

On the calibration of continuous, high-precision $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements using an off-axis integrated cavity output spectrometer

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Received 7 October 2008; Revised 4 December 2008; Accepted 4 December 2008

The ^{18}O and ^2H of water vapor serve as powerful tracers of hydrological processes. The typical method for determining water vapor $\delta^{18}\text{O}$ and $\delta^2\text{H}$ involves cryogenic trapping and isotope ratio mass spectrometry. Even with recent technical advances, these methods cannot resolve vapor composition at high temporal resolutions. In recent years, a few groups have developed continuous laser absorption spectroscopy (LAS) approaches for measuring $\delta^{18}\text{O}$ and $\delta^2\text{H}$ which achieve accuracy levels similar to those of lab-based mass spectrometry methods. Unfortunately, most LAS systems need cryogenic cooling and constant calibration to a reference gas, and have substantial power requirements, making them unsuitable for long-term field deployment at remote field sites. A new method called Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) has been developed which requires extremely low-energy consumption and neither reference gas nor cryogenic cooling. In this report, we develop a relatively simple pumping system coupled to a dew point generator to calibrate an ICOS-based instrument (Los Gatos Research Water Vapor Isotope Analyzer (WVIA) DLT-100) under various pressures using liquid water with known isotopic signatures. Results show that the WVIA can be successfully calibrated using this customized system for different pressure settings, which ensure that this instrument can be combined with other gas-sampling systems. The precisions of this instrument and the associated calibration method can reach $\sim 0.08\text{‰}$ for $\delta^{18}\text{O}$ and $\sim 0.4\text{‰}$ for $\delta^2\text{H}$. Compared with conventional mass spectrometry and other LAS-based methods, the OA-ICOS technique provides a promising alternative tool for continuous water vapor isotopic measurements in field deployments. Copyright © 2009 John Wiley & Sons, Ltd.

The ^{18}O and ^2H of water vapor can be used to investigate couplings between biological processes (e.g., photosynthesis and transpiration) and hydrologic processes (e.g., evaporation and precipitation) and serve as powerful tracers in hydrological cycles.¹ Rapid and accurate determination of atmospheric water vapor isotope ratios is important for a broad range of biological and hydrological questions from leaf-scale to global-scale. The typical method for determining water vapor $\delta^{18}\text{O}$ and $\delta^2\text{H}$ involves the cryogenic method (using liquid nitrogen or dry ice) for trapping atmospheric water vapor. The major disadvantage of this method is the intensive labor and time involved, which have limited most studies to either single plants,^{2,3} or temporally coarse observations.⁴ The challenge is even higher for ecosystem level isotopic composition of evapotranspiration (δ_{ET}) estimates using flux gradient approaches and the cryogenic trap method, mainly because fractionation accompanying

inefficient vapor trapping can lead to measurement uncertainty⁵ that is comparable with typical atmospheric isotopic vapor gradients at the surface,⁶ particularly at low humidity. Although recent advances allow for faster sampling⁷ or alternative trapping methods⁸ (e.g. molecular sieves), these techniques are still not fast enough to achieve a continuous measurement mode (defined here as minutes to hourly resolution) and require additional laboratory analyses. In recent years, a few groups have developed continuous approaches for measuring water vapor $\delta^{18}\text{O}$, $\delta^2\text{H}$ and ecosystem δ_{ET} that achieve accuracy levels similar to lab-based cold trap/mass spectrometry methods.^{6,9} These continuous approaches rely on laser absorption spectroscopy (LAS), which allows direct measurement of water vapor isotopologues at high temporal frequency.¹² Unfortunately, the need for cryogenic cooling, constant calibration to a reference gas and substantial power requirements preclude long-term field deployment at remote field sites. However, the accuracy of these new LAS techniques is quite good ($0.07\text{--}0.66\text{‰}$ for $\delta^{18}\text{O}$ and $1.1\text{--}11.3\text{‰}$ for $\delta^2\text{H}$)¹¹ and comparable with those achieved using conventional laboratory-based cold trap water vapor collection/mass spectrometry ($\sim 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $\sim 5\text{‰}$ for $\delta^2\text{H}$, assuming complete vapor recovery).¹⁰

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Contract/grant sponsor: Startup Grant from Princeton University.
Contract/grant sponsor: The Office of Science (BER), US Department of Energy; contract/grant number: DE-FG02-07ER64371.

