

$\delta^2\text{H}$ & $\delta^{18}\text{O}$ -water isotopic analysis by “*headspace equilibration*”

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Overview:

Although equally applicable to waters of low TDS, the $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of high TDS waters (> 10,000 mg/L) such as saline, brackish or brine waters are determined using headspace equilibration with H_2 and CO_2 gas mixtures respectively, and analyzed using Continuous Flow – Isotope Ratio Mass Spectrometry (CF-IRMS).

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 0.45 μM ,
- 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>

Online (CF-IRMS) technique:

250 μl of water is placed with a Hokko bead stick into an Exetainer vial (Labco p/n: 038W), then capped and flushed with either a 0.5% CO_2 + balance helium or 2% H_2 + balance helium gas mixture respectively. If samples contain dissolved organics, activated charcoal may also be added to the auto-sampler vial. If samples contain H_2S , copper rods may also be added to the auto-sampler vial. If samples are highly charged with dissolved CO_2 , 10 μl of concentrated *ortho*-phosphoric acid (Coplen et al., 1983) may also be added to the auto-sampler vial. Vials are flushed for ~10 minutes at ~70ml/min with the respective gas mix (CO_2 or H_2) then placed in the heated block of the GasBench-II[®] at 25°C and left to react for ~20hrs and ~2hrs for CO_2 and H_2 respectively. The CO_2 or H_2 headspace is then sampled automatically using a 50 μl sample loop and inlet to the ion source of

a DeltaV^{Plus}® stable isotope ratio mass spectrometer for analysis of ¹⁸O/¹⁶O and ²H/¹H ratios. The headspace of each vial is sampled 6 times by loop injection. The first peak is discarded and the subsequent 5 injections are acquired. If the first peak is >30 [V], the subsequent 5 injections are automatically diluted. Measurement of δ²H and δ¹⁸O are made in two separate sequences, optimizing the ion source first for ²H and then for ¹⁸O respectively. The instruments are fully automated and computer controlled using ISODAT 3.88 software. Prior to sample analysis instrument conditions: oven temperatures, carrier gas flows, ion beam background(s), ion source stability and signal linearity are checked and recorded (“Daily check” routine).

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.

Selected internal reference waters are analyzed multiple times within the sequence and are used to normalize the data as well as correct for any instrument drift. The internal ISL references are periodically calibrated against International Reference Materials (table below) to assure accuracy to the VSMOW-SLAP scale. All results are reported in the per mille notation relative to the international VSMOW reference material for δ²H and δ¹⁸O respectively.

	δ ¹⁸ O	SD	δ ² H	SD
VSMOW2	0	0.02	0	0.3
GISP	-24.76	0.09	-189.5	1.2
GRES	-33.39	0.04	-257.8	0.4
SLAP2	-55.5	0.02	-427.5	0.3

Further comments:

- Internal references are analyzed every 9th and 10th position throughout the sequence
- An internal lab QA/QC is analyzed at 1 standard per every 7 unknowns throughout the sequence
- USGS LIMs is used for drift correction, normalization and data management (<http://water.usgs.gov/software/LIMS/>)
- Corrected δ²H_{H2O} and δ¹⁸O_{H2O} values are reported in the usual per mil (‰) notation

Accuracy and Precision:

Accuracy and precision of δ²H determinations are generally better than ±2.0‰ (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).

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