Improved throughput for $\delta^{18}O$ and δD measurements of water with Cavity Ring-Down Spectroscopy.

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INTRODUCTION

- Oxygen ($^{18}O/^{16}O$) and deuterium (D/H) isotopes are a widespread tool to trace physical and chemical processes in hydrology and bio-geosciences. Precision and throughput are key parameters for water isotope analysis.
- Picarro presents two new methodologies for the L2130-i CRDS water isotope analyzer that allow the user to increase the throughput without compromising data quality.
- The Picarro ***Express Method*** distinguishes between a memory reduction stage and a sample analysis stage and allows the user to measure up to 50 samples per day while maintaining the excellent precision of CRDS (i.e., 0.01‰ for $\delta^{18}O$ and 0.05‰ for δD). This corresponds to doubling the throughput compared to the standard Picarro methodology.
- The Picarro ***Survey Method*** makes use of ultrafast injections and sorts the samples by their measured isotopic values, enabling a powerful new strategy to reduce memory effects.

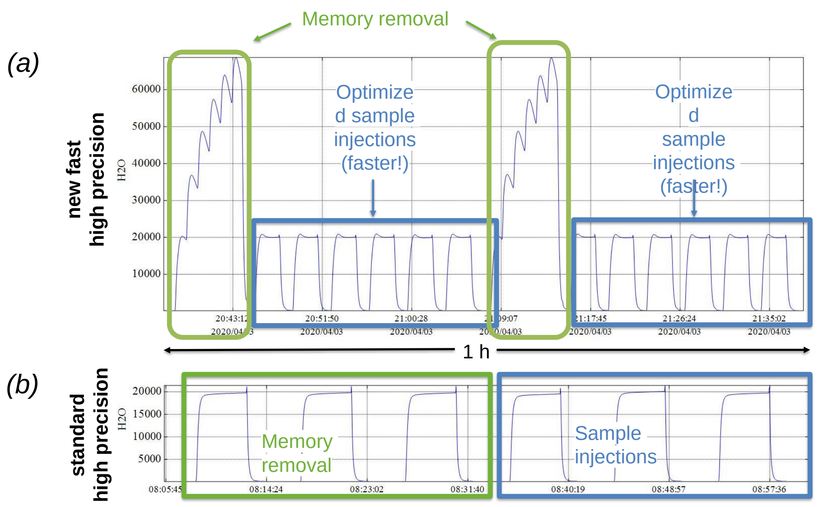
INSTRUMENTATION

Picarro L2130-*i* water isotope analyzer

- Analyzer is coupled to an autosampler and vaporizer (see picture top right)
- Current specification: 15 permeg (SD of averages of 6 injections, i.e., 1 h measurement)
  - ➢ The current 15 permeg precision specification is limited by the reproducibility of the water injections, not by the precision of the analyzer.
  - ➢ An improved injection procedure (see box below) allows significantly higher throughput (see results).

METHODS

Methodological Improvements in Water Isotope Analysis



NEW fast high precision

Memory removal:
- ➢ Continuous wet flushing of vaporizer and analyzer

Sample injection:
- ➢ Improved water vapor preparation ($T_{vaporizer}$=140°C)
- ➢ Faster transfer from vaporizer to analyzer
- ➢ Shorter sample measurement
- ➢ Improved syringe injection speed

Fig. 1 ***Standard vs. Express mode.*** *(b)* Standard water injection procedure for a Picarro water isotope analyzer (L2140-*i* / L2130-*i*) coupled to an autosampler and vaporizer. All injections show the same peak shape. The first three injections are discarded due to memory effects. *(a)* The new injection procedure (Express) distinguishes between memory removal and sample injections. The six memory removal injections are done within a few minutes so that the water vapor peak reaches up to 70,000 ppm. The actual sample measurements are still done at 20,000 ppm H_2O but with a shorter integration time on the peak and a faster transfer from the vaporizer to the analyzer.

