

Demonstration of high-precision continuous measurements of water vapor isotopologues in laboratory and remote field deployments using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) technology[†]

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This study demonstrates the application of Wavelength-Scanned Cavity Ring-Down Spectroscopy (WS-CRDS) technology which is used to measure the stable isotopic composition of water. This isotopic water analyzer incorporates an evaporator system that allows liquid water as well as water vapor to be measured with high precision. The analyzer can measure H₂¹⁸O, H₂¹⁶O and HD¹⁶O content of the water sample simultaneously. The results of a laboratory test and two field trials with this analyzer are described. The results of these trials show that the isotopic water analyzer gives precise, accurate measurements with little or no instrument drift for the two most common isotopologues of water. In the laboratory the analyzer has a precision of 0.5 per mil for δD and 0.1 per mil for δ¹⁸O which is similar to the precision obtained by laboratory-based isotope ratio mass spectrometers. In the field, when measuring vapor samples, the analyzer has a precision of 1.0 per mil for δD and 0.2 per mil for δ¹⁸O. These results demonstrate that the isotopic water analyzer is a powerful tool that is appropriate for use in a wide range of applications and environments. Copyright © 2009 John Wiley & Sons, Ltd.

Measurements of the stable isotopic composition of water have historically facilitated a greater understanding of many physical processes in hydrology, meteorology, ecology and more recently, global climate change to name just a few. Specifically, the stable isotopes of hydrogen and oxygen (hereafter denoted by the common δD and δ¹⁸O) have given rise to deeper understanding of transport and exchange processes in hydrological systems at many scales. Acting as indicators, integrators, tracers and recorders they have, for example, allowed us the ability to reconstruct paleoclimate records from ice cores^{1,2} that form one of the pillars of global climate change science today. In other applications hydrogen and oxygen isotopes act as natural tracers driving models of soil water content and pore water that produce information about near-surface water dynamics.

Although a vast amount of literature exists on δD and δ¹⁸O measurements of liquid meteoric water,^{3–9} fewer isotopic measurements of meteoric water vapor have been performed.^{10–15} This is because isotopic analyses are typically done with isotope ratio mass spectrometry (IRMS) systems in a laboratory setting, which precludes convenient real-time field use and limits the samples to those which can be reliably prepared manually in the field and transported to the lab. Recently, isotopic water vapor analyzers based on laser spectroscopy have advanced to the point where field deployment is now possible. The relatively small size, weight, and ruggedness of these laser-based analyzers could transform the way in which scientists think about acquiring δD and δ¹⁸O measurements of meteoric water vapor. This technology will enable systematic, continuous studies of the isotopic composition of meteoric water vapor to be performed at locations never before possible. In addition, the wide deployment of such analyzers will help greatly improve the coverage of isotope data associated with hydrological cycling and recycling.¹⁶

The objective of this paper is to demonstrate the ability of a recently developed isotopic water analyzer to make precise measurements of the isotopic content of water samples in the

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liquid phase as well as in the vapor phase. Here, we report the results of three trials undertaken with the Wavelength-Scanned Cavity Ring-Down Spectroscopy (WS-CRDS) isotopic water analyzer that test and confirm its performance and also identify any shortcomings. Laboratory testing of the stability, memory, and drift of this analyzer for liquid samples was undertaken at the University of Colorado Institute for Alpine and Arctic Research (INSTAAR) Stable Isotope Laboratory. Two separate field campaigns were undertaken to test the water vapor analysis mode of the instrument. One was a 10-day field trial undertaken at the Woods Hole Oceanographic Institute where the ambient air was very humid and temperatures were warm. The second, a more strenuous test, was a 26-day field trial undertaken at the National Oceanographic and Atmospheric Administration's Mauna Loa Observatory in Hawaii. The range of variation in δD and $\delta^{18}O$, and generally low H_2O concentrations at Mauna Loa, make for a particularly challenging environment for measurements and so it is an ideal site at which to assess the performance of the analyzer. Together, these three trials demonstrate the practical performance of the isotopic water analyzer in making continuous and calibrated measurements of liquid water and ambient vapor samples.

EXPERIMENTAL

The isotopic water analyzer has three components: a gas-phase instrument that measures the concentration and isotopic content of water in vapor form, a liquid evaporator that converts liquid water samples into water vapor and an autosampler that injects liquid water samples into the evaporator. Although the measurement of water vapor samples only requires the gas-phase instrument, the instrument should be calibrated periodically to compensate for any instrumental drift. In order to calibrate the instrument, known water standards were measured every few hours so that the data could be scaled, based on the true versus measured values of these standards. While isotopic standards exist in vapor form for other isotopic analyses (e.g. CO_2 gas), the primary standards (e.g. VSMOW, SLAP, GISP) for water exist only in liquid form. Hence, the calibration process requires that these liquid standards be vaporized so that they can be measured by the gas-phase instrument.

The introduction of liquid water samples for vapor analysis provides two major challenges. First, the water must be vaporized with little or no isotopic fractionation during sample preparation otherwise there will be systematic errors in the measurement. Second, both the vaporized liquid sample and the water vapor samples must be measured identically.

