Performance of the Picarro CRDS water isotope analyzer for tracer applications using highly enriched and depleted δ^2H samples.

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INTRODUCTION and OBJECTIVE

- The Picarro water isotope analyzers (L2130-*i*/L2140-*i*) have become a standard technique to measure the natural abundance of δ^{18}O, δ^2H and ^{17}O-Excess of water isotopes in climate, environment, and hydrological studies. In addition, some applications require to measure highly enriched and depleted δ^2H water isotope samples, e.g., when tracing water flows in hydrology. The current work is aimed to demonstrate the best methods to perform such measurements and identify the challenges and advantages of Picarro system.
- Measuring highly enriched and depleted water samples with optical spectroscopy comes along with challenges to address (i) the memory effect and (ii) the spectroscopic limits of the analyzer. Our experiments show that the recently launched **Picarro Express Mode** helps to address both these challenges without compromising precision, accuracy, or throughput time.

METHODS

- Picarro L2140-i water isotope analyzer coupled to an autosampler and vaporizer (see picture top right).
- All samples were analyzed using the recently developed express mode.
- Analyzed enriched samples range from +6000‰ to +130,000‰ and depleted samples were between -900‰ to -1000 ‰ of δ^2H.
- Different combinations of injections, wet flushes, injection volumes have been utilized to address different specifications.

