Report on memory tests during liquid injections

FARLAB, UiB
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1   Overview

A memory effect is visible during liquid injections when switching between vials, in particular if the stable isotope concentration difference is large (Penna et al. 2010, 2012; van Geldern and Barth 2012). This memory effect in the current configuration extends over several injections, sometimes up to 5. These injections have to be discarded and thus waste analysis time and resources, including dry gas, syringes, and septa. Removing as much as possible of this memory effect is thus highly desirable to save time and money during routine sample processing. A suite of measures has been tested in the lab during several days during the visit of Pascal Graf from ETH Zürich in February/March 2016. Also in discussions with Pål Tore Mørkved, we identified a number of factors that can potentially cause such memory effects, and measures that can potentially reduce them.

The potential causes of a memory effect are:

1. Sample remaining in the syringe
2. Sample remaining on the outside of the syringe
3. Sample remaining in the septum
4. Sample remaining in the vapourizer
5. Sample remaining in the analyzer
6. Sample remaining in the septum

The measures that have been tested to reduce the memory focus either on influences related to the syringe, i.e. autosampler aspects (Section 3), or on influences related to water remaining in the measurement system, i.e. vapourizer aspects (Section 4, 5). The isotopic difference between the adjacent samples also plays a role on the amplitude of memory effect (Penna et al. 2012), but will not be discussed in this context. The same two samples, VATS (δ^{18}O $\approx$ -16.45, δD $\approx$ -127.52) and DI (δ^{18}O $\approx$ -7.71, δD $\approx$ -49.71), are used through all the tests.

Results from all tested measures are compared to a default setup. The memory effect of this default setup is identified and quantified in Figure 1.

2   Quantification of memory effects

2.1   Data pre-process

The raw data from measurements were calibrated for both water concentration and isotopic dependency on water concentration (Tremoy et al. 2011; Aemisegger et al. 2012).

Water concentration calibration: Water concentration measured by Picarro L2140-*i* was calibrated against dew point generator LI-610 on 2016-06-06. The calibration function was found to be:

$$W_{true} = 0.84784 W_{Picarro} - 682.5519.$$

Calibration of isotopic dependency on water concentration: The isotopic compositions (δ^{18}O, δD) measured by CRDS have a dependency on water concentration levels. According to the manual of
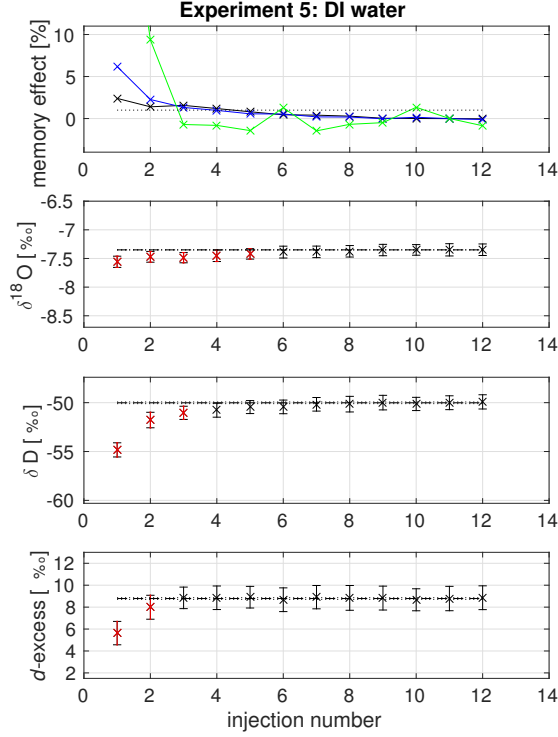
Figure 1: Example for memory effect of the default setup (1 pre rinse, 1 sample rinse, 0 fill strokes, no other modifications) for $\delta^{18}O$, δD and d-excess.