In order to overcome these challenges, a liquid water evaporator (Picarro Inc., Sunnyvale, CA, USA) has been developed for use with the gas-phase instrument. The evaporator allows for flash evaporation of the liquid water samples and subsequent equilibration of the resulting vapor with dry carrier gas to minimize isotopic fractionation. It is intended to enable the measurement of liquid water samples with great precision and also facilitate switching between ambient atmospheric gas sampling and liquid samples. This

capability permits the use of liquid standards for real-time recalibration even in the field. With the help of this evaporator, variations in the isotopic content of samples taken from a variety of environmental sources can be measured with high precision and confidence.

Gas-phase instrument – WS-CRDS technology

WS-CRDS has emerged as a proven cavity-enhanced optical method for detecting trace quantities of gases^{17,18} and is now beginning to be applied to stable isotope measurement. The technology employs absorption spectroscopy using an infrared laser to detect the various isotopologues of water. A full description of the method can be found elsewhere.¹⁸ The temperature and pressure of the ring-down cavity are monitored and actively stabilized at $80^\circ C \pm 20$ mK and 35 ± 0.1 Torr, respectively. This stability is required for two reasons. First, the strengths of the absorption peaks of the various water isotopologues have different temperature sensitivities, so an unstable temperature could result in unstable and erroneous isotopologue measurements. Second, this stability enables the absolute concentration (mole fraction) of $HH^{18}O$ ($\text{conc}[H_2^{18}O]$), HDO ($\text{conc}[HD^{16}O]$) and $HH^{16}O$ ($\text{conc}[H_2^{16}O]$) in air samples to be simultaneously measured. In addition, a wavelength monitor, built into the gas-phase instrument, is continuously used to target specific wavelengths of the spectrum with about 1 MHz precision, helping to counteract laser drift.

WS-CRDS aims to measure the rate loss of light emerging from an optical cell that contains the gas sample. Because WS-CRDS is a time-based measurement, several orders of magnitude of dynamic range of loss can be measured without changes to the analyzer. The decay time constant can be expressed as:

$$\tau = \frac{1}{c(L + A)} \quad (1)$$

where τ is the laser light decay time constant, c is the speed of light, L is the loss in the empty cavity and A is the absorption loss due to the gas species to be measured. Assuming an empty cavity loss of 1 ppm/cm, an absorption loss of 0.001 ppm/cm gives a decay time constant, $\tau = 33.3 \mu s$, while an absorption loss of 1 ppm/cm gives a decay time constant of $16.67 \mu s$. This dynamic range allows for accurate measurements of both high and low abundance isotopologues.

The ratios of the concentrations, $R^{18}O$ and RD , of the two isotopologues are defined as (currently the $H_2^{17}O$ data is not recorded):

$$R^{18}O = \frac{\text{conc}[H_2^{18}O]}{\text{conc}[H_2^{16}O]}, RD = \frac{\text{conc}[HD^{16}O]}{\text{conc}[H_2^{16}O]} \quad (2)$$

and can be used to express the 'delta values' (δ) defined as:

$$\delta = \left(\frac{R}{R_{\text{standard}}} - 1 \right) \times 1000 \quad (3)$$

where δ is given in parts per thousand or the more commonly used 'per mil' (‰). The international reference standard for isotopic water which defines $\delta^{18}O = \delta D = 0$ is Vienna Standard Mean Ocean Water (VSMOW).

Liquid evaporator

The WS-CRDS gas-phase instrument measures water samples only when they are in the vapor phase. Analysis of liquid samples therefore requires complete vaporization of the samples and subsequent transport to the WS-CRDS instrument. Therefore, a liquid evaporator was developed which is intended to facilitate vaporizing of the entire liquid water sample in a controlled fashion to prevent or minimize isotopic fractionation. This was achieved by making the evaporation chamber a small (~150 cc) volume, with hydrophobic coatings, and maintaining a constant hot (140°C) temperature of the wetted parts.

The evaporator (see Fig. 1) consists of a hollow cylindrical chamber, a solenoid valve for the carrier gas inlet line, a solenoid valve for the vacuum port, an injection port, a three-way valve and fittings to connect them. A dry carrier gas, such as nitrogen or zero-grade dry air, enters the cylinder through the inlet valve. A vacuum valve at the exit end of the cylinder is connected to a small diaphragm vacuum pump which enables full evacuation of the evaporator when needed. The injection port, through which liquid samples are injected into the evaporator, is sealed and isolated from room air through a 9.5 mm septum (Restek, Bellefonte, PA, USA). The three-way valve in the evaporator has two operating positions: when it is powered it connects the gas-phase instrument to the evaporator and when it is not powered it connects the instrument to a dry gas supply.

While measurement of water vapor samples only requires the gas-phase instrument, calibration of this instrument requires use of the evaporator. Hence, when measuring vapor samples the inlet of the gas-phase instrument is connected to the vapor source through an external solenoid valve. This valve can switch the input of the WS-CRDS instrument from the vapor sample to dry gas. The instrument is connected to dry gas prior to being connected to the evaporator for measuring liquid water standards so that any traces of the vapor sample are removed from the measurement cell. The standards can then be manually or automatically injected into the evaporator and measured using the protocol described in the following section.

Operation with an autosampler

The WS-CRDS instrument and the liquid evaporator can be coupled with a CTC HTC-Pal liquid autosampler (LEAP Technologies, Carrboro, NC, USA) to make automated measurements of liquid water samples. The autosampler is fitted with a 5- μ L glass syringe (SGE Inc., Austin, TX, USA) and programmed to provide injections of 2- μ L water samples from 2-mL glass vials fitted with Teflon/silicon septa (MicroLiter Analytical Supplies, Suwanee, GA, USA). If cleaned on a daily basis with organic solutions, the syringes can make up to 3000 consistent injections before their plungers start to malfunction due to clogging.

