

MEASUREMENT INFORMATION

PREPARED FOR: Pennsylvania State University

Cylinder: JB03428

Date: 2/3/15



The Stable Isotope Lab (SIL) at INSTAAR, University of Colorado, has measured this cylinder for  $\delta^{13}\text{C}$  of  $\text{CH}_4$  in cooperation with the Global Monitoring Division of the National Oceanic and Atmospheric Administration. **This measurement is offered as an unofficial calibration**, for reasons that are discussed below. This document includes specific information regarding methods used to make these measurements. If you have any further questions, please contact the Stable Isotope Lab directly: Bruce Vaughn (303-492-7985, [bruce.vaughn@colorado.edu](mailto:bruce.vaughn@colorado.edu))

The table below summarizes the results of the measured composition of  $\delta^{13}\text{C}$  in atmospheric  $\text{CH}_4$  in your tank. Please note that these numbers are considered informational and are provided only as an initial  $\delta^{13}\text{C}$  in atmospheric methane value.

Informational $\delta^{13}\text{C}$ of Methane				Stable Isotope Lab INSTAAR, Univ. of Colorado, Boulder
Cylinder ID	JB03428			
Date filled	6/19/2014			
Date Analyzed	n $\delta^{13}\text{C}$	Mean $\delta^{13}\text{C}$	1 $\sigma$ $\delta^{13}\text{C}$	$\delta^{13}\text{C}$ Uncertainty*
12/10/14	3	-46.851	0.027	0.057
12/12/14	3	-46.828	0.064	0.061
12/17/14	3	-46.830	0.079	0.059
12/19/14	3	-46.843	0.008	0.061
12/31/14	8	-46.795	0.038	-0.009
1/8/15	4	-46.821	0.053	0.089
1/22/15	3	-46.861	0.030	0.086
1/27/15	3	-46.785	0.064	0.085
	Total n $\delta^{13}\text{C}$	$\delta^{13}\text{C}$		Std error
Final Value	<b>30</b>	<b>-46.821</b>		<b>0.009</b>

\* Standard deviation of “trap tank” (a cylinder of known value) over roughly 10 days of analysis. (-0.009 value indicates trap did not run that day)

### *Measurement details*

Measurements are made using an Isoprime (Elementar Group) continuous flow stable isotope mass spectrometer (CF-IRMS) that is primarily used for measuring stable isotopes of carbon in methane. The methods used are described in detail in **Miller et al. (2002)**. Sample analysis can be summarized in a few general steps: methane extraction and pre-concentration; cryo-focusing; chromatographic separation; combustion and drying; and continuous flow mass spectrometric analysis. Samples from cylinders are introduced the same way reference and trap tank (see below) air is introduced into the system.

All isotopic measurements expressed here for  $^{13}\text{C}/^{12}\text{C}$  are in delta notation  $\delta^{13}\text{C}$ , which is defined as the part per thousand deviation of the  $^{13}\text{C}/^{12}\text{C}$  ratio in a sample to that in a standard

$$\delta^{13}\text{C} \equiv [(R_{\text{sample}}/R_{\text{reference}})-1] \times 1000 \text{ ‰}$$

where  $R=^{13}\text{C}/^{12}\text{C}$  and reference is V-PDB [*Craig, 1957*]. The scale used is set using international standards NBS-19 and NBS-20 for carbonates.

The procedure for measuring tanks is to analyze at least three sets of five extractions that are performed over a period of several weeks to check for drift in the isotopic value. Typically, the first values from a newly filled tank are rejected. The precisions for  $\delta^{13}\text{C}$  quoted with your tank are standard errors calculated from these analyses. The value reported is the unweighted mean of all retained analyses.

Daily instrument runs include measurements from a cylinder, treated as an unknown, whose isotope value is known: this "trap" tank alerts us to any problems with the mass spectrometer or extraction system. We also use this cylinder to calculate uncertainty, which we define as the standard deviation of ten analyses of trap measurements. Typically we measure four trap samples per day, of which all but the first are used (due to known irregularities caused by the tank regulator). For each set of analyses, the uncertainty is calculated from the trap data from that run.

