Comparison of Three Measurement Principles on Water Triple Oxygen Isotopologues

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The widespread method for measuring $\Delta^{17}$O (17O-excess) is an offline CoF$_3$ (Cobalt tri-fluoride) conversion of water to molecular oxygen with subsequent isotope determination by dual inlet mass spectrometry. High precisions for $\Delta^{17}$O measurements, using CoF$_3$ water conversion, are so far only possible with off-line methods. Here we report on an improved and modified online continuous flow method intended for high precision triple oxygen isotope analysis. This method is improved by optimizing the reactor (site for conversion of H$_2$O into oxygen through the chemical reaction) compositions, size of the fused silica capillary, flow regulator, and data treatment. Our modified online continuous method was further compared with the recently developed cavity ring down measurement principle. The precision is significantly better for the commercially available laser-based system than our current version of improved online CoF$_3$ conversion method using mass spectrometry. Factors identified for limiting precision in our continuous flow system are: (i) compaction of the reactor with time that leads to the restriction of flow rate of carrier gas, (ii) the CoF$_3$ treatment, (iii) the amount of CoF$_3$ inside the reactor, (iv) the pore size of the steel frit, and (v) the metallic tube. Changes in all of these items as well as the dimension of the fused silica capillary, the positioning of the fused silica capillary in the open split, and the memory effect can also lead to a declining precision. These limiting factors for precision still provide us enough space for further improvement of our improved online method which will be worthwhile for the measurement of smaller aliquot samples as fluid inclusions for palaeoclimatic applications. With present improvement, multiple injections ($n = 15$ or even more) should be applied to obtain a precision better than 10 per meg for $\Delta^{17}$O. Furthermore, a comparison of the laser-based system with an improved conventional equilibration method has been made on precipitation samples originating from Jungfraujoch.

Keywords: Continuous flow, CoF$_3$ method, triple oxygen isotope, 17O-excess, laser-based system

INTRODUCTION

Water stable isotopes (primarily oxygen isotopic ratio) are being used as an ideal tracer to reveal the underlying processes in the hydrologic cycle as well as past climatic information through their sensitive character during evaporation, condensation, mixing, and moisture transport (Dansgaard, 1964; Galewsky et al., 2016). Water is a naturally circulating resource that is constantly recharged...
and helps to control the masking effect of the equilibration process of the isotopologues (HH$^{16}$O, HH$^{17}$O, HD$^{18}$O, etc.) of the water during phase changes result in isotopic fractionations (mass dependent) that is being used as a tool to understand the hydrological cycle and its link to climate (Epstein and Mayeda, 1953; Dansgaard, 1954; Craig, 1961). For mass dependent fractionation (also known as terrestrial fractionation) changes in $^{17}$O would be approximately half of the changes in $^{18}$O relative to $^{16}$O (Luz et al., 1999). The isotopic ratios of $^{18}$O/$^{16}$O or $^{17}$O/$^{16}$O in samples are denoted with $^{18}$R or $^{17}$R which is commonly reported to an international reference (i.e., VSMOW) standard through eqs. 1 and 2 where delta values have become a standard tracer for environmental studies generally denoted in permil ($\%$) (Dansgaard, 1954).

$$\delta^{18}O = \frac{^{18}R}{^{18}R_{ref}} - 1 \times 1000$$ \hspace{1cm} (1)

$$\delta^{17}O = \frac{^{17}R}{^{17}R_{ref}} - 1 \times 1000$$ \hspace{1cm} (2)

Anomalies from an assumed dependence are expressed by eq. (3), in which $\lambda$ corresponds to an arbitrary number obtained from the scaling, i.e., 0.528 from meteoric waters.

$$\Delta^{17}O = \ln(\delta^{17}O + 1) - \lambda \ln(\delta^{18}O + 1)$$ \hspace{1cm} (3)

High precision and accuracy (0.02 to 0.03$\%$, 95% confidence) are required for the above-mentioned hydrological applications related to water stable isotope exchange (Barkan and Luz, 2005) in order to understand the underlying processes.

Several methods were investigated for water stable isotope analysis that includes conventional equilibration with CO$_2$, fluorination, or electrolysis to O$_2$ with subsequent isotope determination by mass spectrometry or laser-based systems and direct laser-based isotope analysis on water vapor briefly summarized in the following.