## RESULTS (Enriched Samples)

slope: 0.99
$R^2 = 0.99$
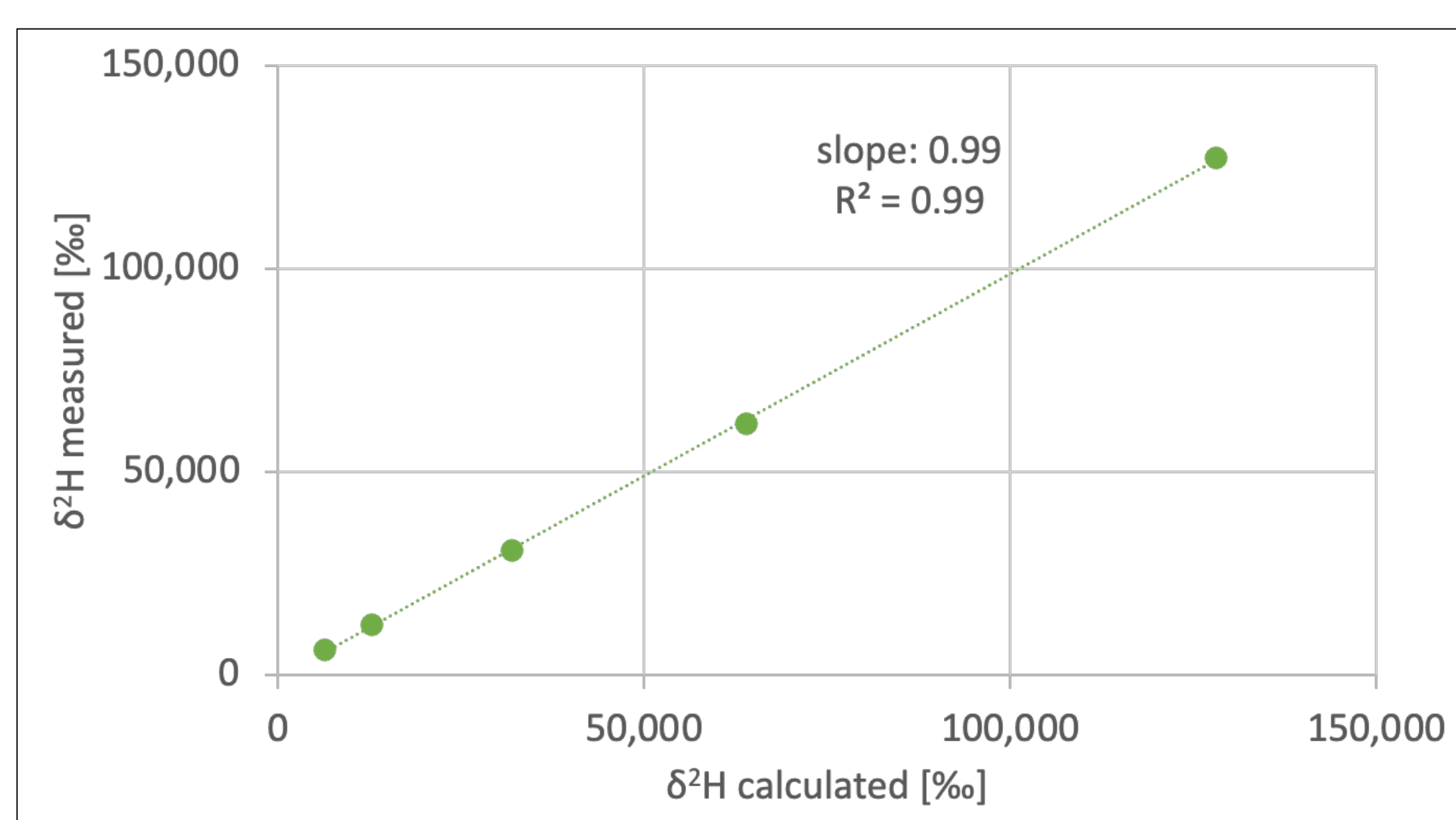
Linearity

- Samples are measured in Express Mode with 40 wet flushes and 12 normal injections. Only the last 3 injections were used for data evaluation.
- The analyzer shows an excellent linearity over the tested δ^2H range.