RESULTS

Sample Sorting Can Reduce Memory Effect

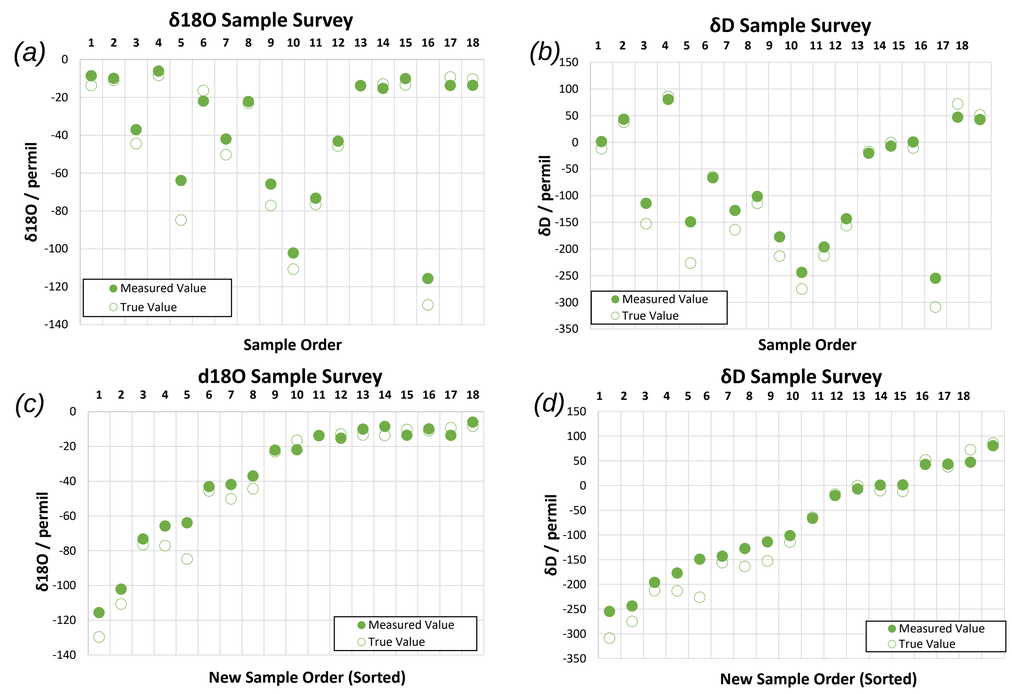


Fig. 2 ***Survey Method.*** Water vapor is sticky; the memory is hard to eliminate, even with multiple wet flushes. 18 different water samples were measured using Standard (o) or Survey (●) modes. The difference between two consecutive samples is significant in the original order for both ^{18}O *(a)* and δD *(b)*. The best memory reduction efficiency is achieved when the samples are sorted by the δD values surveyed in the original sample order. Both the real $\delta^{18}O$ *(c)* and δD *(d)* values follow the new sample order nicely in a monotonic way, which indicates a good sorting.

Increase Throughput Without Compromise on Data Quality

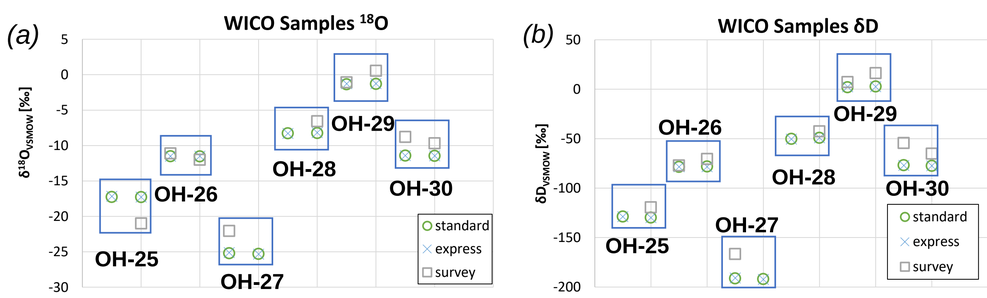


Fig.3 ***Express Method.*** WICO 2020 samples were measured using the new survey (□), Express (x), and Standard(o) modes. Both ^{18}O *(a)* and δD *(b)* measurements showed excellent correlation between the Standard and the Express mode, suggesting similar precision. Measurements done using Survey mode correlate with the true value and can be used to re-sort samples.

CONCLUSIONS

The new water injection procedure allows increased measurement precision and sample throughput.

- ➢ Using Express mode can increase sample throughput by a factor of 2 and reach the same precision for $\delta^{18}O$ and δD as Standard mode.
- ➢ Using Survey mode allows for re-sorting of samples to reduce memory effect resulting in better precision.

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