Analysis of low-concentration gas samples with continuous-flow isotope ratio mass spectrometry: eliminating sources of contamination to achieve high precision


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Developments in continuous-flow isotope ratio mass spectrometry have made possible the rapid analysis of $\delta^{13}C$ in CO$_2$ of small-volume gas samples with precisions of $\pm 0.1\%$. Prior research has validated the integrity of septum-capped vials for collection and short-term storage of gas samples. However, there has been little investigation into the sources of contamination during the preparation and analysis of low-concentration gas samples. In this study we determined (1) sources of contamination on a Gasbench II, (2) developed an analytical procedure to reduce contamination, and (3) identified an efficient, precise method for introducing sample gas into vials. We investigated three vial-filling procedures: (1) automated flush-fill (AFF), (2) vacuum back-fill (VBF), and (3) hand-fill (HF). Treatments were evaluated based on the time required for preparation, observed contamination, and multi-vial precision. The worst-case observed contamination was 4.5% of sample volume. Our empirical estimate showed that this level of contamination results in an error of 1.7$\%$ for samples with near-ambient CO$_2$ concentrations and isotopic values that followed a high-concentration carbonate reference with an isotope ratio of $\delta^{13}C$C$_{0}$ (IAEA-CO-9). This carry-over contamination on the Gasbench can be reduced by placing a helium-filled vial between the standard and the succeeding sample or by ignoring the first two of five sample peaks generated by each analysis. High-precision (SD $\pm 0.1\%$) results with no detectable room-air contamination were observed for AFF and VBF treatments. In contrast, the precision of HF treatments was lower (SD $\pm 0.2\%$). VBF was optimal for the preparation of gas samples, as it yielded faster throughput at similar precision to AFF.

The development of continuous-flow isotope ratio mass spectrometry (CF-IRMS) in the 1980s and its commercial appearance in the 1990s made possible the high-precision isotope measurement of large numbers of samples.$^1$ In 1991, Prosser et al.$^2$ described an automated method for rapid isotopic analysis of high-concentration CO$_2$ from breath samples collected in 13-mL septum-capped vials. The technique involved the use of an autosampler where the headspace gas was transferred to the helium carrier stream using a double-holed needle probe. More recently, Tu et al.$^3$ described an analogous method but focused on the isotopic analysis of near-ambient CO$_2$ samples from 10-mL septum-capped vials for Keeling plot applications. Without cryogenic pre-concentration, Tu et al.$^3$ achieved a precision of 0.08$\%$ $\delta^{13}C$ for ambient concentration air samples using a Gasbench II headspace sampler coupled to an IRMS instrument. This application of CF-IRMS techniques to low-concentration gas samples allows for higher throughput and reduced sampling costs compared with traditional dual-inlet IRMS.

Despite several studies$^3$–$^5$ using continuous-flow preparation devices for the CF-IRMS analysis of low-concentration gas samples, methods for sample introduction into vials have not yet been standardized. Several methodological developments have focused on improving vial integrity and storage$^3$–$^7$ but all had different parameters for sample introduction into the mass spectrometer. Common methods are through a flushing technique or glove bags, but flushing durations and flow rates vary among laboratories. Tu et al.$^3$ flushed their vials manually with a double-holed needle for 10 s at a flow rate of $\sim$1 L min$^{-1}$. Midwood et al.$^5$ flushed their specially designed metal vials for 190 s at a flow rate of 80 mL min$^{-1}$ while Knohl et al.$^4$ did not mention the flush-fill duration and flow rate during the preparation of their calibration gases. Standardized methods for vial filling are

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required not only for unknown gas samples, but also for true internal standards and quality control samples. For flush-filling techniques, it is essential that the procedure results in complete volumetric turnover.\textsuperscript{8} Residual room air in the vial clearly results in inaccurate measurement. To date, contamination due to insufficient flushing times has been discussed in detail only for the analysis of high-concentration carbonate samples.\textsuperscript{8}

Improving precision in the analysis of low-concentration gas samples using CF-IRMS techniques requires optimization of all steps of the analysis; vial preparation and filling, instrument method, and normalization. We compared two sources of contamination: memory effects on the Gasbench II and room-air contamination for three sample preparation methods. These vial-filling methods were: (1) automated flush-fill (AFF), (2) vacuum back-fill (VBF), and (3) hand-fill (HF). The specific objectives of this work were to: (1) analyze and eliminate contamination during preparation and analysis, (2) compare methods for the preparation of gas samples, and (3) determine the optimal sample preparation method evaluated by the absence of contamination, speed of preparation, and vial-to-vial uncertainty.