As an alternative to traditional LAS methods, Cavity Ringdown Spectroscopy (CRDS) uses the intensity of light decay within an optical cavity to directly determine absolute concentrations of trace gases (or trace gas isotopologues) without the need for a reference gas.¹³ However, CRDS lasers require high power and achieve low frequency resolution due to difficulties in dealing with cavity resonance. To address these issues, a new method called Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) has been developed.^{14–17} OA-ICOS uses a narrowband continuous-wave laser that systematically disrupts cavity resonances using a laser that is placed in an off-axis configuration with respect to the cavity. The OA-ICOS absorption cell effectively traps the laser photons so that they make thousands of passes on average before leaving the cell. As a result, the effective optical path length may be several thousands of meters using high-reflectivity mirrors and the measured absorption of light as it passes through the optical cavity is significantly enhanced. The OA-ICOS method provides a high-frequency resolution LAS with low power requirements (<100 W) that operates at ambient temperatures without need for a reference gas. These attributes make OA-ICOS methods ideal for integration with existing micrometeorological applications. However, despite all these advantages, there have been no reports that describe calibration processes for OA-ICOS water vapor sensors or assess the precision of this technique within a field application. Therefore, the objectives of this study are (1) to develop a feasible method to calibrate a commercially available OA-ICOS for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements, especially for micro-meteorological applications; and (2) to access the precision of this new type of laser-based $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements using our calibration method.

EXPERIMENTAL

Water vapor isotope analyzer and principles of the calibration

In this study, we focused on the calibration and precision assessment of the Los Gatos Water Vapor Isotope Analyzer DLT-100 (WVIA, Los Gatos Research Inc.) which is based on the OA-ICOS technique. The calibration method that we developed is based on the relationship between instrument measurements and Rayleigh fractionation predictions for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$.^{6,11} In our framework, the Rayleigh fractionation predictions were treated as 'true' values¹¹ and the instrument was calibrated by correcting for the difference between the instrument measurement and Rayleigh fractionation prediction. To assess the precision of the instrument and to obtain a calibration at the same time, we did not use the 'calibration' option of the instrument, which instantaneously corrects the instrument readings based on the typed in 'correct values' for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Instead, we first made continuous calibration measurements for around 12 or 24 h, depending on the sampling air pressure, and used these to compare the instrument measurement data with the Rayleigh fractionation predictions in order to correct for measurement bias. After the initial calibration run, we reran the instrument to assess precision and repeatability using exactly the same setup and the correction factors obtained in

the calibration run for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$. A Li-610 dew point generator (DPG, Li-Cor, Lincoln, NE, USA) and a liquid water working standard with known isotopic signatures ($\delta^{18}\text{O} = -11.4\text{‰}$ and $\delta^2\text{H} = -79.0\text{‰}$, Los Gatos Research Inc.) were used in the calibrations. The DPG is a completely self-contained instrument that produces a saturated air stream with a known dew point (and therefore a known vapor pressure). The condenser stability of the DPG is around $\pm 0.01^\circ\text{C}$ according to the manufacturer, and this ensures a stable vapor pressure in the DPG head space ($\pm 2\text{ Pa}$). The DPG was used as a Rayleigh fractionation device, producing water vapor with a known isotopic signature. The instantaneous water vapor isotope signature (R_v) is calculated by Rayleigh fractionation:

$$R_v = (R_{l,o}/\alpha) \times ((m_o - Qt)/m_o)^{(1/\alpha-1)} \quad (1)$$

where $R_{l,o}$ is the initial liquid water isotope signature [unitless], α is the isotope-specific fractionation factor (α_{H} or α_{O}), m_o is the initial liquid water mass [g], Q is the flow rate of water vapor out of the system [g/s], and t is the elapsed time in seconds since the initiation of the flow.⁶ In these calibrations, we assumed a constant flow rate that is determined by:

$$Q = (m_o - m_f)/t_f \quad (2)$$

where m_o is the initial liquid water mass in g, m_f is the final liquid water mass in g, and t_f is the total duration of the calibration period.⁶ Because the air in the DPG headspace is saturated, the fractionation factor α should be equal to the equilibrium fractionation factor, which is only a function of the water reservoir temperature. The α values for ^2H (α_{H}) and ^{18}O (α_{O}) are calculated by:

$$\alpha_{\text{H}} = \exp[24844/(t_d + 273)^2 - 76.248/(t_d + 273) + 52.612 \times 10^{-3}] \quad (3)$$

$$\alpha_{\text{O}} = \exp[1137/(t_d + 273)^2 - 0.4156/(t_d + 273) - 2.0667 \times 10^{-3}] \quad (4)^{11,18}$$

where t_d ($^\circ\text{C}$) is the temperature of the water reservoir of the DPG.

Once R_v is known, the isotope ratios of the water vapor (both the $\delta^{18}\text{O}$ and $\delta^2\text{H}$) generated by the DPG can be determined according to:

$$\delta_v = (R_v/R_{\text{vsmow}} - 1) \times 1000 \quad (5)$$

where δ_v is the water vapor isotope ratio produced by the DPG (either $\delta^{18}\text{O}$ or $\delta^2\text{H}$), and R_{vsmow} is the isotope ratio of the international standard (VSMOW).

