Isotope ratio infrared spectroscopy analysis of water samples without memory effects

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Rationale: Since their introduction more than a decade ago, isotope ratio infrared spectroscopy (IRIS) systems have rapidly become the standard for oxygen ($\delta^{18}$O) and hydrogen ($\delta^2$H) isotope analysis of water samples. An important disadvantage of IRIS systems is the well-documented sample-to-sample memory effect, which requires each sample to be analyzed multiple times before the desired accuracy is reached, lengthening analysis times and driving up the costs of analyses.

Methods: We present an adapted set-up and calculation protocol for fully automated analysis of water samples using a Picarro L2140-i cavity ring-down spectroscopy instrument. The adaptation removes memory effects by use of a continuously moisturized nitrogen carrier gas. Water samples of 0.5 $\mu$L are measured on top of the water vapor background, after which isotope ratios are calculated by subtraction of the background from the sample peaks.

Results: With this new technique, single injections of water samples have internal precisions ($1\sigma$) below 0.05‰ for $\delta^{18}$O values and 0.1‰ for $\delta^2$H values, regardless of the isotope ratio of the previous sample. Precision is worse, however, when the isotope difference between the sample and background water is too large (i.e., exceeding approximately 9‰ for $\delta^{18}$O values and 70‰ for $\delta^2$H values). Isotope ratios show negligible drift across the four weeks within which the experiments were performed. The single-injection $1\sigma$ precision for $^{17}$O excess ($\Delta^{17}$O) determined with this method is 60 per meg.

Conclusions: Our experiments demonstrate that by removing sample-to-sample memory effects with a moisturized carrier gas, the time for measurement of $\delta^{18}$O and $\delta^2$H values using an IRIS system can be reduced markedly without compromising the analytical precision and accuracy. Thorough replication is needed to achieve sufficiently low uncertainties for $\Delta^{17}$O.

1 INTRODUCTION

Oxygen ($\delta^{18}$O) and hydrogen ($\delta^2$H) isotope ratios of water are important tracers of processes in the hydrological cycle.1,2 Water isotope analysis is widely applied across the fields of hydrology, oceanography, geochemistry and biochemistry.3 The first techniques for water isotope analysis emerged in the 1950s and were based on isotope ratio mass spectrometry (IRMS) instruments. For water
isotope analysis with an IRMS instrument, water needs to be converted into separately measurable oxygen and hydrogen species. In the early years, water was typically equilibrated with CO₂ at a known oxygen isotope fractionation factor, after which the δ¹⁸O value of the CO₂ gas was measured.⁴ Hydrogen extraction is less straightforward and was usually achieved through the reduction of water by reaction with metals such as zinc, manganese, and chromium.⁵,⁶ Later, water isotope analysis using IRMS instruments was simplified through the implementation of on-line pyrolysis units that allow for rapid and automated analysis in continuous-flow mode, yielding both δ¹⁸O and δ²H values from a single water injection.⁷ The analytical precisions (1σ) of IRMS systems are of the order of 0.1‰ for δ¹⁸O values and 1‰ for δ²H values.⁸

About two decades ago, a fundamentally new technique for water isotope analysis was developed that relies on isotope ratio infrared spectroscopy (IRIS).⁹ An infrared laser is operated in a cavity that contains sample water vapor, and the resulting wavelength-specific absorption spectrum reflects the isotope composition of the sample. For this reason, the technique is also commonly referred to as laser absorption spectroscopy. The two most-used techniques based on IRIS are cavity ring-down spectroscopy (CRDS)¹⁰ and off-axis integrated cavity output spectroscopy.¹¹ A major advantage of IRIS is that δ¹⁸O and δ²H can be measured simultaneously at high precision without prior reactive separation of oxygen and hydrogen. The ease of use of IRIS systems led to the emergence of several commercial instruments, which are generally more cost-efficient than IRMS instruments. Laser absorption spectrometers are also more compact and can even be deployed in the field for real-time monitoring.¹² Analyzers and analytical schemes have improved rapidly since extensive development started about 10 years ago.¹³,¹⁴ Currently, methodologies employed for the analysis of water samples using IRIS systems typically rely on repetitive analysis of samples to bring the precisions of the pooled data down to 0.04‰ for δ¹⁸O values and 0.1‰ for δ²H values.¹⁵,¹⁶

Some IRIS instruments are also able to simultaneously measure δ¹³C compositions. The δ¹³C isotope is found in trace amounts in natural water bodies, and its abundance relative to ¹⁸O and ¹⁶O is typically reported as ¹⁷O excess or Δ¹³¹⁷O values.¹⁷,¹⁸ Despite the low abundance of ¹⁷O, further development of analytical techniques and protocols over the last decade has allowed increasing precision for Δ¹³¹⁷O measurements,¹⁹ leading to a growing interest in the use of the high-resolution triple oxygen isotope compositions (¹⁶O, ¹⁷O and ¹⁸O) to investigate the hydrological cycle.¹⁹,²⁰ The Δ¹³O record provides information pertaining to kinetic fractionation during phase changes within the hydrologic cycle, such as evaporation and ice formation.²¹–²⁵

The main limitations of IRIS systems center around interferences related to organic contaminants²⁶,²⁷ and sample-to-sample memory effects.²⁸ While organic contaminant interferences can be reduced by sample cleaning procedures applied prior to analysis, the memory effect is inherent to the instrument and cannot be solved by any sample preparation protocol that we know of. Due to memory effects, the standard analytical procedure requires each sample to be analyzed multiple times before reproducible isotope ratios are reached. Memory effects become even more persistent when the system becomes contaminated, for example due to salt deposition when analyzing saline samples.²⁹ For this reason, regular cleaning of the injection unit is considered an essential step in keeping memory effects manageable. In this context, numerous methodologies and calculation protocols have been developed to streamline raw data processing and account for memory effects.²⁸,³⁰–³³