Picarro L2140-i, the water concentration operating range is 17,000~23,000 ppmv and for best results, liquid sample injections should be provided to the instrument at a concentration of 20,000±1,000 ppmv. Typically, isotopic compositions measured by CRDS are reported at a water concentration of 20,000 ppmv (Gkinis et al. 2010). A linear fit was found to correct the isotopic response at the section of 16,000 21,000 ppmv (after water concentration calibration). For each data point, the correction term for the isotopic composition will be given by:

$$\Delta\delta^{18}O = 0.000156\Delta w,$$

$$\Delta\delta D = 0.000088\Delta w,$$

where Δw [ppmv] is the deviation of water concentration relative to 20,000 ppmv; $\Delta\delta^{18}O$ and $\Delta\delta D$ isotopic correction terms.

2.2 Quantification method 1: Relative deviation (*t*-test)

To compare the impact of different measures a statistical testing procedure has been devised that is similar to *t*-test based outlier testing. From a sample sequence of e.g. 12 injections from the same vial an average of the last 4 injections has been calculated for both the mean and standard deviation, the so-called target mean value. For each injection is then calculated the deviation of the injection mean value from the target mean value ($\delta_{inj} - \delta_{target}$). This deviation divided by the standard deviation from obtaining the target mean value (σ_1), or the average standard deviation of the mean value (σ_2), resulting in two *t*-values.

σ_2 is rather consistent while σ_1 can vary a lot for different runs depending on the measurement quality. To maintain a consistent reference through the whole experiment, σ_2 is chosen for the calculation of *t*-value.
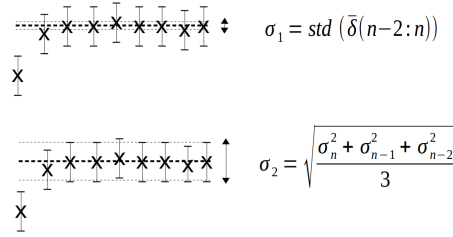
$$\sigma_1 = std\left(\bar{\delta}(n-2\!:\!n)\right)$$

$$\sigma_2 = \sqrt{\frac{\sigma_n^2 + \sigma_{n-1}^2 + \sigma_{n-2}^2}{3}}$$

Figure 2: Schematic indication of σ_1 and σ_2. σ_1 is standard deviation from obtaining the target mean value, σ_2 is the average standard deviation of the mean values.

Data quality: Due to the changing measuring conditions (environmental conditions and instrument performance), the measurements could be unstable. The ratio $\frac{\sigma_1}{\sigma_2}$ can be used as an indication of the data stability. In this experiment, the runs with $\frac{\sigma_1}{\sigma_2} > 0.5$ will be regarded as unstable runs and will thus be excluded in the following evaluation procedure.

Injections affected by memory: If the t-values exceed some defined threshold, they are considered as outliers, i.e. as affected by memory from the previous vial. An improved injection method will reduce the number of injections affected by memory in a sequence. The threshold for t-value is defined to be 0.5 by observing the raw data. That is to say, the injection with $t > 0.5$ will be regarded as being affected by memory from previous sample.

First injection memory: As an additional measure of the memory effect the first t-value in an injection series is retained. This measure should in particular be sensitive to wet flushes and sample rinses.

Both measures are calculated for δD, δ^{18}O and d-excess. In order to evaluate the effect of a measure, the different methods are shown in graphs with the number of injections affected by memory on the vertical axis, and the first injection difference on the horizontal axis (Figure 6). Improved methods will shift the measures towards the lower left corner of the evaluation graph.

2.3   Quantification method 2: Memory effect in percent

Memory effect can be quantified directly in percent (Gröning 2011). For each pair of adjacent vials, the isotopic difference (d) between the mean of the last 4 injections of each sample was considered as the true isotopic difference of these two samples ($d = true_1 - true_2$). The isotopic difference (e) between each previous injection and the mean of the last 4 injections of the second sample was calculated ($e = meas_2 - true_2$). The ratio $f = e/d * 100\%$ was then considered as the total memory contribution (in percent) from the previous sample (Figure 3).
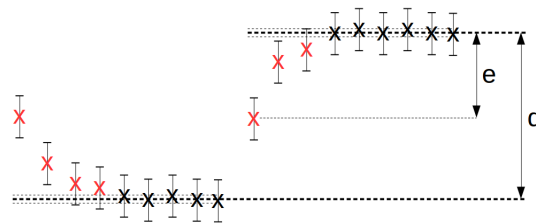

Figure 3: Schematic presentation of quantification method 2: memory effect in percent.