Equilibration method was for long the method of choice for water stable oxygen isotopes, in particular for $\delta^{18}$O. Yet, it was limited for $\delta^{17}$O analysis due to the $^{13}$C interferences of the used CO$_2$ during the equilibration process. Elsig and Leuenberger (2008) improved the equilibration method for measurements of $\delta^{18}$O and $\delta^{17}$O using a chemical buffering of the water samples to keep the pH value lower than 4.3 for which the carbon is by far present as carbonic acid (H$_2$CO$_3$) or dissolved CO$_2$ compared to bi-carbonate (HCO$_3^-$) or carbonate (CO$_3^{2-}$) and helps to control the masking effect of the 14 times more abundant $^{13}$C on mass 45. Therefore, fractionation during the equilibration process of the $^{13}$C remains constant. They estimated the precision of $\delta^{18}$O to be 0.03$\%$o, while for $^{17}$O-excess better than 0.1$\%$ at 95% confidence interval. Although precision improved in Elsig and Leuenberger (2008) equilibration method, the amount of samples (5000 µL) required for analysis is still very large for the above-mentioned application. Irrespective of this improvement, precision is not good enough to clearly disentangle the relevant influences on water samples, as documented in Elsig and Leuenberger (2008). Only recently, a further significant improvement of the equilibration method by freezing out the CO$_2$ under liquid nitrogen temperature (Affek and Barkan, 2018) was published. Unfortunately, it was too late to be applied to our method, since we already performed all the measurements discussed in the present study.

O’Neill and Epstein (1966) were the first to use water fluorination with BrF$_5$ for oxygen isotopic measurements of water samples by following the reaction:

$$\text{BrF}_5 + \text{H}_2\text{O} \rightarrow \text{BrF}_3 + 2\text{HF}+1/2\text{O}_2$$ \hspace{1cm} (4)

Using micro-liter sized water samples with isotope ratio reproducibilities for both $\delta^{17}$O and $\delta^{18}$O of ±0.1$\%$ (95% confidence interval), this method is free of fractionation and memory effects. Instead of BrF$_5$, Brenninkmeijer and Röckmann (1998) used a fluorination method using 5% F$_2$ in helium rather than pure F$_2$ in order to enhance safety procedure. Instead of BrF$_5$ and F$_2$, a less hazardous solid reagent CoF$_3$ was first used by Lantz (1967) who produced molecular oxygen through the following reaction:

$$2\text{H}_2\text{O}+4\text{CoF}_3 = 4\text{CoF}_2 + 4\text{HF} + \text{O}_2$$ \hspace{1cm} (5)

In his first study, the precision for $\delta^{18}$O was only moderate with $\sim 0.7\%$ (95% confidence).

New developments by Sano et al. (1976) and Matthews and Hayes (1978) that were the first to use an online application of isotopic ratio mass spectrometry by using a continuous flow of the carrier gas for the preparation and analysis of the samples opened up new versions of the above-mentioned conversions. Namely, CoF$_3$ method became attractive for reasons of safety and was later applied by Baker et al. (2002) to determine $\delta^{18}$O and $\delta^{17}$O through a continuous flow isotope ratio technique using 0.02 µL of the H$_2$O sample. The reproducibility for $\delta^{18}$O and $\delta^{17}$O was 0.54$\%$ and 0.33$\%$, respectively (68% confidence interval). Franz and Röckmann (2004) successfully modified this method for direct air sample application and extended it to hydrogen isotopes for small samples ($\sim$120 nL of water) but with less precision ($\sim 0.7$ and $\sim 1.3\%$ for $\delta^{17}$H and $\delta^{18}$H, respectively).

Barkan and Luz (2005) successfully modified the method of Baker et al. (2002) using a molecular sieve and liquid helium for trapping and storage of the produced oxygen, so as to obtain the highest precision through the dual inlet mass spectrometer technique. The precision obtained for $\delta^{18}$O and $\delta^{17}$O is 0.003 and 0.006$\%$ (at 95% confidence interval), respectively. Although results by this method are excellent and were already successfully applied to the above-mentioned applications related to water stable isotope exchange processes in hydrologic cycle, it is laborious and quite costly, in particular the liquid helium. To our best knowledge, high precision determination like Barkan and Luz (2005) has not been obtained by the continuous flow principle using IRMS. Here we will try to explain in detail of the continuous flow principle using an open split transfer in order to reach high precision results for further applications.

Using the electrolysis method, with CuSO$_4$ as an electrolyte, Meijer and Li (1998) determined the $\delta^{17}$O and $\delta^{18}$O variations in meteoric waters with a precision of 0.07 and 0.1$\%$, respectively, but the required sample amount is relatively large.
(700 μL) which is often limiting. Furthermore, δ17O with a precision of ±0.3‰ in CO2 gas was obtained by Assonov and Brenninkmeijer (2003) but this precision is insufficient for the above-mentioned applications.

A new method based on laser absorption spectroscopy has been developed in recent years and is known to achieve the precision (Steig et al., 2014) close to the dual inlet IRMS (Barkan and Luz, 2005). The working principle and technical setup to obtain the triple oxygen isotopic composition of water from laser-based absorption spectroscopy have already been discussed in detail (Schoenemann et al., 2013; Affolter et al., 2014, 2015; Steig et al., 2014) and therefore is beyond the scope of this article. In this article, three measurement principles, namely continuous flow method (ConFlow), laser-based system (LBS), and CO2-H2O equilibrium method were run to test their precision and comparison among each other’s, whereas real samples were intentionally run only using already established laser-based system (PICARRO L2I40i) (Schoenemann et al., 2013; Steig et al., 2013; Affolter et al., 2015) and CO2-H2O equilibrium method (Elsig and Leuenberger, 2008) to avoid precious sample shortage during several trial and error test on ConFlow optimization.