Reduction of memory effects would decrease sample throughput time and improve the data reliability. Great potential for decreasing and possibly even eliminating memory effects in continuous-flow CRDS analyzers was shown in experiments using a moisturized carrier gas.³⁴–³⁷ These experiments used a Picarro system specifically for isotope analysis of minute amounts of water liberated from fluid inclusions in mineral samples. In such a system, manually injected water samples were shown to produce isotope data at 1‰ precisions of 0.1‰ for δ¹⁸O values and 0.4‰ for δ²H values, while memory effects were not observed.³⁶

Based on the analytical system presented by De Graaf et al.,²⁶ we here present an adapted set-up and calculation protocol for fully automated analysis of water samples using a Picarro L2140-i instrument. The system comprises a custom-made injection port that replaces the standard A0211 vaporizer unit and runs on a continuously moisturized nitrogen carrier gas to remove memory effects. Isotopically contrasting water samples are analyzed to quantify memory effects, optimize the analytical procedure and determine the precision and accuracy of water isotope data produced with this system.

2 | METHODOLOGY

2.1 | Technical set-up

The system runs using a CRDS instrument (L2140-i, Picarro, Santa Clara, CA, USA) that is equipped with an autosampler (ALS-G 3D robotic autosampler, part number: 601-201,101, Applied Instruments, Tuttingen, Germany). The L2140-i instrument measures δ¹⁸O and δ²H values, while also having a specific operating mode for additional measurement of δ¹³C values. The main adaptation of the set-up that we present lies in the use of a moisturized carrier gas that serves to remove memory effects. Water samples are measured on top of a stable water vapor background, and isotope ratios are calculated by subtracting the background from the sample peaks.³⁴

A custom-made injection unit (Figure 1) was built to replace the standard A0211 evaporation unit delivered by Picarro. A peristaltic pump (Elemental Scientific (ESI, Omaha, NE, USA) MP2-6 Precision Micro Peripump) supplies background water from a 50 mL glass vial into the nitrogen carrier gas via a tee-piece connector at the start of the line. A mass flow controller (FC-260, Tylan GmbH, Eching, München, Germany) maintains a stable 300 mL/min inflow of nitrogen carrier gas. The components and tubing in the preparation unit are maintained at a temperature of 120°C to vaporize the water.
The background water vapor is first guided to an in-house-built 2 L homogenization volume of electropolished stainless steel, which acts to reduce fluctuations in the background water vapor pressure. As the gas consumption of the analyzer is about 40 mL/min, a purge is used at the outflow end of the 2 L volume to discard the ca 260 mL/min excess flow. The tubing leading to the 2 L volume and the purge tubing is 1/8 inch with an inner diameter of 1/16 inch, while the other tubing in the system is 1/16 inch with an inner diameter of 1 mm.

Most of the set-up is identical to the system recently published by De Graaf et al. with the exception of the custom-made injection port installed in place of the crusher cell described by De Graaf et al. Water samples can be injected directly into the moisturized carrier gas through a septum (11 mm Thermogreen LB-2, Sigma-Aldrich, St Louis, MO, USA) in the injection port, which is installed in one of the autosampler trays to allow for fully automated sample injections. Injections are performed with a 0.5 μL microsyringe (SGE Analytical Science, model BNR-5/0.63, part no. 00300; Trajan Scientific, Ringwood, Australia) that is mounted in the autosampler. Injected water aliquots are vaporized and flushed with the moisturized carrier gas into a 40 cm³ volume (304L-HDF2-40, Swagelok, Solon, OH, USA) before entry into the Picarro analyzer. This volume serves to spread out the sample peak over a wider time interval, which facilitates precise data integration over the sample peak. The total length of the tubing from the injection unit to the analyzer is 1.2 m.

The injection port and the tubing leading to the injection port and the analyzer are heated by heating tape. All other components in the system are heated in an oven (UNE 400, Memmert GmbH, Schwabach, Germany).

Throughout the experiments, the peristaltic pump maintained a flow rate of 0.9 μL/min to generate a stable background water vapor concentration of around 14 500 ppmv, with a standard deviation of 10 to 25 ppmv over an hourly period. In the standard operating mode, the standard deviation of the isotope ratios of the background over an hourly period is 0.09‰ for δ¹⁸O values and 0.3‰ for δ²H values. In the δ¹⁷O operating mode, standard deviations are higher at 0.28‰ for δ¹⁸O values and 0.56‰ for δ²H values, while the standard deviation of the δ¹⁷O values is around 0.35‰. The values in the δ¹⁷O operating mode are recorded every second, compared with every 0.7 s in the standard operating mode. Two different background waters were used in the experiments. By default, “Mainz Milli-Q” water (Millipore, Burlington, MA, USA) was used to produce a background with values of −9.0‰ for δ¹⁸O and −65.1‰ for δ²H. A second background water is named “BG-Depleted” and produces a background level of −47.1‰ for δ¹⁸O values and −382.9‰ for δ²H values. All the experiments were performed running on nitrogen carrier gas; the use of dry air as carrier gas was not tested in this study.