Data quality: The same as in quantification method 1. The runs with $\frac{\sigma_1}{\sigma_2} > 0.5$ will be regarded as unstable runs and will thus be excluded in the following evaluation procedure.

Injections affected by memory: The same principle as in quantification method 1. However, the thresholds defined here will be 0.5%, 1%, and 5% (i.e. the δ value of this injection represents 99.5%, 99%, and 95% of the target mean value).

First injection memory: The same principle as in quantification method 1, only indicated in percent.

3 Changing syringe (autosampler) aspects

The measures that have been tested to remove previous sample water from the syringe are:

1. rinsing with DI water (pre rinses, Section 3.1),
2. rinsing with new sample (sample rinses, Section 3.2),
3. rinsing with new sample to the sample vial (fill strokes, Section 3.3).

Combinations of these effects above in Section 3.4. Finally, removing liquid from the syringe by placing a vacuum pump to the waste port has also been tested (Section 3.5).

Rinsing is by default done between each injection, but can be chosen to be done only between vials.

3.1 Pre-rinses

Experiments with 5 pre-rinses of DI water instead of the default value 1 have been run. DI water is then injected directly to the waste port. This measure should remove memory effects from a previous sample from the syringe. This measure increases the number of strokes of the syringe, as well as the time until an injection arrives at the injector port.

3.2 Sample rinses

Experiments with 5 sample-rinses have been run instead of the default value 1. Sample water is then injected directly to the waste port. The advantage to the pre-rinses is that the previous sample's signal in the syringe is overwritten with the current sample's values. This measure increases the number of strokes of the syringe, as well as the time until an injection arrives at the injector port.

3.3 Fill strokes

Experiments with 5 fill strokes (instead of the default value 0) have been run. Sample water is then injected back into the vial. Fill strokes do not consume sample, but potentially pollute sample. This is particularly critical when measuring standards repeatedly from the same vial. Fill strokes should therefore be generally avoided. This measure increases the number of strokes of the syringe, as well as the time until an injection arrives at the injector port, but less so than for sample rinses.

3.4 Combined sample rinses and pre-rinses (No. 2-5)

Combinations of the above parameters are also possible. This further increases the number of plunger strokes, and the injection time. Repeated pre-rinses are expected to be dominated by the number of sample rinses following thereafter.

3.5 Vacuum at waste port

A vacuum pump was attached to the waste port in order to extract any liquid possibly remaining at the needle tip and outside for some of the tests. This increases noise level if run permanently. If effective as a measure, the pump should only be activated during injections to the waste port if possible.

4 Changing vaporizer aspects

The measures that have been tested to remove previous sample from the vapourizer are:

1. injecting liquid without measuring it (wet flushes),

2. repeating the ordinary cleaning sequence,

3. modifying the flow pattern of the ordinary cleaning sequence. Combinations of these measures have also been tested.
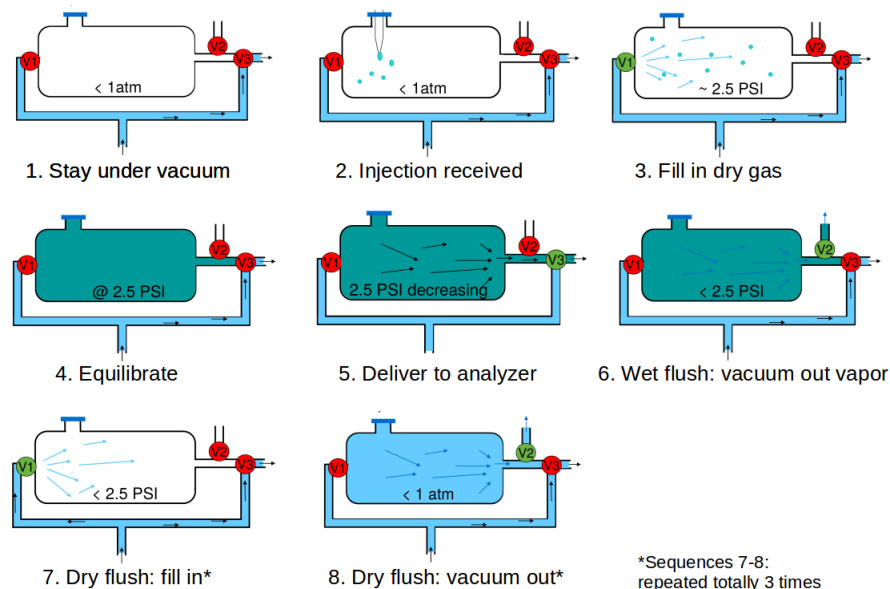