### *Measurement Scale*

Cylinders of compressed whole-air that have isotopic  $\delta^{13}\text{C}$  values assigned to them can be used as secondary standards for environmental measurement applications. By far the most demanding application is tracking modern-day changes in atmospheric methane as differences are quite small, and stability of the long-term calibration is important. Consequently, measuring stable isotopes in  $\text{CH}_4$  with the precision needed for atmospheric  $\text{CH}_4$  budgeting is difficult and only performed by a few laboratories worldwide. The large difference between atmospheric  $\delta^{13}\text{C}-\text{CH}_4$  (approximately -47%) and the primary  $\delta^{13}\text{C}$  standard (NBS-19, 1.95‰) places stringent requirements on a laboratory's ability to maintain the integrity of an internal calibration scale over decades. Given this large difference between carbon reference materials and atmospheric values, ties to primary reference materials can vary, and slight offsets have been observed between the principal laboratories making these measurements. Without inter-laboratory comparisons, crucial for quality control, interpretation of combined  $\delta^{13}\text{C} - \text{CH}_4$  records from different laboratories in modeling studies may yield wrong conclusions (Levin et

al., 2012). Efforts to further tighten this link are ongoing with a handful of international labs, including INSTAAR.

For reasons described above, we cannot claim that our scale is any more accurately tied to primary reference materials than other labs. However, our scale along with several other key labs has been linked to the V-PDB scale via Dr. Stanley Tyler at University of California Irvine, using traditional, dual-inlet, off-line techniques based on that of Stevens and Rust [1982; Tyler, 1986; Lowe *et al.*, 1991]. We also use internal standards to verify that our scale has not drifted over time. At INSTAAR, we maintain four reference cylinders that have been calibrated at UC Irvine in this manner. The  $\delta^{13}\text{CH}_4$  of these whole-air reference cylinders was measured relative to pure  $\text{CO}_2$  reference gas that had been calibrated against IAEA-NZCH, a Barium (?) Carbonate solid standard with an isotopic value near that of atmospheric methane [see e.g. Lowe *et al.*, 1999]. Therefore, the isotopic composition of any of our samples and one additional reference air tank are determined relative to these calibrated references in any analysis run. All measurements are reported relative to V-PDB [Coplen, 1995]. Comparisons confirm that our scale is very close to that of other international laboratories.

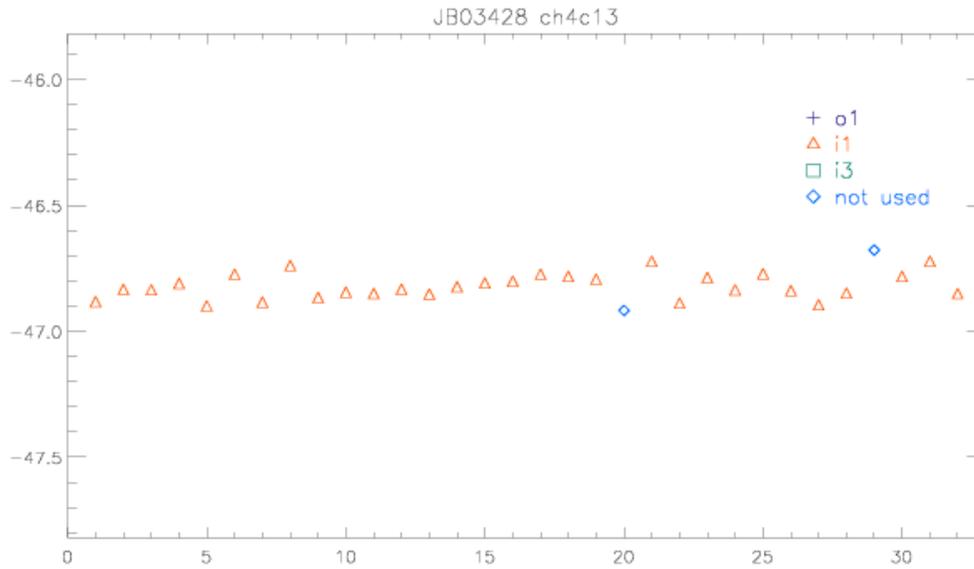
In summary, **our direct tie to V-PDB scale is not as robust as we believe is required, which is why we offer these measurements as informational only.**