Water injections of 0.5 μL were used in the experiments to produce maximum peak heights of around 40 000 ppmv (sum of background and sample; Figure 2). Although this maximum water

**FIGURE 1** Analytical line for water isotope ratio analysis on a moisturized background. The incoming nitrogen carrier is moisturized by a peristaltic pump at the start of the line. A 2 L mixing volume is used to reduce instabilities in the water vapor mixing ratio. Water can be injected into a port that is mounted in one of the autosampler trays. Prior to entry into the analyzer, the water vapor passes through a second smaller-sized volume that acts to widen the sample peaks. The line is maintained at a temperature of 120 °C. The injection port can be decoupled from the line at the straight connectors to flush and clean the inside. Heating tape around the injection port is not shown for clarity.
vapor concentration is higher than the recommendations of Picarro, earlier work showed that injections in a crusher unit produce highest precisions for injected amounts of between 0.3 and 0.8 μL. Injections larger than 1 μL are undesirable as the system could then potentially pass the maximum water vapor concentration at which reliable isotope analysis is possible with a Picarro instrument. The injected amounts are less than one-third of the amounts injected when operating the standard Picarro injection unit (A0211) in factory settings (i.e., ca. 1.8 μL).

2.2 Analytical procedure and data calculation

The analytical protocol is largely identical to the standard protocol for water isotope ratio measurement using a Picarro instrument with an autosampler. A detailed step-by-step description of the protocol is provided in the supporting information. Thorough rinsing of the syringe is of particular importance, since contamination of the syringe can be a source of memory effect. For the experiments presented here, the syringe was set to draw and dispose 1 μL of sample water three times to flush out any residue from previous samples. The syringe was then rinsed with sample water by performing nine fill strokes before injection into the septum port. The rinsing procedure was set within the autosampler software and is, therefore, similar to rinsing in the standard operation mode.

A custom Python script (see supporting information) is used to calculate isotope ratios directly from the raw data files (.dat format) produced by the Picarro software. An exemplary .dat file is included in the supporting information that can be used for testing the Python code.

Injection of a water sample creates a peak on top of the stable water vapor background. The peak duration depends on the size of the volume downstream from the injection port. With the 40 cm³ volume in our set-up, background values are restored again after approximately 8 min. The script calculates the slope over the water vapor concentration trace to define the timing of the peak starts and ends (Figure 2). Isotope ratios are calculated by subtracting the background from the sample peak, which consists of a mix of sample and background water. Equation 1 shows the theoretical calculation for determining δ¹⁸O values:

\[
\delta^{18}O = \frac{\int_{t_0}^{t_1} δ^{18}O(t) \cdot H_2O(t) - \int_{t_0}^{t_1} δ^{18}O_{BG}(t) \cdot H_2O_{BG}(t)}{\int_{t_0}^{t_1} H_2O(t) dt - \int_{t_0}^{t_1} H_2O_{BG}(t) dt}
\]

where BG refers to the background and t₀ and t₁ to the start and end of the peak, respectively. Analogous equations apply to δ²H and δ¹⁷O values. The script uses a Riemann sum as an integral approximation, which is justified considering the high rate at which the Picarro records data. In practice, background values cannot precisely be determined, since the background is below the sample peaks and can, thus, not be isolated. For this reason, average background values are determined per peak over two intervals, directly before and after the peak (Figure 2). Factual calculations for the background integrations are then reduced to Equations 2 and 3:

\[
\int_{t_0}^{t_1} δ^{18}O_{BG}(t) \cdot H_2O_{BG}(t) dt \approx δ^{18}O_{BG} \cdot H_2O_{BG} \cdot (t_1 - t_0)
\]

\[
\int_{t_0}^{t_1} H_2O_{BG}(t) dt \approx H_2O_{BG} \cdot (t_1 - t_0)
\]

The extent to which this simplification leads to increased uncertainty depends on the stability of the isotope ratios and the concentration of the background water vapor. Taking into account the intervals for
determining the background values, the total time for a single analysis is approximately 11 min. Measured $\delta^{18}O$, $\delta^2H$ and $\delta^{17}O$ values have a systematic offset with respect to true isotope ratios. A scale normalization is applied to raw isotope ratios to account for this offset. The calibration line for this normalization procedure is determined by measuring a series of reference standards and performing a linear regression on the relationship between measured and true isotope ratios. The slope and intercept of this linear relationship are then used to normalize measured values of unknown samples to the VSMOW-SLAP scale.

The normalization adds an extra error that needs to be propagated into the final isotope results. The equations used for the scale normalization and error propagation are supplied in the supporting information. However, where we speak of “precision” or “uncertainty” in this paper, we generally refer to the internal 1σ measurement precision of series of samples measured, unless it is specified that the uncertainties are based on propagation of the error associated with the scale normalization.

Earlier work of De Graaf et al. determined the linearity of a similar fluid inclusion isotope analytical system for water injections over a range from 0.04 to 0.8 μL. The linearity is especially strong for injected amounts below 0.3 μL. For higher amounts, the linearity is insignificant when the injections stay within a range of 0.1 μL. For this reason, a high-precision 0.5 μL microsyringe was used in this study to maintain injected amounts within a total range of 0.02 μL, making a linearity correction irrelevant.

Equation 4 is used to calculate $\Delta^{17}O$ values in per meg (ppm) notation from the normalized $\delta^{17}O$ and $\delta^{18}O$ data in ‰:

$$\Delta^{17}O = 10^6 \left[ \ln \left( \frac{\delta^{17}O}{1000} + 1 \right) - 0.528 \cdot \ln \left( \frac{\delta^{18}O}{1000} + 1 \right) \right]$$

(4)

3 | RESULTS

3.1 | Quantification of memory effects

The performance of the set-up was tested by measuring isotopically different waters. International reference standards SLAP-2, GRESP, VSMOW-2 and IAEA-607 were taken from freshly opened ampoules (Table 1). We further prepared three new batches of isotopically distinct waters, intended to demonstrate the performance of the system in the isotope range of most commonly measured fresh water samples. These three batches are named Mainz-2020, Andes-2020 and MIX-2020 and cover an isotope range from about –14‰ to –6‰ in $\delta^{18}O_{VSMOW-SLAP}$ and –110‰ to –40‰ in $\delta^2H_{VSMOW-SLAP}$. The batches were not a priori calibrated and have been run as unknown samples through the experiments.

