Simple, precise and accurate measurements of ^{17}O, ^{18}O and ^{2}H for water applications
Los Gatos Research (LGR)

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Measurement made easy

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Introduction

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Key benefits
- Benchtop instrument eliminates need for outsourcing to expensive, dedicated measurement laboratories
- First simple route to address ^{17}O
- Simultaneously measures ^{17}O, ^{18}O and ^{2}H, d-excess and ^{17}O-excess
- Direct injection of liquid or vapor samples
- High accuracy and precision
- Smart software package simplifies data analysis

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Overview

This application note demonstrates that a different type of stable isotope analyzer – the Triple Isotope Water Analyzer (TIWA-45EP) from LGR – can measure δ^{17}O, δ^{18}O, δD, d-excess and even ^{17}O-excess with equal or better precision and accuracy compared to isotope ratio mass spectrometry (IRMS). The cited comparative data was recently published in a peer-reviewed journal. Furthermore, in contrast to IRMS, this benchtop instrument can derive all five isotope parameters simultaneously from directly injected water samples. Because of these capabilities, this instrument delivers faster results and reduces costs for researchers who have typically outsourced the measurements of δD and δ^{18}O in their samples to specialized isotope labs. Furthermore, this system enables direct measurement of δ^{17}O, which has usually been prohibitively costly and complex, even though there is growing evidence that it provides unique and valuable information in many diverse water applications.
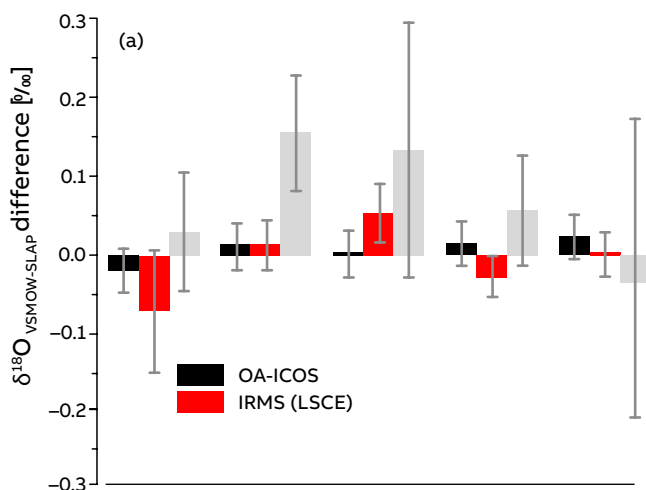

Figure. 1   Compelling evidence of the accuracy and simplicity of the OA-ICOS based TIWA-45EP instrument from LGR. These data show deviations (and error bars) of δ^{18}O data from literature accepted values for several different water samples, when measured indirectly by two different IRMS labs and by direct sample injection into LGR's TIWA-45EP with no sample processing. As published in reference[1].

Applications of stable isotopes in water

Every process involving water, from photosynthesis to seawater evaporation, has a characteristic isotope fractionation ratio, i.e., how much it favors heavier or lighter isotopes of oxygen and hydrogen. Thus, measurements of these ratios reveal much about the history and source of natural water samples. Additionally, in many life- and geo-sciences studies, known amounts of these stable isotopes are actively introduced as labels to track water through various pathways and biological processes.

The abundance of each isotope is expressed as its concentration in the sample relative to its concentration in an accepted standard. For ^{18}O and deuterium, these ratios are written as δ^2H (also often written δD) and d^{18}O in units of per mill (per thousand, ‰). The standard for natural water samples was originally "Standard Mean Ocean Water" (SMOW) as defined by Craig [2]. But today we more commonly use a newer standard, specifically the Vienna Standard Mean Ocean Water 2 (VSMOW2). (Note that VSMOW was replaced by VSMOW2 recently) In his landmark study, Craig also showed that there is a close relationship between the two trace isotopes:

$$\delta^2H \approx 8 \times \delta^{18}O + 10.$$

Since then, researchers have studied deviations from this relationship. These deviations arise from subtle interplay between thermodynamic and kinetic fractionation processes and are defined by the quantity d-excess, which was originally formulated by Dansgaard [3] in 1964 as:

$$d\text{-excess (in permil)} = \delta^2H - 8\,\delta^{18}O$$

This is also measured in units of per mil (per thousand, ‰). As an example of its use and value, d-excess in rainwater is strongly dependent on the humidity and temperature at the point of evaporation.