Figure 4: Schematic diagram of the vapourizer sequence. V1, V2, V3 indicating valves (red colour means disabled and green colour actuated). Blue filling and arrows indicate the flow of dry gas. Green filling indicates the distribution of vapour sample. (According to Vaporizer A0211 Operation Diagram, Picarro, Inc., 2011.)

Table 1: Commands to activate the valves and flow pattern. "0x03" and "0x05" are the new flow patterns that were tested in the experiment.

Command	V1	V2	V3	Valve state	Flow pattern
0x00	0	0	0	All valves disabled	Break
0x01	1	0	0	Valve 1 actuated	Fill in vaporizer with dry gas
0x02	0	1	0	Valve 2 actuated	Vacuum vaporizer
0x04	0	0	1	Valve 3 actuated	Vacuum vaporizer & analyzer
0X03	1	1	0	Valve 1 & 2 actuated	Flush vaporizer with dry gas
0X05	1	0	1	Valve 1 & 3 actuated	Flush vaporizer & analyzer with dry gas

4.1 Wet flushes (No. 6)

Wet flushes denote sample injections into the vapourizer that are processed as for sampling, but then discarded and evacuated to vacuum. This procedure primes the vapourizer in the same way as usual sampling would, but saves the time required for a complete sampling sequence. By default, wet flushes are deactivated in the Picarro vapourizer software.

The code of the coordinator was first modified in order to allow for wet flushes between each sample. Then the code was further modified to allow for wet flushes only at the change to a new vial.

4.2 Vaporizer flush to vacuum (No. 7)

The vapourizer software was modified to allow for throughflow of the vapourizer from the dry gas inlet to the vacuum pump.

4.3 Vaporizer flush to analyzer (No. 8)

The vapourizer software was modified to allow for throughflow of the vapourizer from the dry gas inlet to the analyzer.

4.4 Combined vaporizer flush sequence and wet flushes between vials (No. 9)

All of the above measures have also been combined into one sequence, with additional switches of the valves V2 and V3 to extract moisture potentially remaining in the valves themselves.

4.5 Additional dry flushes (No. 10)

The vapourizer software was modified to increase the length of the pumpout sequence, carried out before each new sample. The time of the usual sequence was increased from 25 s to 50 s, and duplicated with a 10 s break with closed valves in between. During this run the DI rinses were turned off in addition. Measures 3.2 and 3.3 were included in this sequence, but no wet flushes.

5 Cleaning vaporizer, filter and cavity

5.1 Wet flush through filter and cavity (No. 11-19)

The vaporizer sequence was modified to allow for the throughflow of wet flush from vaporizer through filter and cavity to vacuum. The number of wet flushes (1, 2 or 3), the pattern through filter and cavity (one pulse or three pulses), the water concentration of the pulse ($\sim$20,000 ppmv with 1 injection, $\sim$50,000 ppmv with 2 injections), and the length of the pulse (half or double the time) have been tested for their efficiency on reducing memory effect.

6 Memory effect of ^{17}O mode measurements (No. 20-22)

The memory effect and the measures to reduce the memory has also been investigated for the ^{17}O mode measurements. The tested measures include the default mode and the wet flushes.

7 Summary of findings

The evaluation results are presented in this section. Results from quantification method 1 and 2 (Section 2) are rather similar disregarding the different approaches they used. In the following only the evaluation results from method 2 are shown.

Figure 5 shows the averaged memory effect for each group of measures, which gives an overview of the memory effect for all the measures.