We also tested the instrument performance under various pressures in anticipation of being able to combine the sensor with gas-sampling systems operating at a range of mainline pressures (e.g. eddy covariance systems, soil chambers). For example, for the eddy covariance system, the sampling line pressures of an eddy covariance system may vary from ambient pressure to 60 kPa, depending on the tower height and the air flow rate. To address this need, we developed a dynamic pumping system that is able to achieve different mainline pressures. The system included three pumps, two control valves, one flow meter, one pressure pump and

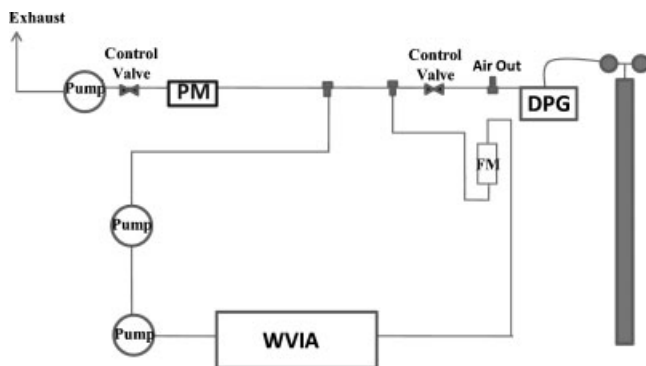


Figure 1. System design used to achieve various pressure settings for the water vapor isotope analyzer. DPG: dew point generator (Li-610, Li-cor Inc.), WVIA: water vapor isotope analyzer (Los Gatos Research DLT-100), FM: flow meter (Cole-Parmer), PM: pressure meter (Li-7000, Li-cor Inc.).

multiple Teflon tubes (Fig. 1). The system is relatively easy to assemble inside a laboratory with minimum instrumental requirements. Using this system, pressures ranging between 20 kPa and ambient (98 kPa) can be achieved by adjusting the positions of the two controlling valves. We tested the instrument performance at a pressure of 60 kPa (a common system pressure for the eddy covariance system on high towers >30 m in height) and ambient pressure (98 kPa). A tee-split ('Air out' in Fig. 1) was used in the outlet of DPG to avoid over-pressurization of the DPG.

Calibration procedures

Filling the dew point generator

The calibrations were conducted inside a climatically controlled laboratory. Because the calibration is based on the initial isotopic signatures of the liquid water standard (e.g. $R_v = R_{l,0}/\alpha$), the completeness of water replacement inside the DPG condenser determines the accuracy of liquid water isotope signatures in the DPG and governs the accuracy of the calibration method. Therefore, the DPG condenser block is first rinsed with the water standard (the same isotope signatures as used for calibration) at least six times. Each rinsing consisted of 20 mL of water standard injected into the condenser and then removed by a syringe. To completely drain the condenser block, it was necessary to use the syringe to withdraw water multiple times (>10 times) after each injection. The total rinse process required about 30 min to complete.

After the rinsing procedure was complete, the DPG condenser block was filled with 25–30 g of water from the same standard as used for rinsing. The exact weight of the water injected into the DPG condenser was recorded as m_0 in Eqn. (1) using a lab balance with an accuracy of at least 0.1 g. Alternatively, the volume added could be determined exactly using a fixed volume pipette or graduated cylinder assuming a known density for a particular standard. Any bubbles attached to the condenser tube walls were removed by pumping air in using the syringe. During the rinsing and filling process, the DPG inlet and outlet were left open to prevent backflow of the water standard outside the

condenser. After the filling, both the inlet and outlet were capped to allow the water isotopes to equilibrate within the DPG for at least 12 h.

Performing the calibration

After the 12-h equilibration period, the DPG inlet was connected to a tank of ultra-purity nitrogen, and the gas pressure was set to 5 psi using a brass two-stage gas regulator with 0–10 psi output range (Scott Specialty Gases, Plumsteadville, PA, USA; part No:5114B590). The DPG power and the DPG cooler switch were turned on first at the same time, followed by activation of the WVIA. The DPG temperature was allowed to reach a set dew point temperature of 13.4°C which usually took less than 5 min when the ambient temperature was around 25°C. After the temperature had stabilized, the DPG 'air pump' was turned on and the DPG outlet was connected to the WVIA to start measurements. The exact measurement starting time was noted. For the ambient pressure measurement, the flow rate of the DPG was set to 800 mL/min; for the 60 kPa measurement, the flow rate was set to 1500 mL/min to avoid backflow of ambient air into the tee-split. The purpose of setting the flow rates faster than the WVIA flow rate (480 mL/min) was to exclude the possibility of liquid drops flowing into the WVIA, which would permanently damage the laser.