In operation, a needle-rinsing protocol is employed that involves aspirating several aliquots of the sample water and dispensing it into a waste port. While the needle is rinsing, the evaporator and the analyzer are purged with dry gas and evacuated multiple times to clean the surfaces and remove any memory of the previous sample. When the various components have completed this cleaning cycle, the needle collects the final 2 μ L of the water sample and injects it into the evaporator through the injection port.

Within a few seconds after injection of the liquid water sample, the sample is completely vaporized because the evaporator is maintained at 140°C and is under vacuum. The water vapor sample is then mixed with dry carrier gas to form a uniform, homogenous mixture of all the isotopologues of water vapor. Mixing the water vapor sample with dry gas facilitates the flow of the sample from the evaporator into the WS-CRDS analyzer with limited adsorption on the various surfaces and it also dilutes the vapor sample going into the gas-phase instrument. It is advantageous to dilute the sample as there is an optimum water concentration that gives the highest possible precision from the WS-CRDS instrument, although the instrument is designed to meet specifications over a wide concentration range.

After equilibration with itself and the carrier gas for ~2 min, the homogeneous mixture of the sample and dry gas flows to the WS-CRDS instrument at a constant flow rate via the three-way valve, where its isotopic content is repeatedly measured over the next few minutes. The 2- μ L injection of

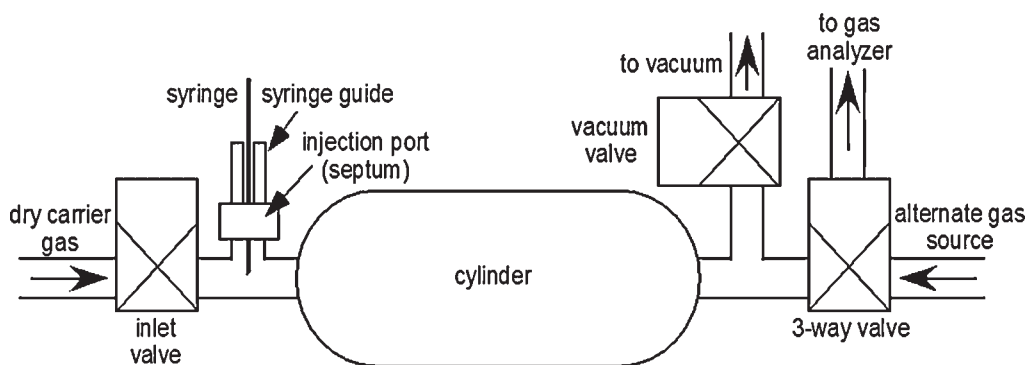


Figure 1. Schematic of the evaporator. The evaporator facilitates vaporization of liquid water samples in a controlled fashion to prevent isotopic fractionation. Dry carrier gas is introduced into the cylinder through the inlet valve and the vapor sample equilibrates with it to form a homogeneous gas sample. The three-way valve allows this equilibrated sample to flow from the evaporator to the analyzer.

water, after dilution in the evaporator, yields a pulse of approximately $20\,000 \pm 220$ ppm (5.9×10^{17} water molecules per cm^3) water vapor in the measurement cell held at ~ 35 Torr during analyses. Since the sample has a uniform concentration and the flow rate into the gas phase instrument is constant, the pulse of water measured by the analyzer is flat, as shown in Fig. 2. Measurements made during the flat part of this concentration profile are used to determine the isotopic ratios in the sample. After a few minutes of measurement time, the evaporator is isolated from the gas-phase instrument again and the two components go through their automatic cleaning cycle in parallel to remove any memory of the old sample. Once the components are clean again, the new sample is injected into the evaporator which goes through the measurement cycle and so on. When using an autosampler, the entire measurement of more than 100 samples is fully automated and requires no user intervention.

The isotopic water analyzer is designed to have minimal drift and as such the measurement of the delta values can be calibrated to the internationally accepted VSMOW scale by intermittently measuring standards. When liquid samples are being measured, standards can be interspersed within the unknown liquid samples. The data can then be scaled using a linear fit of the true versus measured delta values of the standards.

Laboratory test

The isotopic water analyzer was tested in a laboratory environment at the University of Colorado Institute of Alpine and Arctic Research (INSTAAR) Stable Isotope Laboratory. For the tests, a suite of five internal lab standards was used that had previously been calibrated by IRMS to primary reference materials VSMOW, SLAP and GISP supplied by IAEA, Vienna, Austria. The IRMS method used