The number of memory affected injections is plotted against the memory effect of the first injection in Figure 6. Improved methods will shift the measures towards the lower left corner of the evaluation graph. For all of δ^{18}O, δD and d-excess, the measures with changing autosampler (i.e. cleaning syringe) mainly stay in the middle and to right side (black to bluish colors) while the measures with cleaning

Table 2: Summary of all the experiments. (No. 1 test group has only 6 injections for each vial and is disregarded here. Test groups No. 2-22 have 12 injections for each vial.)

| No.	Method	Time per vial	Note
Syringe (autosampler) aspect			
2	1 pre-rinse, 1 sample rinse	0.5 min	10 sec x2
3	5 pre-rinse, 1 sample rinse	1 min	10 sec x6
4	1 pre-rinse, 5 sample rinse	1 min	10 sec x6
5	5 pre-rinse, 5 sample rinse	1.5 min	10 sec x10
Vaporizer aspect			
6	1 Wet flush between injections	24 min	2 min*inj
7	Open V1,V2 simultaneously	9 min	22 sec x2*inj
8	Open V1,V3 simultaneously	9 min	22 sec x2*inj
9	3 Wet flush between vials + V1,V2 + V1,V3	24 min	2 min x3 + 22 sec x2x2*inj
10	Additional dry flush + V1,V2 + V1,V3	37.5 min	1.5 min + (1.5 min + 22 sec x2x2)*inj
Vaporizer + Filter + Cavity			
11	1 Wet flush: 3 pulse	5 min	1 min + 4 min
12	2 Wet flush: 3 pulse (bad quality)	10 min	5 min x2
13	2 Wet flush: 3 pulse + LastClean (dry flush)	12 min	(5 min + 50 sec)x2
14	1 Wet flush: 3 pulse (x2 Conc.)	6 min	5 min + 50 sec + 10 sec
15	1 Wet flush: 1 pulse (x2 Conc.)	6 min	
16	2 Wet flush: 1 pulse (x2 Conc.)	12 min	6 min x2
17	2 Wet flush: 1 pulse (x2 Conc., x2 time)	17 min	(6+2.5 min) x2
18	3 Wet flush: 1 pulse (x2 Conc., x0.5 time)	15 min	(6-1 min) x3
19	3 Wet flush: 1 pulse (x2 Conc.)	18 min	6 min x3
^{17}O mode			
20	^{17}O mode high precision (default)	9 min	
21	^{17}O 2 Wet flush: 1 pulse (x2 Conc.)	12 min	6 min x2
22	^{17}O 1 Wet flush: 1 pulse (x2 Conc., x3 time)	10 min	6+4 min
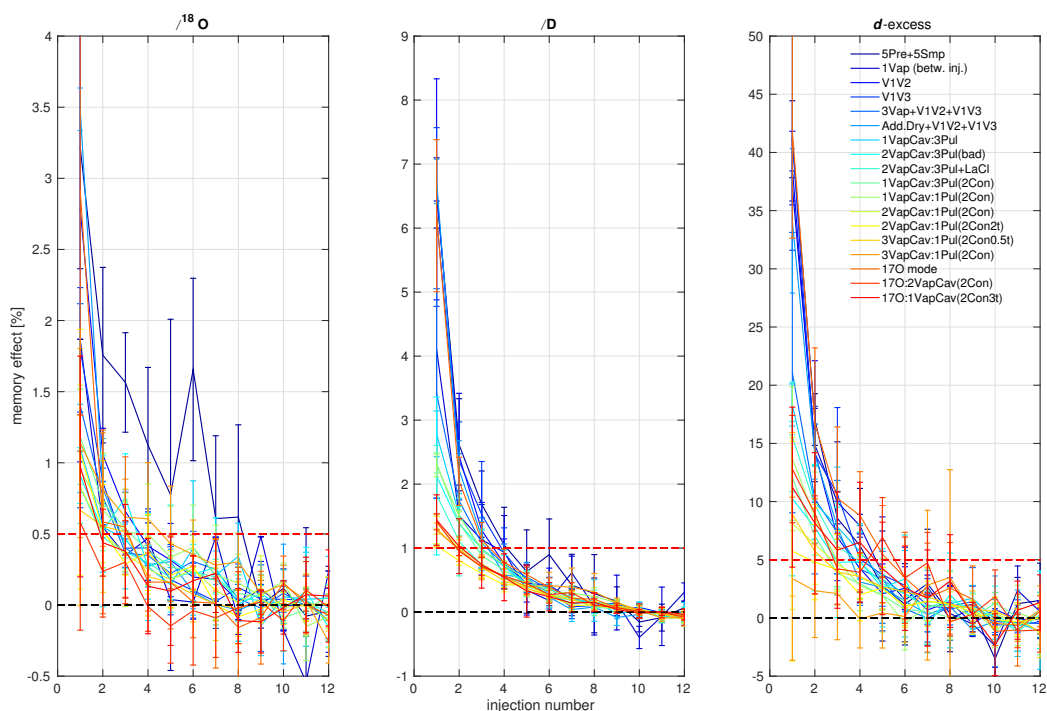
Figure 5: Evaluation of memory effect for the different tested measures: the averaged memory effect for each group of measures. The groups are indicated by lines in color and standard deviation by bars. Red dashed lines indicate the thresholds for detecting memory affected injections.

