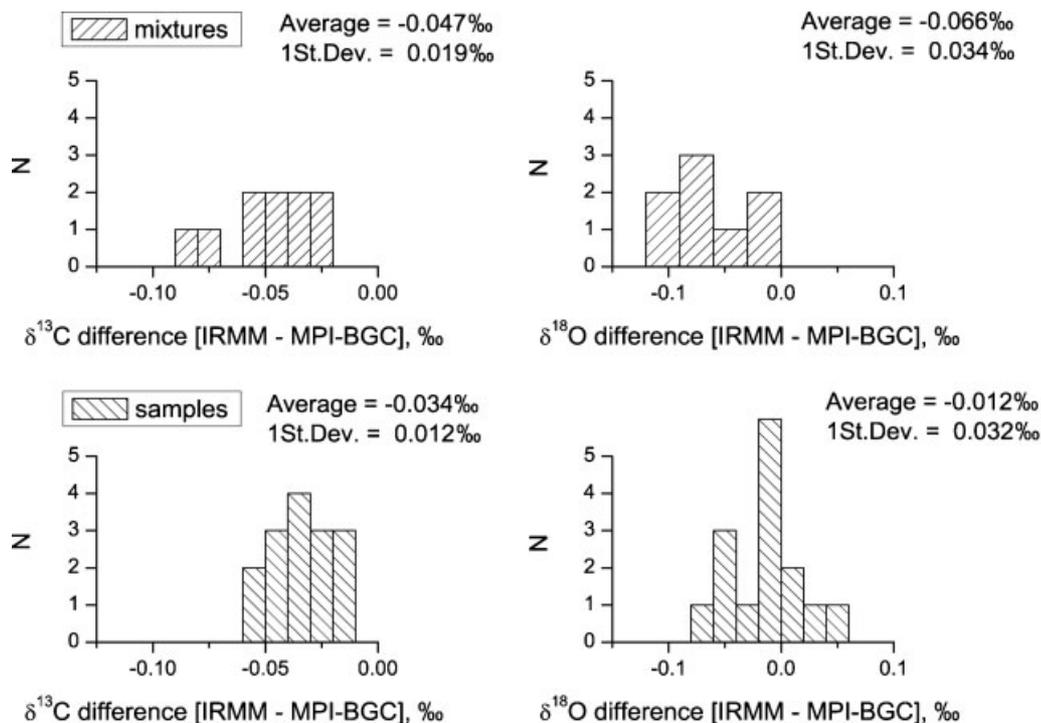
Figure 7. A difference in $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ between IRMM and MPI-BGC obtained on gas mixtures (upper panels) and 13 CARIBIC samples (lower panels). Two samples of 13 have been analysed in duplicate.

We cannot give an explanation for these discrepancies, and a more detailed study is required. However, given the different calibration approaches at IRMM and MPI-BGC and that the IRMM laboratory is only recently established, the scale difference observed is reasonable and it is much smaller than inter-laboratory scale discrepancies observed by long-established laboratories, e.g., by SAUSAGE round-robins.[30]

CO₂-air mixtures in high-pressure cylinders

Several 'CO₂-air' mixtures were prepared based on isotopically 'known' CO₂ gases as follows:

(i) In April 2007, two CO₂-air mixtures with synthetic air were prepared at MPI-CH (Mainz), in 10-L aluminium cylinders (Scott-Marrin Inc., Riverside, CA, USA – filled to ∼85 bar). Each mixture was prepared in duplicate. The first mixture (two cylinders) was based on high-purity AGA-CO₂ ($\delta^{13}C = -3.058 \pm 0.032$‰ and $\delta^{18}O = -14.389 \pm 0.056$‰, 2-$\sigma$). Aliquots of the stock CO₂ gases were taken in 2.5-L SS electropolished cans with dosing valves, enabling a direct analysis of 'mother' gas vs. WR-CO₂ in symmetrical DI mode. The 'twin' AGA-CO₂ mixtures extensively used in 2007–2008 agree well in $\delta^{13}C$ and show a constant offset in $\delta^{18}O$ of 0.106‰.

(ii) The second mixture prepared at MPI-CH was based on the mixture (0.1% N₂O in CO₂) from Messer Griesheim (Sulzbach, Germany). This CO₂-air mixture was used for memory tests (see Fig. 6 and Supplementary Figure S1 in Supporting Information).

(iii) In March 2008 and June 2008 Air Liquide prepared 'CO₂ + N₂O-air' mixtures for us, each of 7.5 m³ in 50-L high-pressure aluminium cylinders. Mixture 2008-0122 (one gas cylinder) was based on the aliquot of WR-CO₂ and mixture 2008-1640 (two gas cylinders) on another aliquot of AGA-CO₂.