Concentration dependence

- Each sample was analyzed with 6 wet flushes and 12 normal injections. The last 3 injections were used to calculate the mean and SD error.
- The analyzer shows a negligible concentration dependence at high enrichment levels.
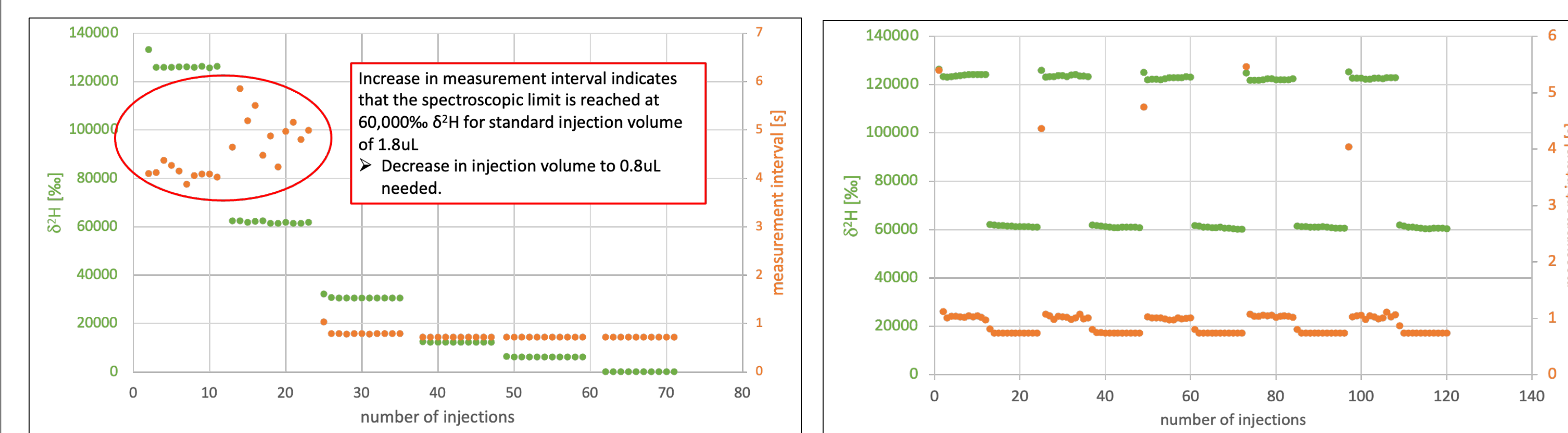- The analyzer was first stabilized at a value of around 30,000 ‰.
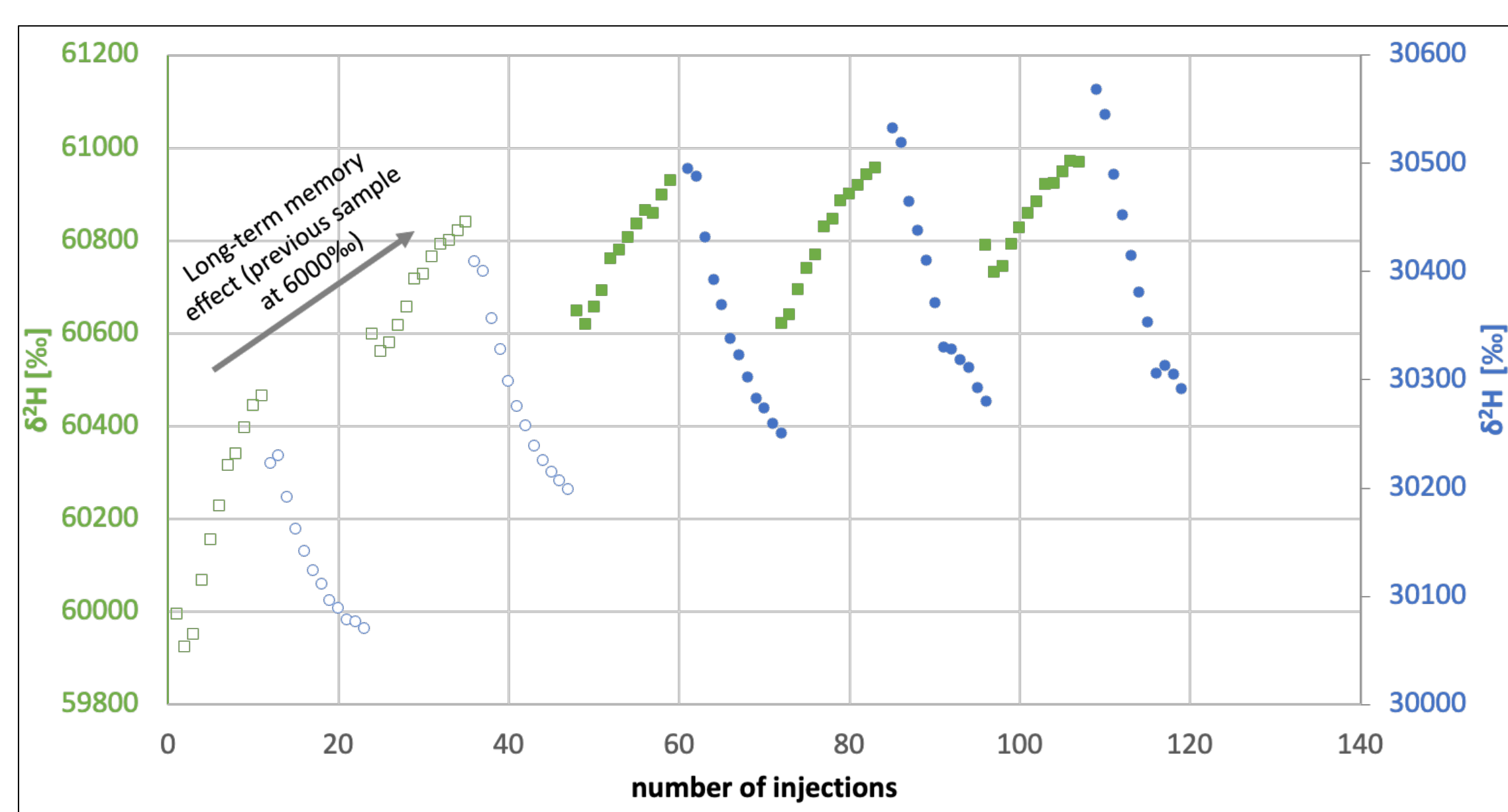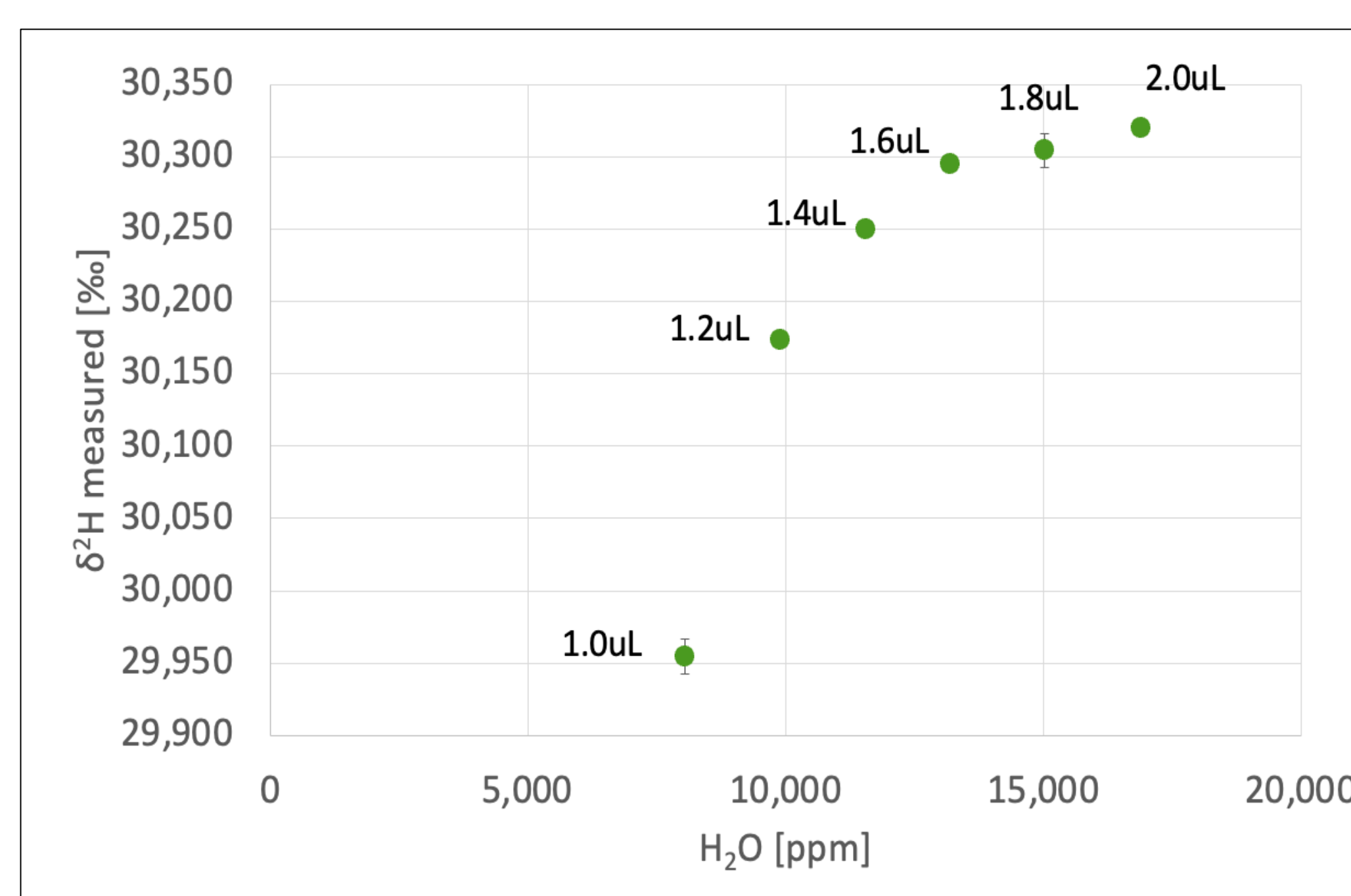
Reproducibility