**EXPERIMENTAL**

**Isotopic analysis**

Isotopic measurements were performed at the Laboratory for Biotechnology and Bioanalysis II, Stable Isotope Core at Washington State University, Pullman, WA, USA. The carbon isotope ratio of low-concentration CO\textsubscript{2} gas samples was measured using a Gasbench II interface (ThermoFinnigan, Bremen, Germany) with a GC-PAL autosampler (CTC Analytics, Zwingen, Switzerland) connected to a Delta plus XP IRMS instrument (ThermoFinnigan, Bremen, Germany). The autosampler was equipped with a double-holed needle that samples the headspace from 12-mL borosilicate vials (Labco Ltd., High Wycombe, UK; #938W) capped with butyl rubber septa. The total run time for each sample was 875 s. Included in the total run time was a 20-s transfer time to allow the analyte gas and helium carrier to fill the sampling line. These gases then passed through an inline Nafion water trap and into a 100-μL sampling loop for 80 s. During the load cycle of the sampling loop, three pulses from a pure CO\textsubscript{2} tank were introduced into the mass spectrometer through an open split as an external reference. The third peak of the monitoring gas was used for all initial calculations of isotope ratios by arbitrarily defining the monitoring gas as 0% δ\textsubscript{13C}VPDB. After 80 s of filling the sampling loop, an eight-port valve (VICI Valco, Houston, TX, USA) was switched to inject for 60 s. This process was repeated five times, to ultimately provide five sample peaks. During the injection phase, gas samples passed through a Poraplot Q gas chromatography (GC) column (25 m long × 0.32 mm i.d., 10 μm thickness; Varian, Inc., Walnut Creek, CA, USA) held at 40 °C followed by another Nafion trap. After the GC column, analyte gas and helium entered the mass spectrometer through a movable sample open split. Moving the open-split capillary could be achieved through the software, thus diluting the sample entering the mass spectrometer. We used the split out/dilution setting to achieve consistent signal among samples and standards, and to remove earlier eluting N\textsubscript{2}O which has isobaric interference for mass-to-charge ratio, m/z 44, 45 and 46. For experiments where the purpose was to observe maximum contamination in the system and for blank vials, the dilution was turned to off/split in.

Prior to every sample sequence, the stability of the instrument was verified to be <0.06% δ\textsubscript{13C}VPDB from ten or more injections from the CO\textsubscript{2} monitoring tank, and at least five conditioning samples from the one blank vial were run through the system. The linearity was verified to be within the manufacturer’s recommendations of <0.06% per volt for the range of 500–8000 mV for m/z 44. The isotopic values were expressed in terms of the delta notation (in ‰) relative to the Vienna Pee Dee Belemnite (VPDB) standard:

\[
\delta_x = \left( \frac{R_x}{R_{\text{std}}} - 1 \right) \times 1000
\]

where \( R_x \) and \( R_{\text{std}} \) are the ratios of 13C relative to 12C in the CO\textsubscript{2} in the sample and in the VPDB standard, respectively.

Three carbonate standards that covered a range of delta values were used to reduce uncertainty in the isotope measurements.\textsuperscript{9–11} The span of calibration standards was −47.32‰ (IAEA-CO-9) to +1.95‰ (NBS19). NBS18 (−5.01‰) was used as a quality control (QC). The carbonate standards were prepared according to Revesz and Landwehr:\textsuperscript{12} the standards were transferred into 12-mL septum-capped exetainers, flush-filled with helium for 5 min, digested with 100% H\textsubscript{3}PO\textsubscript{4} in a CO\textsubscript{2}-free environment, and allowed to equilibrate for 24 h. The vials were flush-filled in the gas bench with tank air at 26 mL min\textsuperscript{−1} using the double-holed needle. The internal pressures of all vials were equilibrated with atmospheric pressure to reduce the variability of the results.\textsuperscript{3} The flush-fill needle was left in the vial for 60 s after shutting off the supply of the flushing gas to achieve atmospheric equilibrium. A pressure gauge (model HHP701-2; Omega Engineering, Stanford, CT, USA) fitted with a needle was used to verify internal vial pressure.