All gas cylinders were equipped with high-purity single-stage pressure regulators (Parker and Scott, Cleveland, OH, USA). Having been well flushed and shown to be stable (stable $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ on the extracts from the mixtures), the regulators have never been inter-changed. The CO₂ and N₂O contents on mixtures have been determined by MPI-CH, Mainz, on the NOAA/CMDL scale (Supplementary Table 1, see Supporting Information).

Because aliquots of CO₂ used for the mixtures (the aliquots of AGA-CO₂ and WR-CO₂) were taken, they can be assayed in the symmetrical DI mode directly vs. WR-CO₂. This gives the first estimate for $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ of the mixtures. However, the preparation might have resulted in small isotope modification, especially for $\delta^{18}O(CO_2)$ as, for example, observed for the twin AGA-CO₂ mixtures prepared at MPI-CH, Mainz.

Use of mixtures based on 'known' CO₂ with and without N₂O doping can assist in testing the following:

(i) The isotope distances [AGA-CO₂ mixture vs. WR-CO₂] and [air samples mixture vs. WR-CO₂] are approximately the same but of opposite sign, making the correction magnitude for samples similar to that determined on the AGA-CO₂ mixture.

(ii) Given that mixture preparation introduces no contamination, the mixture based on WR-CO₂ doped with N₂O can provide/prove an estimate of the N₂O correction coupled with the extraction-related correction (Fig. 8). The agreement is excellent for
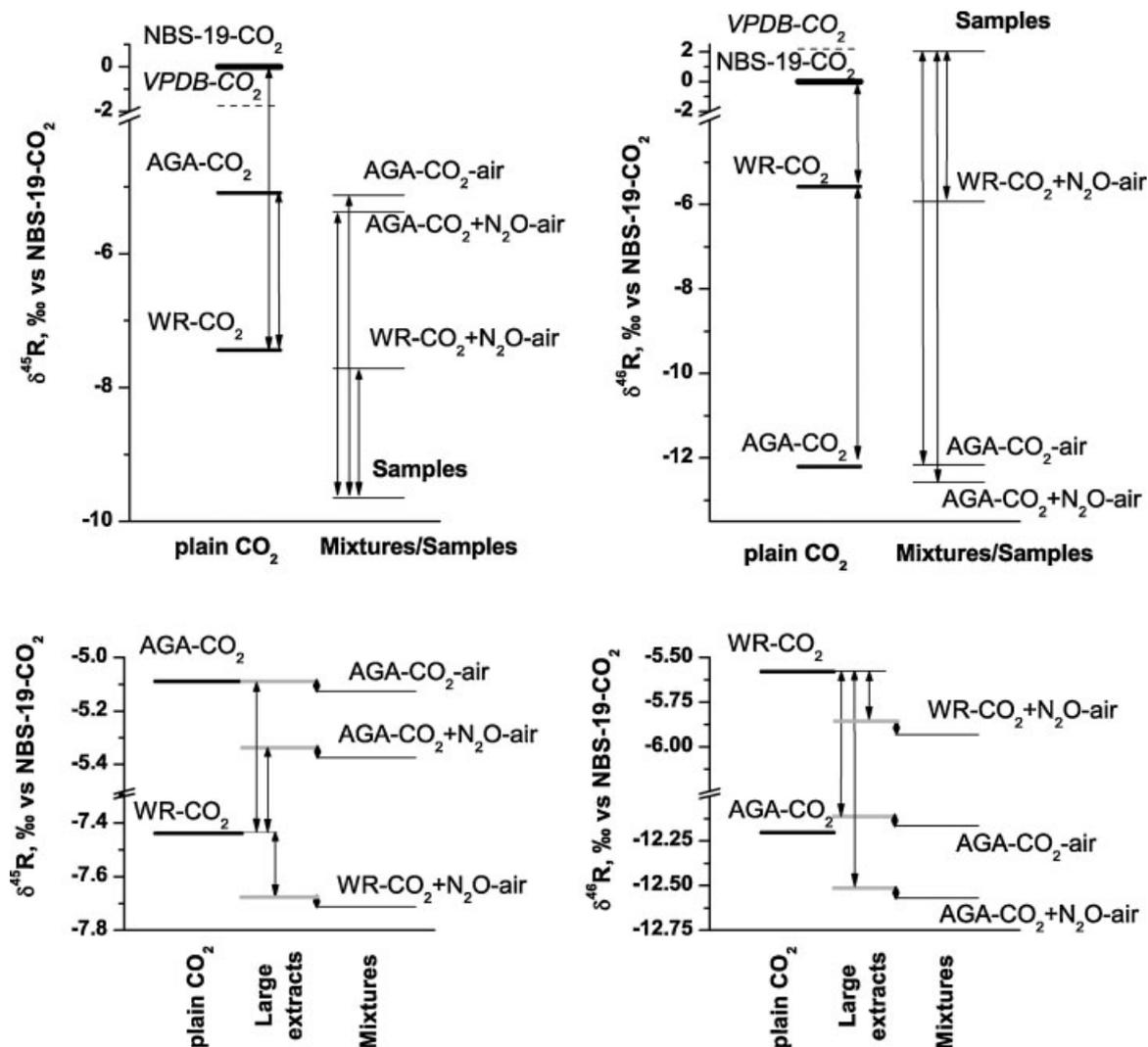
Figure 8. The approach of using mixtures based on 'known' CO_2 with and without N_2O doping. The upper panel shows the calibration on plain CO_2 gases and air samples vs. CO_2-air mixtures. Here the calibration link between plain CO_2 and CO_2-air mixtures is missing. The lower panel shows practical realisation of this link by using large extracts from the mixtures analysed in DI mode; the distance between each mixture and large extracts (small arrows) gives a correction magnitude. Other distances have also been measured, proving our calibration approach.