Table 2 presents normalized δ values of two water samples that were measured in a single run together with VSMOW-2. The results show good precision and simultaneously demonstrate that no obvious memory effects occur when switching between isotopically different samples. There is no observable drift in the isotope ratios throughout the run, and the same values are measured independent of the isotope ratios of the preceding water sample.

The absence of detectable sample-to-sample memory effects was tested more rigorously in a series of alternating measurements of SLAP-2 and IAEA-607, which differ isotopically by more than 150‰ for $\delta^{18}O$ values and 1200‰ for $\delta^2H$ values (Figure 3). The data of this run were normalized with a calibration of the day before. In Figure 3, the overall average values of SLAP-2 (–55.37‰ for $\delta^{18}O_{VSMOW-SLAP}$ and –426.7‰ for $\delta^2H_{VSMOW-SLAP}$) compare well with averages of only the first SLAP-2 injections after switching: –55.37‰ and –426.0‰. Similarly for IAEA-607, the overall averages (99.05‰ for $\delta^{18}O_{VSMOW-SLAP}$ and 802.4‰ for $\delta^2H_{VSMOW-SLAP}$) are similar to the averages of only the first injections after switching: 99.16‰ and 802.5‰. This confirms that, despite the extreme isotopic difference, the measurements show no memory effect throughout the run.

3.2 | Scale normalization

Calibration lines for normalizing raw $\delta^{18}O$ and $\delta^2H$ data while running on Mainz Milli-Q background water in the standard operation mode were determined in four different weeks. The calibrations are based on linear regressions over the four international reference standards. The slopes and intercepts of the calibration lines are reported in Table 3 along with associated uncertainties. The parameters of the calibration lines do not show meaningful drift through time, but do slightly differ as to whether Mainz Milli-Q water or BG-Depleted water was used as background. The calibration line of the system for $\delta^{17}O$ was determined only once when running samples in the $\delta^{17}O$ operation mode.

3.3 | Analytical precisions

$\delta^{18}O$ and $\delta^2H$ data were acquired running the Picarro in its standard operating mode, because it gives more precise results than the $\delta^{17}O$ operating mode. The results of these runs in Table 2 and Figure 3 show

| Table 1 | Reference delta values of standard waters used in the experiments |
|---------|---------------------------------------------------------------|
| Standard | $\delta^{18}O_{VSMOW-SLAP}$ (‰) | SD (‰) | $\delta^2H_{VSMOW-SLAP}$ (‰) | SD (‰) | $\delta^{17}O_{VSMOW-SLAP}$ (‰) | SD (‰) |
| SLAP-2   | –55.50 | 0.02 | –427.5 | 0.3 | –29.70 | 0.02 |
| GRESP    | –33.39 | 0.04 | –257.8 | 0.4 | 0 | 0.05 |
| VSMOW-2  | 0 | 0.02 | 0 | 0.3 | 0 | 0.05 |
| IAEA-607 | 99.02 | 0.13 | 802.4 | 0.4 | 3.6 | 0.4 |
TABLE 2  
Isotope results of a run with injections of Mainz-2020 water, measured after either VSMOW-2 standard water or Andes-2020 water. Identical values are recorded for Mainz-2020 regardless of the water that was measured directly before, showing that the system is free of memory effects and machine drift throughout the run. The internal repeatabilities ($1\sigma$) of measurements in this series are shown at the bottom of the table and are similar to long-run precisions (Table 4) despite the frequent switching between the different waters.