All sequences were normalized using the Laboratory Information Management System (LIMS) for Light Stable Isotopes (USGS, Reston, VA, USA) with NBS19 and IAEA-CO-9 as anchor points. LIMS uses ordinary least-squares regression (OLS) to normalize isotopic values and perform hourly drift corrections if needed. An hourly drift correction was applied to the data only if all the references and QC samples showed improvement. The final isotopic composition of each sample was evaluated from the best three of five sample peaks, with vial precision typically <0.1‰ (1 standard deviation (SD)). The first two peaks were typically ignored because they were the most likely to be affected by carry-over from the previous sample. Occasionally, the last peak was ignored due to helium dilution of the signal. In cases where the goal was to measure prior sample carry-over, the area and δ\textsubscript{13C}VPDB values of all peaks were used. We chose 10 mV as a minimum peak detection parameter because it was the smallest peak above typical background fluctuations that our system could reliably detect. Since diagnostic tests encompassed 500–8000 mV only, it should be noted that some additional bias might exist for sample peaks with signals <500 mV. We present only the mean values for such peaks, normalized in the same way as other samples.
Description of gas sample preparation methods

We compared three filling techniques to prepare gas samples: (1) automated flush-fill (AFF), (2) vacuum back-fill (VBF), and (3) hand-fill (HF). All vials were initially open to room air and the caps were tensioned prior to all treatments. In the AFF method, the vials were flush-filled using the GC-PAL autosampler on the Gasbench II for 5 and 10 min at a flushing rate of 26 mL min\(^{-1}\). The autosampler was programmed to leave the flushing needle in the vial for 60 s after turning off the flush gas. This was determined previously to keep the vials at only a slightly positive pressure. We combined AFF with vial pre-cleaning treatments, where individual vials were pre-evacuated and filled with helium one or three times.

For the VBF technique, the vials were evacuated and filled via a vacuum back-fill manifold (Fig. 1). The line was constructed of \(1/4''\) stainless steel tubing with 8 valved ports designated V1 (\(1/4''\) turn Swagelok plug valves, part # SS-4P4T, The Swagelok Co., Solon, OH, USA) which reduce into 28G needles. Both ends of the line have separate valves, designated V2 (Swagelok \(1/4''\) integral bonnet needle valve, part #SS-1RS4) which allow the user to control connection to a vacuum pump (RV 1.5; Edwards, Tewksbury, MA, USA) and the flush gas. The flush gas for the VBF technique was helium in the case of blank preparation or a gas tank filled with actual sample. The VBF manifold and the connection to the regulator of the flushing tank were initially evacuated. The vacuum was measured with a thermocouple type 0531 sending unit (Varian, Walnut Creek, CA, USA) and model 801 analog gauge. The pressure was measured with a pressure transducer and digital readout (MKS 122A-1123, PDR-D-1; MKS Instruments, Andover, MA, USA). After each evacuation, the manifold was isolated from the vacuum pump and the vials were filled with the tank gas to atmospheric pressure by slowly adjusting the tank regulator. The VBF method was applied in two treatments: one evacuation/back-fill, and three evacuations/back-fills.

In the HF method, vials were evacuated with the VBF line, left under vacuum and manually filled with the tank gas using a 30-mL syringe. The syringe was used to pierce an empty septum-fitted Swagelok \(1/4''\) nut that was attached to the tank regulator, set at 138 kPa (20 psi). After three rinses of the syringe, the sample vials were initially over-pressurized by injecting 20 mL of sample gas into the 12-mL exetainers. Excess vial pressure was released by briefly puncturing the vial septum with a needle, allowing the pressure to equilibrate with ambient pressure. The HF method was applied in three treatments: one evacuation/hand-fill, and three evacuations/hand-fills.

In summary, the three sample introduction methods (AFF, VBF, HF) in combination with vial pre-filling procedures (no evacuation, one evacuation, and three evacuations) yielded a total of ten treatments. These treatments were: 5-min AFF with no evacuation, 5-min AFF with 1 evacuation, 5-min AFF with 3 evacuations, 10-min AFF with no evacuation, 10-min AFF with 1 evacuation, 10-min AFF with 3 evacuations, HF with 1 evacuation, HF with 3 evacuations, VBF with 1 evacuation, VBF with 3 evacuations. The HF and VBF techniques were not used with the no-evacuation procedure because these techniques always require an evacuated vial.