$\delta^{13}C(CO_2)$ and, to a lesser degree, for $\delta^{18}O(CO_2)$, see Table 3.

(iii) The two mixtures, AGA-CO_2 doped with N_2O and the AGA-CO_2 mixture, can also provide an estimate for the N_2O correction. The difference between the AGA-$CO_2 + N_2O$ mixture and the WR-$CO_2 + N_2O$ mixture should also give the $\delta^{13}C(CO_2)$ difference between AGA-CO_2 and WR-CO_2 (Fig. 8).

The 'method-related' correction

The difference between the $\delta^{45}R$ and $\delta^{46}R$ measured on extracts of CO_2-air mixtures and the 'true' values gives the correction magnitude. This is the overall correction and it includes effects like non-symmetrical capillary crimping, impurities introduced by the line, effects due to air traces and NO_2 produced in the ion source, isotope modifications due to incomplete extraction (if any), etc. Given that the

Table 3. Calibration: 'True' $\delta^{45}R$ and $\delta^{46}R$ values (vs. WR-CO_2) obtained in symmetric DI mode on large extracts from CO_2-air mixtures, values for 'Mother' CO_2 and $\delta^{13}C$ and $\delta^{18}O$ obtained (1-σ values)

Mixture	$\delta^{45}R$, ‰	$\delta^{46}R$, ‰	$\delta^{13}C$, ‰	$\delta^{18}O$, ‰
Large extracts from AGA-CO_2 mixture, cylinder #9, MPI-CH (Mainz, Germany)	2.369 ± 0.007	−6.574 ± 0.014	−3.060 ± 0.010	−14.298 ± 0.014
Large extracts from Mixture 2008-1640 (AGA-CO_2-N2O-air), Air Liquide, Belgium	2.119 ± 0.006	−6.978 ± 0.014	−3.065* ± 0.017	−14.358* ± 0.026
'Mother' AGA-CO_2	2.367 ± 0.008	−6.665 ± 0.014	−3.058 ± 0.016	−14.389 ± 0.028

* Based on $\delta^{13}C_{N2O} = -358‰$ and $\delta^{18}O_{N2O} = -496‰$ as found for N_2O.[31]

Table 4. Test for N$_2$O correction: δ^{45}R-δ^{46}R values obtained on WR-CO$_2$-N$_2$O mixture vs. WR-CO$_2$ agree with the N$_2$O-correction estimate (1-σ values)

Mixture	δ^{45}R, ‰, 'method-related' correction applied	δ^{46}R, ‰, 'method-related' correction applied	N$_2$O correction*, Δ^{45}R, ‰	N$_2$O correction*, Δ^{46}R, ‰
WR-CO$_2$-N$_2$O-air, Mixture 2008-0122, Air Liquide, Belgium	-0.238 ± 0.010 (n = 82)	-0.304 ± 0.021 (n = 82)	-0.234 ± 0.007	-0.331 ± 0.010

* *Based on δ^{13}C$_{N_2O}$ = −358‰ and δ^{18}O$_{N_2O}$ = −496‰ as found for N$_2$O.[31]

extraction line has a negligible memory effect and that the IT principle was fulfilled, the correction determined on mixtures can be applied to samples.