EXPERIMENTAL

Instrumentation for the Continuous Flow System

In our experiment, an Isoprime mass spectrometer (GV Instruments, Manchester, United Kingdom) is used with an accelerating voltage of 4.1 kV to measure the isotopic abundance in O2. Ion currents are collected continuously by Faraday cups for 32, 33, and 34 m/z with resistors being set at 5 × 10−8, 5 × 10−10, and 1 × 10−8 Ω, respectively. With these settings, we found an overall ionization efficiency of our mass spectrometer of 0.5‰, corresponding to the detection of a single O2 molecule out of 2,000 molecules entering the mass spectrometer. The number of detected O2 molecules can only be increased at the expense of overall precision. Sample and reference gas were allowed to pass through a single open split. We used an open split closed at one end, i.e., a glass tube with a length of 7.3 cm having inner and outer diameters of 1 and 2 mm, respectively. Since fractionations are associated with open split settings (Elsig and Leuenberger, 2010), care must be taken with the correct referencing as well as with the protection against contamination with laboratory air. Five fused silica capillaries with varying diameter were used: (i) the reference capillary, attached to a movable piston, allows admission of a working standard (pure O2); (ii) the background capillary is set to a fixed position, with a constant flow of a working standard of known isotopic composition in order to minimize adsorption effects; (iii) the He capillary, a high flow of helium enters the open split, acting as a dynamic seal to the laboratory air; (iv) the mass spectrometer capillary, connected to the mass spectrometer inlet valve; (v) the sample capillary, eluted O2 signals from H2O conversion are transferred through it. Only the reference capillary can be lifted and lowered within the open split. The dimensions and fluxes of all capillaries used in our experiment are summarized in Supplementary Table 1.

The setup used for this study is shown in Figure 1, manual or autosampler (H/Device) injections (2 μl H2O) are possible. Prior to injection into a purified (carbagas, purity, 99.999%) helium flow through a high temperature septum (GBG analytic, part no SM11), the syringe (Hamilton, part no 80300-00) is flushed two times with 5 μL of the water sample to minimize the memory effect. The helium flow is maintained at a constant level by a mass flow controller (Analyt-MTC, model no 35827). Sample and helium lines are attached to the injection port (Swagelok, T-union). The reaction of H2O with CoF3 takes place in a nickel tube (0.250” outer diameter (hereafter o.d.) × 0.056” inner diameter (hereafter, i.d.) of 5.4” in length). The upper and the lower end of the nickel tube are attached to the 1.7” (0.250” o.d × 0.056” i.d.) and 2.2” (0.250” o.d × 0.056” i.d.) length of a stainless steel tube through connectors (Swagelok, part no SS-400-6), respectively. 10 μm of steel frit (Grace, part no 703125) is attached to the lower end of the upper steel tube for the convenient filling of a new batch of CoF3 to the inside of the nickel tube. Nickel wool (Säntis analytical) is placed at ~2 cm above the bottom end of the nickel tube after filling CoF3 (approximately 3 g) and Ni grains in such a way that the reagents are ideally placed to reach a constant temperature of 643 K (370 °C) in the reaction furnace. The HF produced as a byproduct of the reaction is removed by a NaF trap (Franz and Röckmann, 2004) by the following reaction:

\[
\text{NaF + HF} \rightarrow \text{NaHF}_2
\]  

(6)

The NaF trap consists of a 6 cm, 0.250” o.d. 0.056” i.d. nickel tube with a 10 μm steel frit at the front end and nickel wool at the rear end. It is completely filled with NaF (approximately 170 mg). A subsequent liquid nitrogen trap (coiled steel tube with ~ 70 cm length 0.250” o.d.) acts as a backup trap to remove any condensable left in the gas stream for safe venting. To minimize the chances of any condensable escaping from the liquid N2 trap, a 7 μm filter (Swagelok, part no SS-F-7) is additionally attached with a 0.125” o.d. steel tube to prevent fused silica capillaries. A manually operated 4-port valve (Swagelok, part no SS43Y6FS2) allows switching between waste and measuring mode. It has a sample inlet and outlet as well as waste and helium flushing port, the latter have a pressure gauge (Kistler) and a Pfeiffer vacuum pump attached (0.125” o.d. steel tube) to read the pressure of the produced O2 signal after the chemical reaction and to evacuate the sample line, respectively. A homemade gas coupling system (open split) is attached to the 4-port sample outlet by a 0.0265” o.d. steel tube. The helium capillary leading to the open split is set to a flow rate of 6.25 ml/min while the background capillary is controlled through a mass flow controller at a flow rate of 0.2 ml/min. The reference capillary is set to 7.5 ml/min while the sample capillary is controlled through another mass flow controller at a flow rate of 15 ml/min for an improved Gaussian type sample peak. Only the reference capillary is attached to a movable piston to admit pulses of the working standard.
Measurement Procedure of the Continuous Flow System

Filling and Preconditioning of Reactor Furnace
An argon ventilated chamber is used for filling solid CoF$_3$ into the nickel tube. Prior to loading, CoF$_3$ was heated to 70°C for ~5 h in an argon atmosphere for water removal. As per recommendation by Baker et al. (2002) we conditioned the CoF$_3$ by gradually increasing the temperature to 400°C within 2 days while maintaining the helium flow through the loaded nickel tube at 0.2 ml/min in order to insure the removal of adsorbed water and remaining contaminants. Thereafter, the temperature is reduced to its operating value of 370°C.