Experiment 1: Identification of sources of contamination

The contamination was assessed using helium-filled vials (blanks) for the ten treatments previously described. Three replicates (designated as blanks 1, 2 and 3) were prepared for each treatment and successively positioned after an IAEA-CO-9 (\(-47.32\%)\) carbonate standard. The default minimum peak detection parameter was lowered from 50 to 10 mV. The \([\text{CO}_2]\) for gas samples can be determined from the area of the voltage signal peak.\(^{13,14}\) Therefore, the magnitude of contamination was estimated by taking the ratio of the maximum sample area of the blanks over the maximum area of a 380-ppm \(\text{CO}_2\) sample for this instrument. The source of contamination was identified using the \(\delta^{13}\text{C}\) values of the blank vials. Memory effects (carry-over contamination) in the Gasbench were associated with the depleted \(\delta^{13}\text{C}\) values of the IAEA-CO-9 standard; in contrast, contamination due to

![Figure 1. Schematic diagram of the vacuum back-fill manifold. The line consists of \(1/4''\) stainless steel tubing with 8 valved ports designated V1 which reduce into 28G needles. Both ends of the line have separate valves, designated V2, which allows the user to control connection to a vacuum pump and the flush gas.](image-url)
laboratory air had a significantly more enriched $\delta^{13}C$ ($\approx -9\%$).

The CF-IRMS instrument sampled each vial and analyzed it five times. The gas in the vial was diluted as helium was injected to transfer the sample into the mass spectrometer. Therefore, our ability to detect small contaminations in the blanks decreased over the analysis time required for each sample: room-air contamination might have been detected in the first sample peak but would probably disappear in the remaining peaks. A common practice for post-processing isotope data is to discard the first sample peak because it is subject to large errors. We decided to use the third peak in our analysis of blanks 2 and 3 to identify the treatments with room-air contamination that would still be present even after post-processing.

**Experiment 2: Application to gas samples of near-ambient CO$_2$ concentrations**

The results obtained from Experiment 1 (blanks) were used to select among each category (AFF, HF and VBF) the treatment that (1) produced minimum contamination, and (2) required the least preparation time. The selected treatments were 5-min AFF with 1 evacuation/helium fill, VBF with 3 evacuations/back-fills, and HF with 3 evacuations/hand-fills. Those three treatments were used for further testing with the CO$_2$ tanks to evaluate the best method for gas standard preparation. Three sample vials were prepared per filling treatment. To avoid carry-over contamination, a blank (helium-filled) vial was positioned between the carbonate standard and the CO$_2$-filled sample vials. This experimental set-up enabled us to attribute any observed residual contamination to the sample preparation method.

The CO$_2$ tanks were dilutions prepared by mixing carbon isotope reference gases with instrument grade zero air. Carbon isotope reference gases were: tank 1, $-23.5\%$ (Cambridge Isotope Laboratories Inc., Andover, MA, USA) and tank 2, $-38.9\%$ (Oztech Trading Corporation, Safford, AZ, USA). The CO$_2$ concentrations were 396.4 ppmv ($\pm 1\%$) and 383.7 ppmv ($\pm 1\%$) for tanks 1 and 2, respectively.

**RESULTS**

**Experiment 1: Identification of sources of contamination**

The highest contamination ($\approx 4.5\%$ of the area of a 380-ppm sample) occurred in the 5-min AFF method when no vial pretreatment was carried out (Fig. 2). The contamination was reduced (<4%) by either flushing for 10 min or rinsing the vials with helium before flushing. No improvement was observed by rinsing the vials three times instead of one. For both the VBF and the HF method the contamination was about 4% and this was not reduced by applying more evacuations (Fig. 2). One replicate for the 10-min AFF with 1 evacuation was not included in Figs. 2 and 3, as the observed voltage area for this treatment was almost twice as large as those observed for the other treatments. An outlier test using orthogonal distance regression on the $\delta^{13}C$ and peak areas of

![Figure 2. Maximum contamination on low-concentration CO$_2$ gas samples as a function of the various gas filling treatments. The three sample introduction methods (AFF = automated flush-fill, VBF = vacuum back-fill, HF = hand-fill) were combined with vial pre-filling procedures (no evacuation, 1 evacuation, and 3 evacuations) for a total of ten treatments. The HF and VBF techniques were not used with the no-evacuation procedure because these techniques always require an evacuated vial. Data for the 10-min AFF with 1 evacuation were not included as the observed voltage area for this treatment was almost twice as large as those observed for the other treatments. An outlier test using orthogonal distance regression on the $\delta^{13}C$ and peak areas of all treatments confirmed that the result for the 10-min AFF with 1 evacuation was an outlier in the data set.](image-url)
all treatments confirmed that the result for the 10-min AFF with 1 evacuation was an outlier in the data set.