Determination of the 'true' δ^{45}R and δ^{46}R of CO$_2$-air mixtures is complicated. The δ^{45}R and δ^{46}R of extracted CO$_2$ depends on the quantity of CO$_2$, mostly because of non-symmetrical capillary crimping and traces of air. The intercept of the δ^{45}R trend and the inverse of the CO$_2$ amount (Supplementary Figure S3, see Supporting Information) can be considered as the first estimate for 'true' δ^{45}R; the intercept of the δ^{46}R trend often gives an elevated value. A correct approach to determining the 'true' δ^{45}R and δ^{46}R on mixtures is to extract a larger CO$_2$ amount (>1.5 cc compared with 0.3 cc in a typical run) followed by transfer to the sample bellow (cryogenic distillation to a small volume followed by CO$_2$ expansion to bellow) and measurement in a symmetrical DI mode; test #10 (see above) has proven this approach. In this way, the 'true' δ^{45}R and δ^{46}R values of gas mixtures were determined (Table 3). The agreement in the previous test (Table 4), where the 'method-related' correction was applied, proves this approach.

Based on data of CO$_2$-air mixtures, the 'extraction-related' correction is typically about 0.035‰ for δ^{45}R and 0.040‰ for δ^{46}R. The dynamic mixing experiments, where the 'true' δ^{45}R and δ^{46}R values are zero, gave the same correction magnitudes.

N$_2$O correction

The δ^{45}R-δ^{46}R values obtained first must be corrected for cross-contamination and the 'method-related' correction must then be applied. The next correction applied is for N$_2$O interference (m/z 44, 45 and 46 as CO$_2$). (For practical reasons, the ^{17}O-correction is applied first and then the N$_2$O correction. This change of order has a negligible effect.) The magnitude of the N$_2$O correction is (the same for δ^{18}O):

$$\delta^{13}C_{correction} = [\delta^{13}C_{N_2O} \cdot N_2O/CO_2 \cdot E_{N_2O}] \quad (2)$$

where δ^{13}C$_{N_2O}$ is a formal value calculated for atmospheric N$_2$O as if it were CO$_2$; N$_2$O/CO$_2$ is the concentration ratio, and E$_{N_2O}$ is the relative ionisation efficiency of N$_2$O vs. CO$_2$. E$_{N_2O}$ was determined by the product ion spectra[31] on m/z 30 using low concentration N$_2$O-CO$_2$ mixtures[b]. The mixtures were prepared volumetri-cally,[31] with the uncertainty of mixing ratios of ±2%.

[b]E$_{N_2O}$ determined by using the ratio of m/z 44 signals on pure N$_2$O and CO$_2$ gases filling to the same pressure in the same bellow is not representative for air samples and diluted N$_2$O/CO$_2$ mixtures (see refs in Ref. 31). Moreover, E$_{N_2O}$ determined on pure N$_2$O on our MAT-252 does not give reproducible values.

The value for E$_{N_2O}$ = 0.670 obtained in October 2007 agrees, to within 3%, with that of 0.689 obtained in October 2008. The mean E$_{N_2O}$ = 0.680 was used, making the relative uncertainty ±3% relative.

For the Air Liquide Mixture 2008-0122 which is based on WR-CO$_2$ with N$_2$O, the actual δ^{45}R and δ^{46}R deviations from WR-CO$_2$ are in agreement with the estimates of the N$_2$O-correction (Table 4). The δ^{13}C values for the AGA-CO$_2$ mixtures, with and without N$_2$O, then agree with each other and also agree to within 0.007‰ with the mother CO$_2$ (Table 3); deviations in δ^{18}O are expected due to mixture preparation. This thus validates our N$_2$O correction.

THE OVERALL SYSTEM PERFORMANCE AND DATA QUALITY

An overall performance (CO$_2$ extraction plus IRMS) can be evaluated by plotting δ^{13}C and δ^{18}O obtained on CO$_2$-air mixtures (a working reference mixture) over time. The performance charts by Brand, ISOLAB, MPI-BGC, Jena, Germany[25] cover more than 6 years; the data obtained on a working reference mixture are scaled by using a second mixture (CSIRO reference air) which served as an anchor for establishing the δ^{13}C and δ^{18}O scale vs. VPDB-CO$_2$. This is the second calibration approach (see above) which links the air sample (or a mixture) to a reference mixture and thus eliminates uncertainty due to determination of the 'method-related' correction as well as to WR-CO$_2$ refilling. A drift-correction over a single analytical sequence is already included. Quoting from the above website, ''Since the start of the measurements in October 2000, the single-analysis precision between our working gas tank and the QA air standard on 'Matty' were 0.013‰ (δ^{13}C) and ~0.025‰ (δ^{18}O)''.