IRMS Setting and Testing
Center and magnetic scans were performed to optimize our isotopic ratio mass spectrometer. Afterward, a leak test was performed with the working standard (pure O$_2$) in an on-off mode. In case of a leak, higher currents for mass/charge ratios 28 (N$_2$) and 40 (Ar) are detectable by mass spectrometer, documenting the intrusion of laboratory air into the system. The performance of the IRMS cup collector can easily be seen (Supplementary Figure 1) by monitoring the correlation between the ion mass of 33 and 34. Prior to analysis, the flow of the carrier gas is maintained at 15 ml/min through the reactor and the open split by the mass flow controller.

Calibration of Conversion Yield
For estimating the eluted O$_2$ from the H$_2$O conversion, Barkan and Luz (2005) measured the 32/40 m/z ratio by adding a known amount of Ar to O$_2$ collected in the sample tube. We injected ~5.95 ml of compressed ambient air, i.e., equivalent to the O$_2$ amount in 2 µl of H$_2$O, and calculated the peak areas of 32 m/z of air and eluted O$_2$ from the H$_2$O conversion, respectively. Conversion yields obtained from this procedure were quantitative (100% ± 5%), indicating complete conversion of the H$_2$O sample. Since the transfer yield of eluted O$_2$ to the IRMS depends on the dimensions as well as the positions of the different capillaries in use they need to be optimized. The helium capillary is placed near the bottom end of the open split mainly to seal against laboratory air. The background capillary, placed above the helium capillary, transferring pure O$_2$ for a constant...
background signal, results in a significant improvement of the isotope ratios in particular during the start and the end phases of the O$_2$ signal produced from the H$_2$O sample. To monitor pure machine drift and shifts in the background level, we used the reference (working standard on-off pulse of pure O$_2$ with a known isotopic value) at the beginning and end of the sample analysis. Two references at the beginning and two at the end were performed for five sample injections in each acquisition run (Figure 2). The reason for using more than one sample and reference peak in a single acquisition is to improve the results through statistics and to save time. Reference peaks from the on-off mode switching of the reference capillary in the open split are obtained in a rectangular shape, in contrast to the Gaussian-like shape of the sample peak.

### Data Processing of the Continuous Flow System

The IonVantage software of the Isoprime mass spectrometer allows us to store the signals for beams 32, 33, and 34 m/z with a time step of 0.1 s. This raw data are passed to a template compiled by us that largely follows the steps described by Bock et al. (2010). Individual background correction and drift correction are considered in our template to improve the dataset.

The peak shape observed in the continuous flow system is not truly rectangular or Gaussian due to the rapidly moving capillary and the sticking nature of the H$_2$O molecule inside the tube (Franz and Röckmann, 2004), respectively. For the background correction of 32, 33, and 34 m/z, values are always taken before the beginning of each rectangular as well as the Gaussian peak. We observed that the signal depends on the determination of the peak start. Bock et al. (2010) believe that this observation relates to the fact that real peaks are not truly Gaussian and therefore the peak margins, in particular, are isotopically inhomogeneous even after a time shift correction (Elsig, 2009). To sort out these problems, each peak is individually evaluated in the template. To select the start and endpoint for the calculation, raw mass/charge (m/z) data are processed to get their time derivatives $[d(m/z)/dt]$. Two different procedures were performed for the reference calculation. The first one
Table 1 | $\delta^{17}$O, $\delta^{18}$O, and $\Delta^{17}$O of O$_2$ (reference) for the continuous flow method by changing reference peak area calculations by using the whole reference area and only plateau of the reference area.

| (i) Ref. Peak area (Start to End) | (ii) Reference peak (Plateau) |
|----------------------------------|-------------------------------|
| $\delta^{17}$O (mean) [%]        | $-0.010 \pm 0.612$            |
| $\delta^{18}$O (mean) [%]        | $0.027 \pm 0.20$              |
| $\Delta^{17}$O (mean) [per meg]  | $0.131 \pm 0.203$             |
|                                  | $0.081 \pm 0.63$              |
|                                  | $79 \pm 550$                  |
|                                  | $16 \pm 13$                   |

(Supplementary Figure 2A) is a calculation of the reference peak from its start to end. The second is based on the calculation of the reference peak when the time derivative gets stable which is the case on the plateau of the rectangular reference peak (Supplementary Figure 2B). The whole peak and plateau results of our internal St-91 standards are shown in Table 1. A better precision was obtained for plateau evaluation which may indicate that fractionations at the peak start lead to the poorer precision. However, the second calculation type can’t be used for the sample peaks due to its Gaussian shape peak character. Start and endpoint for the peak calculations were chosen according to the time derivatives of the mass/charge ratio (Figure 3) and are valid for each individual run $[d(m/z)/dt$, where $x$ corresponds to 32, 33, and 34].