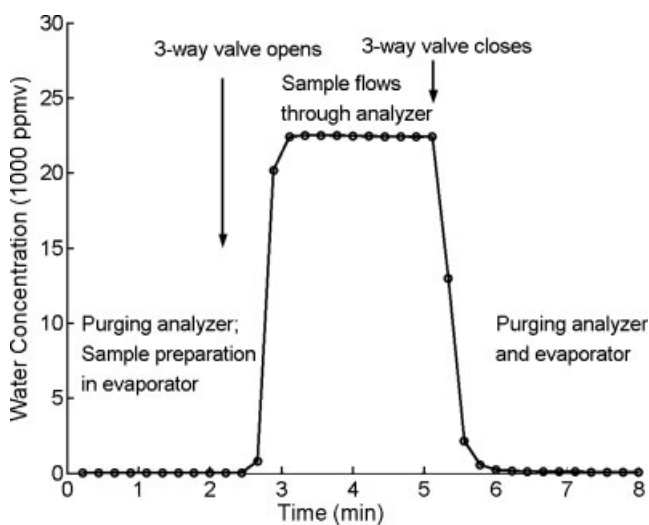


Figure 2. Sample data showing a pulse of water vapor. The analyzer is purged with dry gas while a new sample is prepared in the evaporator. The three-way valve then opens to let this homogeneous sample into the analyzer. After a few minutes of sampling, the three-way valve closes and the evaporator and analyzer are both purged to remove any memory of the sample.

for $\delta^{18}\text{O}$ was $\text{CO}_2/\text{H}_2\text{O}$ head-space equilibration, and the method for δD determination was an automated uranium reduction system.¹⁹ The isotopic range of the lab standards was approximately 430 per mil for δD (over 55 per mil $\delta^{18}\text{O}$), as shown in Table 1.

Determinations of sample precision and drift were made by making 90 injections (2- μL sample volume each) of pure waters (deionized local waters) over a period of 48 h. The standard deviations were 0.29‰ for δD and 0.05‰ for $\delta^{18}\text{O}$ ($n = 90$), and the drift over the entire 48-h period was towards lighter values for both isotopes, but was very small (0.26‰ δD and 0.05‰ for $\delta^{18}\text{O}$ over 48 h). No drift corrections have been applied and the results of this experiment are plotted in Fig. 3. There also appears to be random noise over the period and, while the origin of this noise is unknown, the stability and reproducibility over this time period appear to exceed those obtained with the other IRMS methods in this paper. The hydrogen results are similar to those found by Lis *et al.*²⁰ for an off-axis integrated cavity output spectroscopy (OA-ICOS) instrument, but the oxygen results in this study appear to be more reproducible, by a factor of 3 ($\pm 0.16\%$ by Lis *et al.* to $\pm 0.05\%$ in this study).

In any system that converts liquid water into vapor there will be residual water molecules retained in the system and thus any one analysis will contain some small fraction of the previous water injected into the system.¹⁹ To quantify this system memory, multiple analyses of isotopically differing waters were made. Figure 4 shows the memory effect for both hydrogen and oxygen obtained from 25 experiments, moving from 15 injections of one water to 15 injections of an isotopically different water. In all cases, the true value of the water samples was taken to be the average of the last 4 of the 15 measurements (injections), and it was assumed that this is the asymptotic value. In theory, the measured value M is a function of $X * T + (1 - X)P$, where M is the measured value of current injection, X is the unknown memory coefficient of this n^{th} injection, T is the true value of the current water sample and P is the true value of the immediately previous water sample. Therefore, the memory coefficient X for this n^{th} injection is $(M - P)/(T - P)$. For comparison, it is useful to express a memory coefficient as a percentage of the previous sample, or $1 - X$.

We found that the memory for hydrogen over the first three injections is significantly greater than for oxygen over the same span. The reason for this is not well understood, but may possibly relate to interactions at the molecular level between the water and the hydrophobic coatings on the

Table 1. The isotopic water standards and corresponding delta values used in the laboratory tests

Isotopic standard	$\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ ($\delta^{18}\text{O}$)	$\text{HD}^{16}\text{O}/\text{H}_2^{16}\text{O}$ (δD)
	(‰)	(‰)
Florida	-0.56 ± 0.15	-3.75 ± 1
Boulder*	-16.73 ± 0.15	-124.39 ± 1
WAIS*	-26.07 ± 0.15	-205.08 ± 1
Greenland*	-38.43 ± 0.15	-300.41 ± 1
Vostok	-56.13 ± 0.15	-437.52 ± 1

* Internal laboratory standards.

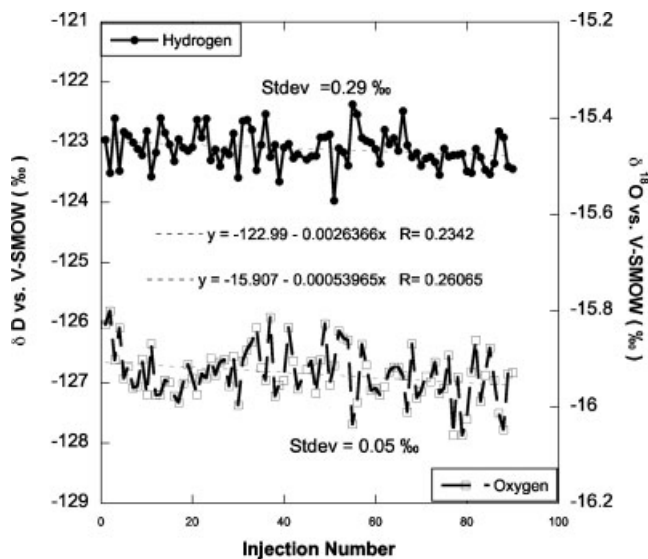


Figure 3. Plot of 90 analyses of deionized water, performed over a 48-h period. The standard deviations of the determinations are 0.05‰ for oxygen and 0.3‰ for hydrogen. Drift is towards lighter values over the 48-h period, but it is very small, and is easily normalized with periodic standards during the analysis run.

