Wavelength-Scanned Cavity Ring Down Spectroscopy:

Opening New Doors for Tracing Water Isotopes in the Hydrosphere, Biosphere, and Atmosphere

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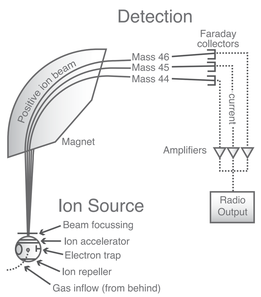
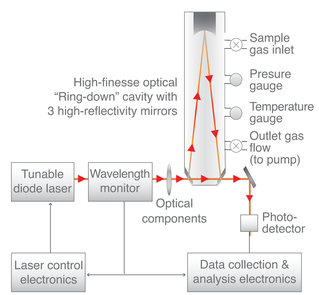
Abstract

Stable isotopes of water are proven indicators, tracers and recorders of processes that affect the hydrologic cycle. Until recently, calibrated measurements of stable isotopes (δD and $\delta^{18}O$) of ***liquid water*** have been limited to the laboratory. In addition, calibration of isotopic measurements of ***water vapor*** have been extremely difficult. We present results of a new field-deployable isotopic water - liquid and vapor - analyzer based on Wavelength-Scanned Cavity Ring-Down Spectroscopy (WS-CRDS). Unlike Isotope Ratio Mass Spectrometry (IRMS), WS-CRDS measures both $\delta^{18}O$ and δD simultaneously. Of particular interest is the improved reproducibility of $\delta^{18}O$ using WS-CRDS, breaking the ~0.1 ‰ barrier. ***The WS-CRDS analyzer can be configured to analyze vapor only, liquid only, or to alternate between vapor and liquid. The alternating configuration enables the periodic recalibration of water vapor measurements using liquid water isotopic standards.*** We demonstrate that the WS-CRDS analyzer has reproducibility, memory, and drift that are equal or superior to laboratory-based IRMS.

Comparison of entrenched technology (IRMS) with new technology (WS-CRDS)



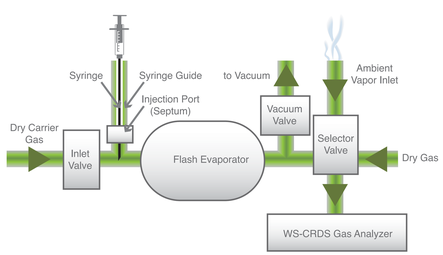
Isotope Ratio Mass Spectrometry (IRMS)



Schematic of Picarro WS-CRDS analyzer showing optical cavity and sample gas flow.

Instrument foot print: 54 cm x 60 cm
Instrument weight: ~ 40 Kg
Power consumption: 300 watts @ 110V

Analyzer can accept either liquid or vapor samples or alternate between them



Whole assembly is maintained at a constant 140 °C

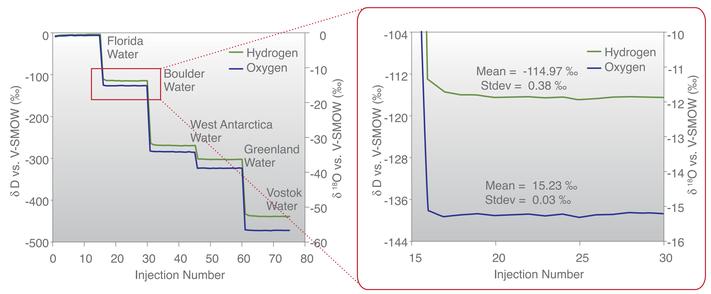
Performance Summary

	Precision [‰]	Drift [‰ / hr]	Memory [‰ change]
$\delta^{18}O$ Vapor	<0.2 (30 sec)	–	–
δD Vapor	<0.5 (30 sec)	–	–
$\delta^{18}O$ Liquid	<0.1	<0.005	2
δD Liquid	<0.5	<0.02	5

Laboratory Test at INSTAAR University of Colorado:

