



Measuring Stable Isotopes of Water in Both Gas and Liquid Phase Using a Single Field-Deployable Analyzer

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Abstract:

We present results from field trials at Woods Hole Oceanographic Institute and laboratory tests at INSTAAR of a newly available analyzer capable of performing continuous measurements of stable isotopes (δD and $\delta^{18}O$) of liquid water and / or water vapor samples.

The analyzer is designed such that it does not require frequent calibration; it maintains high linearity, precision, and accuracy for long periods of time, over changing environmental conditions, with little or no sample preparation. The complete system is small and portable enough for field use.

WS-CRDS Analyzer for Isotopic Water – Model L1102-i

Liquid Water Specifications

- Precision

δD : < 0.5 %

$\delta^{18}O$: < 0.1 %

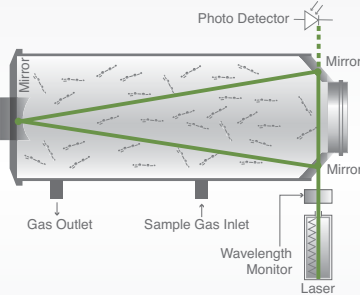
Water Vapor Specifications

- Precision

δD : < 1.0 % in 30 seconds

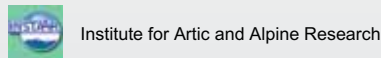
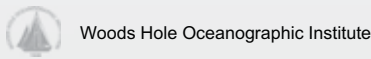
$\delta^{18}O$: < 0.2 % in 30 seconds

WS-Cavity Ring-Down Spectroscopy



- Light from a semiconductor diode laser is directed into a high finesse optical resonator cavity containing the analyte gas.
- When the laser is shut off, the energy decays from the cavity, or “rings-down” with a characteristic decay time τ .
- The ring-down time is measured as a function of laser wavelength. When the gas in the cavity is strongly absorbing, the ring-down time is short; when the gas does not absorb, the ring-down time is long.
- The in-line high precision optical wavelength monitor permits extremely detailed, highly reproducible spectral scans.

Acknowledgements



Field Trial at Woods Hole Oceanographic Institute:

The Problem:

How do you produce water vapor measurements tied to stable isotopes standards (δD and $\delta^{18}O$) in the field?

- Measurements typically done with IRMS systems which preclude real-time field use.
- Recently isotopic analyzers, based on laser spectroscopy, have advanced to the point where field deployment is now possible.
- However, a critical need for field use is to compare the isotopic vapor phase measurement results against standards.
- Although such standards exist for CO_2 gas, they exist for water only in liquid form.

The Solution:

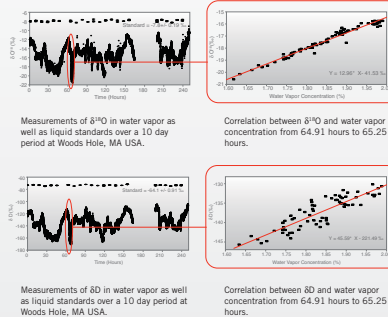
An analyzer that can, on command, measure either water vapor in ambient air or liquid water calibration standards.

- Field deployable
- Run unattended for long periods of time

Measurements 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.



Summary of Woods Hole Results

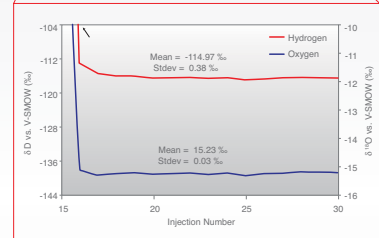
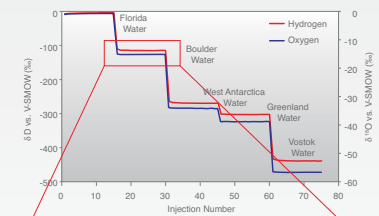
A high positive correlation was found between the δD and $\delta^{18}O$ and water vapor concentrations. Based on the conclusions of other work*, it is likely that the lowest isotopic values occur when cool, dry Canadian air that is stable aloft moves southeastward, while much higher values occur in hot, more humid air that is unstable aloft.

* James, W. C. White & Stanley David Gedzelman, *Journal of Geophysical Research*, Vol 89, No. D3. Pages 4937-4939 (June 20, 1984)

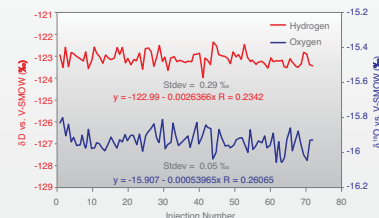
Laboratory Test at INSTAAR University of Colorado:

We analyzed a variety of isotopically differing waters, all previously calibrated via Isotope Ratio Mass Spectrometry to primary IAEA water isotope standards: V-SMOW, 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 $\delta^{18}O$. Dry nitrogen (ultra high purity) was used as a carrier gas, and water volumes of 2 μl were injected. Results from analyses of 15 injections each of 5 waters with widely varying isotopic values are plotted here:



Using a 6-injection run mode, and ignoring the first 3 to remove memory, the remaining injections 4, 5, & 6 are reproducible to typically ± 0.33 % and ± 0.03 % for δD and $\delta^{18}O$ respectively. The longer term stability of the analyzer/flash-evaporator system was tested by making over 50 injections of each of 2 waters, in alternating 15 injection blocks. The results show a very small amount of instrument drift over the 26 hour run, as shown here for Boulder tap (D1) water:



Summary of INSTAAR Results:

Measurements were made to test the overall stability and reproducibility of the instrument. While the sample delivery to the analyzer is likely the source of most noise and small memory effects, results that compare very favorably with mass spectrometry methods can be obtained by either ignoring the first three injections, as is often done with IRMS, or by post-processing a memory correction. Inclusion of calibrated water standards in each run can also serve as a check on the calibration.