**CO$_2$-H$_2$O Equilibration Method**

We also have used an improved CO$_2$-H$_2$O equilibration method that measures the triple oxygen isotopes of water sample. The detailed technical setup and experimental design of this method are available in Elsig and Leuenberger (2008) and are briefly summarized in the following:

A CO$_2$-H$_2$O equilibrium is necessary for precise isotope ratio measurements in particular for oxygen-17 and $\Delta^{17}$O. This can be achieved through the admission of an isotopically known CO$_2$ gas and proper shaking of the sample for time-efficient equilibration. A scaling factor $r$ is used to determine the delta value correction which summarizes effects such as cross contamination or mass spectrometry sensitivity. Care must be taken during the optimization of the scaling factor since stretching or compressing of the $r$ factor can increase or decrease its value from unity. For precise $\Delta^{17}$O measurements through the equilibrium method, 5 mL of the water sample was taken, equilibrated with about 7–8 mL STP of CO$_2$ ($185 \pm 10$ mbar of CO$_2$), and admitted to a glass flask of 45 cm$^3$ at 20°C temperature. The sample pH was optimized ($<4.3$ pH units) because it is also one of the most critical factors for the $\Delta^{17}$O value for this method. Applying the equilibrium method for samples with a $\Delta^{17}$O non-zero signal, the $\delta^{18}$O value has to be corrected. Assuming a false $\delta^{18}$O value of the admitted CO$_2$ leads to wrong $\Delta^{17}$O and $\delta^{18}$O values which also requires correction. Therefore, to obtain better precision through this method, all measurements were performed under a strict pH regulation, optimum sample amount, and a well-determined scaling factor to limit cross contamination.

**Laser-Based Method (Picarro L2140-i)**

Samples were measured at our division Climate and Environmental Physics (CEP), the University of Bern. Measurements were performed using state-of-art Picarro L2140-i wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) instrument (Picarro Inc., United States). Before an isotopic analysis, samples were transferred into 2 mL glass vials and sealed with rubber/aluminum caps to mount on a PAL COMBI-xt autosampler (CTC Analytics AG, Zwingen, Switzerland) that is connected to the Picarro L2140-i for $\delta^{17}$O, $\delta^{18}$O and $\delta$D analysis (Affolter et al., 2015). Six times injections were performed, and the first three injections were discarded to reduce the memory effect and obtained the reproducibility of typically 0.1% for $\delta^{18}$O and $\delta^{17}$O. The obtained precision for $\Delta^{17}$O is under 7 per meg.  

**RESULTS**

**Continuous Flow System and CoF$_3$ Method**

To characterize potential influences of the carrier gas on the eluted O$_2$ sample signal, we performed an experiment where a 2 μl H$_2$O sample was allowed to react with CoF$_3$ and pass through the cryogenic cool trap without any carrier gas (Supplementary Figure 3). A pressure gauge was attached to the sample line to record the amount of O$_2$ as a function of time; an increase of 53.3%, 17%, 14.8%, 7.7%, and 7.3% in the eluted O$_2$ signal (pressure percentage) was observed at the time interval of 0–10, 10–20, 20–40, 40–60, and 60–90 min, respectively. Two-third of the sample signal were obtained within 30 min from the sample injection, while a small percentage of the sample was still obtained at the end of measurements (after 90 min) which indicates the sticky nature of water that can lead to fractionation effects within our system line and hence reduce precision. These results document the importance of using a carrier gas in an online system to obtain a Gaussian shape sample signal that significantly helps to minimize fractionation effects and reducing measurement time. The different behavior of the reactor composition on the 32 $m/z$ ratio is shown in Figure 4. Multiple tests indicated that the carrier gas flow was dependent on the reactor composition. To maintain constant flow conditions, these experiments strongly suggest to use a mass flow controller in the carrier gas line (see Figure 1), since the reactor filled with CoF$_3$ and metallic frit at the bottom of the nickel tube generates high pressure inside the reactor that is most probably due to compaction of the reactor. The byproduct gas HF (HF is acidic and produced as a byproduct, see eq. 5) was able to back diffuse onto the injector and to react with the septum resulting in its damage. Hence, the lab air contamination probability increased which could easily be checked via N$_2$ detection in the IRMS. To solve this problem, we used nickel grains after CoF$_3$ chemical filling. Ni grains are non-reactive with CoF$_3$ and water. Blocking of the pores of the steel frit by CoF$_3$ particles resulted in a significant lowering of the carrier gas flow as observed in many of our experiments. To sort out this problem, Ni grains which have
a bigger grain size compared to CoF$_3$ were placed at the bottom before CoF$_3$ fillings for each experiment.