From June 2007 to August 2008, sample runs at IRMM have been linked to a single mixture only (in fact, two twin AGA-CO$_2$ mixtures in 10-L Scott-Marrin cylinders). The δ^{45}R and δ^{46}R data obtained on this mixture vs. the WR-CO$_2$ (Fig. 4(a)) provide a simplified performance chart. First, the data are not corrected for a trend over a single day (example in Supplementary Figure S2, see Supporting Information) and, second, some additional, day-to-day scatter might have arisen from WR-CO$_2$ refilling (and would be cancelled out by data normalisation to a CO$_2$-air mixture). The data scatter over a single sequence (Fig. 4(a)) gave the error estimation (the 4-σ range) of a single determination. After cleaning the system in July 2007, a typical 1-σ is about 0.01‰ for δ^{45}R and 0.015‰ for δ^{46}R (Fig. 4(a)). After December 2007, the system demonstrated more stable performance, probably due to

achieving a better vacuum in the IRMS instrument and in the pumping system.

We assumed a zero-trend of the twin AGA-CO$_2$ mixtures, based on the high quality of Scott-Marrin cylinders and because the cylinders have been used to store dry air samples for several years. The fact that from June 2007 to October 2008 the twin mixtures have demonstrated a consistency in $\delta^{45}R$ and a constant offset in $\delta^{46}R$ supports this assumption. The 'true' $\delta^{45}R$ determined on the twin AGA-CO$_2$ mixtures in October 2008 (1.5 years after mixture preparation) also agrees with the $\delta^{45}R$ of the 'mother' AGA-CO$_2$. Thus, the variability of data scatter in Fig. 4(a) is considered as a gradual improvement of the overall system characteristics (cleaning, installing better pumps, etc.).

At present (January 2009), only a limited data set has been generated for two further mixtures.

The data of the mixture 2008-1640, corrected as if it were a sample air with the AGA-CO$_2$ mixtures used as a reference, agree well with the expected values (Fig. 4(b)). The results also support the conclusion made above regarding the 4-σ range. More detailed analyses will require (i) a longer observation and (ii) proving a zero-trend for these two mixtures.

An important aspect of isotopic accuracy is the sampling quality. Ground-based sampling programmes typically provide an internal quality check by taking and analysing samples in duplicate and also by analysing the same samples on different days.[32] This is a check for water-CO$_2$ exchange in the sampling flasks (if any), for storage effects and for the system performance. For the aircraft, duplicate sampling is not possible and re-analysing the same sample after long storage is difficult (TRACs must be circulated to other labs). Some CARIBIC samples have been re-analysed within a few days following the first run, giving $\delta^{45}R$ and $\delta^{46}R$ values within 0.020 and 0.035‰, close to the 2-σ range estimated above.

