

$\delta^2\text{H}$ & $\delta^{18}\text{O}$ -_{water} isotopic analysis by Laser Spectroscopy

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Overview

The $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ 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_2O 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.

Sample collection:

- Water samples should be collected in Nalgene, HDPE or glass sample bottles. Cap liners should be plastic or rubber (cardboard or foil coated cardboard are to be avoided)
- Sample bottle caps should be secured using parafilm/electrical tape (wrapped counter to the thread) to ensure caps do not relax during transport
- 20 ml is a reasonable volume (if water isotopes are the only request, do not send bottles larger than 100ml)
- Smaller sample quantities can be accommodated (please consult with lab manager before hand)
- Bottles should be filled to capacity to minimize headspace
- Samples should be filtered to at least 0.45uM,
- No biocide is needed
- Samples should be kept cool (refrigerate or ice)
- A completed sample submission form must accompany the samples
<https://www.ucalgary.ca/labs/isotope-science-lab/sample-submission>

Stable isotope ratios are expressed as delta (δ) and are measures of a ‘per mille’ (‰), or parts per thousand difference between the isotope ratio of a sample and that of a known (International) standard material.

Further comments:

- The syringe used is a Hamilton 7701.2 N CTC (p/n 203185/01)
- In order to overcome “memory”, each vial (unknown and/or standard) is injected nine times, but the first four data points are discarded
- Internal ISL references used as Normalization standards (“high std” & “low std”) are analyzed every six unknowns
- The internal ISL references are periodically calibrated against International Reference Materials (table below) to assure accuracy to the VSMOW-SLAP scale
- An Internal (QA/QC) lab standard is analyzed every six unknowns
- USGS LIMs is used for drift correction, normalization and data management (<http://water.usgs.gov/software/LIMS/>)
- Corrected $\delta^2\text{H}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values are reported in the usual per mil (‰) notation

	$\delta^{18}\text{O}$	SD	$\delta^2\text{H}$	SD
VSMOW2	0	0.02	0	0.3
GISP	-24.76	0.09	-189.5	1.2
GRESP	-33.39	0.04	-257.8	0.4
SLAP2	-55.5	0.02	-427.5	0.3

Accuracy and Precision:

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

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

References:

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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:

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

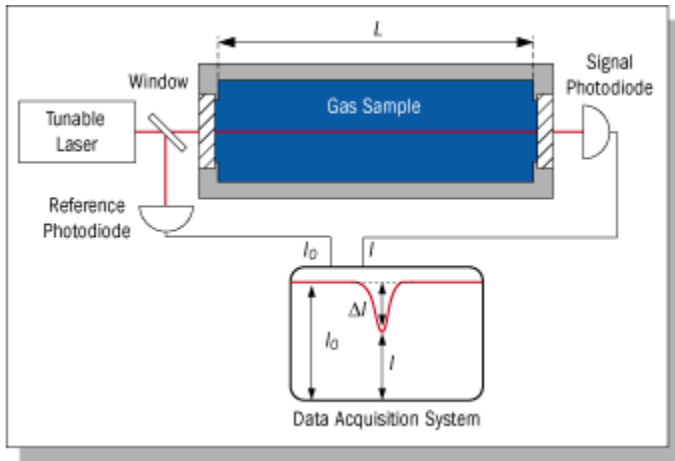
where I_ν is the transmitted intensity through the sample at frequency ν , I_0 is the (reference) laser intensity prior to entering the cell, P is the gas pressure, S is the absorption line strength of the probed transition, L is the optical path length, χ is the mixing ratio, and ϕ_ν is the lineshape function of the transition at frequency ν . 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

Figure 1

Typical laser absorption spectroscopy setup.



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:

$$\chi = \frac{1}{SLP} \int \ln \left(\frac{I_0}{I_\nu} \right) d\nu$$

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

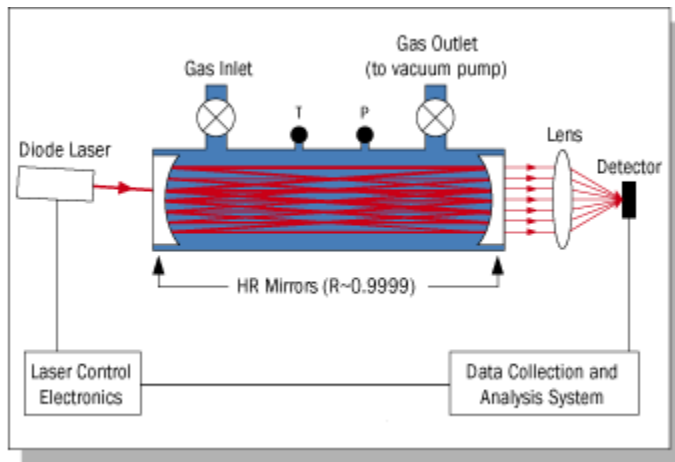
the mid-infrared region where absorption features are strong. LGR's advances in cavity-enhanced absorption-spectroscopy techniques provide dramatic increases in the optical path length (as described below) and, as a result, enable ultrasensitive trace-gas measurements using robust, reliable, room-temperature 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

Figure 2

Schematic diagram of an Off-Axis ICOS Instrument.



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.