In the case of Figure 4i, 2 micron steel frits and Ni grains were used at the top and the bottom, respectively, while a $<2$ g of CoF$_3$ amount was filled in between. However, a sample peak with a long tail was observed. This might be due to the sticking nature of water on the larger surface area of the nickel tube exposed to the H$_2$O molecule because of the lower CoF$_3$ filling ($<3$ g of CoF$_3$) resulting in a tailing of the eluted sample signal (Franz and Röckmann, 2004); 38 ml/min of the flow rate was measured at the end of the sample line. The signal obtained with this setup is higher in amplitude compared to other fillings but the long tailing of the eluted O$_2$ signal is the limiting factor for obtaining better precision.

In Figure 4ii, 2 micron steel frits were used at the top and the bottom and $>3$ g CoF$_3$ were filled together with Ni grains at the top, the middle, and the bottom of CoF$_3$. The reason for filling in more chemicals was to reduce the tailing effect of the eluted sample signal by reducing the surface area exposed to the H$_2$O molecule in the nickel tube. Nickel grains were also filled into the middle of the chemical to reduce compactness. However, no O$_2$ was eluted because of the high restriction ($<1$ ml/min of the flow rate) of the reactor most probably due to the increased chemical amount. Because of the restricted flow of helium through the reactor, reference signals (rectangular shape) with higher amplitude were observed due to a lower dilution effect by the very low carrier helium flow.

In Figure 4iii, nickel grains were mixed with CoF$_3$ and 2 micron steel frits were replaced with 5 micron steel frits to increase the flow rate of the carrier gas and hence to increase the amplitude of the eluted sample signal. The idea behind mixing CoF$_3$ with Ni grains was to allow the carrier gas along with the eluted O$_2$ signal to easily pass through the reactor. A flow rate $>5$ ml/min was measured in parallel to a lower amount of the eluted sample signal and higher amplitudes of reference signals which shows us that the compactness of the reactor remained high even though the size of the steel frits was increased. Obviously, the mixture restricts the flow contrary to expectation.

In Figure 4iv, 5 micron filters as well as nickel grains at the top and the bottom of the reactor were used, with smaller amounts of Ni grains at the bottom than at the top. Eluted Gaussian shape sample signals were recorded with 30 ml/min of the carrier gas flow rate. A wider sample signal is observed due to the insufficient flow of the carrier gas which is unable to push the sample through the reactor to obtain an optimal eluted signal. Although the eluted O$_2$ signal obtained from this setup is not bad, a further improvement of the peak form yielded better isotope results.

Therefore, in Figure 4v, 5 micron steel frits at the top and nickel wool instead of steel frit at the bottom were used in the nickel tube reactor to increase the flow of the carrier gas with an eluted signal and to avoid compactness of the reactor. A flow rate of 60 ml/min was obtained with an improved Gaussian shape eluted sample signal. We also tested with 10 micron filters (figure not shown) at the top and nickel wool at the bottom with the same amount of chemical filling; however, the eluted O$_2$ signal area and shape were similar to Figure 4v, setup. Therefore, we continued with the reactor setup of version (v). Based on all these experimental designs, 5 and 10 micron steel frits and nickel wool are a better option to obtain optimal eluted Gaussian shape sample signals and along with it an improved precision.

After optimizing the reactor setup for the eluted O$_2$ peak, the mass flow controller was connected to the sample injection

![FIGURE 3](image-url) Calculation of the delta ($\delta^{17}$O, $\delta^{18}$O) value for the sample signal is taken in between the range of the two red crosses while for the background calculation (black crosses) for better precision based on the time derivative of the mass/charge ratio $[d(m/z)/dt]$. 
Comparison of Three Measurement Principles

FIGURE 4 | The different reactor compositions (upper panel) and the corresponding evolution of the O₂ signal (mass 32, lower panel) dependent on the reactor compositions (The number (i–v) in the upper and lower panel corresponds to the different reactor setup and its associated eluted O₂ peak after chemical reaction from the corresponding reactor). The higher the compactness of the reactor (peak color and peak number color corresponds to the reactor number), the lower the eluted O₂ signal, and at the same time, higher compactness leads to the higher reference signals because of an increased dilution effect.

line to carry a constant flow and multiple sample injections were performed afterward which is shown in Figure 2.

Comparison of H₂O-CO₂ Equilibrium and Laser-Based Method
Measurements with the equilibration method have been performed on precipitated water sampled at the High Altitude Research Station Jungfraujoch. They are compared to the measurements on the same water samples with the laser-based system (Picarro L-2140i) as shown in Figure 5.

