Measure ^{17}O-excess on water with a precision of 6 permeg within 3 h per sample.

Improved precision and throughput for ^{17}O-excess measurements on water with Cavity Ring Down Spectroscopy

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INTRODUCTION

- Triple oxygen isotope data (denoted as ^{17}O-excess = ln [δ^{17}O+1] - 0.528 ln [δ^{18}O+1]) have been used to constrain meteorological processes, plant fractionation processes, animal metabolism, and a variety of other physical and chemical processes. Measurement precision is key in order to successfully apply this promising new tracer to a range of scientific questions.
- To date, the ^{17}O-excess measurement precision of CRDS was limited to 10-15 permeg (e.g. [1]). Here, we will present a new methodology that allows to reach a similar or even better precision compared to the mass spectrometric approach [2]. The improved methodology does not require any hardware changes but is solely based on modifications of the injection procedure.

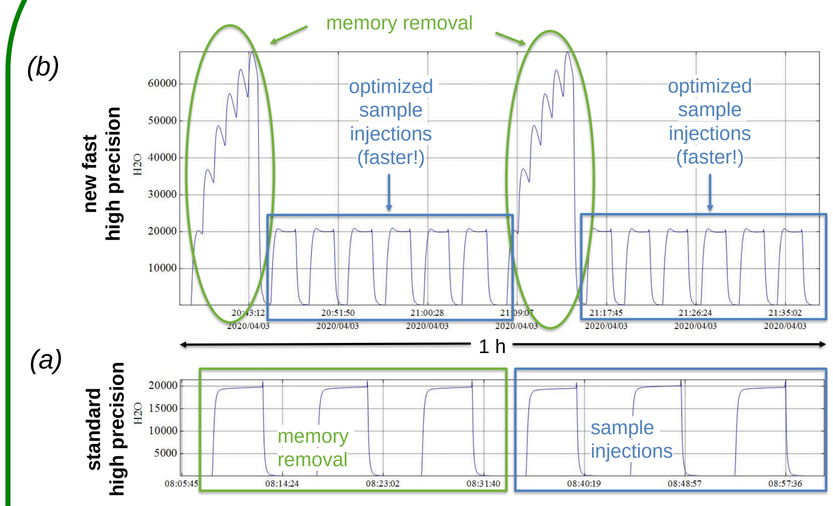
INSTRUMENTATION

Picarro L2140-*i* water isotope analyzer

https://www.picarro.com/l2140_i_isotope_and_gas_concentration_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 to reach a significantly higher precision or throughput (see results).

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: *(a)* 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 and usually the first three injections are discarded due to memory effects. *(b)* The new injection procedure 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 about 70,000 ppm. The actual sample measurements are still done at around 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

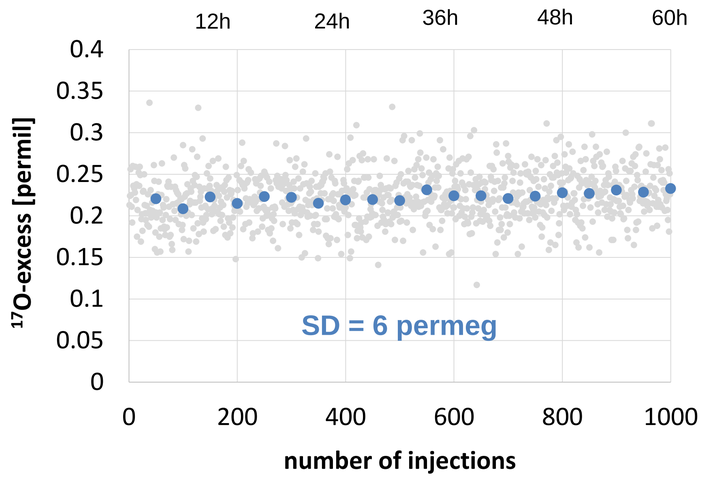


Fig. 2: Reproducibility test for ^{17}O-excess measurements on water with the new injection procedure. The grey data points show the ^{17}O-excess value for the single injections (each injection takes 3.7 min, SD = 30 permeg). The blue data points show the ^{17}O-excess value for averages of 50 injections. The standard deviation over the averages of 50 injections is only 6 permeg.

Injections to average	Time (h)	Time (min)	^{17}O-excess precision (permeg)
1	0.1	3.7	30
6	0.4	22	12
12	0.7	44	9
20	1.2	73	8
50	3.1	183	6

Table 1: The new injection procedure allows more injections in a shorter time: Previously it took about 1 h to reach a ^{17}O-excess precision of 15 permeg, now the same precision can be reached in about 20 min. Injecting the same sample for 3 h allows to reach a precision of about 6 permeg.

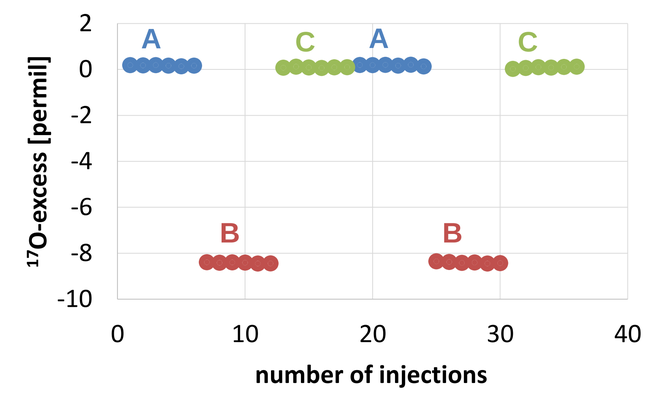


Fig. 3: Memory removal test. Alternating between sample A, B and C does not show any significant memory effect for ^{17}O-excess due to the improved memory removal procedure (SD_A = 23 permeg, SD_B = 28 permeg, SD_C = 27 permeg).
These measurements were performed by Len Wassenaar from IAEA as part of a beta testing collaboration.

CONCLUSIONS

- The new water injection procedure allows to increase significantly measurement precision and/or sample throughput.
  - ➢ The sample throughput can be increased by a factor of 3 and still reach the same precision for ^{17}O-excess, δ^{18}O and δD as before.
  - ➢ Alternatively, the ^{17}O-excess measurement precision can be increased to 6 permeg when averaging over 50 injections (i.e. 3 h).
- The same approach also allows to improve the precision and/or throughput for common δ^{18}O and δD analysis.

REFERENCES

[1] A. Pierchala, K. Rozanski, M. Dulinski, Z. Gorczyca, M. Marzec, R. Czub, High-precision measurements of δ^2H, δ^{18}O and δ^{17}O in water with the aid of cavity ring-down laser spectroscopy. *Isotopes Environ. Health Stud.* **55**, 290–307 (2019).
[2] E. Barkan, B. Luz, High precision measurements of ^{17}O/^{16}O and ^{18}O/^{16}O ratios in H_2O. *Rapid Commun. Mass Spectrom.* **19**, 3737–3742 (2005).

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