Because the DPG works well when the water volume in the condenser block is between 20 and 25 mL, the duration of calibration and precision assessment was confined to about 24 h for the ambient pressure setup and 12 h for the lower pressure (high flow rate) setup. The ending time was noted to calculate the exact running time (t_r in Eqn. (2)). All the water left in the condenser block was completely withdrawn and weighed to calculate the water flow rate (Q in Eqns. (1) and (2)). The hourly- and minute-averaged $\delta^{18}\text{O}$ and $\delta^2\text{H}$ 'true' values (δ_v in Eqn. (5)) were calculated using Eqns. (1) and (5), and these 'true' values (δ_v) were compared with hourly- or minute-averaged instrument measurements.

Precision assessments

To assess the WVIA precisions across a range of averaging times and to attribute calibration error between the WVIA and the DPG, we created Allan Variance curves for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$. The curves were calculated for three components: (1) the theoretical Rayleigh distillation (Eqn. (1)), (2) observed values measured by the WVIA, and (3) the difference between theoretical prediction and observed values. If we assume that the DPG is a perfect Rayleigh distillation device, the difference between the theoretical prediction and observed values represents the precision of the WVIA itself. The Allan Variance ($\sigma_A^2(\tau)$) measures the average temporal variability of a signal over a certain averaging time, τ , and is defined as:

$$\sigma_A^2(\tau) = 1/(2(n-1)) \sum (Y(\tau)_{i+1} - Y(\tau)_i)^2 \quad (6)$$

where Y_i is the average value of the measurement in averaging interval i ; and n is the total number of averaging intervals for a given τ . This method of precision analysis has been successfully applied to determine the accuracy of other LAS-based methods.¹¹ For the Allan Variance curves of the precision assessments, we excluded the first 2 h of the runs

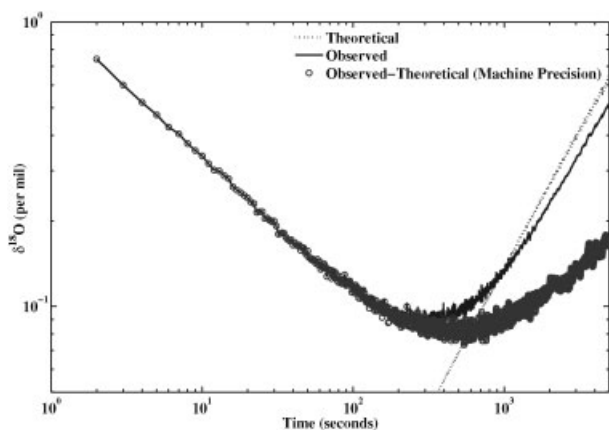


Figure 2. Allan Variance curves of the theoretical Rayleigh distillation (dashed line), observed WVIA values (solid line) and the difference between theoretical prediction and observed values (WVIA precision, circles). Data shown are for $\delta^{18}\text{O}$ of calibration 1 at ambient pressure.

to remove obvious departures from theoretical predictions during these periods. Figure 2 provides Allan Variance curves for the three $\delta^{18}\text{O}$ components of ambient pressure calibration 1. The curves show a clear pattern for the effect of increasing averaging time on total instrument precision; at low averaging intervals, the measurement variance is much higher than theoretical predictions due to sensor noise, but the precision rapidly increases with larger averaging intervals. We use these Allan Variance curves to provide information on the maximum precision that the combined WVIA and DPG calibration method can achieve.

RESULTS

Figure 3 depicts two calibration curves obtained under the ambient pressure (98 kPa) (corresponding to a sensor chamber pressure of 21 Torr) with an interval of 1 day between each of the two calibration runs. Both the calibrations use the exactly same correction factors (the differences between the Rayleigh fractionation predictions and the measured values) for $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Under this pressure setting, the correction factor for $\delta^{18}\text{O}$ is +1.7‰ and for $\delta^2\text{H}$ is +6.7‰. After the simple linear corrections, in both calibrations, both the $\delta^{18}\text{O}$ and the $\delta^2\text{H}$ of water vapor closely follow the Rayleigh fractionation curve predictions ($R^2=0.996/0.998$, $p<0.001$ for $\delta^{18}\text{O}$ and $R^2=0.996/0.997$, $p<0.001$ for $\delta^2\text{H}$ in both calibrations) (Fig. 3). In particular,