| Time       | Sample | Amount (μL) | $\delta^{18}$O$_{\text{VSMOW-SLAP}}$ (‰) | $\delta^{2}$H$_{\text{VSMOW-SLAP}}$ (‰) |
|------------|--------|------------|--------------------------------|----------------------------------|
| 17:15:34   | VSMOW-2 | 0.501      | 0.06                          | 0.1                              |
| 17:26:40   | VSMOW-2 | 0.500      | 0.12                          | 0.0                              |
| 17:37:47   | Mainz-2020 | 0.500 | –8.71                         | –63.3                           |
| 17:48:54   | Mainz-2020 | 0.502 | –8.71                         | –63.6                           |
| 18:00:01   | Mainz-2020 | 0.502 | –8.73                         | –63.6                           |
| 18:11:07   | Mainz-2020 | 0.501 | –8.73                         | –63.5                           |
| 18:22:14   | Andes-2020 | 0.498 | –13.58                        | –106.2                          |
| 18:33:21   | Andes-2020 | 0.502 | –13.54                        | –106.4                          |
| 18:44:27   | Andes-2020 | 0.502 | –13.60                        | –106.3                          |
| 18:55:33   | Andes-2020 | 0.497 | –13.52                        | –106.4                          |
| 19:06:40   | Mainz-2020 | 0.500 | –8.79                         | –63.5                           |
| 19:17:45   | Mainz-2020 | 0.502 | –8.78                         | –63.7                           |
| 19:28:52   | Mainz-2020 | 0.489 | –8.84                         | –63.9                           |
| 19:39:59   | Mainz-2020 | 0.501 | –8.76                         | –63.5                           |
| 19:51:06   | VSMOW-2   | 0.500      | 0.05                          | 0.0                              |
| 20:02:12   | VSMOW-2   | 0.501      | 0.05                          | 0.2                              |
| 20:13:19   | VSMOW-2   | 0.501      | 0.14                          | 0.4                              |
| 20:24:26   | VSMOW-2   | 0.499      | 0.11                          | 0.2                              |
| 20:35:32   | Mainz-2020 | 0.502 | –8.79                         | –63.5                           |
| 20:46:39   | Mainz-2020 | 0.498 | –8.78                         | –63.5                           |
| 20:57:46   | Mainz-2020 | 0.496 | –8.74                         | –63.6                           |
| 21:08:52   | Mainz-2020 | 0.500 | –8.75                         | –63.5                           |
| 21:19:59   | Andes-2020 | 0.499 | –13.55                        | –106.3                          |
| 21:31:05   | Andes-2020 | 0.498 | –13.59                        | –106.4                          |
| 21:42:11   | Andes-2020 | 0.498 | –13.55                        | –106.5                          |
| 21:53:18   | Andes-2020 | 0.500 | –13.56                        | –106.3                          |
| 22:04:24   | Mainz-2020 | 0.499 | –8.82                         | –63.7                           |
| 22:15:31   | Mainz-2020 | 0.501 | –8.78                         | –63.5                           |
| 22:26:39   | Mainz-2020 | 0.501 | –8.73                         | –63.5                           |
| 22:37:44   | Mainz-2020 | 0.501 | –8.78                         | –63.5                           |
| 22:48:51   | VSMOW-2   | 0.500      | 0.04                          | 0.1                              |
| 22:59:59   | VSMOW-2   | 0.500      | 0.06                          | 0.2                              |
| 23:11:06   | VSMOW-2   | 0.500      | 0.06                          | 0.3                              |
| 23:22:13   | VSMOW-2   | 0.498      | 0.10                          | 0.7                              |
| 23:33:19   | Mainz-2020 | 0.501 | –8.75                         | –63.5                           |
| 23:44:26   | Mainz-2020 | 0.499 | –8.73                         | –63.5                           |
| 23:55:32   | Mainz-2020 | 0.504 | –8.81                         | –63.6                           |
| 00:06:39   | Mainz-2020 | 0.501 | –8.73                         | –63.6                           |
| 00:17:45   | Andes-2020 | 0.502 | –13.58                        | –106.3                          |
| 00:28:51   | Andes-2020 | 0.501 | –13.49                        | –106.3                          |

SD VSMOW-2 ($n = 10$) | 0.036 | 0.22 |
SD Mainz-2020 ($n = 20$) | 0.037 | 0.12 |
SD Andes-2020 ($n = 10$) | 0.033 | 0.09 |

*Injected amounts are calculated from an empirical relation between injected amounts and integrated peak areas of the water vapor concentration.*
that single-injection precisions are variable between the different waters analyzed. Single-injection precisions over long measurement runs with two distinct background waters are presented in Table 4. The data appear to be less precise for water samples that are isotopically further away from the background water. The best analytical precisions \((1\sigma)\), at around 0.03‰ for \(\delta^{18}O\) values and 0.06‰ for \(\delta^{2}H\) values, are achieved for samples that are isotopically close to the background water used. Figure 4 shows that the analytical precision broadly has a linear relation to the isotope difference from the background water.

### 3.4 Measurement of \(\delta^{17}O\) values

The L2140-i instrument was switched briefly to the \(\delta^{17}O\) analytical mode to determine the performance of the system for measuring \(\delta^{17}O\) and \(\Delta^{17}O\) values. These values were determined over long runs for several waters (Table 5). The internal precision \((1\sigma)\) on a single injection for \(\delta^{17}O\) is between 0.11 and 0.15‰ and for \(\Delta^{17}O\) between 50 and 60 per meg. Standard water IAEA-607 shows clearly higher uncertainties, which probably relate to it being isotopically furthest away from the \(\Delta^{17}O\) value of the background water.

### 4 Discussion

#### 4.1 Removal of memory effects

For IRIS systems, the common problems of sample-to-sample memory effects and, to a lesser extent, machine drift complicate the conversion of precise measurements to accurate isotope ratios. Techniques to

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**FIGURE 3** Isotope ratios of single injections measured when switching between the standard waters SLAP-2 and IAEA-607. The system does not display detectable memory effects for either \(\delta^{18}O\) (orange) or \(\delta^{2}H\) (blue), while the standards have a true isotope difference of 155‰ for \(\delta^{18}O\) and 1230‰ for \(\delta^{2}H\). Horizontal bars represent single standard deviation confidence intervals, as determined per standard for each isotope ratio. The standard deviations of the SLAP-2 measurements are 0.14‰ for \(\delta^{18}O\) and 1.21‰ for \(\delta^{2}H\). The IAEA-607 standard has standard deviations of 0.21‰ for \(\delta^{18}O\) values and 1.66‰ for \(\delta^{2}H\).

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**TABLE 3** Slopes and intercepts (with their \(1\sigma\) uncertainties) of the calibration lines used to normalize raw isotope data to the VSMOW-SLAP scale. Calibration lines are based on the linear relationship between measured and accepted values of the international reference standards SLAP-2, GRESP, VSMOW-2 and IAEA-607. The goodness-of-fit \((R^2)\) of all regression lines is 1.00