- The reproducibility varies from 31‰ to 740‰ for low and high enrichment levels, respectively.
- It was limited by a long-term memory effect, which can be tackled by keeping samples at a similar enrichment level within one sequence.


Spectroscopic limit

- The analyzer reaches its spectroscopic limit at around 60,000‰ δ^2H when using the standard injection volume of 1.8uL.
- This is indicated by a reduction in measurement interval, leading also to a reduced precision.

Increase in measurement interval indicates that the spectroscopic limit is reached at 60,000‰ δ^2H for standard injection volume of 1.8uL.
➤ Decrease in injection volume to 0.8uL needed.

RESULTS (Depleted Samples)

- A set of two depleted δ^2H samples (5 ppm and 10 ppm **D2O**) were analyzed on a L2140-i connected to an autosampler and vaporizer.
- Measurements were done in express mode, with 6 wet flushes, 6 injections and last 3 injections were used for samples' data evaluation.
- Resultant standard deviation was ~0.4 ‰ for both samples.
- The use of standards in the depleted range would have been more appropriate and would result in enhanced accuracy for this type of samples.
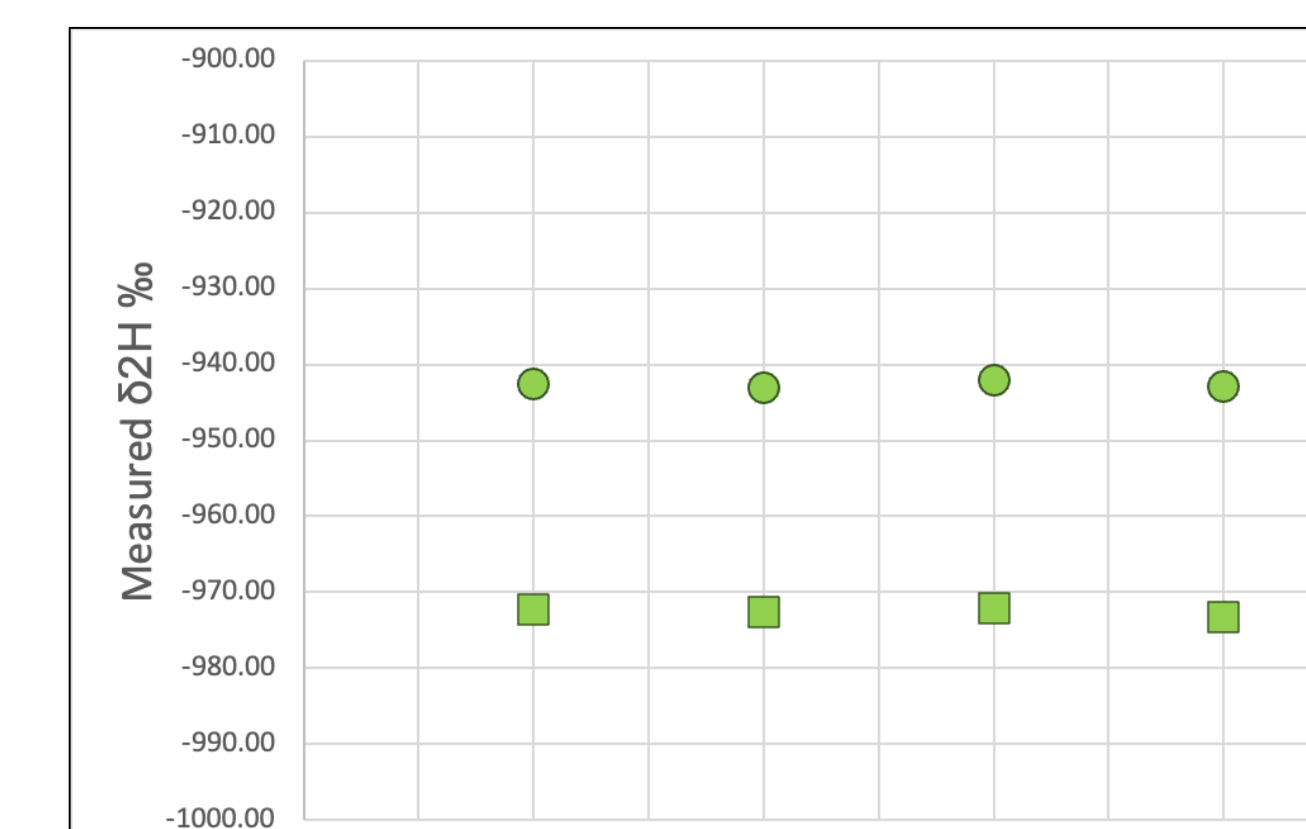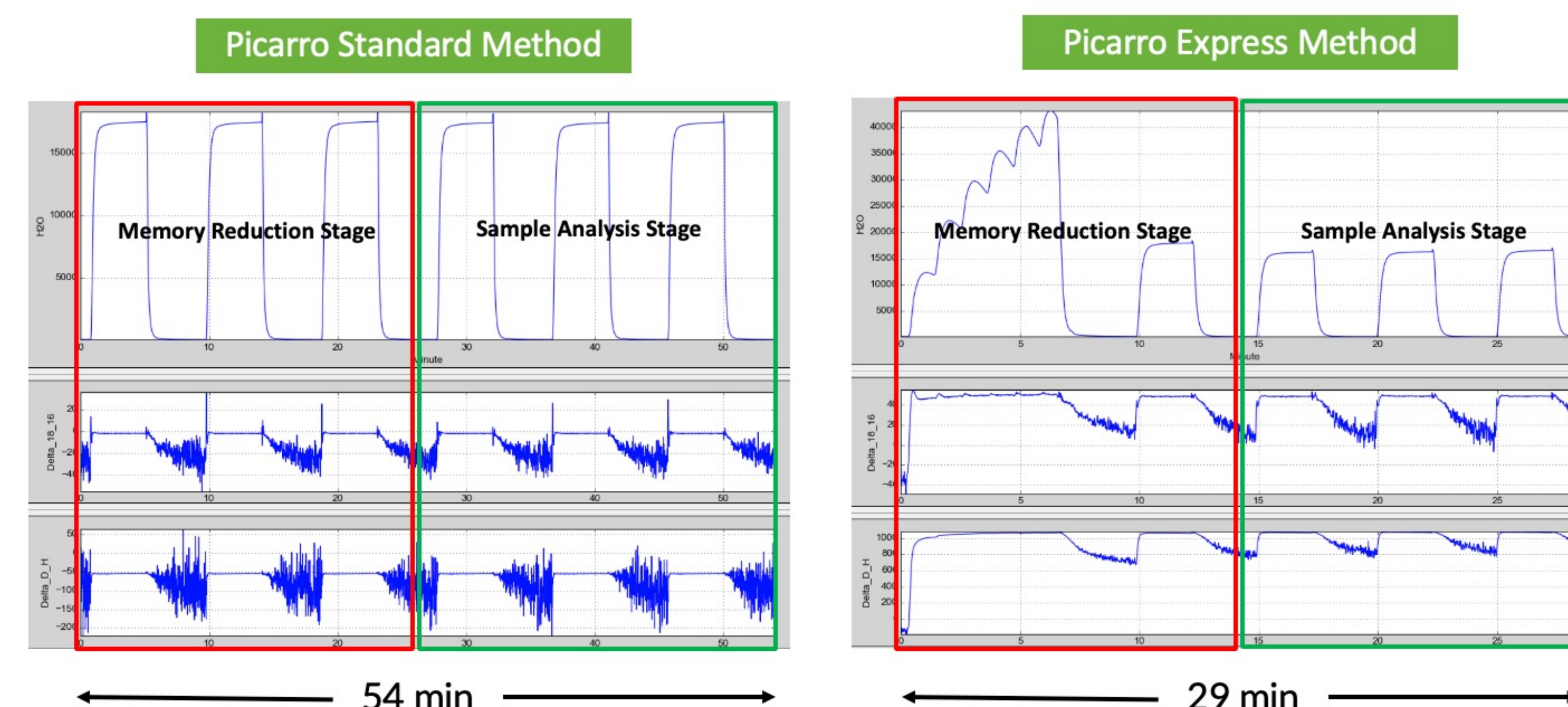

Sample type	Calculated (per mil)	Picarro-Measured (per mil)	Measured (ppm)
5 ppm sample	-967.90	-972.51	~4.3 ppm
10 ppm sample	-935.80	-942.66	~9 ppm

CONCLUSIONS and RECOMMENDATIONS

- Excellent linearity is seen over a high δ^2H range (up to 130,000‰ on the enrichment side and up to -1000 ‰ in the depletion side).
- Negligible concentration dependence at high enrichment levels.
- Reduction in injection volume (<1.8uL) beneficial to avoid measurement gaps at high enrichment levels.
- It is recommended to keep samples at a similar enrichment level within one sequence to enhance reproducibility and avoid memory effects.
- The analyzer should be calibrated with appropriate standards.
- When switching regularly between highly enriched samples and natural abundance levels or depleted samples and enriched samples, it is beneficial to use two separate vaporizers.
- Express mode, increased number of wet flushes, is the key to obtain excellent results even for extremely enriched/depleted water samples.

METHODOLOGICAL IMPROVEMENTS in water isotope analysis

Picarro Standard Method

Memory Reduction Stage   Sample Analysis Stage

54 min

Picarro Express Method

Memory Reduction Stage   Sample Analysis Stage

29 min

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