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Applications of Cavity-Enhanced Absorption Spectrometry for Water Isotope Monitoring in Hydrology, Medical Diagnostics, and Wine Authentication

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Abstract: *Measurements of the $^{18}O/^{16}O$ and $^{2}H/^{1}H$ isotope ratios in water are commonly used in hydrology, medical diagnostics, and food verification. Until recently, these measurements required transporting samples to dedicated laboratories and quantifying them using isotope ratio mass spectrometry, a complicated and expensive process. Advances in cavity-enhanced absorption spectrometry have enabled the development of automated, field-deployable water isotope analyzers that are considerably faster, simpler, and more economical. This article describes the utilization of these analyzers for studies of groundwater migration, energy expenditure, and wine authentication. Beyond water isotopes, this technology can also be extended to address other species, including carbon dioxide, methane, and nitrous oxide for climate studies, energy exploration, and wastewater attribution.*

Keywords: *Cavity Enhanced Laser Absorption Spectrometer, Applications of CEAS to Water Isotope Measurements, Isotope Hydrology, Medical Diagnostics, Wine Authentication*

1. Introduction:

In a sample of liquid water, the vast majority of water molecules consist of two hydrogen-1 atoms and an oxygen-16 atom. The hydrogen-1 atoms contain 1 proton and the oxygen-16 atom contains 8 protons and 8 neutrons. A small fraction of water molecules will include other stable isotopes of hydrogen and oxygen which contain extra neutrons. For example, ocean water will typically contain 2005 parts-per-million (ppm) oxygen- 18 (found as 1H18O1H) and 156 ppm hydrogen-2 (found as 2H16O1H). The quantities of these stable isotopes are often expressed as the atomic ratios (i.e. for ocean water, 18O/16O = 2.005e-3 and 2H/1H = 1.56e-4). Natural processes, like evaporation and condensation, change these isotope ratios in a process called fractionation, and the measured isotope ratios can be used to help determine water sources and transport. Measurements of water isotopes have been used in a wide variety of environmental, medical, and forensic applications. They are often used in isotope hydrology1 to help determine water source, pathways, and residence times. Likewise, isotopic measurements of melted ice cores2 from Greenland, Antarctica, and equatorial glaciers are used as a proxy for the Earth's historical temperature record. In addition to these environmental applications, water isotope measurements have also been used in medical diagnostics to determine total body water content3, total energy expenditure,4 and glycolysis rates5. Finally, water isotope analysis is also employed for forensic applications, helping to determine sources of food6 and bacteria7.

Until recently, water isotopes were measured by transporting samples to a dedicated laboratory and utilizing isotope ratio mass spectrometry (IRMS) to quantify $^{18}O/^{16}O$ and $^{2}H/^{1}H$.

Typically, the samples are first equilibrated with a headspace of carbon dioxide, where oxygen-18 atoms are exchanged between the water and CO_2 for 12–24 hours. This CO_2 is then measured via IRMS against isotopically-calibrated CO_2 gas standards to determine the $^{18}O/^{16}O$ ratio. For $^{2}H/^{1}H$, the water sample typically is reduced by passing it through a hot chromium or palladium reactor held at 850 °C. The resulting hydrogen gas is measured by the IRMS against isotopically-calibrated hydrogen gas standards to determine the $^{2}H/^{1}H$ ratio. This conventional IRMS technology requires a dedicated operator, frequent calibration, and sample transportation. It frequently has very long lead times (e.g. 1–6 months) and costs $30–$50/sample. Due to these limitations, water isotope measurements have been limited in their scope and frequency, despite their high utility. Cavity-enhanced laser absorption spectrometry (CEAS) has revolutionized the measurement of water isotopes[8]. These new instruments directly measure water with no sample handling or conversion. They provide immediate results and can be operated on-site by minimally-trained personnel. The measurement requires virtually no consumables and the analyzers can make measurements at less than $2/sample. Recent advances have even permitted these sensors to be deployed directly in the field for continuous measurements of water sources. CEAS water isotope analyzers are dramatically

increasing the applicability of water isotope measurements for isotope hydrology, medical diagnostics, and forensics.

2. Technology: Cavity-Enhanced Laser Absorption Spectrometry:

The technology has been described in detail elsewhere9, and only a brief overview will be provided below.