| Date       | Background water | \(n\) | Slope \(\delta^{18}O\) | Intercept \(\delta^{18}O\) | Slope \(\delta^{2}H\) | Intercept \(\delta^{2}H\) | Slope \(\delta^{17}O\) | Intercept \(\delta^{17}O\) |
|------------|------------------|------|------------------------|----------------------------|----------------------|------------------------|------------------------|------------------------|
| 09-09-2020 | Mainz Milli-Q    | 39   | 0.937 ± 0.0006          | −0.55 ± 0.037              | 0.946 ± 0.0005        | −3.57 ± 0.228          |                         |                       |
| 16-09-2020 | Mainz Milli-Q    | 154  | 0.935 ± 0.0006          | −0.59 ± 0.037              | 0.945 ± 0.0004        | −3.52 ± 0.213          |                         |                       |
| 22-09-2020 | Mainz Milli-Q    | 127  | 0.934 ± 0.0013          | −0.64 ± 0.080              | 0.943 ± 0.0006        | −3.75 ± 0.278          |                         |                       |
| 01-10-2020 | Mainz Milli-Q    | 83   | 0.934 ± 0.0008          | −0.62 ± 0.051              | 0.943 ± 0.0005        | −3.50 ± 0.251          |                         |                       |
| 27-09-2020 | BG-depleted      | 199  | 0.934 ± 0.0012          | −1.76 ± 0.079              | 0.943 ± 0.0005        | −8.47 ± 0.270          |                         |                       |
| 19-09-2020*| Mainz Milli-Q    | 120  | 0.935 ± 0.0005          | −0.88 ± 0.020              | 0.955 ± 0.0010        | −2.42 ± 0.298          | 0.930 ± 0.0022         | −0.74 ± 0.049          |

*Measured in the \(\delta^{17}O\) operation mode and based on the reference standards SLAP-2 and VSMOW-2. Calibration lines of the other days were determined in the standard operation mode and using all four reference standards.
account for drift and memory effects so far have included replicate analysis of individual samples (up to 15 times)\textsuperscript{13,31} and adapted analytical procedures coupled to computational schemes.\textsuperscript{28,30,33} For the state-of-the-art techniques developed for automated water isotope analysis with IRIS equipment, data must typically be based on at least four injections per sample to achieve reliable results.\textsuperscript{28}

**TABLE 4** Long-run 1σ repeatability for uninterrupted measurement series with injections of 0.5 μL. The data were acquired in the standard operation mode of the Picarro with either Mainz Milli-Q or BG-depleted water for the background. Mainz Milli-Q water is isotopically comparable with Mainz-2020 water. The table shows both internal single-injection precisions and uncertainties with the error propagated from the scale normalization. Data are normalized using in-run calibrations based on the international reference standards SLAP-2, GRESP, VSMOW-2 and IAEA-607.

| Sample water | Background water | n | δ\textsuperscript{18}O raw (‰) | δ\textsuperscript{18}O VSMOW-SLAP (‰) | SD (‰) | SD (‰, error prop.) | δ\textsuperscript{2}H raw (‰) | δ\textsuperscript{2}H VSMOW-SLAP (‰) | SD (‰) | SD (‰, error prop.) |
|--------------|-----------------|---|------------------|------------------|-------|-----------------|------------------|------------------|-------|-----------------|
| SLAP-2       | Mainz Milli-Q   | 30 | −58.69           | −55.54           | 0.11  | 0.12            | −448.9           | −427.7           | 0.77  | 0.82            |
| GRESP        | Mainz Milli-Q   | 30 | −35.15           | −33.53           | 0.07  | 0.08            | −269.4           | −258.1           | 0.48  | 0.54            |
| Andes-2020   | Mainz Milli-Q   | 30 | −13.88           | −13.65           | 0.05  | 0.06            | −108.6           | −106.1           | 0.14  | 0.26            |
| Mainz-2020   | Mainz Milli-Q   | 50 | −8.69            | −8.79            | 0.03  | 0.09            | −63.7            | −64.0            | 0.06  | 0.29            |
| MIX-2020     | Mainz Milli-Q   | 30 | −5.72            | −6.01            | 0.03  | 0.09            | −42.1            | −43.6            | 0.09  | 0.29            |
| VSMOW-2      | Mainz Milli-Q   | 30 | 0.71             | 0.01             | 0.04  | 0.05            | 4.3              | 0.2              | 0.17  | 0.27            |
| IAEA-607     | Mainz Milli-Q   | 30 | 106.51           | 98.92            | 0.26  | 0.27            | 853.1            | 802.7            | 2.17  | 2.21            |
| SLAP-2       | BG-depleted     | 30 | −57.34           | −55.32           | 0.06  | 0.12            | −444.0           | −426.7           | 0.15  | 0.58            |
| BG-depleted  | BG-depleted     | 30 | −48.60           | −47.14           | 0.04  | 0.11            | −397.5           | −382.9           | 0.11  | 0.51            |
| Mainz-2020   | BG-depleted     | 30 | −7.60            | −8.86            | 0.17  | 0.19            | −58.6            | −63.7            | 0.80  | 0.80            |
| VSMOW-2      | BG-depleted     | 30 | 1.83             | 1.06             | 0.19  | 0.20            | 8.5              | 0.5              | 0.87  | 0.87            |
| IAEA-607     | BG-depleted     | 30 | 107.96           | 99.07            | 0.40  | 0.43            | 860.6            | 802.2            | 3.43  | 3.48            |

**FIGURE 4** Standard deviations of single injections in relation to the absolute isotope difference between sample and background water, shown for δ\textsuperscript{18}O values (A) and δ\textsuperscript{2}H values (B). The plotted data are from the runs of Table 4. Highest precisions are achieved when the sample and background water are isotopically similar.

| Sample water | δ\textsuperscript{17}O VSMOW-SLAP (‰) | SD (‰) | Δ\textsuperscript{17}O VSMOW-SLAP (per meg) | SD (per meg) |
|--------------|--------------------------------------|--------|------------------------------------------|--------------|
| SLAP-2       | −29.70                               | 0.15   | 1                                        | 54           |
| Andes-2020   | −7.13                                 | 0.11   | 33                                       | 56           |
| Mainz-2020   | −4.55                                 | 0.11   | 46                                       | 51           |
| MIX-2020     | −3.04                                 | 0.12   | 48                                       | 58           |
| VSMOW-2      | 0.00                                  | 0.13   | 0                                        | 63           |
| IAEA-607     | 3.25                                  | 0.10   | −46,567                                  | 103          |