DISCUSSION

Comparison of Equilibration (EQUI) With Laser-Based System (LBS)
To see the consistency between CO₂-H₂O equilibration (EQUI) and LBS system, a comparison of the last three decades (1983–2011) was performed for precipitation samples originating from Jungfraujoch station (JFJ: altitude 3580 m.a.s.l.). Here, we are restricting us to discuss only a comparison between EQUI and LBS using JFJ precipitation records (Figure 5). The detailed descriptions about the JFJ precipitation records can be found in a companion manuscript (Leuenberger and Ranjan, 2021, under review in this issue). For the EQUI method, δ¹⁷O, δ¹⁸O and Δ¹⁷O exhibit precisions of 0.0470, 0.0194, and 0.0458‰, respectively, while LBS shows a precision of 0.0140, 0.0174, and 0.007‰ for δ¹⁷O, δ¹⁸O, and Δ¹⁷O, respectively. These indicate that the EQUI method documents limited precisions for δ¹⁷O and Δ¹⁷O compared to δ¹⁸O which are significantly deviating from precisions to be expected under ideal conditions as discussed in Elsig and Leuenberger, 2008. However, recent work by Affek and Barkan (2018) claimed to achieve the precision of EQUI method close to the offline fluorination method (Barkan and Luz, 2005) using hot platinum for an isotopic exchange between O₂ and CO₂. The excellent correlation between δ¹⁷O and δ¹⁸O (r² > 0.9919) is not sufficient for getting good Δ¹⁷O values as obtained with the laser-based system for which the
same correlation is significantly stronger ($r^2 > 0.999957$). Furthermore, correlation among isotopic records from both systems indicates that $\delta^{17}O$ ($r^2 > 0.937, p < 0.05$) and $\delta^{18}O$ ($r^2 > 0.945, p < 0.05$) show a strong correlation while no correlation was found for $\Delta^{17}O$. The poor correlation exhibited by $\Delta^{17}O$ indicates the inconsistency and poor precision from EQUI methods (see Figure 5) in particular for $\delta^{17}O$. It is interesting to note that the uncertainty of $\Delta^{17}O$ correlates neither with $\delta^{17}O$ nor with $\delta^{18}O$ and its uncertainty but shows a positive correlation with the uncertainty in $\delta^{17}O$. Based on the sensitivities investigated by Elsig and Leuenberger, 2008, it might point to an influence of the temperature control.
TABLE 2 | δ\textsuperscript{17}O, δ\textsuperscript{18}O, and Δ\textsuperscript{17}O of ST-91 values against ORSMOW (Winkler, 2012) in ‰ with average, standard deviation, and standard deviation by using students factor by 5% confidence limit.

| Sample peak number |  \( \Delta^{17}\text{O} \) |  \( \delta^{17}\text{O} \) |  \( \delta^{18}\text{O} \) |  \( \Delta^{17}\text{O} \) |  \( \delta^{17}\text{O} \) |  \( \delta^{18}\text{O} \) |
|--------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                    | [ORSMOW per meg] | [ORSMOW ‰]     | [ORSMOW ‰]     | [ORSMOW per meg] | [ORSMOW ‰]     | [ORSMOW ‰]     |
| Sample peak No. 1  | −464            | −6.750          | −11.879         | 166             | −6.336          | −11.998         |
| Sample peak No. 2  | −179            | −6.698          | −12.314         | 164             | −6.412          | −12.137         |
| Sample peak No. 3  | 49              | −6.342          | −12.068         | 157             | −6.447          | −12.191         |
| Sample peak No. 4  | 4               | −6.459          | −12.204         | 166             | −6.423          | −12.162         |
| Sample peak No. 5  | −23             | −6.491          | −12.214         | 156             | −6.442          | −12.179         |
| Average of 5 peak  | −123            | −6.548          | −12.136         | 13              | −6.412          | −12.133         |
| Average of last 4 peak | −38            | −6.498          | −12.200         | 12              | −6.431          | −12.167         |
| Average of last 3 peak | 10             | −6.431          | −12.162         | 11              | −6.437          | −12.177         |
| Average of last 2 peak | −10            | −6.475          | −12.209         | 12              | −6.432          | −12.170         |
| Std. dev. of 5 peak | 209             | 0.171           | 0.168           | 5               | 0.045           | 0.078           |
| Std. dev. of last 4 peak | 99              | 0.148           | 0.101           | 5               | 0.016           | 0.023           |
| Std. dev. of last 3 peak | 36              | 0.078           | 0.081           | 5               | 0.013           | 0.015           |
| Std. dev. of last 2 peak | 19              | 0.023           | 0.007           | 7               | 0.013           | 0.012           |
| Std Dev (t factor) of 5 peak | 93              | 0.077           | 0.075           | 2               | 0.020           | 0.035           |
| Std Dev (t factor) of 4 peak | 49              | 0.074           | 0.050           | 2               | 0.008           | 0.012           |
| Std Dev (t factor) of 3 peak | 21              | 0.045           | 0.047           | 3               | 0.007           | 0.008           |
| Std Dev (t factor) of 2 peak | 13              | 0.016           | 0.005           | 5               | 0.010           | 0.009           |

FIGURE 6 | Memory effect of the continuous flow (ConFlow) system during the sample acquisition. Memory effect can easily be seen on the first peak for δ\textsuperscript{17}O (ConFlow, black circle), δ\textsuperscript{18}O (ConFlow, blue circle), and Δ\textsuperscript{17}O (ConFlow, red circle) in comparison to laser-based system (LBS, square box), PICARRO. The last two peaks of each acquisition were not much influenced by the memory effect.

as this is the only positive dependence they state; yet, in this case one also would expect a correlation with the uncertainty in δ\textsuperscript{18}O. Additionally, the calculated offset of 36 per meg between LBS and EQUI methods cannot be taken as robust due to the high uncertainty of the EQUI method. Even increasing the number of injections for the EQUI method to match the precision of the EQUI method to LBS (Picarro L2140i) through statistics is not guaranteed due to...
the fact that we do not understand where the limitation is coming from.