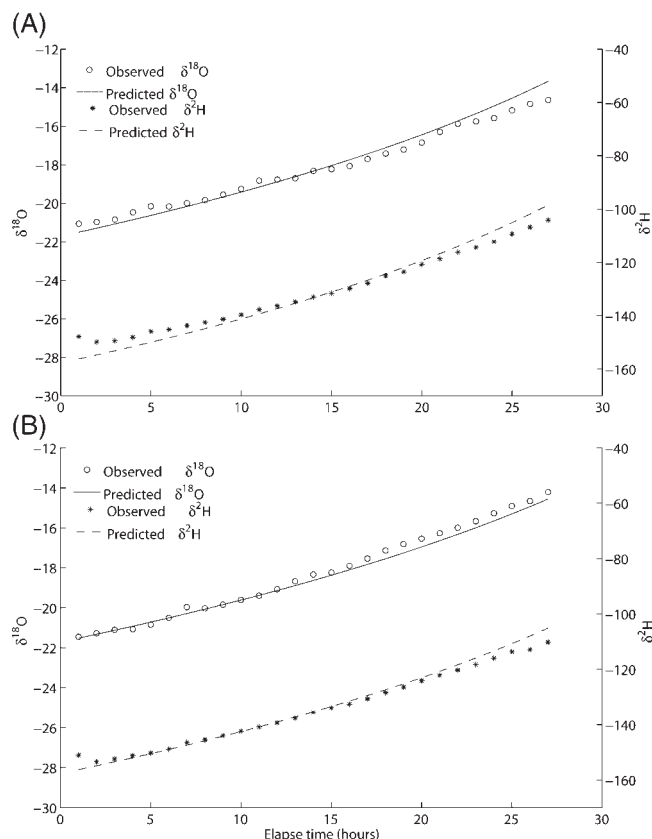


Figure 3. Calibration curves for observed (circles) and predicted (solid line) values of $\delta^{18}\text{O}$ as well as observed (asterisks) and predicted (dashed line) values of $\delta^2\text{H}$ at the ambient pressure setting. Both calibrations use the exactly same correction factors: +1.7‰ for $\delta^{18}\text{O}$ and +6.7‰ for $\delta^2\text{H}$.

both the $\delta^{18}\text{O}$ and the $\delta^2\text{H}$ of water vapor follow the Rayleigh fractionation very well between 10 and 15 h ($R^2=0.926/0.978$, $p<0.002$ for $\delta^{18}\text{O}$ and $R^2=0.996/0.999$, $p<0.001$ for $\delta^2\text{H}$ in both calibrations) (Fig. 3). Based on these calibrations, under the ambient pressure, the precision of the WVIA measurement is 0.1‰ for $\delta^{18}\text{O}$ and 1.0‰ for $\delta^2\text{H}$ at hourly averages, and 0.2‰ for $\delta^{18}\text{O}$ and 1.0‰ for $\delta^2\text{H}$ when averaging over 1 min (Table 1). These precisions are close to the conventional laboratory-based cold trap water vapor collection/mass spectrometry method ($\sim 0.2\%$ for $\delta^{18}\text{O}$ and $\sim 5\%$ for $\delta^2\text{H}$)¹⁰ and other LAS-based measurements (0.07–0.66‰ for $\delta^{18}\text{O}$ and 1.1–11.3‰ for $\delta^2\text{H}$)¹¹

Figure 4 depicts two calibration curves at the 60 kPa pressure setting (corresponding to an instrument chamber pressure of 14 Torr). As with the 98 kPa calibrations, these

Table 1. Water vapor isotope analyzer precisions calculated by the Allan Variance differences between the modeled values according to the Rayleigh distillation equation and the instrument measurements

Pressure settings		Calibration 1		Calibration 2	
		Hour average	Minute average	Hour average	Minute average
98 kPa (ambient pressure)	$\delta^{18}\text{O}$	0.1	0.2	0.1	0.2
	$\delta^2\text{H}$	1.0	1.0	1.0	1.0
60 kPa	$\delta^{18}\text{O}$	0.4	0.3	0.4	0.3
	$\delta^2\text{H}$	2.9	2.0	2.5	2.0