**TABLE 5** Analytical performance for δ\textsuperscript{17}O and Δ\textsuperscript{17}O. The data are from a single run on a background of Mainz Milli-Q water. Each sample was measured 40 times. The data are given with internal 1σ precisions on single injections. The δ\textsuperscript{17}O and δ\textsuperscript{18}O data used for calculating Δ\textsuperscript{17}O values are normalized with an in-run calibration that is based on the reference standards SLAP-2 and VSMOW-2.
Running a Picarro CRDS instrument on a moisturized nitrogen carrier gas was shown to effectively remove sample-to-sample memory effects for manual water injections in a preparation system designed for fluid inclusion isotope analysis.34,36 The experiments in the present study show that a Picarro L2140-i instrument with autosampler operated with a moisturized carrier gas also lacks detectable sample-to-sample memory in long automated runs of isotopically different waters (Table 2). Even switching between the isotopically light SLAP-2 standard and the heavy IAEA-607 standard over a large range of 150‰ for δ18O values and 1200‰ for δ2H values shows no sample-to-sample memory effects that exceed the single-injection uncertainty (Figure 3). It appears that the stable water background in the carrier gas effectively purges any sources of memory effect in the Picarro instrument that affect the system when run on a dry carrier gas.

4.2 Analytical precisions

A relationship exists between analytical precision and the isotope difference between sample and background water (Figure 4). This effect is probably related to small uncertainties in determining the background water vapor concentration under a peak. The relative contributions of sample and background water are important factors in the calculation (Equation 1). Theoretically, when a sample is isotopically the same as the background, it does not matter if there are uncertainties in the determination of the background water vapor concentration. However, as the difference between sample and background isotope composition increases, the impact of uncertainties in the background water vapor concentration proportionally increases. For this reason, it is recommendable to use a background water that is isotopically similar to the samples analyzed.

Our data show that within a range of 70‰ for δ2H values and 9‰ for δ18O values from the background water values, samples can be measured at excellent precision. Long runs of the Andes-2020, Mainz-2020, MIX-2020 and VSMOW-2 waters – covering a range typical for most natural samples and measured on a background of Mainz Milli-Q water – all give internal precisions below 0.05‰ for δ18O values and 0.17‰ for δ2H values. The precisions, based on single sample injections, are comparable with the precisions of pooled injection data reported for Picarro L2140-i analyzers in standard operation mode15,16 and generally better than for IRMS systems.8 If we pool the data from our study per four consecutive injections to make a better comparison with data from pooled injections in standard operation mode, the 1σ uncertainties of the long runs of the Andes-2020, Mainz-2020, MIX-2020 and VSMOW-2 waters are between 0.01‰ and 0.02‰ for δ18O values and 0.05‰ and 0.12‰ for δ2H values. The adaptation in our set-up to remove memory effects and shorten analytical times, thus, does not compromise analytical precisions.

4.3 Long-term stability of the system and accuracy

Arguably more important than daily repeatability is the long-term (months to years) reproducibility of the system, as this will eventually be the more important factor determining the external reproducibility of the system. An important factor for system stability is the extent to which the calibration line for normalizing the data changes through time. An unstable calibration line will lead to inaccurate corrections and a drift in isotope ratios. Many laboratories have developed protocols to ensure stable running conditions by performing calibrations on a daily basis.28 In our own laboratory when running the Picarro analyzer in standard operation mode on a dry carrier gas, we have so far adopted a strategy in which every 24 h run contained enough water standards to determine the calibration line for each individual run. This takes extra time and effort, but is necessary to keep track of drift in the correction parameters between runs.

The current wet carrier gas set-up has been running for approximately one month. Parameters for the data normalization while running on Mainz Milli-Q background water were determined multiple times (Table 3) and shown to be remarkably stable over several weeks. This is also evident from Table 6, which reports precisions determined over all isotope measurements of VSMOW-2 and Mainz-2020 water that were made during the four-week course of experiments for this study. The data in Table 6 were normalized with a single averaged calibration line. The resulting single-injection precisions are around 0.06‰ for δ18O value and 0.3‰ for δ2H values, suggesting a good long-term stability of the system.

The long-term reproducibility reported in Table 6 spans no more than a month of analyses, simply because this is a new method in our laboratory. Nevertheless, a similarly good long-term stability was obtained for the results of manual water injections into a fluid inclusion isotope analysis unit within the same analytical system that were run over the course of several months earlier this year.36 We take these data to suggest that the system presented here, running on a moisturized nitrogen carrier gas, not only eliminates memory effects efficiently, but also shows promising long-term analytical stability.

| Sample water | Time span            | n   | δ18O<sub>VSMOW-SLAP</sub> (‰) | SD (‰) | δ2H<sub>VSMOW-SLAP</sub> (‰) | SD (‰) |
|--------------|----------------------|-----|-------------------------------|--------|-------------------------------|--------|
| VSMOW-2      | 7 September to 1 October | 97  | 0.00                          | 0.068  | 0.02                          | 0.243  |
| Mainz-2020   | 7 September to 1 October | 176 | −8.77                         | 0.046  | −63.55                        | 0.299  |
4.4 | Performance for measurement of $\delta^{17}O$ values

