

Performance of L2140-*i* Analyzer (Picarro, Inc.) for δ^{18} O and δ D analyses of freshwater, plant extracted waters and methanol or ethanol-water mixtures

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Introduction

Isotope-ratio infrared spectroscopy (IRIS) represents a cheaper alternative to isotope-ratio mass spectroscopy (IRMS) for stable isotope analyses of waters and could significantly enhance the application of stable isotopic data of waters in a variety of disciplines. However, the presence of organic contaminants in liquid samples causes spectral interferences and erroneous measurements.

We assessed the performance of a new commercially available IRIS instrument (L2140-i, Picarro, Inc., Santa Clara, CA) designed with improved spectroscopy and on-line module for oxidation of organic compounds (Micro-Combustion Module, or MCM) in order to overcome the problems as mentioned above.

Materials and methods

We compared isotope data obtained by L2140-*i* to IRMS data for different types of samples: freshwaters (n = 65), plant-extracted waters (n = 10), and methanol (n = 8, at 0, 0.3, 0.7 and 1% MeOH) or ethanol-water mixtures (n= 12, at 0, 0.3, 0.7, 1, 1.5 and 2% EtOH). MCM cartridge lifetime was assessed analyzing the same batches of samples with new and used (up to 500 samples) cartridges. Carryover effects were evaluated on a sub-set of samples analyzed with a new MCM cartridge and based on the last 3 injections of a total of 6 and 12 injections. Freshwater samples were also analyzed without on-line MCM.

Precision and accuracy

Precision and accuracy of our lab water standard with on-line MCM improved and were similar to what was obtained without on-line MCM when septa were changed every \leq 200 samples. On average, δ^{18} O matched the IRMS reference value, but δD was approximately 1 ‰ more depleted than the IRMS reference value.

| Mode of analysis | n | | δ ¹⁸ Ο (‰) | δD (‰) |
|--|----|------------------------|-----------------------|--------|
| MCM, overall | 63 | Average | -5.06 | -37.22 |
| | | SD | ± 0.28 | ± 1.89 |
| MCM, septa < 200 samples | 18 | Average | -4.99 | -36.65 |
| | | SD | ± 0.13 | ± 0.52 |
| no MCM, septa < 200 samples | 22 | Average | -4.99 | -36.58 |
| | | SD | ± 0.11 | ± 0.55 |
| | | IRMS Reference values* | -4.77 | -35.50 |
| *calibrated against IAEA water standards | | | | |

Conclusions

- Changing septa at ≤ 200 samples helped improve L2140-*i* precision (based on quality control data).
- Accuracy and precision of L2140-*i* data were better for δ^{18} O compared to δD , but were influenced by sample type.
- > L2140-*i* represents a good alternative to IRMS for freshwater samples, especially if used without on-line MCM.
- > MCM proved unable to completely eliminate the organic interferences in plant-extracted waters or alcohol-water mixtures leading to unsystematic δD discrepancy between IRIS and IRMS measurements even while using a new cartridge.
- We are currently testing the effect of adding activated carbon to the samples and/or filtering them.

Freshwater samples



- from 6 injections with on-line MCM.
- MCM.
- cartridge for up to 500 samples.

Plant-extracted waters and methanol or ethanol-water mixtures



- cartridge; acceptable cartridge lifetime is for \leq 300 samples.
- dependent.
- identification of non-problematic samples.

 \succ δ^{18} O measurements of freshwater samples with on-line MCM and 6 or 12 injections were comparable, while data from 6 injections without MCM were more similar to the IRMS data and had smaller standard deviations than data obtained

 \blacktriangleright More accurate δD measurements of freshwater samples were attained without

> Freshwater data were not affected by the number of samples previously run on the

| Mode of analysis | IRMS - L2140- <i>i</i> Difference | | | | | |
|---------------------|-----------------------------------|-----------------------|--------|--|--|--|
| | | δ ¹⁸ Ο (‰) | δD (‰) | | | |
| MCM 6 inj | Average | 0.50 | 1.67 | | | |
| | SD | ± 0.43 | ± 2.10 | | | |
| MCM 12 inj | Average | 0.50 | 1.32 | | | |
| | SD | ± 0.21 | ± 1.41 | | | |
| no MCM 6 inj | Average | 0.13 | 0.55 | | | |
| | SD | ± 0.13 | ± 0.93 | | | |

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> Laser measurements of plant extracts and alcohol-water mixtures were affected by the number of samples already run on the MCM cartridge and the nature of the sample. Best results were obtained by using a new

 \blacktriangleright However, even using a new cartridge, δD data were less consistent than $\delta^{18}O$ data with the IRMS data, with the discrepancies unsystematic and sample

Screening data for organic contamination running the ChemCorrect software was unreliable due to missed identification of problematic samples (high discrepancy between the IRMS data and the L2140-*i*) and erroneous

| Mode of analysis | IRMS - L2140-i Difference | | | |
|---|---------------------------|-----------------------|---------|--|
| | | δ ¹⁸ Ο (‰) | δD(‰) | |
| New Cartridge | Average | 0.18 | 1.48 | |
| | SD | ± 0.21 | ± 1.53 | |
| Used Cartridge (330 sa) | Average | -0.04 | 0.94 | |
| | SD | ± 0.88 | ± 2.83 | |
| Used Cartridge (500 sa) (only plant extracted waters) | Average | 1.95 | 5.95 | |
| | SD | ± 1.28 | ± 1.35 | |
| Used Cartridge (500 sa) (includes MeOH-water mixtures) | Average | 22.66 | 35.38 | |
| | SD | ± 36.39 | ± 53.20 | |