vaporizer and analyzer are gathered on the left side (greenish to yellowish colors). This indicates that the main memory source stays in the part from vaporizer to analyzer and cleaning this section efficiently reduces the memory effect. For δD, it can be seen that the number of memory affected injections has also been reduced. Tests with ^{17}O mode shows the same tendency. It is worth noting that the large drop of memory effect from nearly 50% to below 10% for *d*-excess.
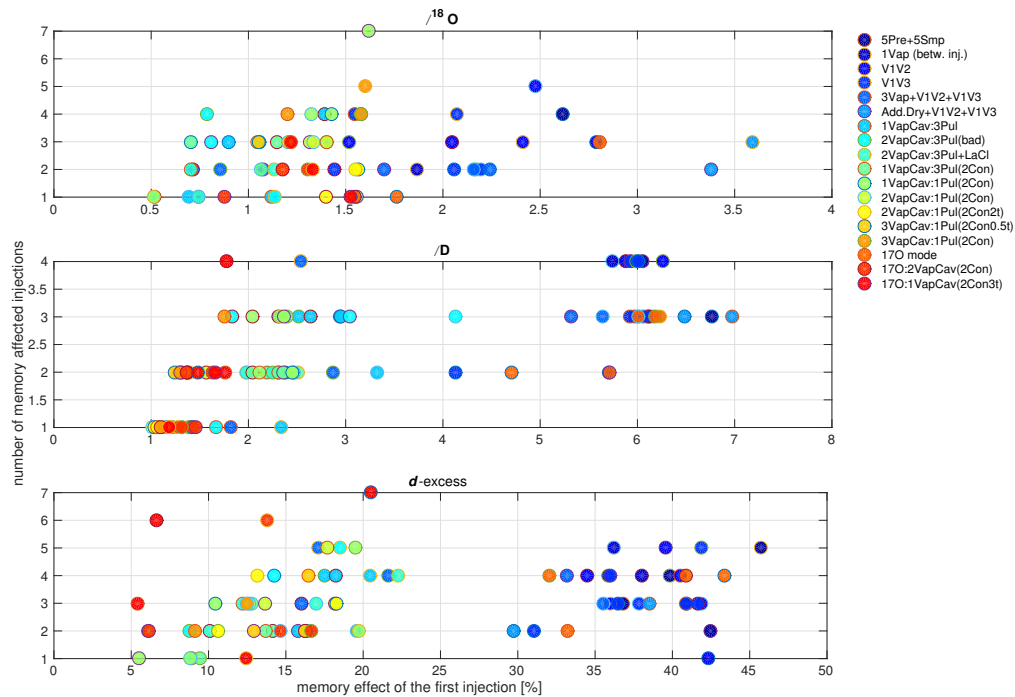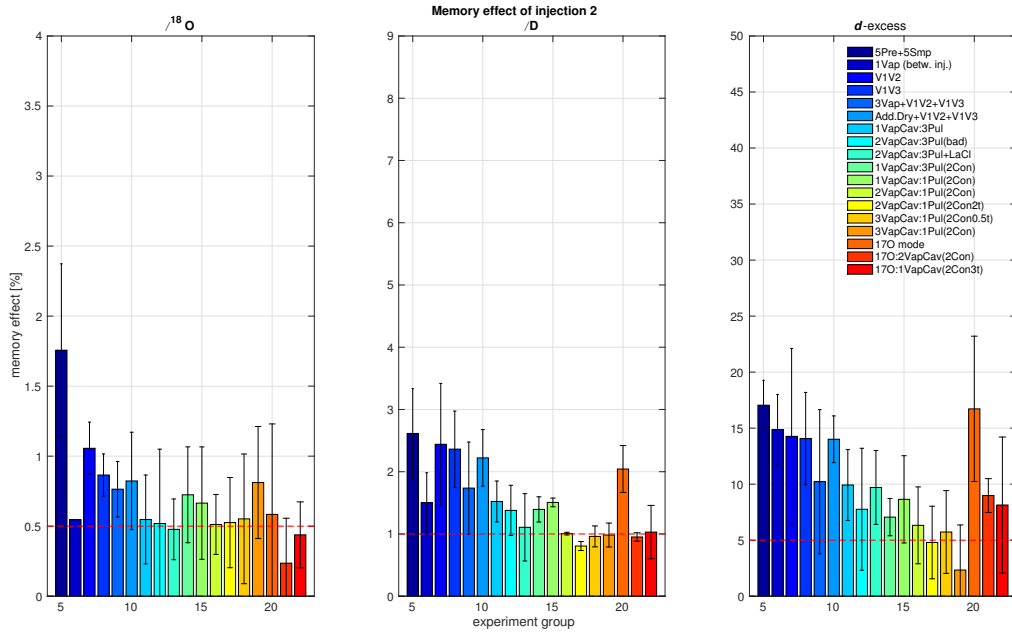

