

AN017

Calibration Routine for Picarro Water Isotope Analyzers

The unmatched stability and linearity of Picarro’s WS-CRDS water isotope analyzers enables simple data scaling by measuring only a few standards concurrently within each sample set. This minimizes the frequency of calibration and the instrument time dedicated to measuring standards.



Summary and Relevance:

Since the Picarro analyzer is extremely linear, it is only necessary to use three calibration standards across the intended span of isotope values to calibrate each isotope ratio (two points define the calibration line, and a third intermediate point is used for verification). The exact value of each calibration standards is not of particular importance as long as they span a representative range of values over which the analyzer will typically be operated. (Although it is not necessary to use more than three standards, additional standards can be used to further constrain the linear calibration coefficients.)

It is best to measure three or more standards, bracketed around the delta values of the unknown samples, in order to construct a calibration line whose regression coefficients can be used to scale the unknown sample data. For example, assuming ten unknown samples numbered 1-10 and the three standards S1, S2, S3, the following arrangement of samples in the autosampler tray is recommended:

S1	S2	1	2	3	4	5	S3	6	7	8	9	10	S1	S2
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Plot the true values of the standards used above against the measured values recorded by the analyzer. Two separate plots should be made, one for $\delta^{18}\text{O}$ and one for δD .

Fitting a straight line through each of the two plots yields an equation of the form:

$y = m \cdot x + b$ where m is the slope and b is the intercept.

For each plot, the equations correspond to:

$$\delta^{18}\text{O}_{\text{calibrated}} = m_{\delta^{18}\text{O}} \cdot \delta^{18}\text{O}_{\text{measured}} + b_{\delta^{18}\text{O}}$$

and

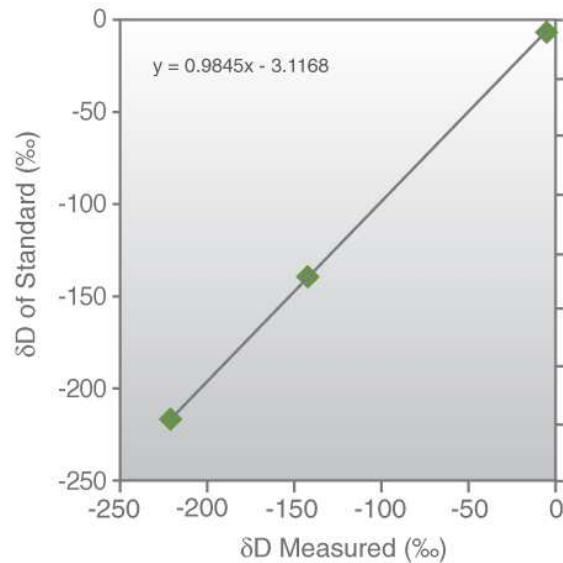
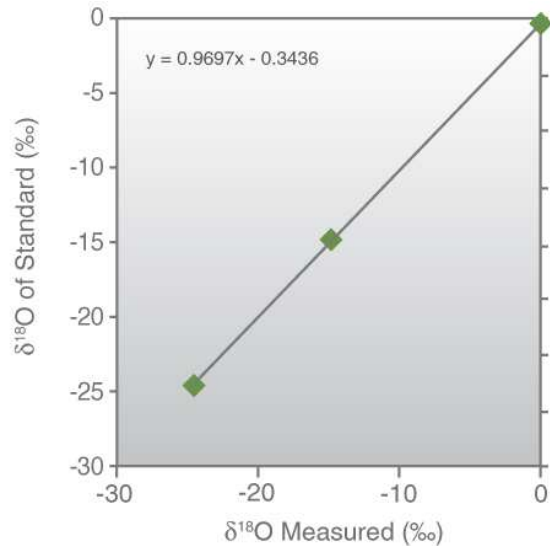
$$\delta\text{D}_{\text{calibrated}} = m_{\delta\text{D}} \cdot \delta\text{D}_{\text{measured}} + b_{\delta\text{D}}$$

Use the slopes and intercepts in the equations above to calculate the calibrated isotope ratios from the measured values.

Analyzer Measurements of Standards			
	S1	S2	S3
$\delta^{18}\text{O}$	-0.35	-17.00	-26.46
δD	0.35	-122.93	-205.28

Known Values of Standards			
	S1	S2	S3
$\delta^{18}\text{O}$	-0.72	-16.72	-26.07
δD	-2.67	-124.39	-205.08

Regression Coefficients	
$\delta^{18}\text{O}$ slope:	0.9697
$\delta^{18}\text{O}$ intercept:	-0.3436
δD slope:	0.9845
δD intercept:	-3.1168



The number of samples between the standards S2 and S3 and between S3 and S1 may vary depending on the specific samples being measured and the user's desired level of accuracy, as well as the number of injections measured per sample, with fewer samples interleaved between the standards corresponding to the highest accuracy measurements. As an example, the Picarro liquid water isotope analyzer has guaranteed specifications regarding drift (i.e. accuracy relative to a measured standard) over a particular temperature range and over a 24-hour period without calibration. This means for example that without measuring standards during a 24-hour run of samples, the absolute values of the delta measurements could vary from the beginning to end of the run by an amount consistent with this specification. By interleaving the samples with standards, however, the delta

values can be constrained by appropriately scaling them relative to nearby measured standards – again, this adjustment is undertaken after the run has been completed.

To calibrate water vapor isotope measurements, liquid standards are measured periodically and the water vapor isotope data scaled in the manner described above. It is not recommended that the analyzer itself necessarily be recalibrated but rather, during sample runs, standards be measured and the data scaled accordingly. The reasoning for scaling the data with standards (interspersed among samples) rather than re-calibrating the analyzer itself is because a re-calibration prior to a sample run ensures only that those samples measured near in time to the recalibration will be of the highest accuracy. In other words, not running standards along with samples – but rather relying on a one-time recalibration of the analyzer – does not allow the user to maximally constrain all the measurements throughout the sample run to known standards.