The $\Delta^{17}O$ record is a promising data source for studying fractionation processes in the hydrological cycle.\(^{17}\) Now that two of the currently available IRIS systems (Picarro L2140-i and Los Gatos TIWA-45EP, Los Gatos Research, San Jose, CA, USA) are capable of measuring $\delta^{17}O$ values of water samples, $\Delta^{17}O$ data are increasingly becoming available to a wider scientific community. Hydrological systems typically have spatial and temporal differences in $\Delta^{17}O$ in the range of 60 per meg.\(^{23}\) Analytical uncertainties must, therefore, be well below 60 per meg for the $\Delta^{17}O$ record to be meaningful (i.e., less than ca 15 per meg). In our experiments, standard deviations for $\Delta^{17}O$ on single injections are between 50 and 60 per meg ($1\sigma$) and, thus, not precise enough to be useful. Achieving sufficiently high measurement precision on single injections with IRIS equipment is currently impossible, and commonly replicate analyses are performed to improve the analytical uncertainties.\(^{31}\)

Berman et al.\(^{31}\) published one of the first analytical protocols for precise $\delta^{17}O$ measurements with an IRIS system, requiring 80 injections and a total analysis time of 4 h to achieve a standard error of the mean for $\Delta^{17}O$ of 10 to 11 per meg. Steig et al.\(^{15}\) reported precisions for $\Delta^{17}O$ of 8 per meg after 10 repeated injections with a CRDS system. More recent studies also achieve uncertainties of around 10 per meg for $\Delta^{17}O$ with IRIS systems through repetition of sample water injections.\(^{16,19,40}\)

In the system presented here, the statistical uncertainty on $\Delta^{17}O$ can be reduced to the 10 per meg level by determining standard errors of the mean of 20 single injections, which corresponds to 3.5 h analysis time per sample. This should merely be taken to provide an indication; we did not venture into further statistical evaluation of the $\Delta^{17}O$ data in this investigation. Altogether, the comparison shows that the performance of our system for acquiring precise $\delta^{17}O$ data is not better than that of previously published studies using IRIS systems. Because of the inherent need of replication to obtain precise $\Delta^{17}O$ data, the advantage of removing the memory effect that characterizes our system does not outweigh the better single-injection precision of recent publications using standard IRIS techniques. Further optimization of our system would be needed for rapid and precise analysis of $\Delta^{17}O$, but is beyond the scope of this study.

4.5 | Proposed measurement procedure

In the absence of memory effects and significant instrumental drift, the analytical procedure for routine isotope analysis of water samples could be shortened considerably from the analytical procedure previously used in our laboratory. We have devised a routine in which a run starts with three standard waters that cover the expected isotope range for the samples to be measured. Each of the standards is injected and analyzed three times. Next come 20 unknown samples that are each injected and analyzed twice. Then, the three standards are repeated, followed by another set of 20 unknown samples, all injected twice. The run is ended with a final repeat analysis of the three standards, again as triple injections.

In the current analytical scheme, such a run is completed in less than 22 h, allowing for cleaning and maintenance every day, before the machine is restarted for the next batch. The standards in each run serve to monitor system stability and provide a first-order check on the applied scale normalization. Once a week, a run should contain standards spanning a wide range of isotope ratios, so that normalization parameters can be re-determined at high precision. When a specific set of samples requires a change to an isotopically different background water, the measurement procedure should start with a high-precision calibration, as minor yet significant changes in the normalization parameters occur when switching between isotopically different background waters.

Salt waters (e.g., ocean water samples) are known to cause complications in IRIS injection systems because of salt crystallization in the injection unit.\(^{29}\) The hygroscopic behavior of salt may affect later water injections, and salt build-up can block carrier gas flow or internally corrode metal parts of the injector unit. Deteriorating performance throughout long runs of seawater samples in IRIS systems is the rule rather than the exception, and regular cleaning of the injector unit is required.

For salt water samples, our system has two main advantages over how we previously operated the Picarro analyzer in its standard operation mode. First, the injection volume is only 0.5 $\mu$L, which is less than one-third of that used in the standard method. Furthermore, we need only one or two injections per sample, where previously we needed at least seven injections. Altogether, we inject less salt water into our injection port per sample, leading to less salt deposition in the injection unit. Second, the internal design of our injection port is simpler than that of the vaporizer unit provided by Picarro for automated water isotope analysis. Removing accumulated salt from our custom injection unit is done through a quick rinse with Milli-Q water that takes less than 10 min. This means that it can be included in the daily maintenance routine between runs, which ensures salt-free operating conditions at all times.

5 | CONCLUSIONS

Experiments using moisturized nitrogen carrier gas with an IRIS instrument show that sample-to-sample memory effects are effectively removed for oxygen and hydrogen isotope analysis of water samples. Application of this technique using a Picarro L2140-i CRDS analyzer yields single-injection $1\sigma$ precisions below 0.05$\%$ for $\delta^{18}O$ values and 0.1$\%$ for $\delta^2H$ values when analyzing water samples that are isotopically close to the background water used to moisturize the nitrogen carrier gas. The single-injection precision with the same methodology for $\Delta^{17}O$ is 50 to 60 per meg, making replicate measurements necessary to acquire meaningful data.

Significant machine drift was not observed over a time period of four weeks. The long-term stability of the system thus allows for accurate calibration of isotope data while running comparatively few
water standards with the samples. A data reduction scheme is presented in the form of a Python code that uses the raw output files of the Picarro L2140-i analyzer to identify sample peaks and correct for the isotope contribution of the water background. Finally, the scheme performs a normalization on the resulting data to report isotope data per injection relative to VSMOW.

In summary, our experiments demonstrate that the use of a moisturized carrier gas in an IRIS analyzer with liquid autosampler can reduce throughput times of water samples without compromising the analytical performance for both $\delta^{18}O$ and $\delta^4$H values. If each sample is duplicated, at least 40 samples can be run per day. Based on the effective removal of memory effects, one can even decide to run samples in a single-injection-per-sample analytical scheme. Doing so will double the analytical capacity to 80 individual samples per day at high analytical precision.

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