Figure 6: Evaluation of memory effect for the different tested measures: 2D plot. The tests are indicated in solid circles with colors. The first black color indicates measure regarding to changing autosampler (i.e. cleaning syringe); bluish colors for cleaning the vaporizer; greenish to yellowish colors for the cleaning including vaporizer, filter and cavity; three reddish colors for tests measured in ^{17}O mode.

To further compare the different measures in detail, the memory effect of the first 4 injections are individually averaged and shown in Figure 7-10.

1. The responses for δ^{18}O and δD are slightly different and the standard deviations for δ^{18}O are rather big.

2. The memory effect and thus the impact of the measures on reducing memory effect are most significant on the first injection. Despite the rather big standard deviations for δ^{18}O, it can be seen from Figure 7-8 that cleaning including filter and cavity (No. 11-19) reduces memory effect much more efficiently compared to cleaning syringe (No. 5) or vaporizer only (No. 6-10).

3. It seems that dry flush has limit to reduce the memory (No. 10), while wet flush works much more efficiently (No. 6, 9).

4. Regarding to the cleaning including vaporizer, filter and cavity (No. 11-19): the pattern through filter and analyzer (1 pulse or 3 pulses) does not seem to play a role (No. 14-15 in Figure 7); wet flush with higher water concentration (2Con) seems to contribute to reduce the memory (No. 11,14 in Figure 7: δD, *d*-excess); the time length of the wet flush to flow through filter and cavity (No. 15-19: t, 2t, 4t, 1.5t, 3t) plays an important role - the more time it flushes the more memory it reduces (No. 15-19 in Figure 7: δD, *d*-excess).

5. The measures present a very similar impact on reducing the memory effect for the measurements on ^{17}O mode.

6. The difference between the impact of the measures is biggest on the 1st injection (Figure 7), and significantly drops on the following injections. The difference becomes already insignificant on the 4th injection (Figure 10). This indicates that most of the memory will be cleaned anyway after the first several injections, rather independent on the different measure that was adopted.

