AN020

Exceptional Reproducibility from a Picarro Isotopic Water Analyzer

Measuring the same water samples on two consecutive days using the Picarro L1102-*i*, without calibration, yields highly consistent data.

Keywords:

Material: Water samples, reproducibility, low drift
Process: Stable isotopes, $\delta^{18}O$ and δD, delta-18O, delta-D

Summary and Relevance:

The ability to measure the $\delta^{18}O$ and δD isotopic content of water has long relied on cumbersome methods that require well equipped laboratories, highly qualified technicians and frequently calibrated instruments. The advent of commercial analyzers based on Wavelength Scanned Cavity Ringdown Spectroscopy (WS-CRDS) for isotopic water measurements has opened up new possibilities for mobile laboratory and field deployable isotopic instruments. For these environments the consistency or reproducibility of data over days of operation provides tremendous savings in calibration time and effort and, perhaps more importantly, provides confidence in data collected in challenging environments. In this application note we present data from two runs of the same sample set that were measured on two consecutive days without any instrument calibration during or between the runs. The results of this study clearly confirm that the reproducibility of the Picarro system is very high and will enable additional methods development for faster and more robust studies.

Picarro Analyzer Used:

L1102-*i* equipped with autosampler option

Process:

The samples used for this study were collected from various locations in the Sacramento River. The samples were pipetted into 2 mL vials and arranged in an autosampler tray in a random order (no bracketing). The isotopic content of each sample was measured by analyzing 6 injections from each sample, discarding the data from the first three injections and taking the mean of the remaining three. A total of 26 samples were run in a 24 hour time window. At the end of the first run, the same samples were re-tested in the same order over a further 24 hours. No changes were made to the sample tray or the method. The instrument was not corrected for any drift and no calibration was performed at any time during this experiment.

Results:

As shown in Figure 1, the data from the second run overlaps with the data from the first run, demonstrating that the Picarro implementation of time-based optical analysis using WS-CRDS and high temperature vaporization provides very low drift and, consequently, highly reproducible data for isotopic water analyses over long time periods.

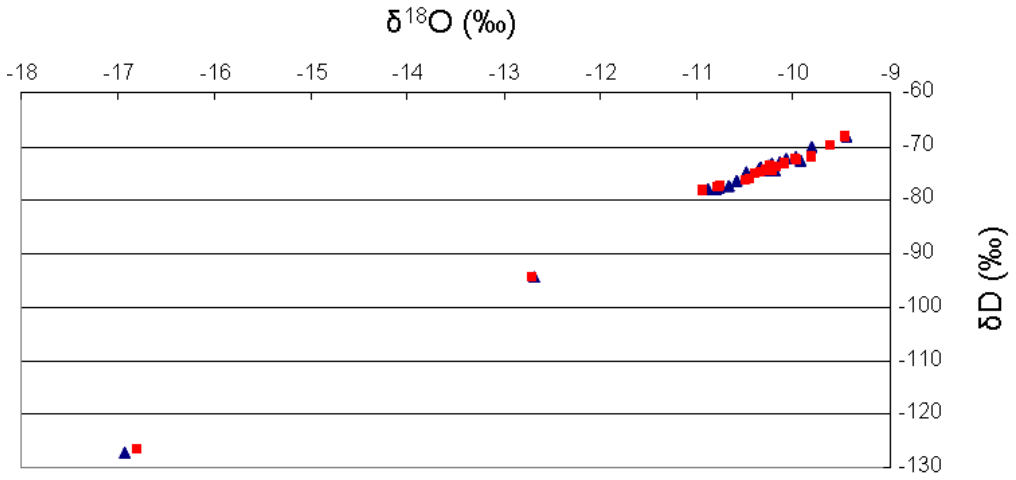

Fig 1. The blue triangles represent a suite of Sacramento River samples run on a Picarro L1102-i on Day 1 of a 2 day experiment. The red squares represent the same samples re-run on Day 2. The instrument was not calibrated during or between the runs, yet the data shows incredible reproducibility and effectively zero drift.

For systems that have more systematic drift problems, the Day 2 data would demonstrate a clearly different intercept than the Day 1 data (since the samples were randomized) and, experimentally, would require additional calibration methods adding significant time to the analysis.

Figure 2 shows an expansion of the congested region from ca. -9 to -11 ‰ $\delta^{18}O$ and -65 through -80 ‰ δD. The data points for the same samples are represented by a different shape for each day, and are also coded with the same color. The plot provides a clear indication that the drift over the two-day run is well within the guaranteed performance specification. The standard deviation of the differences in the isotopic measurements between day 1 and day 2 is 0.07‰ for $\delta^{18}O$ and 0.3‰ for δD.

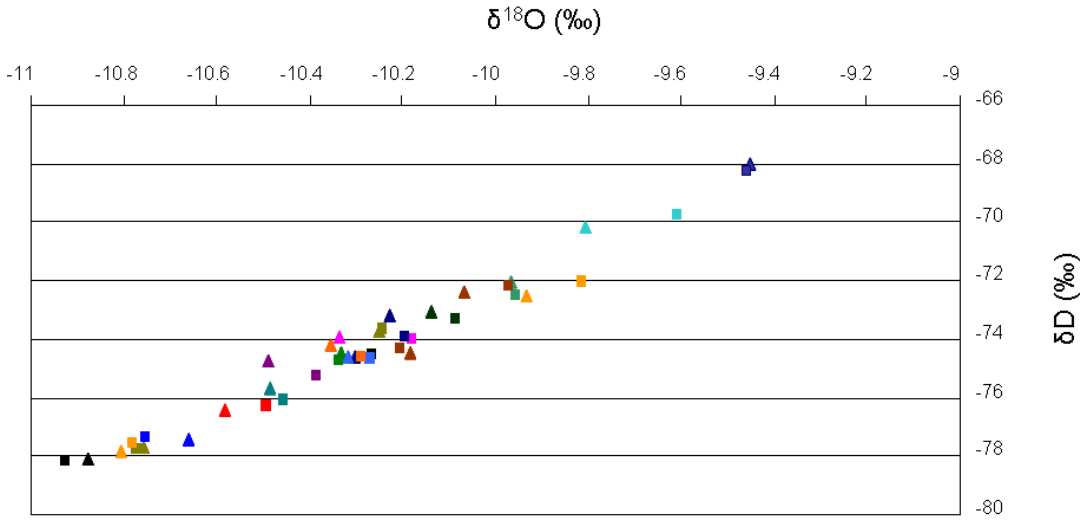

Fig. 2. An expansion of the upper right portion of the data from Figure 1. The data sets from the same sample now have the same color for the Day 1 (squares) and Day 2 (triangles) runs. Note that the data from all samples is well within the guaranteed drift performance of the instrument.

Comments:

WS-CRDS instruments now provide simple access to stable isotope ratio measurements for hydrogen and oxygen. The ease-of-use of these instruments coupled with the no-compromise performance is enabling the utility of isotopic measurements to be explored afresh.