2.1 Conventional Laser Absorption Spectrometry:

Recently, laser absorption spectrometry (LAS) has been used to develop instruments for a wide array of analytical applications. In LAS, a light from a tunable laser is passed through a gas sample and focused onto a detector. The laser wavelength is tuned over a small range by varying its injection current. Specific molecules absorb at particular laser frequencies, resulting in a decrease in transmitted intensity at those frequencies. The measured transmission trace can then be converted to an absorption spectrum, and the integrated area under the absorption peak can be directly related to the concentration of the targeted species via Beer's Law. This technology has several advantages over conventional analytical methods. Foremost, the technique is highly selective and exhibits minimal cross-interferences due to other background gases. By measuring all of the relevant parameters, Beer's Law can be directly used to calculate the gas concentration, with little to no calibration or consumables. Finally, by leveraging telecommunications grade equipment, LAS analyzers can be quite robust and cost competitive compared to existing technologies. These analyzers have been gaining acceptance in a wide variety of applications and several vendors have successfully commercialized the technology. However, for many isotopic measurements, the targeted isotopes (^{18}O and ^{2}H) are present in very low concentrations and conventional LAS cannot provide sufficient sensitivity, so more advanced techniques are required.

2.2. Cavity-Enhanced Laser Absorption Spectrometry:

A simple method of improving the sensitivity of LAS involves increasing the optical pathlength over which the laser interacts with the gas sample. Traditionally, this is has been implemented by using a multi-pass optical cell (e.g. White or Herriott cell) in which the laser beam bounces back and forth through the gas sample many times (typically 30–100 times). Despite this enhancement, accurate quantification of water isotopes requires an even more sensitive measurement.

An alternate method involves using a high-finesse optical cavity to provide an extraordinarily long (5–10 km typical) effective optical pathlength. In this scheme, the windows of the gas cell are replaced by highly-reflective

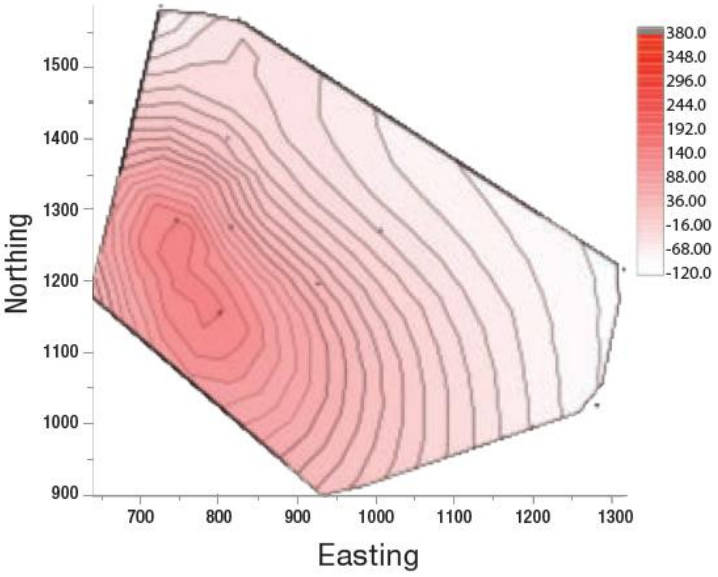


Figure 1. The Off-Axis ICOS Liquid Water Isotope analyzer is interfaced to an autosampler to enable autonomous measurements of 150 unknown samples per day. The measured cavity-enhanced absorption spectra are shown on the computer screen.

mirrors (R > 99.99 %). The laser light passes through the mirror and reflects back and forth in the cavity over 10,000 times, providing a large effective optical pathlength, and enhancing the molecular absorption. In Off-Axis Integrated Cavity Output Spectroscopy (Off-Axis ICOS)[10],a particular variant of cavity enhanced LAS, the laser is aligned off-axis with respect to the cavity to prevent optical interference within the cavity and optical feedback to the laser from the mirrors A typical laser scan takes 10 ms (100 Hz) and involves turning on the laser, scanning over the absorption feature, and turning the laser off. The last step simultaneously provides a measurement of both detector offset and effective optical pathlength via the established cavity ringdown technique[11].

This technology retains all of the benefits of traditional LAS (e.g. selectivity, speed, minimal calibration/consumables, robustness, and cost-effectiveness), but improves the analyzer sensitivity by a factor of 10000, allowing for the accurate quantification of water isotopes. Moreover, the technology is highly robust. The exact trajectory of the laser into the cavity is not critical, helping make the system immune to small changes in optical alignment due to mechanical and thermal perturbations (e.g. vibrations, shock, relative motion, etc.). Furthermore, due to advances in optical coating, the cavity mirrors can be produced inexpensively. Thus, as a result of decreasing components costs and manufacturing simplicity,

For measurements of water isotopes, the Off-Axis ICOS analyzer is integrated with a liquid autoloader (Figure 1). Approximately 1 microliter of liquid is injected through a septum into a heated block held at low pressure.