In contrast to ^{18}O and ^{2}H, scientists have almost universally neglected the other trace stable isotope found in water, ^{17}O. The primary reasons for this neglect are its low natural abundance (nearly an order of magnitude less than ^{18}O) and the fact that its measurement is particularly costly and complex, even for specialized IRMS laboratories (see below). In the past decade, there has been a growing interest in measuring ^{17}O, in spite of this difficulty. In addition to measuring δ^{17}O, researchers have also defined and measured the quantity ^{17}O-excess. Analogous to d-excess, this quantifies the small deviations from the expected relationship in rainwater between δ^{17}O and δ^{18}O, as measured by Luz and Barkan [4] – specifically:

$$^{17}\text{O-excess} = \ell n\,(^{17}\text{O} + 1) - 0.528\,\ell n\,(^{18}\text{O} + 1)$$

Because of its low magnitude, ^{17}O-excess is defined in units of per meg (per million). Many applications for this subtle parameter remain to be discovered. One example of its use is in climatology, where d-excess is known to have a dependence on both humidity and temperature at the source of evaporation. Since it has been shown that ^{17}O-excess is only strongly dependent on humidity, the measurement of both excess values enables humidity and temperature to be separately interpolated. However, this application places extreme demands on the measurement accuracy and precision: near the limits of existing IRMS protocols. In particular, the variation in ^{17}O-excess in meteoric waters is, at most, one hundred per meg. Even though this is similar to the quoted IRMS precision for δ^{18}O and δ^{17}O, it has been shown that ^{17}O-excess can be measured with a precision better than 10 per meg for hydrology applications. The reason is that the limit on precision is typically due to any fractionation that occurs during sample handling. This fractionation affects δ^{18}O and δ^{17}O almost equally, if they are near typical meteoric values [5] and thus allow higher resolution measurements of ^{17}O excess to be recorded.

Limitations of traditional (IRMS) methods

Isotope ratio mass spectrometry (IRMS) has long been the de facto standard for measuring stable isotopes. Samples such as rainwater are carefully sealed and typically then sent to specialized IRMS laboratories. Here the ^{18}O and ^{2}H are processed separately. One reason is that water is a very "sticky" material that should not be injected into delicate high vacuum equipment like an IRMS; it persists on surfaces for a very long time, continuing to corrupt subsequent measurements.

The oxygen is usually processed by equilibrating water with CO_2 gas of known O isotope composition, leading to eventual equilibration of the oxygen atoms between the two species. The CO_2 is then extracted, dried and introduced into the IRMS instrument. The amount of ^{18}O (relative to ^{16}O) is observed from the ratio of the mass 46 and mass 44 peaks. The hydrogen isotopes are measured by passing the vaporized water over a hot metal catalyst to obtain hydrogen gas. This is then measured in an IRMS that has been optimized for low mass species; the amount of ^{2}H is obtained from the ratio of the mass 3 and mass 2 peaks. Alternatively, both isotopes can be measured by temperature conversion elemental analysis (TC/EA) IRMS instruments. Although this all sounds cumbersome for the non-expert, IRMS laboratories have often mastered this process.

The lower abundance isotope ^{17}O is quite another matter. The established CO_2 equilibration method is problematic because this would require observing the ratio of the mass 45 and mass 44 peaks. But mass 45 can also arise from the much more abundant ^{13}C which thus serves to mask the ^{17}O measurement and only low precision data (±0.3 ‰) is possible at best via this route. Instead, for the past decade, the relatively sparse ^{17}O data has been obtained by reducing water with electrochemistry or powerful reducing agents like C_oF_3. Of course, this added complexity makes sample analysis a higher cost service and places stable isotope analysis even further from the capabilities of the average hydrologist.

Benchtop OA-ICOS instruments

Instead of IRMS, all LGR trace gas and stable isotope analyzers are based on an extremely sensitive optical absorption technique called Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS). Nearly every small molecule, including CH_4, CO_2 and H_2O, has a near-infrared/infrared absorption spectrum consisting of a series of sharp lines. By measuring the intensity of one or more of these lines, an instrument can determine the concentration of the molecules in the sample region between the light source and the detector. Moreover, where there is an isotopic substitution (e.g., ^{18}O instead of ^{16}O) the absorption lines are shifted and can be separately observed providing the measurement tool has sufficient wavelength resolution. Tunable laser diodes are narrow linewidth sources that can be operated with very low noise and are ideal for this purpose. The challenge is to measure the absorption when only a low concentration of the target molecule, e.g., HOD, is present. As demonstrated in 1988 by the founder of LGR, Anthony O'Keefe, this can be achieved using cavity enhancement to produce effective path lengths through the sample exceeding 20 kilometers.