*Important note on regulators:*

There are known isotopic problems with some types of high-pressure regulators used for the cylinders. Lower cost models that have seals made with elastomers such as Viton or butyl rubber are particularly problematic. These materials can contaminate the standard air with compounds that contribute to masses 45 and 46. We recommend using a high purity regulator that has a minimum of non-metallic surfaces, preferably stainless steel. We have chosen for use on all our standards the Air Products model E11-C444A (CGA-590) stainless steel single stage regulator with Kel-F and Teflon seals. The two stage version works equally well, and both have proven to be a more stable regulator than other models. Single stage regulators may lack the long-term pressure stability that can be found with two stage regulators, but since very little gas is used in the analysis process for even our daily standards, the necessary adjustments of outlet pressure are infrequent. The single stage model also has the advantage of fewer wetted parts and is more economical (~approx. \$550 USD). No doubt there are likely other brands of regulators that would also perform adequately, but are untested by our analysis process.

*References:*

- Coplen, T. B., (1995) Reporting of stable carbon, hydrogen, and oxygen isotopic abundances, in Reference and intercomparison materials for stable isotopes of light elements, pp. 31-34, International Atomic Energy Agency, Vienna, 1995.
- Coplen, T.B., (1995) Discontinuance of SMOW and PDB, *Nature*, 375(6529), 285-285, 1995.
- Levin, I., Veidt, C., Bruce H. Vaughn, Brailsford, G., Bromley, T., Heinz, R., Lowe, D., Miller, J. B., Poss, C., James W. C. White, 2012: No inter-hemispheric  $\delta(\text{CH}_4)\text{-C-13}$  trend observed. *Nature*, 486(7404): E3-E4. DOI: [10.1038/nature11175](https://doi.org/10.1038/nature11175)
- Lowe, D.C., C.A.M. Brenninkmeijer, S.C. Tyler, and E.J. Dlugokencky, (1991) Determination of the Isotopic Composition of Atmospheric Methane and Its Application in the Antarctic, *J. Geophys. Res.*, 96(D8), 15455-15467, 1991.
- Lowe, D.C., M.R. Manning, T. Bromley, W. Allen, G. Brailsford, D. Ferretti, A. Gomez, R. Knobben, R. Martin, M. Zhu, R. Moss, (1999) Shipboard determinations of the distribution of  $\delta_{13}\text{C}$  in atmospheric methane in the Pacific, *J. Geophys. Res.*, 104, 26, 125-26, 135, 1999.
- Miller, J. B., K. A. Mack, R. Dissly, J. W. C. White, E. J. Dlugokencky, and P. P. Tans (2002), Development of analytical methods and measurements of  $^{13}\text{C}/^{12}\text{C}$  in atmospheric  $\text{CH}_4$  from the NOAA Climate Monitoring and Diagnostics Laboratory Global Air Sampling Network, *J. Geophys. Res.*, 107(D13), 4178, doi:10.1029/2001JD000630.
- Tyler, S.C., (1986) Stable Carbon Isotope Ratios in Atmospheric Methane and Some of its Sources, *J. Geophys. Res.*, 91(D12), 12,232-12,238, 1986.



Any samples that had analysis problems and were determined to be non-representative of the sample were removed from calculations of the average isotope values (blue diamonds, above). In addition, the first data point for each run is always removed to allow the cylinder one ‘warm-up’.