To identify the sources of contamination we analyzed the δ¹³C values of the blanks. For each filling technique three replicates (blanks 1, 2 and 3) were placed in sequential order after an IAEA-CO-9 standard. Blank 1, positioned immediately after IAEA-CO-9, had more negative δ¹³CVPDB values and larger voltage areas (Fig. 3). We found contamination in blank 1 for nine treatments (data for 10-min AFF with 1 evacuation was not included in the figure). For blank 2 only four treatments presented contamination and for blank 3 only three treatments had detectable contamination (Fig. 3). In cases where we still observed contamination in blanks 2 or 3, the δ¹³CVPDB values were similar to those of laboratory room air (Fig. 3). These results clearly show that: (1) the carry-over contribution from IAEA-CO-9 was observed in the sample positioned immediately after the carbonate (blank 1), and (2) the residual room-air contamination in blanks 2 and 3 was only observed for some treatments; i.e. not all treatments were susceptible to room-air contamination. When we analyzed the third peak of blanks 2 and 3, only the two HF and the 5-min AFF methods exhibited the presence of contamination (Fig. 4). This residual contamination in the HF and 5-min AFF methods was clearly an artifact of the sample preparation method. Flush filling for 5 min (no evacuation) was insufficient to turn over the gas in the vial, while doubling the flush fill time to 10 min or rinsing the vial with helium before filling completely removed the residual room air. Puncturing the HF vials to release excess pressure may have introduced room air during pressure equilibration.

Simulation using a two-source mixing model predicts that a 4.5% contamination (maximum contamination measured in Experiment 1) translates to as much as ~1.7% error. This error would result when the differential isotopic composition of the sample gas and the contaminant is about ~37% (Fig. 5), as in the case where the contamination is carry-over from IAEA-CO-9 (~47%) and the sample gas is room air with an isotopic signature of ~9.3% (Fig. 5). As the stable isotope composition of contamination becomes more similar to that of the sample, there is less added uncertainty. The error decreased when the carbon isotope ratio of the contaminant approached that of the sample. This result suggests that carry-over contamination can be masked whenever the carbon isotope ratio of the contaminant is similar to that of the sample. For the case where the contamination is isotopically very different (e.g. ~47%) and of very low concentration (nominally equal to the minimum peak detection limit of 10 mV), the contamination contribution is about 0.4% of the area of a 380-ppm sample. Simulation
Recall that the carbon isotope ratio of room air in our laboratory was measured as $\delta^{13}C = -9.3\%o$, which was the average measured $\delta^{13}C$ of room air in our laboratory.

Predicates that this contribution translates to an error of $\sim 0.15\%o$, which is of the same order as the precision of CF-IRMS systems.

**Experiment 2: Application to gas samples of near-ambient CO$_2$ concentrations**

The AFF and VBF techniques yielded similar precisions ($\leq 0.1\%o$) while the largest variability in results was observed for the HF method ($\geq 0.2\%o$) (Fig. 6). The carbon isotope ratio for tank 2 obtained with the HF method was slightly enriched ($-38.3\%o$) relative to the AFF ($-38.9\%o$) and VBF ($-38.8\%o$) methods. This result is consistent with the introduction of room air ($\sim -9.3\%o$) into the more depleted HF samples ($\sim -38\%o$) during pressure equilibration. We did not observe the same isotopic enrichment for tank 1 samples prepared with the HF technique. This observation is consistent with the result of the two-source mixing model simulation shown in Fig. 5. Since the carbon isotope ratio of the sample (tank 1, $-23.5\%o$) was closer to that of the ambient samples, the small contamination introduced by the HF technique did not significantly alter the $\delta^{13}C$ estimated for the sample.