A number of commercial instruments are available based on variants of this cavity enhanced laser absorption spectroscopy approach, from first-generation (conventional) cavity ringdown spectroscopy (CRDS) to fourth-generation OA-ICOS. However, of all these techniques, OA-ICOS is unique in its ability to deliver superior performance (simultaneously providing sensitivity, precision and absolute accuracy) in large part because it does not need the extreme (nanometer!) thermo-mechanical stability of the earlier embodiments. As implemented by LGR engineers and scientists, OA-ICOS instruments like the benchtop Triple Isotope Water Analyzer (TIWA-45EP) also provide exceptional reliability, rugged portability and lower cost per measurement. And, with over a thousand OA-ICOS instruments installed on seven continents, including in harsh field conditions and factories, these benefits are now well-proven and documented in many peer-reviewed journals.

Unlike with IRMS instruments, all the necessary skills to obtain maximum performance from the TIWA-45EP can be learned in a few hours. Samples of water and reference water standards can then be directly injected into the instrument using a conventional chromatography syringe. Or, water vapor can be continuously flowed into the instrument using the supplied connectors. The instrument simultaneously automatically generates data for δ^{17}O, δ^{18}O and δD, from which d-excess and ^{17}O-excess can be calculated. The combination of a fast measurement time and virtually no sample preparation now enables scientists to measure stable isotopes of water in their own labs and to process large numbers of water samples. And unlike IRMS, there is no additional cost whatsoever for adding ^{17}O data to the usual ^{18}O data set.

Figure. 2   The TIWA-45EP is very simple to use

Smart Instrument – post-analysis software package

There are two keys to obtaining precise, accurate and reproducible data on low abundance trace isotopes. The first is quantitative sensitivity, which is an inherent attribute of LGR's implementation of OA-ICOS. The second is data processing – including analysis, error screening, calibration, averaging and fitting. In this regard, the TIWA-45EP is a smart instrument, designed to enable the non-expert to reliably generate cutting-edge data quality. For example, one uncertainty in using direct syringe injection is the exact amount of water actually injected. And for injections another potential uncertainty is whether the heater evaporates the sample completely before data acquisition commences. Both can be addressed seamlessly in the TIWA-45EP, which can automatically discard any raw data where the amount of optical absorption indicates the amount of injected water (the number density) is outside the recommended limits for the instrument. And, data are rejected which obviously show a steady increase in number density, indicating ongoing (i.e., incomplete) water evaporation.

The instrument also comes with powerful post analysis software to enable sophisticated data validation, calibration, sorting, fitting, plotting and other functions that increase the instrument utility for both novices and isotope experts. For example, every data point can be screened and qualified beyond the red flags that the instrument itself will notice and discard. This software also ensures the highest possible absolute accuracy for every data point, by fitting the small instrument drift with time using the periodically inserted reference data that are standard in any isotope study, no matter what the technology. Specifically, the smart software will not only fit the drift of these reference data but also will determine on an ad hoc basis what type of fit is best to use, e.g., linear fit, cubic spline and so forth. This means the most accurate possible absolute correction is applied to every single sample measurement.

Comparative study of OA-ICOS and IRMS

In a recent study published in the peer-reviewed ACS journal Analytical Chemistry [1], scientists from LGR collaborated with researchers at two leading stable isotope laboratories to compare the accuracy and precision of the TIWA-45EP with IRMS for oxygen isotope determination. Specifically, a series of water samples were independently analyzed at LGR, at Johns Hopkins University in Baltimore, Maryland and at the Laboratoire des Sciences du Climat et l'Environnement in Gif sur Yvette, France. The two IRMS studies were performed using C_oF_3 fluorination to derive ^{17}O, ^{18}O and ^{17}O-excess. At LGR, water samples were introduced without sample conversion into the OA-ICOS instrument via the included auto-injector equipped with a heated injector block (LGR). In the block, the water samples were evaporated for isotope analysis directly on the resulting water vapor. Liquid water samples were injected into the injector block using a 1.2 μL, zero dead-volume syringe. The LGR instrument output all three stable isotope values (dD, d^{18}O and d^{17}O); the three oxygen parameters were compared to those from the two IRMS studies. The hydrogen isotope parameters, while measured by the LGR instrument, were not compared in this study because the IRMS protocols did not include measurement of hydrogen isotopes.

