# $\delta^{13}$C of Air Liquide carbon dioxide: cylinder preparation and calibration

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## Goal

To describe the process for the filling, preparation and calibration of $CO_2$ in Air Liquide's gas cylinders. This description contains both the validation of cylinder filling uniformity as well as the isotope calibration process and some of the precautions that stable IRMS laboratory practitioners should adhere to when dealing with compressed dual- and single-phase $CO_2$.

## Introduction

Air Liquide has established stable isotope certified $N_2$, $H_2$ and $CO_2$ gases that can be used as isotopically characterized reference gases for isotope ratio mass spectrometers. Using isotopically characterized $N_2$, $H_2$ and $CO_2$ gases is important since nearly all laboratory users connect these gases directly to their IRMS for analysis as laboratory working reference gases for comparison to their unknown samples. The purpose of this technical note is to describe how such gases are filled into the cylinders and the subsequent product uniformity and reliability as it is used.

$CO_2$ and other isotopically characterized gases are filled from a "Source cylinder" into the smaller "Product cylinders": this process is referred to as transfilling. Concerns have been expressed in the IRMS community about the use of isotopically characterized and transfilled gases as standards. This concern derives from gas handling procedures, which include: vaporization, expansion, pressurization, transfer through lines and equipment, storage, etc., which are thought to cause isotope fractionation. Consequently, Air Liquide has rigorously validated gas filling, processing, and storage protocols used in the manufacture of these products. This directly addresses these concerns and essentially eliminates the associated isotopic fractionation that commonly accompanies those processes.

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In this note, we will address the following parameters, with examples shown for $CO_2$ in a gas cylinder:

1. Vaporization of liquefied gas

2. Gas transfilling

3. Gas Pressurization/depressurization—regulation

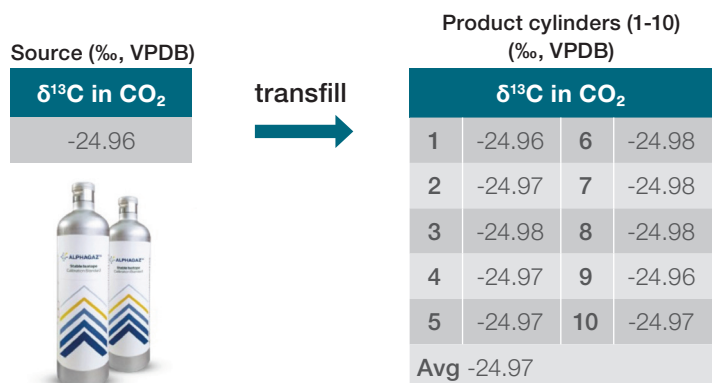4. Isotopic characterization of $CO_2$

## 1. Vaporization of liquefied gas

Isotope fractionation occurs when liquefied gases are vaporized. This is particularly pertinent to gases such as $CO_2$ and nitrous oxide ($N_2O$)—which are also referred to as compressed, liquefiable gases. In order to better understand this phenomenon, a carefully controlled experiment was conducted that involved slowly depleting a 16 L aluminum cylinder which had been filled with 16 kg of research grade $CO_2$ to ensure both a liquid and gaseous phase (dual phase) within the cylinder. The cylinder was depleted of its contents at a withdrawal rate of approximately 50 mL/min to eliminate the possibility of droplet formation in the gas stream while measuring the $^{13}C$ composition periodically over a ~7 month period. The $^{13}C$ composition of dual phase pressurized $CO_2$ was observed to change as the contents of the cylinder was depleted, as illustrated in Figure 1. During the initial stages of cylinder withdrawal, the $CO_2$ showed a slight $^{13}C$ depletion. As the cylinder was emptied, less liquid was present and the cylinder was dominated by a gas fraction, and an enrichment in the $^{13}C$ composition was observed. These observations are consistent with previous data[1,2]. For this reason, a 1.6 L cylinder with 34 bar gaseous $CO_2$ was chosen, as these conditions are known to avoid fractionation.
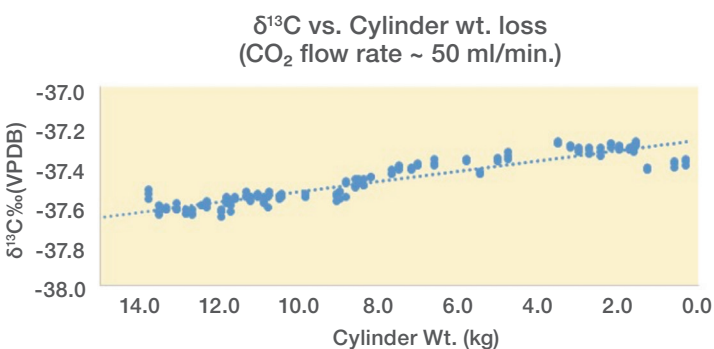
## 2. Gas transfilling

The equipment used to transfill gas from a source cylinder to the product cylinders is referred to as a transfill manifold. The source cylinder is connected to the feed side of the manifold; the product cylinders are on the receiving side. Typically, a source cylinder can fill many product cylinders at a time. Gases flowing through the transfill manifold are then subjected to gas expansion, pressurization and flow direction changes, all of which are possible sources of isotope fractionation. By judicious design of the gas transfill manifold system and controlled gas transfer operations, Air Liquide has tested and successfully shown that isotope fractionation does not occur during the transfill process followed here. Figure 2 illustrates transfilling from a source cylinder with an isotopic signature of $\delta^{13}C$-$CO_2$ = -24.96‰ (VPDB), which was transfilled into 10 cylinders with an average of $\delta^{13}C$ - $CO_2$ = -24.97‰ (VPDB). Of note, these results also show that the position of the product cylinder on the manifold (indicating different gas pathways travelled by the gas) did not appear to affect isotope compositions.