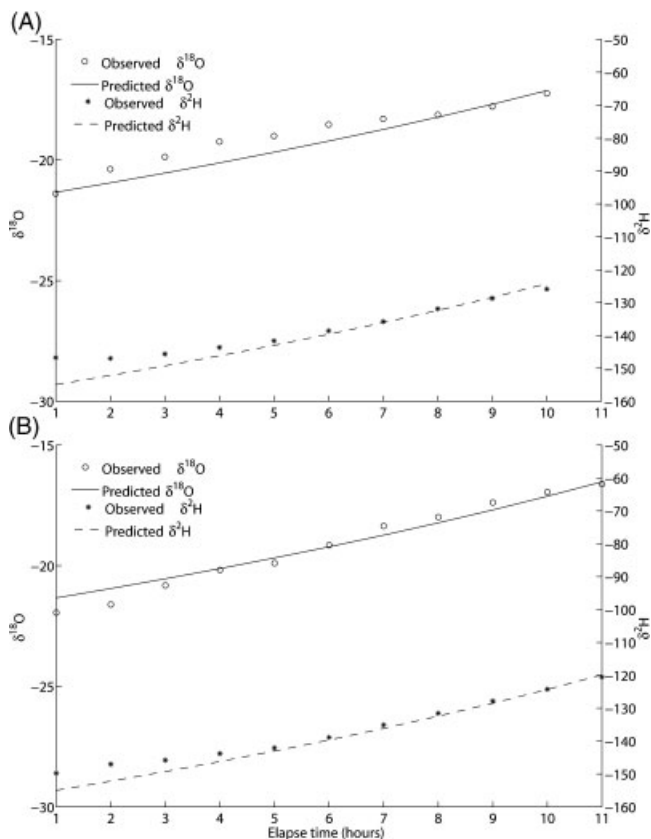


Figure 4. Calibration curves for observed (circles) and predicted (solid line) values of $\delta^{18}\text{O}$ as well as observed (asterisks) and predicted (dashed line) values of $\delta^2\text{H}$ at the 60 kPa pressure setting. Both calibrations use the exactly same correction factors: +0.4‰ for $\delta^{18}\text{O}$ and +4‰ for $\delta^2\text{H}$.

calibrations were conducted with an interval of 1 day between each of the two runs. We find that the patterns are very similar to the ambient pressure setting. After the corrections (+0.4‰ for $\delta^{18}\text{O}$ and +4‰ for $\delta^2\text{H}$), both the $\delta^{18}\text{O}$ and the $\delta^2\text{H}$ of water vapor follow the expected Rayleigh fractionation curves very well ($R^2 = 0.932/0.983$, $p < 0.001$ for $\delta^{18}\text{O}$ and $R^2 = 0.979/0.993$, $p < 0.001$ for $\delta^2\text{H}$ in both calibrations) (Fig. 4). In particular, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water vapor follow most accurately, corresponding to the Rayleigh fractionation expectations between 8 and 10 h in both calibrations ($R^2 = 0.989/0.992$, $p < 0.06$ for $\delta^{18}\text{O}$ and $R^2 = 0.997/1.000$, $p < 0.03$ for $\delta^2\text{H}$ in both calibrations) (Fig. 4). Overall, the precisions of the measurements are slightly lower than the precisions at ambient pressure. They are 0.4‰ for $\delta^{18}\text{O}$ and 2.5–2.9‰ for $\delta^2\text{H}$ during hourly averages, and 0.3‰ for $\delta^{18}\text{O}$ and 2.0‰ for $\delta^2\text{H}$ for minute averages (Table 1).

Figure 5 shows the Allan Variance curves for the differences between theoretical and measured values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ at two pressure settings. For both pressure settings, the highest precisions occur when averaging over minutes. Specifically, for the ambient pressure setting, the highest precisions occur when averaging over ~500 s, while, at 60 kPa pressure, the highest precisions appear at ~200 s. During our testing, the highest precisions of the WVIA and the associated calibration method are 0.08‰ for $\delta^{18}\text{O}$ and 0.4‰ for $\delta^2\text{H}$ (Fig. 5) and they appear at the ambient pressure setting.

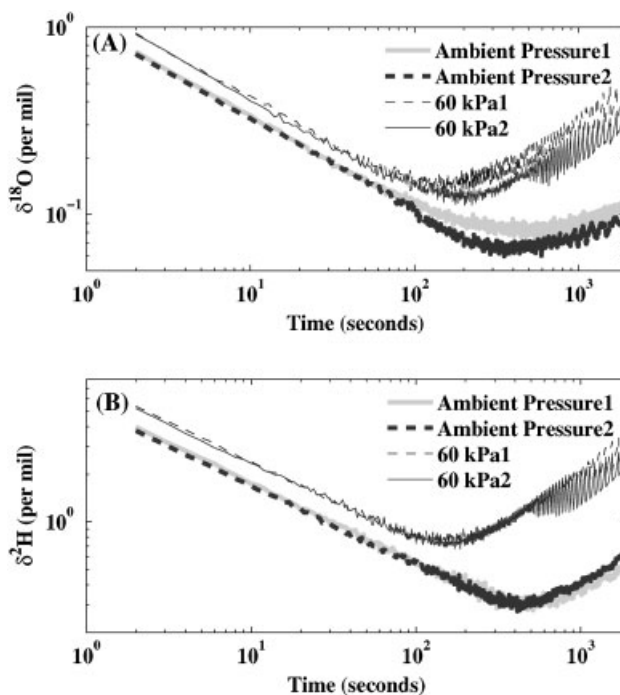


Figure 5. Allan Variance curves of $\delta^{18}\text{O}$ (A) and $\delta^2\text{H}$ (B) precisions at the two pressure settings.