wetted surfaces within the system. The memory coefficients for both isotopes were quite reproducible for both the first and second injections at $(1 - X) = 0.5 \pm 0.06$ and 0.25 ± 0.01 for hydrogen and 0.15 ± 0.02 and 0.08 ± 0.02 for oxygen, respectively. Because of the consistency of the memory coefficients, one could make fewer measurements of any water

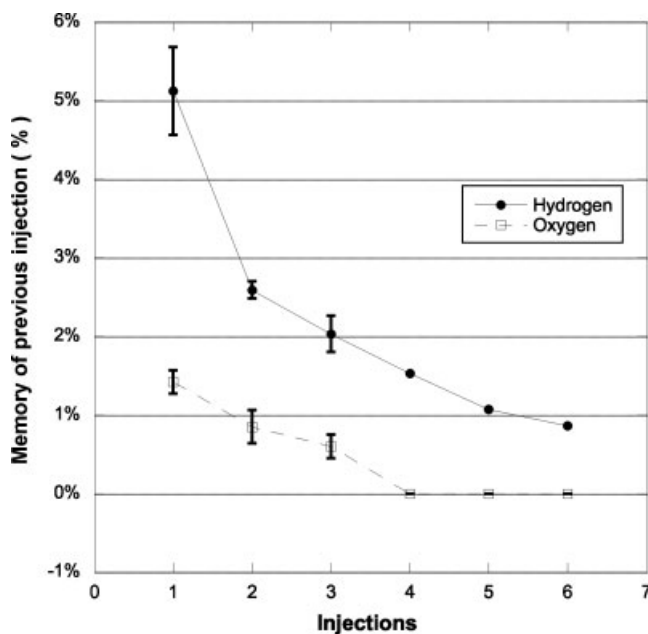


Figure 4. The system memory of previous water, expressed as a percentage of the previous sample, for both hydrogen and oxygen. For oxygen, after the 3rd injection, the memory has been reduced to zero, whereas hydrogen has a slightly more persistent memory. Error bars are standard deviations of multiple determinations ($n = 25$) for each of the first three injections.

sample and calculate the true value using $T = (M - (1 - X)P) / X$ to facilitate a higher throughput with the analyzer.

Earlier efforts on similar systems have shown that small mass variations can adversely and dramatically affect the measured isotope ratios.²⁰ To test this dependence, a series of different size injections was made of the same water into the analyzer. The results showed minimal dependence of the water mass on the delta values. There is a slightly greater dependence on water mass for oxygen isotopes than hydrogen. In both cases, however, the correction is small and was applied in the software, based on these characterizations.

The results of all the bench tests were very reproducible on different days, including tests of stability, memory, drift, and dependence on water vapor concentration. Because of this apparent consistency, it is then possible to apply post-analysis calculations that can correct for memory and scale measurements to isotopic standards to achieve results that are accurately tied to the VSMOW scale. The drift coefficients were found to be very small (less than 0.002‰ δD and 0.0005‰ $\delta^{18}O$ over 48 h), and were too insignificant and within the noise of the instrument to correct on timescales less than 48 h. Memory effects, especially for hydrogen, were much smaller (~5 percent 1st injection) than those observed in other IRMS water injection systems (up to ~9 percent on 1st injection¹⁹) and can be characterized and removed from the final data. The apparatus to convert liquid water into vapor is crucial for calibrating any water vapor isotopic measurements, and because calibrations are an essential element of producing credible isotopic analyses of water or water vapor, this represents an important step forward in non-IRMS water isotope analyses.

Field test at Woods Hole Oceanographic Institute

In an attempt to gain insight into the performance characteristics of the isotopic water analyzer outside the laboratory, a 10-day field trial was undertaken at Woods Hole Oceanographic Institute. The measurement site was on the roof of an ocean-side building roughly 30 m above the water. While the analyzer was installed inside a protective shelter, a 4 m long and 9.5 mm diameter Dekoron line was mounted outside the shelter to take ambient air samples. The stable isotopes δD and $\delta^{18}O$ as well as the water vapor concentrations were continuously monitored; liquid water calibration standards were measured every 8 h. In order to switch between liquid and vapor samples, the three-way valve in the evaporator was configured such that it either connected the vaporized liquid sample in the evaporator to the analyzer or the ambient vapor sample to the analyzer (Note: this configuration is different from the one described earlier). Water vapor measurements were produced every 15 s. Dry carrier gas was provided to the analyzer by flowing ambient air through a dryer (Drierite, Xenia, OH, USA). The H_2O concentration at the exit to the dryer was <250 ppm.