| Source (‰, VPDB) | | Product cylinders (1-10) (‰, VPDB) | | | |
|---|---|---|---|---|---|
| **$\delta^{13}C$ in $CO_2$** | transfill | **$\delta^{13}C$ in $CO_2$** | | | |
| -24.96 | | 1 | -24.96 | 6 | -24.98 |
| | | 2 | -24.97 | 7 | -24.98 |
| | | 3 | -24.98 | 8 | -24.98 |
| | | 4 | -24.97 | 9 | -24.96 |
| | | 5 | -24.97 | 10 | -24.97 |
| | | Avg -24.97 | | | |

Figure 2. $\delta^{13}C$ values for the mother cylinder and product cylinders illustrating uniform transfilling.

## 3. Gas pressurization

The ability to regulate pressure from a compressed gas cylinder without fractionation is important to ensure that the highest quality isotope data are obtained. To evaluate this, pressure from a 16L compressed gas cylinder filled with 57 bar of research grade $CO_2$ was reduced through sequential expansions to avoid the use of a pressure regulator and the $^{13}C$ composition was measured[1,2]. These data were compared with the $^{13}C$ values after pressure reduction using a single stage, low dead-volume regulator. Measurements of pressure reduced samples obtained using the pressure regulator were done in the range of 0.5 to 3 bar. The background measurement refers to $CO_2$ taken from the cylinder



δ¹³C vs. Cylinder wt. loss
(CO₂ flow rate ~ 50 ml/min.)

Figure 1. $\delta^{13}C$ vs. $CO_2$ Cylinder depletion wt. in kg of a liquid-/gas-filled $CO_2$ cylinder. The flow rate of the $CO_2$ throughout the duration of the experiment (~7 months) was kept constant at ~50 ml/min. Change in the C isotope composition (Δ) from most depleted to most enriched is 0.38‰.

without the use of the pressure regulator but only by sequential expansion ($\delta^{13}C$ = -24.50‰ (VPDB)). To arrive at the effect of pressure reduction, the isotope values at the designated pressures were subtracted from the background isotope value (Figure 3). The data very clearly show that over a pressure range of ~4 bar the isotope variations are less than analytical error, i.e. $\leq \delta^{13}C$ variations that can be expected from a zero enrichment measurement on a well-tuned IRMS. We therefore conclude from these data that using the type of regulator described here does not statistically alter the $\delta^{13}C$ values of pressurized $CO_2$ in the pressure ranges evaluated.
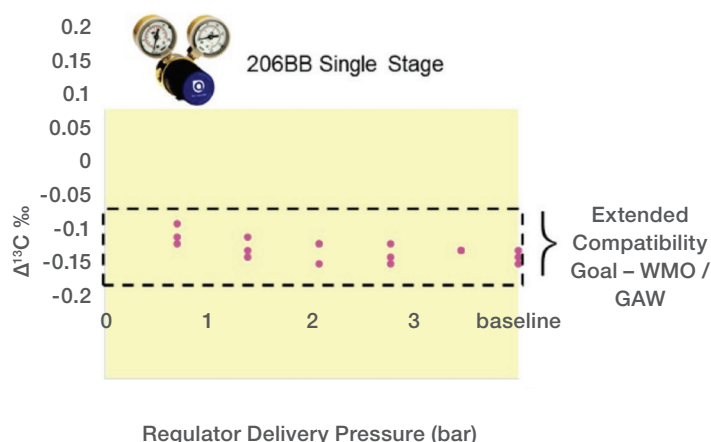


**Figure 3. Background analysis of $\delta^{13}C$-$CO_2$ (VPDB) without the use of a pressure regulator (gas expansion only) and of $\delta^{13}C$-$CO_2$ (VPDB) obtained with the use of a pressure regulator.** $\Delta^{13}C$ ‰ represents the difference between pressure reduction by sequential volumetric expansion and pressure reduction with a pressure regulator.

## 4. Isotopic characterization of $CO_2$

In order to establish the $\delta^{13}C$ of $CO_2$ contained in the compressed gas cylinders filled by Air Liquide, standard analytical protocols were followed. Analysis of the $CO_2$ was performed in the stable isotope facilities at Air Liquide (USA) on a Thermo Scientific™ 253 Plus™ 10 kV

IRMS operated in dual inlet mode. The isotopic value was measured relative to 102% phosphoric acid-extracted $CO_2$ from the NBS-19 calcium carbonate standard whose $\delta^{13}C$ = +1.95‰ (VPDB)[3,4]. The $\delta^{13}C$ value of that $CO_2$ as measured and calibrated was -3.3‰ (VPDB). The same gas that was analyzed at Air Liquide was further analyzed at the United States Geological Survey (USGS), Reston, VA USA also on a dual inlet mass spectrometer. The $\delta^{13}C$ value of that $CO_2$ as measured and calibrated at the USGS was -3.27±0.03‰ (VPDB).

## Summary

Air Liquide has established isotopically characterized $N_2$, $H_2$ and $CO_2$ gases that can be used as reference material for isotope ratio mass spectrometers. By controlling several aspects of cylinder preparation, proper source to product cylinder transfilling techniques, and careful pressure regulation, Air Liquide can assure IRMS end users with isotopic uniformity and reliability in gas standards, not only in the Thermo Scientific™ Start-Up Kit, but also for subsequent use when re-ordered.

## Acknowledgment

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