The CARIBIC measurements themselves provide a check for data quality and quality of sampling. The $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ of some flights are found to closely correlate with the CO$_2$ content (Fig. 9). As these intercontinental flights (Germany–USA–Germany and Germany–China–Germany) covered long distances and met different air masses, such tight correlations are remarkable. Two particular flights (Fig. 9) crossed the tropopause and showed mixing as evidenced by high ozone (not shown). The tight correlations imply a mixture of well-mixed upper tropospheric air and lowermost stratospheric air; interestingly tropospheric variability for these flights forms the same trend as that for the stratospheric-tropospheric mixture. (Data and interpretation will be given elsewhere, manuscript in
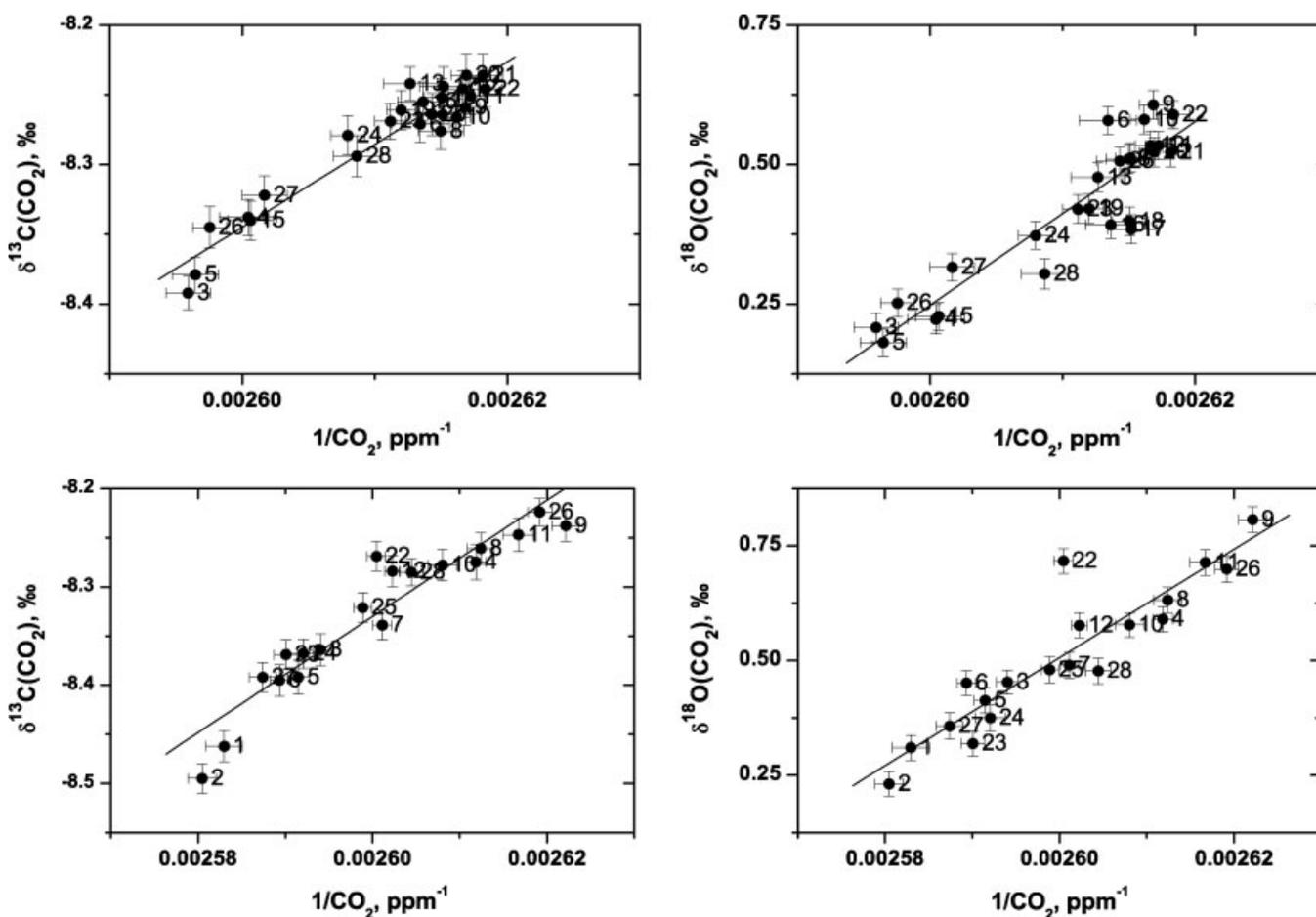

Figure 9. Some CARIBIC flights demonstrate a tight correlation between $\delta^{13}C(CO_2)$, $\delta^{18}O(CO_2)$ and the CO$_2$ concentration (labels correspond to sample numbering in a flight, from 1 to 28). This implies a two end-member mixing, despite the long distances covered by the flights and the different air masses sampled over a route. Variabilities relative to the trend lines are used to give (over)estimations of total errors (analytical errors in CO$_2$ concentrations, isotope analyses, sampling quality and storage, etc.).

Table 5. Estimations of the overall uncertainty (sampling and analytical) by data scatter around trend lines as given in Fig. 9

Flight	No of data points	1 St.Dev. of δ^{13}C(CO$_2$) deviations from the trend, ‰	Max δ^{13}C(CO$_2$) deviation from the trend, ‰	1 St.Dev. of δ^{18}O(CO$_2$) deviations from the trend, ‰	Max δ^{18}O(CO$_2$) deviation from the trend, ‰
218-219	25	0.013	0.028	0.054	0.114
220-223	19	0.025	0.059	0.063	0.205

preparation.) Assuming trends for δ^{13}C(CO$_2$) and δ^{18}O(CO$_2$) (Fig. 9) to be for two-component mixtures and assuming a zero-error for the CO$_2$ concentrations (an oversimplification), one obtains a data quality indicator based on real air measurement (Table 5). The values given are obviously upper limits as they include a degree of natural variability. It also confirms excellent sampling and measurement quality.