**DISCUSSION**

Continuous-flow isotope ratio mass spectrometry is now frequently used to investigate the carbon isotopic exchange between the biosphere and atmosphere, making use of septum-capped vials to collect gas samples from remote field sites followed by laboratory analysis. To reduce errors associated with gas collection and storage, earlier studies focused on improving the reliability of septum-capped vials prior to application in the field. Previous studies have investigated the flushing times required for carbonate standards preparation, but there is no standard protocol for introducing low-concentration gas samples into vials for analysis on the same sampling device. Through improved vial preparation and analysis, we found that error can be reduced in low-concentration samples.

Carry-over contamination associated with the laboratory analysis can add uncertainty to the results. The carry-over contribution was attributed to the transfer of a small portion of sample from the previous to the current vial. The significance of the carry-over depends on both the prior sample concentration and its stable isotope composition. When we diluted our carbonate standard with helium, carry-over contamination was not observed in any of the blank vials (data not shown). Therefore, sequence design must consider sample concentration and expected isotopic composition, and similar samples should be grouped together in the sequence. We found errors due to carry-over as large as $1.7\%o$. Errors in the isotopic ratio of collected gas samples of the order of $0.7\%o$ can potentially introduce significant uncertainty when used in Keeling plot applications to determine signatures of ecosystem respiration. For example, Badeck et al. reported that, on the global scale, an uncertainty in the autotrophic respiration of the order of $1.7\%o$ can translate to as much as $5\%$ change in the estimate of the biospheric sink.

Carry-over can cause significant errors in the analysis of low-concentration samples, such as those at ambient [CO$_2$]. Carry-over can be reduced by placing a blank (helium-filled) vial between a standard and the gas sample or by discarding the first two sample peaks during post-processing of data. We hypothesize that carry-over is a potential artifact of the continuous-flow system. Unlike a traditional off-line analysis where pure gases are transferred in controlled amounts via dual inlet, and then evacuated between samples, the Gasbench system relies on a continuous flow of helium to transfer the analyte gas to the IRMS instrument. In the Gasbench itself, we see the sample gas continually diluted as it is transferred to the mass spectrometer. In a separate test, we compared blanks immediately following carbonates with the sample open split in the 'out' position. Performing this test reduced the carbonate signal in the mass spectrometer.
compared with the split ‘in’ position, but it did not reduce the blank effect of a subsequent vial. Therefore, we think that the carry-over observed is occurring in the Gasbench and not in the mass spectrometer. Memory effects in CF-IRMS systems must therefore be addressed in future efforts to design systems with high reliability and precision.

Ambient air contamination was shown to be an artifact of the sample preparation method. We found that a basic (<10 min or without vial pretreatment) flush-fill method can lead to incomplete volumetric turnover of gas in the vial. This result is consistent with recent findings of Paul and Skrzypek who recommended flushing times of ≥600 s to completely remove air in the vials. Our results indicated that either the 5-min AFF with helium pre-cleaning or the VBF with three sample fills was a satisfactory method for analyzing low-concentration CO2 gas tanks. Accordingly, either technique can be used to prepare gas standards for Gasbench applications. However, we found the VBF technique to be a more efficient method with higher throughput. With the use of the vacuum back-fill manifold, it took approximately the same time to evacuate and fill eight vials as it did to fill one vial on the Gasbench using the AFF method. The variation in the HF data was associated with less uniformity due to manual fills.

We recommend VBF, or AFF with vial pretreatment, for filling low-concentration gas samples into vials. The VBF method can be more readily applied to field measurements. The procedure is a slight modification to the method described by Knohl et al. Vials fitted with Kel-F disks can be simultaneously evacuated using the vacuum back-fill (VBF) manifold and a vacuum pump. The VBF set-up will allow for several vials to be pre-rinsed with canopy air before filling. The approach can facilitate a larger throughput from the field, increasing the statistical robustness of analysis of samples. The vacuum line system could easily be deployed in the field.

All our procedures sampled gas from pressurized tanks and this may not be practical for all field samples. Where low-pressure, low-volume samples are all that is available (and a VBF system is inaccessible), the HF method is the most suitable outlined here. The procedures that we tested provide insight into the differences between the HF technique and what we consider the gold standard, the VBF approach. Therefore, the techniques presented here could be used to prepare multiple gas standards in exetainers or to test HF methods before implementing them in the field. The precision of measurements of low-concentration gas samples with CF-IRMS devices can also be improved by taking steps to reduce carry-over in the device itself. We recommend building sequences with similar samples (concentration and stable isotope composition), incorporating helium blanks, and using post-run data processing to reduce external sources of variation.

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