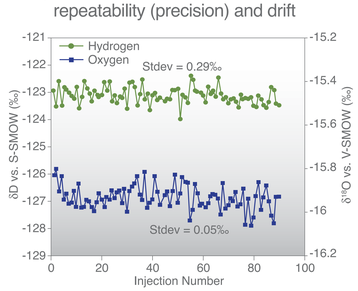
To test for stability, memory, and drift, we analyzed a variety of isotopically differing waters, all previously calibrated via Isotope Ratio Mass Spectrometry to primary IAEA water isotope standards: VSMOW, SLAP and GISP (uranium reduction for δD, and CO_2/H_2O equilibration method for $\delta^{18}O$). Analyses for each injection took approximately 12 minutes to produce both δD and $\delta^{18}O$ measurements. Dry nitrogen (ultra high purity) was used as a carrier gas, and injected water volumes were 2 µl.

Analyzer Performance: Liquid measurement repeatability (precision) and drift



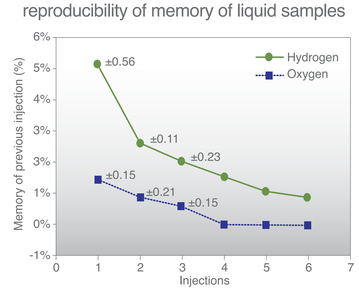
Liquid waters ranging from -3‰ to - 437‰ δD were analyzed for 15 injections each. The ~120‰ transition is enlarged, showing mean of all but the 1st injection.

Analyzer Performance: Liquid measurement repeatability (precision) and drift



Two different waters were analyzed in alternating groups of 15 injections each. Shown here are the hydrogen and oxygen results for just one of the waters over the whole run. Drift over the 36 hour run was 0.25‰ for hydrogen (~0.007 ‰/hr) and 0.047‰ for oxygen (~0.002 ‰/hr).

Analyzer Performance: memory and reproducibility of memory of liquid samples



Memory was tested by alternating between waters differing by 175‰ or more. Mean results are plotted here for 25 measured transitions, and expressed as percent of the previous sample remaining. In each case, by the 3rd injection, memory is significantly reduced. 1σ standard deviations are shown for the first 3 injections. Because this memory for liquid samples is highly reproducible it enables precise memory corrections while maintaining high precision and high throughput.

Test Driving the New Analyzer: Results from its First Field Trial

The Problem: How do you gain a real understanding of the strengths and weakness of this new technology for measuring the stable isotopes (δD and $\delta^{18}O$) in water?

- Testing at the factory does not necessarily prove that the analyzer will work well in under laboratory or field conditions.
- Measurements of (δD and $\delta^{18}O$) require that methods such as syringe cleaning and flushing be fully tested under "real world" conditions.

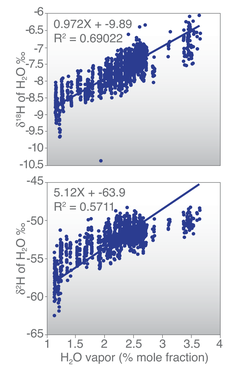
The Solution: Perform a field trial at the Woods Hole Oceanographic Institute with the objective of assessing the analyzers strengths and weaknesses.

- Measure both water vapor in ambient air and liquid water calibration standards.
- Carefully analyze results and correct any problems found with the analyzer or associated methods.
- Derive examples of new information that can be generated using this technology.

Measurements Made at Woods Hole, MA USA

We collected samples of atmospheric water vapor at Woods Hole, MA over a 10-day period the second week of August 2008. The stable isotopes (δD and $\delta^{18}O$) as well as water vapor concentrations were continuously monitored; liquid water calibration standards were momentarily measured every 8 hours. Water vapor measurements were produced every 15 seconds.

Problem Identified and Corrected

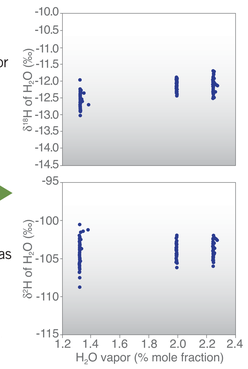


Problem: Measurements of standards biased:

- Buffer gas used in evaporator was not completely dry.
- Gas used to flush out analyzer between samples was wet ambient air.

