

$\delta^{13}\text{C}$ of carbon dioxide, $\delta^{15}\text{N}$ of nitrogen and $\delta^2\text{H}$ of hydrogen: interlaboratory comparison of isotopically characterized gases

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Goal

To compare and validate isotopic values for $\delta^{13}\text{C}-\text{CO}_2$, $\delta^{15}\text{N}-\text{N}_2$ and $\delta^2\text{H}-\text{H}_2$ in the Air Liquide stable isotope certified gases with isotope values obtained by the United States Geological Survey, Reston Stable Isotope Laboratory (USGS RSIL).

Introduction

Air Liquide has established stable isotope certified CO_2 , N_2 and H_2 that can be used as isotopically characterized gases for isotope ratio mass spectrometers. Using isotopically characterized CO_2 , N_2 and H_2 is important since nearly all stable isotope laboratory users connect these gases directly to their IRMS systems for analyses as laboratory working reference gases for comparison to their unknown samples.



The purpose of this technical note is to validate the isotopic composition obtained by Air Liquide by comparing those values to those measured on the same gases by the USGS RSIL, VA, USA.

Comparison

The primary analyses of the sample gases were performed at Air Liquide (USA) on a Thermo Scientific™ 253 Plus™ 10 kV IRMS operated in dual inlet mode. An aliquot of each gas was expanded into the dual inlet and analyzed against calibrated working reference gases. Air Liquide calibration methods for working reference gases (CO_2 , N_2 and H_2) are described in each subsequent section below. Comparison analysis of these gas samples were further made at the USGS RSIL. The data comparison between Air Liquide and USGS RSIL values illustrate that they are statistically identical at the 95% confidence level (Table 1).

Table 1. Comparison of AL and USGS RSIL stable isotopic values for the range of isotopically characterized gases.

Stable isotope ratio/gas	AL measured value	USGS measured value
$\delta^{13}\text{C-CO}_2$	$-3.3\text{‰} \pm 0.5\text{‰}$ (VPDB)	$-3.27 \pm 0.03\text{‰}$ (VPDB)
$\delta^{13}\text{C-CO}_2$	$-24.9\text{‰} \pm 0.5\text{‰}$ (VPDB)	$-24.95 \pm 0.03\text{‰}$ (VPDB)
$\delta^{15}\text{N-N}_2$	$-1.9 \pm 0.5\text{‰}$ (air)	$-1.90 \pm 0.04\text{‰}$ (air)
$\delta^2\text{H-H}_2$	$-253 \pm 5\text{‰}$ (VSMOW-SLAP)	$-250.0 \pm 3.3\text{‰}$ (VSMOW-SLAP)

$\delta^{13}\text{C-CO}_2$

The isotopic value for the gaseous CO_2 was measured relative to 102% phosphoric acid-extracted CO_2 from the NBS-19 calcium carbonate standard, whose certified $\delta^{13}\text{C} = +1.95\text{‰}$ (VPDB)^{1,2}. Table 1 summarizes the $\delta^{13}\text{C}$ value of that CO_2 along with the value obtained by the USGS RSIL.

$\delta^{15}\text{N-N}_2$

The isotopic value for the gaseous N_2 was measured relative to a nitrogen isotope reference working gas that was calibrated against NSVEC (NIST-8552) nitrogen gas¹, whose $\delta^{15}\text{N}$ value = $+2.78\text{‰}$ (Air- N_2). The comparative analysis with the USGS RSIL is found in Table 1.

$\delta^2\text{H-H}_2$

The isotopic value for the gaseous H_2 was measured relative to a H_2 isotope reference working gas that was calibrated by means of water standards measured and normalized to the V-SMOW-SLAP scale according to Reference 2, where VSMOW = 0.0‰ and SLAP = -428‰ . The comparison with the USGS RSIL analysis is located in Table 1.



Summary

At the 95% confidence level, the stable isotope values for the $^{13}\text{C-CO}_2$, $^{15}\text{N-N}_2$ and $^2\text{H-H}_2$ isotopically characterized gases measured by Air Liquide are statistically the same as those made by the USGS RSIL. Therefore, customers can use the isotopic values provided in the certificates of the Air Liquide isotopically characterized gases with confidence.

*For additional information on gas filling, processing, and storage protocols used in the manufacture of isotopically characterized gases, please see Technical Note TN30734.

References

- Brand, W., Coplen, T.B., Vogl, J., Rosner, M. and Prohaska, T., 2014. Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report). Pure and Applied Chemistry, V. 86, 3, pp.425-467.
- Coplen, T.B., 1988. Normalization of oxygen and hydrogen isotope data. Chemical Geology: Isotope Geoscience Section, V. 72, 4, pp.293-297.

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