The H_2O concentration of ambient air over the 10-day period varied from 14 000 ppm to 24 000 ppm while the $\delta^{18}O$ varied from -10‰ to -22‰ and δD spanned from -93‰ to -170‰ , as shown in Fig. 5. Although the ambient

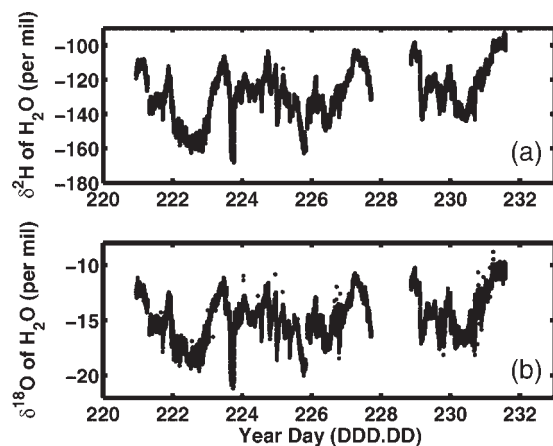


Figure 5. Raw, uncalibrated data from the field trial at Woods Hole. (a) Plot shows the variation of δD during the field trial. (b) Plot shows the variation of $\delta^{18}\text{O}$ during the field trial. The data is raw and uncalibrated where no corrections for drift have been applied.

air measurements of water vapor met analyzer performance specifications, a careful analysis of the isotopic water standards data indicated a problem in which the measured isotopic ratio, particularly for δD , showed a much larger than expected standard deviation over the 10-day period. Careful analysis of the data was performed, including correlation studies with a number of observables that included but was not limited to ambient temperature, ambient water vapor concentration, ambient isotopic values, wavelength monitor offset, sample pressure, and sample temperature. Figure 6 shows a significant positive correlation between water vapor concentration and its isotopic composition. It is unclear what might have been the cause of this correlation in the early configuration of the analyzer but this effect disappeared in a later deployment of the instrument which did not use ambient air to purge the sample cell (described earlier). While it is possible that purging the sample cell with ambient air may have contributed to the problem, the ambient air concentrations show no correlation with the variability of either $\delta^{18}\text{O}$ or δD standards. Correcting for the correlation with water vapor over the 10-day experiment reduced the variability of standards for $\delta^{18}\text{O}$ from 0.43‰ to 0.27‰ and for δD from 1.6‰ to 1.2‰. Assuming that there was no fractionating effect in the evaporator causing this trend with water vapor concentration, similar corrections were made to ambient air sample data by correcting all water samples to a mean water vapor mixing ratio (19 400 ppm). With a range in water vapor concentrations between 14 000 and 24 000 ppm the air sample measurements were corrected by up to 0.4‰ for $\delta^{18}\text{O}$ and 1.3‰ for δD due to variations in water vapor mixing ratios during the experimental period.

The 10-day experiment in Woods Hole demonstrated that this isotopic water analyzer could be deployed in a typical coastal field environment with high variability in water vapor and isotope ratios. An analysis of the measurement resolution indicated that the typical variability in atmospheric water vapor isotopes expected in this environment is well resolved by this instrument. The instrument makes

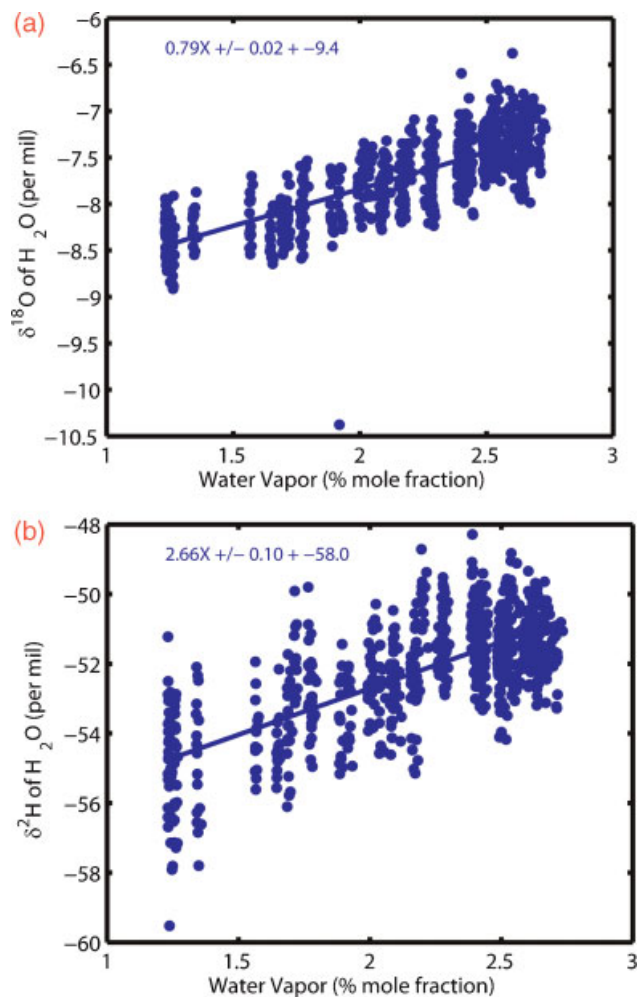


Figure 6. Analysis of field measurements of water vapor from standards versus $\delta^{18}\text{O}$ and δD . An orthogonal least-squares approach shows that the fit of water vapor to (a) $\delta^{18}\text{O}$ and (b) δD is significant. This dependence was, however, corrected in a later deployment of the analyzer by improving the spectral fitting.

reliable continuous measurements and this will allow a better understanding of large-scale processes that control variability in water vapor isotopes in typical coastal environments.