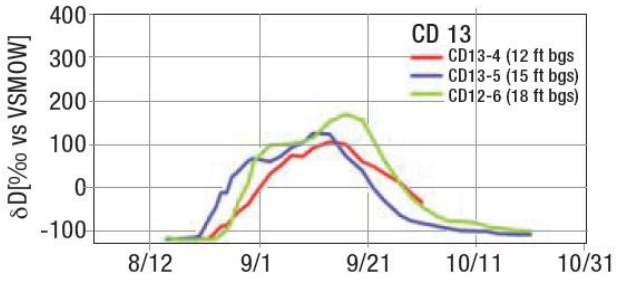


Figure 2.Water isotope measurements taken at the DOE IFRC site in Rifle Colorado during a groundwater tracer experiment. The injected, deuterated water migrates to the south and west (left) as indicated by the isotope readings. Measurements taken at different depths (right) show breakthrough curves that depend on soil porosity as a function of depth.

The sample evaporates, and the resulting water vapor flows into the measurement cell, where Off-Axis ICOS is used to make highly-precise measurements of $^{1}H^{16}O^{1}H$, $^{1}H^{18}O^{1}H$, and $^{2}H^{16}O^{1}H$. These molecular concentrations are converted to atomic ratios ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) and periodic measurements of isotopically-characterized water are used to calibrate the system. Note that, once the measurement run is set up, the system is fully autonomous and there are no consumable gases, with a single analyzer measuring up to 150 unknown water samples per day.

3. Applications of CEAS to Water Isotope Measurements:

3.1. Isotope Hydrology:

The first applications of CEAS for water isotope measurements involved isotope hydrology12. Since the 18O/16O and 2H/1H isotope ratios in water are specific to different sources (e.g. rainfall, snowmelt, lakes, streams, etc.), measurements of water isotopes can help researchers distinguish water sources and better understand water flow. Alternatively, water enriched with 2H16O1H (e.g. deuterated water) can be used as a tracer to identify groundwater flow and track water migration.

A good example is the CEAS Liquid Water Isotope analyzer used at an Integrated Field Research Challenge (IFRC) site in Rifle, Colorado. This site was used for uranium milling until 1958 and the surface layer was removed in 1996 to reduce contamination. Despite this removal, there is still a widespread plume of mobile uranium, U(VI), that is leaching into the groundwater and Colorado River. DOE researchers are working to convert mobile U(VI) into stationary U(IV) using natural bacteria via bioremediation. In order to better optimize the process, these researchers are studying the effects of acetate and pH on this bioremediation..

The injected chemicals are dosed with deuterium (2H) and bromide to track water movement.
The CEAS Liquid Water Isotope analyzer is used to monitor the flow of deuterated water through the system and track the migration of added chemicals. Measurements of 2H/1H (Figure 2) clearly show how the added water migrates through the system as a function of position and depth. These measurements were made on-site in a field trailer and the experimental parameters were revised in accordance with this readings.

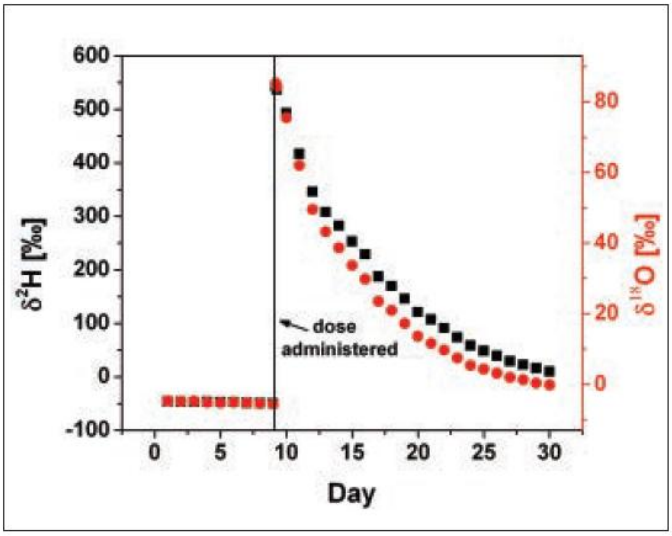


Figure 3.CEAS Liquid Water Isotope Analyzer measured isotope decay of δ2H (black squares, left axis) and δ 18O (red circles, right axis) after dosing for TEE analysis (dose administered on day 9). The difference in the elimination rate of the two isotopes can be used to calculated the subject's total energy expenditure.