Comparison of Continuous Flow (ConFlow) With Laser-Based System (LBS)

The reported $\delta$ values for ConFlow and LBS are shown in Table 2 and this corresponds to a single peak of single acquisitions with respect to water standard (ORSMOW) (Winkler, 2012). In the case of ConFlow, the overall precisions from each acquisition for $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ are 0.077‰, 0.075‰, and 93 per meg, respectively. The reported precision for $\delta^{17}O$ and $\delta^{18}O$ are under 0.1‰ for five peaks and it further improves to 0.050‰ and 0.074‰, respectively, by skipping the first peak to minimize the memory effect (Figure 6). Thus in four peaks, overall precision for $\Delta^{17}O$ improved to 49 per meg, which is two times better than the previous one. By skipping the second and third peak, surprisingly the $\Delta^{17}O$ precision improves by a factor of four and seven (Table 2) while $\delta^{17}O$ improves to two and four times, respectively. A drastic improvement in precision by skipping initial peaks indicates that the H$_2$O sticking nature inside the reactor is a limiting factor. In the case of LBS, the precision obtained by five subsequent injections in a single run ($n = 5$) for $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ are 0.020‰, 0.035‰, and 2 per meg only. The obtained precision for $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ are, respectively, > three times, > two times and > forty times, better than ConFlow system. The $\Delta^{17}O$ precision for LBS is much better than the ConFlow system and the latter can only improve by skipping the first three injections to minimize the memory effect and its associated fractionation. Correlation among $\delta^{17}O$ and $\delta^{18}O$ shows a tight correlation ($r^2 > 0.979$, $p < 0.05$) for continuous flow and laser-based system ($r^2 > 0.961$, $p < 0.05$), respectively (Figure 7). Furthermore, an offset of only 0.136, 0.002, and 0.136‰ were observed between $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ of both systems, respectively. By removing the first two peaks from ConFlow, the offset between ConFlow and LBS becomes insignificant that further confirms the influence of memory effect and its associated fractionation role in $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ precision.

Coherency between continuous flow and laser-based systems were tested using correlation analysis among $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ of both systems. $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ exhibit a significant correlation of 0.680, 0.494, and 0.333, respectively. The observed $\delta^{17}O$ and $\delta^{18}O$ correlation further improve to 0.690 and 0.822 by skipping the first peak while correlation among $\Delta^{17}O$ of both systems further degraded. These results indicate that $\delta^{18}O$ of both (continuous flow and laser-based systems) systems are comparable but $\delta^{17}O$ and $\Delta^{17}O$ need further improvement to match the precision level of laser-based system. Further improvement of the continuous flow system is certainly possible through the optimization of the reactor, tubing replacement from...
a nickel to steel, optimizing the tubing length between the reactor and the detector (IRMS). Therefore, more than 15 injections with the exclusion of the first three peaks should be applied to match the precision of a laser-based system.

CONCLUSION

We successfully developed an online technique for triple water isotope determination for small water aliquots (2 µL). However, precision is not yet acceptable compared to conventional dual inlet methods based on the same conversion of oxygen water stable isotopes to O₂ and requires further improvements. Four factors are mainly responsible for limiting precision in the continuous flow method. (i) The reactor: The behavior of a reactor due to the changing flow rate of the carrier gas, the treatment of the chemical before filling, the amount of chemical inside the reactor, the reactor composition, the dimension of the nickel tube and the pore size of the steel frit influence the eluted sample signal and hence precision; (ii) The dimension of the nickel tube and the pore size of the steel frit influence the inside the reactor, the reactor composition, the dimension of reactor due to the changing flow rate of the carrier gas, the continuous flow method. (i) The reactor: The behavior of a stable isotopes to O₂ in inlet methods based on the same conversion of oxygen water precision is not yet acceptable compared to conventional dual.

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DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

SR and ML developed the concept of technical setup as well as the design of the study. SR performed a technical experiment and wrote the manuscript with help from ML. Both authors contributed to the article and approved the submitted version.

FUNDING

This work was supported by the EU-funded project Initial Training network on Mass Independent Fractionation (Intramif) as well as the Swiss National Science Foundation (SNF-125116 and SNF-135152).

ACKNOWLEDGMENTS

The authors would like to acknowledge Peter Nyfeler for this laboratory assistance and advice on technical issues. We would like to express thanks for the mechanical and electronic workshop staff at the Division of Climate and Environmental Physics Division.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2021.598616/full#supplementary-material
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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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