Field test at Mauna Loa Observatory

NOAA's Mauna Loa Observatory (MLO) is an atmospheric research facility that has been continuously monitoring and collecting data related to atmospheric change since the 1950s. The observatory protrudes through the strong marine temperature inversion layer present in the region, which separates the more polluted lower portions of the atmosphere from the much cleaner troposphere. This high-altitude site presents unique challenges, including the low concentration of water (<500 ppm), as well as the opportunity to directly study free tropospheric air that should have quite different characteristics from the lower atmospheric air. While water vapor in the marine layer is believed to originate from local evaporation of ocean water, the water vapor in the free troposphere will have experienced a long history of

condensation in the region of clouds and it is subject to long-range transport.¹⁴

The isotopic water analyzer was installed in a small room located in one of the temperature-controlled laboratories (standard building heating gave rise to typical daily variations of 5°C) at MLO.²¹ The analyzer was set up to continuously monitor the stable isotope composition (δD and $\delta^{18}\text{O}$) as well as the water vapor concentration in outside air. The analyzer was connected to a pressurized gas cylinder filled with zero air and to ambient air via two separate lines of 1/8" stainless steel tubing. The ambient air inlet was located just outside and above a laboratory window on the roof.

In order to calibrate the measurements of ambient air, liquid water calibration standards were measured every 8–12 h. Three water standards, with $\delta^{18}\text{O}$ values within -15 to -40‰ and δD values within -100 to -300‰ (see Table 2), were used and the analyzer was set up to measure one of these three standards during every calibration period. The concentration of the standards injected was fixed at $\sim 10\,000$ ppm throughout the field trial. The instrument was tested before the start of the field trial to minimize any dependencies of the isotope ratios on sample concentration for water values between 200 ppm and 20 000 ppm. This allowed us to measure the standards at a fixed concentration and to apply the calibration to the water vapor measurements which varied from 200 to 14 000 ppm during the experiment. After the completion of the field trial, the instrument was re-tested to confirm that the isotope ratios still did not have any dependence on the concentration; this was found to be true. This means that both $\delta^{18}\text{O}$ and δD have the same accuracy irrespective of the H_2O concentration.

Figure 7 shows the variation in H_2O concentration and water vapor δD composition measured by the analyzer on the first day that it was installed at the Mauna Loa Observatory. The concentration dropped from 10 000 to 3000 ppm within a few minutes. The δD for vapor in equilibrium with seawater near Hawaii is expected to be around -96‰ , whereas the δD for upper atmospheric air tends to have a large magnitude negative value.^{14,22} During the 1-day period shown in the figure, the measurements captured the collapse of the inversion layer after local sunset (around day 283.2) which caused the measurements to change from purely marine boundary layer air with high δD values to the free tropospheric air with much lower values. Some of the high-frequency variability (less than 2 min) seen in the figure is associated with sampling noise, which can be greatly reduced by averaging the 12-s samples to averages over a few minutes without loss of the scientifically relevant signal.

Table 2. The isotopic water standards and corresponding delta values used in the field trial at Mauna Loa

Isotopic standard	$\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ ($\delta^{18}\text{O}$)	$\text{HD}^{16}\text{O}/\text{H}_2^{16}\text{O}$ (δD)
	(‰)	(‰)
Standard 1	-16.73 ± 0.15	-124.39 ± 1
Standard 2	-26.07 ± 0.15	-205.08 ± 1
Standard 3	-38.43 ± 0.15	-300.41 ± 1

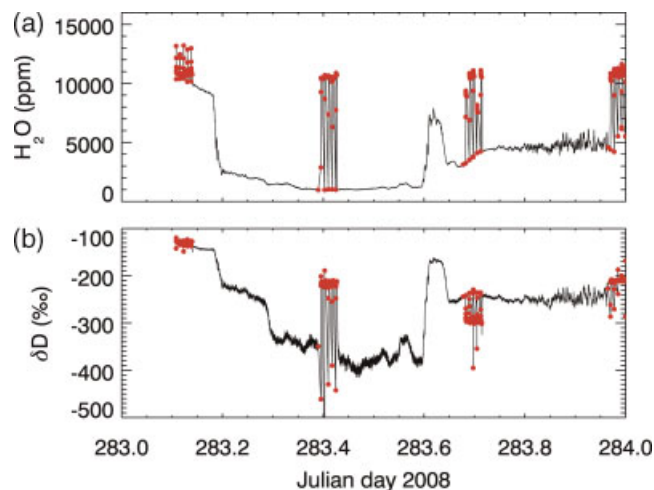


Figure 7. Raw (uncalibrated) (a) water vapor concentration and (b) δD value observations from the first 20 h of operation of a WS-CRDS water isotope analyzer at Mauna Loa on 10 October 2008. The data shown includes four calibration periods (as indicated by the red dots) with three different reference samples.

Based on statistics from the calibration periods, it was found that with ambient conditions of very low water vapor pressure, data from the first hour had to be discarded after calibration with liquid water samples to be certain that any memory effects were removed. Memory effects of up to 45 min were suspected to be associated with the transition from the (arbitrarily) much higher water vapor concentration used when running standards (arbitrarily around 10 000 ppm) back to the ambient conditions. This is seen clearly in Fig. 7 as the series of observations that approaches the ambient conditions following the second calibration. Since this strength of the memory effect is linked to the difference in water concentration between calibration and ambient values, a choice for the calibration concentration that minimizes this difference would be more optimal and easily achieved by changing the rate at which the zero air carrier gas is supplied.