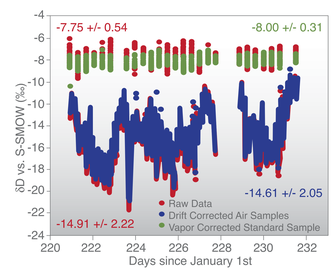
Solution:

- Use completely dry buffer gas when measuring standards.
- Flush out analyzer sample cell with dry gas between measurements of standards.



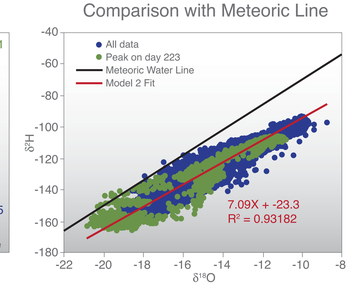
Analysis of field measurements of water vapor from standards verses $\delta^{18}O$ and $\delta^{2}H$ using an orthogonal least squares approach shows the fit of water vapor to δ is significant.

Measurements of water vapor verses $\delta^{18}O$ and $\delta^{2}H$ taken at Picarro's laboratory after analyzer's return from Woods Hole.



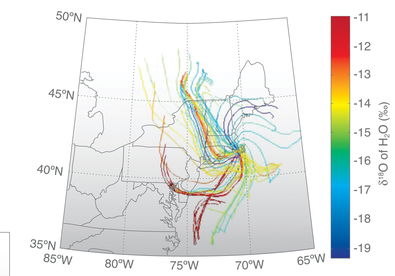
Raw data from the analyzer (red); liquid standard measurements after correcting for water vapor concentration (green); water vapor data (blue) corrected for drift between each standard measurement. green); water vapor data (blue) corrected for drift between each standard measurement. A significant fraction of the variability in the standards (43%) was eliminated by correcting for water vapor. Because the sample $\delta^{18}O$ was corrected to the mean sample water vapor mixing ratio, the standard deviation of water vapor samples throughout the experiment was reduced.

Comparison with Meteoric Line

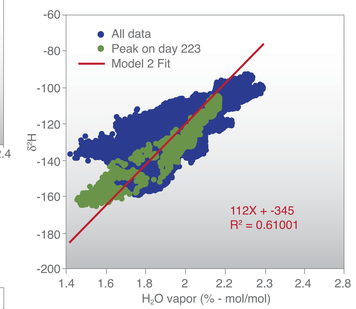


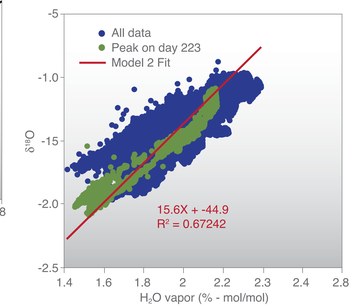
Previous analysis done on rain water indicates that most lie along the Meteoric Water Line (Black). The red line is a fit to all the data collected during the 10-day period. This illustrates a deuterium excess (Dansgaard, 1964) of -23‰, which is significantly lower than the Meteoric water line value of +10‰. More data is needed to understand exactly what is the source of depletion in $\delta^{2}H$. The overall slope of the data suggests that a simple Rayleigh fractionation model may be sufficient to describe the progressive depletion of $\delta^{2}H$ and $\delta^{18}O$.

Providing unique Information about the Origin and Transport of Water Vapor in the Atmosphere



Back trajectories collected from Hisplit back trajectory runs during the 10-day period that data was collected. The general trend that more depleted $\delta^{18}O$ and $\delta^{2}H$ originate from high latitudes is illustrated here.





Water vapor verses $\delta^{18}O$ and $\delta^{2}H$ illustrate that there are two dry sources of air coming into Woods Hole. Further analysis of the back trajectories will be needed to identify the sources of these different dry air masses. The existing back trajectory analysis suggests that one source is over northern Canada (lower $\delta^{2}H$ and $\delta^{18}O$) and the other is the North Atlantic (higher $\delta^{18}O$ and $\delta^{2}H$).

Conclusions

Based on the results of laboratory tests of liquid waters and the field test of water vapor measurements, the WS-CRDS water analyzer should prove to be an extremely valuable tool for both hydrologic and atmospheric investigations. An instrument that provides high precision, at low cost, small size, and low power consumption will no doubt open up new possibilities for research.