DISCUSSION

The method of calibration that we have adopted here is designed for situations where there is limited control over the environmental operating conditions; the sensor is required to operate over a range of specific line pressures, and routine cross-calibration between sensors (e.g. calibration of the WVIA through comparison with traditional mass spectrometry approaches) is not feasible. An important example of such a situation would be the routine calibration of a water vapor isotope analyzer that is part of a micrometeorological instrumentation deployment. To address these constraints, we use a dew point generator as a means to create a vapor source for calibration. The efficacy of our calibration method therefore depends on two critical factors: (1) the accuracy and predictability of the isotopic composition of the vapor generated by the DPG; (2) the accuracy and repeatability of water vapor isotope composition measurement in the WVIA. While we are unable to strictly separate these two sources of error within our calibration approach, it helps to examine each of these two components separately.

A key limitation of this calibration method lies in the fact that it assumes that the DPG is a perfect Rayleigh distillation device for liquid-vapor fractionation. While the good agreement that we obtained between Rayleigh fractionation predictions and instrument measurements at both pressure settings (Figs. 3 and 4) indicates that the DPG is performing quite well as a Rayleigh distillation device, there are conditions that could invalidate this assumption. Most importantly, any liquid-vapor fractionation process is affected by vapor concentration gradients above the liquid surface, which lead to additional kinetic fractionation driven by differential diffusion of isotopologues across

concentration gradients.¹ In the case of water, the result of this additional kinetic fractionation is a deuterium excess in the vapor compared with what would be expected in an equilibrium fractionation process. For water evaporating from the ocean surface, an excess of $\delta^2\text{H}$ enters the vapor because the relative humidity above the ocean surface averages 0.85. This deuterium excess (D_e) averages 10‰ globally, as can easily be seen from the $\delta^2\text{H}$ -intercept of the average global meteoric water line (GMWL): $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$. The Rayleigh distillation process is an equilibrium process which assumes that kinetic contributions to the total fractionation are insignificant. When the air is fully saturated (i.e. relative humidity = 1.0) in the DPG headspace, there should be no gradients of water vapor concentration and kinetic fractionation would be negligible. It is possible that the headspace of the DPG may not be fully saturated. When the water volume in the DPG condenser is extremely low, kinetic fractionation would affect the ability of DPG to produce water vapor exactly following the Rayleigh distillation prediction. Through conventional deuterium excess calculations ($\delta^2\text{H} - 8\delta^{18}\text{O}$), we find that the deuterium excesses for our measurements are 14‰ and 13‰ for ambient pressure and 13‰ and 12‰ for 60 kPa, during the periods that we suggest for calibration (10–15 h for ambient pressure and 8–10 h for 60 kPa pressure). The similarities in deuterium excess between the two calibrations across both pressure settings generally confirm our use of the DPG as a Rayleigh distillation device, at least for this part of the testing period. Despite the apparent suitability of the DPG as a Rayleigh distillation device, we find that the different pressure settings appear to affect the overall performance of the WVIA. First, the correction factors at the 60 kPa setting are different from the ambient pressure setting. At 60 kPa, the correction factors are lower than they are for the ambient pressure setting. In addition, the precisions are generally higher for the ambient pressure setting (Table 1). While the higher precisions under ambient pressure setting may relate to the manufacturer optimizing the instrument for ambient pressure operation, we are not sure why the correction factors are lower for the 60 kPa setting. Nevertheless, these results indicate that, in order to obtain the best performance, the instrument should be calibrated under the particular operating pressure. The consistency in correction factors between two calibrations conducted over a period of 3 days at both pressure settings indicates that the WVIA measurements are stable for at least 3 days. We cannot predict the maximum days of stable performance based on the current data, although the manufacturer suggests that the instrument is stable for at least one week (D. S. Baer, personal communication).

The similarity in precision over hourly and minute averaging periods is explained by the shape of the Allan Variance curves in Fig. 5, which finds its minimum between these two averaging periods. The WVIA precision initially increases due to longer averaging times that increase precision; however, laser drift probably begins to reduce precision over longer averaging periods. We observe oscillations in precision patterns for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ at the 60 kPa pressure setting starting from an averaging interval of ~ 400 s (Fig. 5). Because similar patterns do not exist for the ambient pressure setting, we think that these

patterns are mainly caused by oscillations in the pumping system used to create the lower than atmospheric pressure.