In addition, correlation studies indicated that cross-talk between the water standards and the δD value of ambient air before and during the liquid water measurements was creating a bias in the liquid standards measurements. The cause of this cross-talk was found to be memory effects introduced by flowing ambient air through the analyzer sample cell before every measurement of isotopic water standards. The solution was to reconfigure the analyzer by adding an additional three-way valve enabling zero-air (<5 ppm H_2O) from a gas bottle to flow through the sample cell for a time before each liquid water measurement, as described earlier. This issue appeared to have no impact on the measurements of water vapor isotopic ratios in ambient air and the problem was rectified 2 days after the commencement of this field trial. A correction was applied to the δD and $\delta^{18}\text{O}$ for the water standards measured before this change in the analyzer configuration. As a result, a significant fraction of the variability in the standards (43%) measured within the first 2 days of the trial was eliminated.

Without intervention, the analyzer showed a small, 2‰, drift for δD over the course of the 4-week experiment, which is substantially smaller than the measured water vapor signals of interest. Figure 8 shows the measurements of the three injected standards over a 13-day period while installed at MLO. At each known δD value the drift characteristics are similar, such that one can have confidence that the observed variability over this time period is representative of the true variability. There does remain some question about the ability of the instrument to monitor longer-term variability (on the scale of months) to a precision better than a few per mil, and to do so will require a careful and rigorous calibration strategy to gain confidence in the instrument.

The field results showed that even at this extreme altitude, and with low and rapidly varying water vapor abundance, the analyzer was able to provide reliable measurements of a kind previously unobtainable with traditional (physical sampling) methods. The observed precision of the analyzer (over 30-s windows) for water vapor concentrations >5000 ppm was <0.2‰ for $\delta^{18}O$ and 1.0‰ for δD during this field trial. The precision gradually got worse for lower water vapor concentrations.

Despite the large and rapid variation in the water concentration, as evident from Fig. 7, the analyzer captured the concentration with a precision of better than 0.1%. Using the evaporator, the standards were reproduced to within 1‰ for δD and 0.12‰ for $\delta^{18}O$. This level of reproducibility is as good as that achieved by the isotopic water analyzer in a laboratory setting, and on par with that of IRMS.

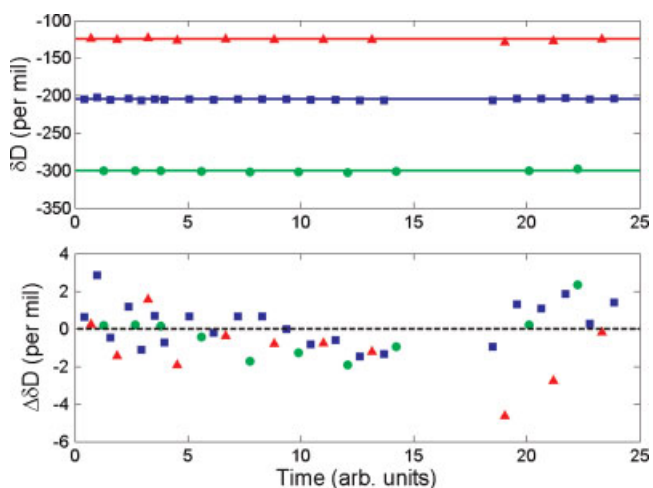


Figure 8. (a) Measured δD of standards while the analyzer was deployed at Mauna Loa. The plotted value is the mean value of the calibration standards scaled to remove any correlation with ambient air; however, it is not scaled to compensate for drift of the instrument. (b) The deviation of each measurement from the known value. The lack of any significant drift in the instrument while it was installed at Mauna Loa is evident from this plot. The gap in the data indicates the time when the dry gas cylinder ran out. This did not have any impact on the water vapor data at all; however, it reduced the quality of the measurement of the liquid water standards until the gas supply was restored.

CONCLUSIONS

An isotopic water analyzer has been developed using WS-CRDS technology. The performance of the isotopic water analyzer matches or exceeds IRMS measurements and its ease of use and lower cost provide significant advantages over IRMS. The precision of the analyzer when measuring liquid samples is <0.5‰ for δD and <0.1‰ for $\delta^{18}O$ and, when measuring ambient vapor samples, is <1.0‰ for δD and <0.2‰ for $\delta^{18}O$. The active temperature and pressure control of the analyzer and the continuous wavelength monitoring are the key to the unmatched drift-free performance of the system.

This analyzer incorporates an evaporator system that has been developed to homogeneously vaporize liquid water samples before they are tested by the gas-phase instrument. This allows measurement of the isotopic content of water whether it is in liquid or vapor form. The evaporator enables automated switching between ambient atmospheric gas sampling and liquid samples. These measurements require no extensive sample preparation (unlike IRMS, which can require CO_2 equilibration, reductions, etc.).

The results of three trials undertaken with the analyzer attest to its advantages over traditional approaches and confirm the precision and repeatability of the measurements, and importantly inform us of its limitations. Future improvements should include investigation and modifications to reduce memory effects within the WS-CRDS instrument as well as the evaporator. A reduction in memory would reduce the sampling time and hence increase the throughput of the analyzer.

The analyzer has proved reliable in both very humid and very dry field settings. The performance of the instrument deployed for *in situ* measurements in the field as well as in the lab is remarkable. The potential for the creation of high-quality, high-density data of water vapor measurements using the continuous analyzer has set the stage for large advances to our understanding of spatial and temporal variations of water isotopes in natural systems and consequently the controls on the hydrologic fluxes in terrestrial ecosystems, and the role of water in climate.

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