Only a few of the 500 samples analysed at IRMM to date (January 2009) have had δ^{18}O(CO$_2$) lower than adjoining samples (for 1‰), which attests to the quality of sampling and storage. The discrepancies may be indicative of water-CO$_2$ exchange in the sampling flasks. Typically, samples for a single flight show δ^{18}O(CO$_2$) values within a compact range, often with tight correlations with CO$_2$ content (Fig. 9). This is in contrast to the CARIBIC-1 measurements where water-CO$_2$ exchange in metal flasks was observed.[33]

Thus, based on numerous tests, on performance charts, and on the trends demonstrated by the CARIBIC data, we conclude that the system for air-CO$_2$ isotope measurements at IRMM is reliable and robust. Using CARIBIC air samples, we have been able to obtain a reliable record for the well-mixed remote troposphere and the upper troposphere/lower most stratosphere mixing region (manuscript in preparation).

ERROR BUDGET CONSIDERATIONS

To construct the error budget, errors corresponding to all measurement and calibration steps, including instrumental corrections, need to be considered. As all analyses are performed on CO$_2$, by measuring relative δ^{45}R-δ^{46}R differences traced to NBS-19-CO$_2$, the budget should be based on errors in δ^{45}R and δ^{46}R values traced back to that reference material. The approach presented by Allison et al.[29] was recently reconsidered[16] and a simplified error budget in terms of δ^{45}R-δ^{46}R values was given. (Note: The VPDB scale defined by the NBS-19 carbonate, the primary RM for δ^{13}C and δ^{18}O of CO$_2$, is realised by CO$_2$ evolved from the NBS-19 carbonate with 100% H$_3$PO$_4$ at 25°C. NBS-19-CO$_2$ is the basis for the VPDB-CO$_2$ scale. As air-CO$_2$ (gas phase) cannot be compared with the NBS-19 solid, data for air-CO$_2$ have always been reported on the VPDB-CO$_2$ scale, thus circumventing arguments related to δ^{18}O(CO$_2$) fractionation by acid conversion and its uncertainty. (All calculation and error propagation steps are made on the VPDB-CO$_2$ level.) The acid conversion may (and in practice does) result in variability of δ^{18}O(CO$_2$)-scale realisation. MPI-BGC (Jena) has been selected as the WMO-GAW central calibration laboratory for air CO$_2$ isotope measurements.[12]

The δ^{45}R-δ^{46}R values obtained vs. WR-CO$_2$ are first corrected for cross-contamination (not required), then for

'method-related' correction and for N$_2$O interference (see above). Thus, an equation for δ^{45}R is:

$$\delta^{45}\text{R}_{\text{sample/NBS19-CO2}} = ((\delta^{45}\text{R}_{\text{sample/WR-CO2}}$$
$$+ [\delta^{45}\text{R}_{\text{CO2-air\_"true"/WR-CO2}}$$
$$- \delta^{45}\text{R}_{\text{CO2-air\_measured/WR-CO2}}] + 1)/ \qquad (3)$$
$$(\delta^{45}\text{R}_{\text{NBS19-CO2/WR-CO2}} + 1) - 1)$$
$$- [\delta^{45}\text{R}_{\text{N2O/NBS-19-CO2}} \cdot \text{N}_2\text{O}/\text{CO}_2 \cdot \text{E}_{\text{N2O}}]$$

The first square-bracketed term is the 'method-related' correction and the second square-bracketed term is the N$_2$O correction; δ^{45}R$_{\text{N2O/NBS-19-CO2}}$ is the isotope composition of atmospheric N$_2$O. The latter value in use is currently considered to have zero uncertainty. This does, however, appear to be incorrect and it thus gives an unrecognised source of error.[31] The N$_2$O and CO$_2$ contents were measured by MPI-CH Mainz, Germany) on the scale of NOAA/CMDL. Finally, by correcting δ^{45}R$_{\text{sample/VPDB-CO2}}$ and δ^{46}R$_{\text{sample/VPDB-CO2}}$ for the ^{17}O contribution,[16] the values δ^{13}C(CO$_2$) and δ^{18}O(CO$_2$) are determined.

Because (δ^{45}R + 1) and (δ^{46}R + 1) are close to unity, the multiplication and additive terms in Eqn. (3) give the following equation for errors (see Allison and Francey[24]):

$$u_{\text{combined}} \cong \sqrt{\sum_{i=1}^{n} u_i^2} \qquad (4)$$

Typical IRMS determination in DI mode gives 1-σ values (internal precision) of 0.008 and 0.015‰ for δ^{45}R and δ^{46}R, respectively. The 'method-related' correction typically has 1-σ values of 0.010 and 0.015‰. Given that the N$_2$O correction to δ^{45}R and δ^{46}R accounts for about 0.20 and 0.30‰, respectively, the N$_2$O and CO$_2$ contents are determined at ±0.1% (relative) and E$_{\text{N2O}}$ is determined with ±3.0% (relative); the final 1-σ values for δ^{45}R and δ^{46}R on the VPDB-CO$_2$ scale are about 0.018‰ and 0.030‰, respectively. For each particular analytical sequence, the error budget can be evaluated individually, based on the actual data scatter obtained for CO$_2$-air mixtures.