… **Comparative study of OA-ICOS and IRMS**

In order to compare the three sets of measurements, each laboratory normalized their data using two primary reference standards (VSMOW2 and SLAP2) in conventional calibration protocols. The full details of the laboratory protocols can be found in the paper in Analytical Chemistry.

By any metric, the data from this study demonstrate that the TIWA-45EP can match or beat the performance of fully optimized IRMS instruments and do this without either sample preparation or the need for special expertise (and, therefore, lower cost per measurement). Perhaps nothing illustrates this better than the study data for δ^{17}O. In fact, the historical difficulties of trace ^{17}O measurements mean there are no internationally recognized reference standards with which to compare δ^{17}O data, as in Figure 1.

As shown in Figure 3, to compare the performance of the TIWA-45EP to IRMS systems, we compare data for all three to a weighted average for each water sample (except GISP, which is compared to an average of previous literature values). Again the precision and accuracy of these data speak for themselves.

Summary

In the field of stable isotopes in water, the development of OA-ICOS instruments represents a paradigm shift. The ability for any laboratory or field application to measure all five isotopic parameters of water, including the difficult δ^{17}O and ^{17}O-excess, will benefit existing applications for water isotopes and also enable their use in applications which previously could not tolerate the cost and complexity of these measurements.
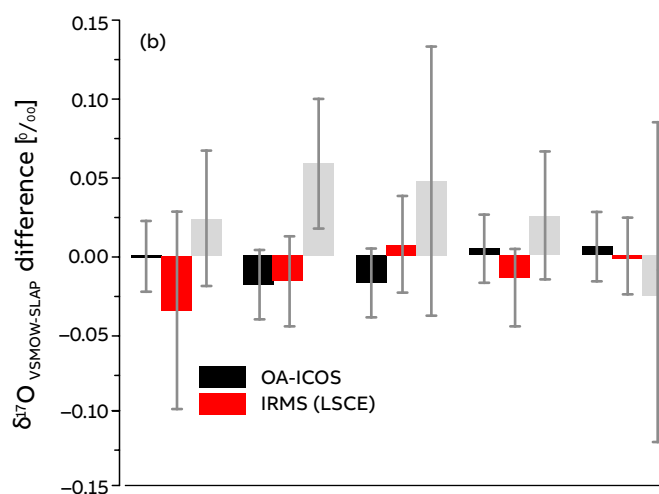

Figure. 3   Measurements of δ^{17}O VSMOW-SLAP (b) for GISP are shown as the difference between each measurement and an average of previously reported values (ref xx). Measurements of δ^{17}O VSMOW-SLAP (b) for USGS isotopic reference waters are shown as the difference between each measurement and the average of the three experimental measurements inversely weighted by the uncertainty. Error bars represent the standard error of the mean for IRMS measurements and the measured limit of instrumental precision for OA-ICOS.

A note about accuracy and precision

The data summarized in Figures 1 and 3 graphically illustrate the achievable measurement accuracy with the TIWA-45EP. The instrument precision (i.e., the data spread or standard deviation) not surprisingly depends on the number of measurements that are averaged for each data point. Consequently, the definitive way to measure the precision is to use an Allan plot. For random errors like white noise, the Allan deviation declines as the square root of the number of measurements averaged; the value of the Allan deviation defines the instrument precision for a given number of averaged measurements. However, an Allan plot, by itself, simply reflects the repeatability of the instrument and does not include memory effects that occur between samples and references in a real measurement sequence. As a result, the apparent precision as shown in an Allan plot is thus obtained at the expense of accuracy. Most applications need high precision and high accuracy, not high precision or high accuracy. That's why at LGR we record all data, including Allan plots, the same way as you record actual high accuracy and precision data – by periodically inserting reference measurements in the data. As a result, you can obtain data that simultaneously deliver the instrument's stated precision and accuracy.

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ABB Inc.
Measurement & Analytics
3400 Rue Pierre-Ardouin
Quebec (Quebec)
G1P 0B2
Canada
Tel: +1 418 877 2944
Fax: +1 418 877 2834
Email: icos@ca.abb.com

abb.com/measurement

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