Previous reports of a laboratory test of the DPG with another type of LAS-based measurement shows a more negative departure (measured values are more depleted than predicted) from Rayleigh prediction through time, especially after a long period of comparison,⁶ and we also observe this behaviour in our 24 h (ambient pressure setting) calibrations (Fig. 3). Furthermore, these negative departures are consistent between the two ambient calibration runs (Fig. 3). The previous report⁶ argues that this negative departure could be caused by either of two factors: (1) the diffusion of water vapor in room air through the wall of Bev-a-line tubes (which are used by the DPG device for water vapor transport), especially if the room air is more depleted than the reservoir water; and (2) by some amount of residual water vapor contained within the dry air feeding to the DPG. In our case, since we do not see such departures for our shorter time calibration (10 h runs, Fig. 4), we suspect that observed departures are more likely to be caused by the lower volume of water in the DPG condenser at the end of the calibration, which will reduce the flow rate, Q , and/or induce a kinetic fractionation effect due to reduced humidity in the DPG headspace. This indicates that the calibration should not be conducted for a period exceeding 20 h at the ambient pressure setting.

Despite the observed departures between theoretical and observed patterns of isotope composition, we find that the DPG method is satisfactory for WVIA calibration. In addition to obtaining excellent overall agreement between the corrected sensor measurements and those obtained from a predicted Rayleigh fractionation process, we find that there are periods during each calibration when the Rayleigh predictions and instrument measurements are almost identical. In our case, the best period for the ambient pressure setting was found to be 10–15 h after the calibration had been initiated (Fig. 3). The best period for the 60 kPa pressure setting was observed to occur 8–10 h after initiating the calibration (Fig. 4). Therefore, we suggest calibrating the WVIA using data collected 10 h after beginning the calibration, which is the overlapping period for the two pressure levels that we tested. This period should consistently provide the best performance regardless of the pressure settings, provided that the pressure is between 60 kPa and 98 kPa (ambient pressure).

Because the Los Gatos WVIA has only been commercially available for about 2 years, there remains a need for more intensive calibrations and comparisons carried out under a wider range of temperature conditions, a more diverse suite of pressure conditions, and even for more individual instruments. In addition, although DPG is a good candidate for WVIA calibration, especially for various pressure needs and for remote field sites applications, we do not think that our tests provide a definitive answer on the issues of evaluating the instrument performance or calibration configuration. To further assess instrument accuracy, methods that can better control the source isotopic signatures should be developed to compensate and cross validate this technique. We have, however, demonstrated the feasibility of calibrating this type of ICOS-based instrument under various

pressures using a relative simple laboratory setup based on a dew point generator. Using this method, we are also able to assess of precision of the instrument, which is comparable with reported conventional lab-based cold trap water vapor collection/mass spectrometry and other LAS-based methods. Based on our results, and considering the many benefits of an OA-ICOS approach compared with other methods, we believe that OA-ICOS-based instruments will compete favorably with traditional mass spectrometry techniques for the measurement of water vapor isotopic compositions and that they have the potential to greatly expand the use of continuous $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements to address a wide range of ecohydrological research topics.

Because the DPG calibration method developed here can calibrate the WVIA under different pressure settings using a portable pumping system it is especially beneficial in micrometeorological applications. The DPG calibration method is also a good candidate for remote field site operations since the DPG itself is a relatively reliable water vapor source with known isotopic signatures and is able to provide 'in situ' calibration.

CONCLUSIONS

We have successfully calibrated the ICOS-based spectrometer (Los Gatos Water Vapor Isotope Analyzer DLT-100) using a commercially available dew point generator and a liquid water standard of known isotopic signatures. We developed a system to calibrate the instrument at various pressure settings, which is important for the integration of this instrument into a range of existing gas sampling systems (e.g. soil chamber measurements and eddy covariance systems). We find that this OA-ICOS instrument is able to obtain continuous measurements with a precision of $\sim 0.1\%$ for $\delta^{18}\text{O}$ and $\sim 1\%$ for $\delta^2\text{H}$, which is close to or better than that obtained using conventional water-trap/mass spectrometry methods, but in a continuous mode. In addition, the differences between our precisions and that of previously published LAS-based methods are $< 0.1\%$ and $< 1\%$ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. While the instrument precision is generally higher at the ambient pressure setting, we find that calibration of the instrument at the specific operating

pressure is needed. The extremely low energy consumption and the absence of a need for either a reference gas or liquid nitrogen/dry-ice cooling make this ICOS-based spectrometer a suitable candidate for remote site operations.

Acknowledgements

This project was funded by a startup grant from Princeton University and was also partially funded through the Office of Science (BER), US Department of Energy, Grant No. DE-FG02-07ER64371. We greatly appreciate the technical assistance of instrumentation scientist Steve Scott at Indiana University. We are grateful for the comments of an anonymous reviewer as well as Dr Feng Dong from Los Gatos Research Inc. for sharing their preliminary calibration procedures and insightful suggestions for precision assessments.

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