δ^{13}C and δ^{18}O can be approximated as linear functions of δ^{45}R and δ^{46}R on the VPDB-CO$_2$ scale.[16] By recommending that the same ^{17}O-correction be consistently used, this correction is assumed to be uncertainty-free (thus all laboratories are on the same scale). Finally, because air δ^{18}O(CO$_2$) is close to zero, the total combined uncertainty of δ^{13}C and δ^{18}O can be approximated[16] as follows:

$$U(\delta^{13}\text{C}) \approx 1.07 \cdot U(\delta^{45}\text{R}) \qquad (5)$$

$$U(\delta^{18}\text{O}) \approx U(\delta^{46}\text{R}) \qquad (6)$$

where all $U(\delta^i\text{R})$ represent the total combined uncertainty, 1-σ values on the VPDB-CO$_2$ scale. Thereafter, 2-σ values for

$\delta^{13}C(CO_2)$ and for $\delta^{18}O(CO_2)$ of 0.040‰ and 0.060‰ can be attained by the system at IRMM (a total combined uncertainty, $k = 2$). As the calibrations of WR-CO_2 vs. NBS-19-CO_2 contribute ~35% and 25% of the total uncertainty, these numbers can be improved further.

We note by using reference CO_2-air mixtures, namely the MPI-BGC reference sets,[12] as a calibration carrier, interlaboratory data comparability exceeding the above estimates above can be achieved. This, however, will require an independent error budget assessment. It is stressed that the uncertainty about the isotope composition of the tropospheric N_2O and the N_2O used for mixtures, and the values currently used for the N_2O correction, appears to be a currently unrecognised error source[31] which is more prominent for $\delta^{13}C(CO_2)$ than for $\delta^{18}O(CO_2)$.

SUMMARY AND RECOMMENDATIONS

1. The system at JRC-IRMM for the extraction of CO_2 from air samples followed by isotope analysis has been optimised and thoroughly investigated. The extraction line was found to modify the $\delta^{13}C$ and $\delta^{18}O$ of analysed CO_2 and a dependence on the CO_2 amount was observed. Among the most crucial effects were (i) a non-symmetrical crimping of capillaries; (ii) $\delta^{46}R$ increase due to traces of air; (iii) initial problems with traces of oil vapor, which can be addressed by using scroll pumps to back-up turbo pumps.

2. The calibration approach at JRC-IRMM is based on the use of a working reference CO_2 as a calibration carrier (calibrated vs. NBS-19-CO_2) and CO_2-air mixtures (another calibration carrier, calibrated vs. the working reference CO_2) to determine an overall 'method-related' correction. The latter includes some fluctuations due to refilling WR-CO_2 as well as possible fluctuations in the behaviour of the capillary. The approach, together with use of a symmetrical DI mode for calibration periods, permitted us to decouple and determine the magnitude of each instrumental effect separately, directly linked to the primary reference (NBS-19-CO_2). This approach is complementary to the calibration principle of using solely CO_2-air mixtures as a calibration carrier as recommended by WMO/GAW.[12]

3. CO_2-air mixtures based on 'known' CO_2 with and without N_2O were tested, in order to independently quantify/prove the overall 'method-related' correction as well as the N_2O correction. The $\delta^{13}C(CO_2)$ values for extracts from mixtures agree within 0.010‰ with values obtained from the 'mother' CO_2 used for the mixtures. This approach is recommended to other laboratories.

4. With pure CO_2 used a calibration carrier, use of a non-symmetrical system for calibration of CO_2-air mixtures was found to be complicated. As extraction from mixtures is 100% efficient and does not contaminate the extracted CO_2, the extracts can be transferred to a bellow and analyzed in a symmetrical DI mode.

5. Based on the data scatter observed for CO_2-air mixtures and a simplified error balance, the total combined uncertainty in $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ on the VPDB-CO_2 scale was estimated as ±0.040‰ and 0.060‰ (2-σ values).

6. Close correlations between $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ and CO_2 were observed for some CARIBIC flights, independently proving a high quality of sampling and isotope analyses. About 500 CARIBIC samples have been analysed from March 2007 to January 2009; the CO_2 isotope data will be published elsewhere (manuscript in preparation).

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

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