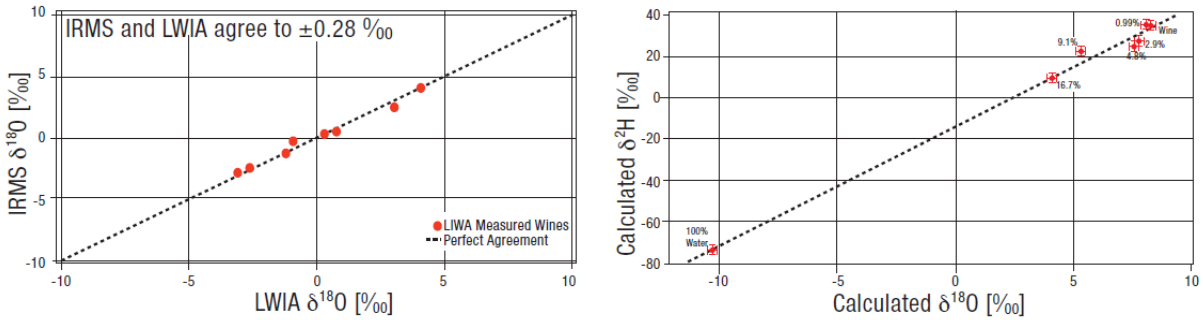


Figure 4.Measurements of wines made by the CEAS Liquid Water Isotope analyzer (LWIA) are in excellent agreement with IRMS readings (left). Moreover, the sensitivity of the CEAS measurements clearly identifies humidification levels of more than 1% (right).

In addition to this application, CEAS Liquid Water Isotope analyzers have also been used to make real-time field measurements[13] of rainfall and streams to study the residence time of hydrological catchments.

3.2. Medical Diagnostics:

Measurements of water isotopes are also used for medical diagnostics. For example, Total Body Water (TBW) can be measured by ingesting deuterated water and measuring the resulting enhancement in the subject's urine. Similarly, in the Doubly-Labeled Water (DLW) test, the subject can ingest water that is enriched in both ^{18}O and ^{2}H. The former leaves the body through breath (as CO_2) and urine (H_2O), whereas the latter primarily exits the body as urine. Thus, by measuring the $^{18}O/^{16}O$ and $^{2}H/^{1}H$ isotope ratios in the subject's urine over several days, the patient's CO_2 output can be quantified, allowing for a measurement of the subject's average Total Energy Expenditure (TEE) in kcal/day. IRMS measurements of urine require extensive sample handling, consumables, and appropriate corrections for the urine saline levels.

CEAS Liquid Water Isotope analyzers enable direct measurements of urine with minimal sample handling[14]. The analyzers provide results that are in excellent agreement with IRMS readings over a very wide dynamic range and have been successfully used to measure TEE (Figure 3). By dramatically simplifying the measurement and reducing costs, the TBW and DLW tests can be further extended for obesity and diabetes research.

3.3. Wine Authentication:

Wine fraud is a multi-billion dollar issue, with counterfeits accounting for up to 5% of the wines sold in secondary markets. Fraud can take many forms, including the addition of water (humidification), label fraud, and wine mixing. Since the isotope ratio of water in wine is specific to the water source and growing conditions, measurements of water isotope ratios in wine can help identify wine fraud[15].

Current international testing[16] involves using IRMS to measure $^{18}O/^{16}O$ ratios and Nuclear Magnetic Resonance (NMR) to measure $^{2}H/^{1}H$ ratios. Recently, CEAS Liquid Water Isotope analyzers have been extended to measure the isotope ratios of water in wine. The wine samples are treated with activated charcoal to remove residual volatile organic carbon
(VOC) compounds and filtered prior to analysis. No further sample treatment is employed. The measured results are corrected for interfering optical absorptions due to methanol, ethanol, and other compounds by using a Spectral Contaminant Identifier[17] that utilizes the cavity-enhanced absorption spectrum to determine correction metrics. Using this technique, the CEAS analyzer measurements are in excellent agreement with IRMS results, and the analyzer can readily identify wines that have been diluted with more than 1% water (Figure 4).

These measurements are now being extended to include fruit juices and other distilled spirits (e.g. whiskey).

4. Future Outlook:

CEAS has greatly widened the accessibility of water isotope measurements. In addition to the applications above, water isotope measurements can be used for climatology, homeland security[18], and plant studies[19]. CEAS is also being extended to address other species and their associated isotopes, including CO_2, CH_4, and N_2O for applications in plant studies, energy exploration, wastewater treatment, and soil studies.

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