Hydrogen and Oxygen isotope analysis ($\delta^2$H & $\delta^{18}$O) of water by Laser Spectroscopy

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Overview

The $^2$H/$^1$H and $^{18}$O/$^{16}$O ratios of low TDS water samples are measured using a Los Gatos Research (LGR), “DLT-100” instrument. Approximately 750nL of water is injected into the heated septum port of a LEAP Technology (CTC) PAL liquid auto-sampler. Upon injection, the water rapidly vapourizes and is expanded into the laser cell of the DLT-100. Unlike mass spectrometry techniques, the H$_2$O molecules are NOT converted to other gases, but rather are measured directly by “Off-Axis Integrated-Cavity Output Spectroscopy (ICOS)”. For more detailed information on this technique please see below and/or visit: www.lgrinc.com.

Further comments on technique

- The syringe used is a Hamilton 7701.2 N CTC (p/n 203185/01)
- In order to overcome “memory”, each vial of water (samples and standards) is injected a minimum of 6 times, but the first 3 data points are discarded
- Normalization standards (“high std” & “low std”) are run every three samples
- An Internal (QA/QC) lab standard is analyzed repeatedly within each sequence (3 standards per 24 samples) to monitor and guarantee quality control

Data normalization

- “raw” $\delta^2$H$_{H2O}$ and $\delta^{18}$O$_{H2O}$ values are normalized using internal, laboratory water standards which have been calibrated against International reference materials: VSMOW, VSLAP & VGISP. (note: all internal lab standards are periodically checked against fresh VSMOW, VSLAP & VGISP)
- USGS LIMs is used for drift correction, normalization and data management (http://water.usgs.gov/software/LIMS/)
- Corrected $\delta^2$H$_{H2O}$ and $\delta^{18}$O$_{H2O}$ values are reported in the usual per mil (‰) notation

Accuracy and Precision:

Accuracy and precision of $\delta^2$H determinations are generally better than $\pm 1.0$‰ (one standard deviation based on n=50 lab standard)
Accuracy and precision of $\delta^{18}O$ determinations are generally better than ±0.2‰ (one standard deviation based on n=50 lab standard)

References:


Further details on ICOS sourced from the LGR website:

Conventional Laser Absorption Spectroscopy

For gas measurements based on conventional laser-absorption spectroscopy (Figure 1), a laser beam is directed through a sample and the mixing ratio (or mole fraction) of a gas is determined from the measured absorption using Beer’s Law, which may be expressed:

$$\frac{I_0}{I_\nu} = e^{-\chi P \phi_\nu}$$

where $I_\nu$ is the transmitted intensity through the sample at frequency $\nu$, $I_0$ is the (reference) laser intensity prior to entering the cell, $P$ is the gas pressure, $S$ is the absorption line strength of the probed transition, $L$ is the optical path length, $\chi$ is the mixing ratio, and $\phi_\nu$ is the lineshape function of the transition at frequency $\nu$. In this case,

$$\int \phi(\nu) d\nu = 1.$$

If the laser linewidth is much narrower than the width of the absorption feature, high-resolution absorption spectra may
be recorded by tuning the laser wavelength over the probed feature. Subsequent integration of the measured spectra together with measured values of gas temperature, pressure, path length and the line strength of the probed transition allow determination of the mixing ratio directly from the relation:

\[
\chi = \frac{1}{SLP} \int \ln \left( \frac{I_2}{I_r} \right) d\nu
\]

This strategy has been proven successful in determining gas concentrations in mixtures containing several species, in flows at elevated temperatures and pressures, and in hostile environments, without using calibration gases or reference standards.

Until recently, high-sensitivity trace-gas measurements have been possible only by using expensive lasers (e.g., lead-salt or quantum-cascade) or broadband lamps that operate in the mid-infrared region where absorption features are strong. LGR’s advances in cavity-enhanced absorption-spectroscopy techniques provide dramatic increases in the optical path length (as described below) and, as a result, enable ultrasensitive trace-gas measurements using robust, reliable, room-temperature diode lasers that operate in the near infrared.

LGR’s Off-Axis Integrated-Cavity Output Spectroscopy (Off-Axis ICOS)

Off-Axis ICOS utilizes a high-finesse optical cavity as an absorption cell (Figure 2). Unlike conventional multipass arrangements
which are typically limited to path lengths less than two-hundred meters, an Off-Axis 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 thus the measured absorption of light after it passes through the optical cavity is significantly enhanced. For example, for a cell composed of two 99.99% reflectivity mirrors spaced by 25 cm, the effective optical path length is 2500 meters.

Since the pathlength depends only on optical losses in the cavity, and not on a unique beam trajectory (like conventional multipass cells or cavity- ringdown systems), the optical alignment is very robust allowing for reliable operation in the field. The effective optical path length is determined routinely by simply switching the laser off and measuring the time necessary for light to leave the cavity (typically tens of microseconds).

As with conventional tunable-laser absorption-spectroscopy methods, the wavelength of the laser is tuned over a selected absorption feature of the target species. The measured absorption spectra is recorded and, combined with measured gas temperature and pressure in the cell, effective path length, and known line strength, used to determine a quantitative measurement of mixing ratio directly and without external calibration.