7. It is worthy pointing out that the remarkable decrease of the memory effect for *d*-excess from 40% to below 10% on the first injection (Figure 7). The difference of *d*-excess between samples are usually not significant. A precise measurement is thus a critical prerequisite for the correct interpretation of *d*-excess.
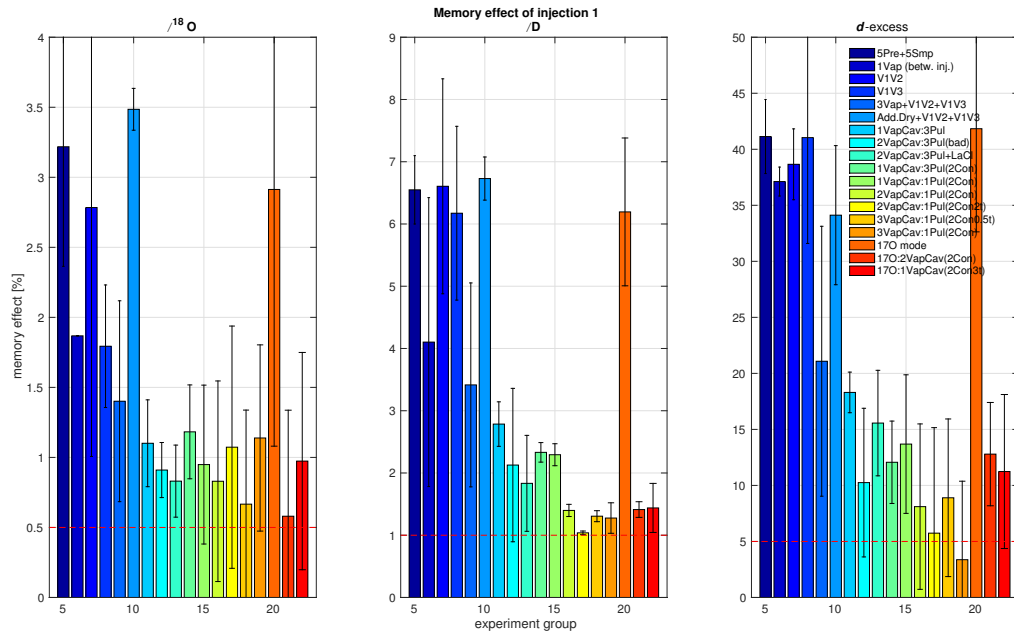
Figure 7: Evaluation of memory effect for the different tested measures: averaged memory effect of the 1st injection. The measures are indicated in coloured histograms and standard deviation in bars. Red dashed lines indicate the thresholds for detecting memory affected injections.

Figure 8: Evaluation of memory effect for the different tested measures: averaged memory effect of the 2nd injection. Legends and y-axis scale same as in Figure 7.
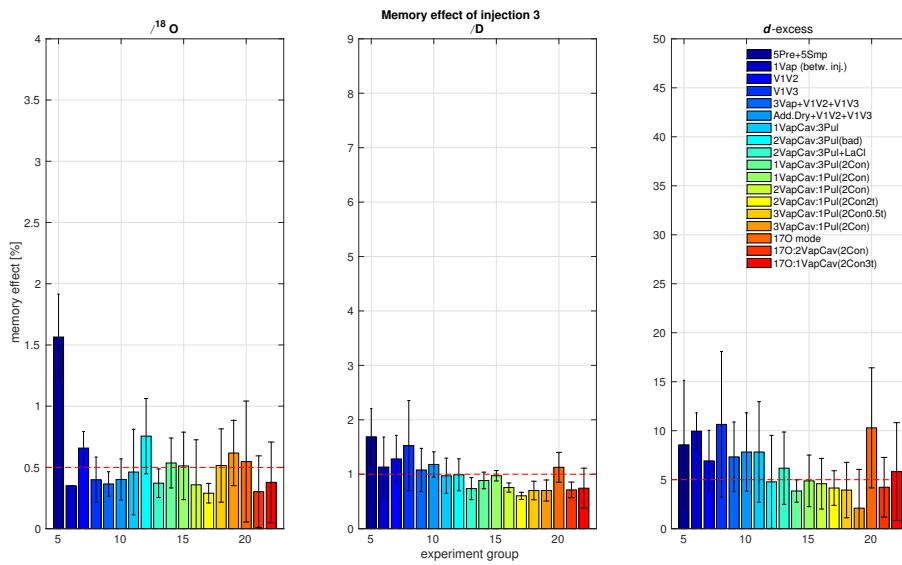

Figure 9: Evaluation of memory effect for the different tested measures: averaged memory effect of the 3rd injection. Legends and y-axis scale same as in Figure 7.
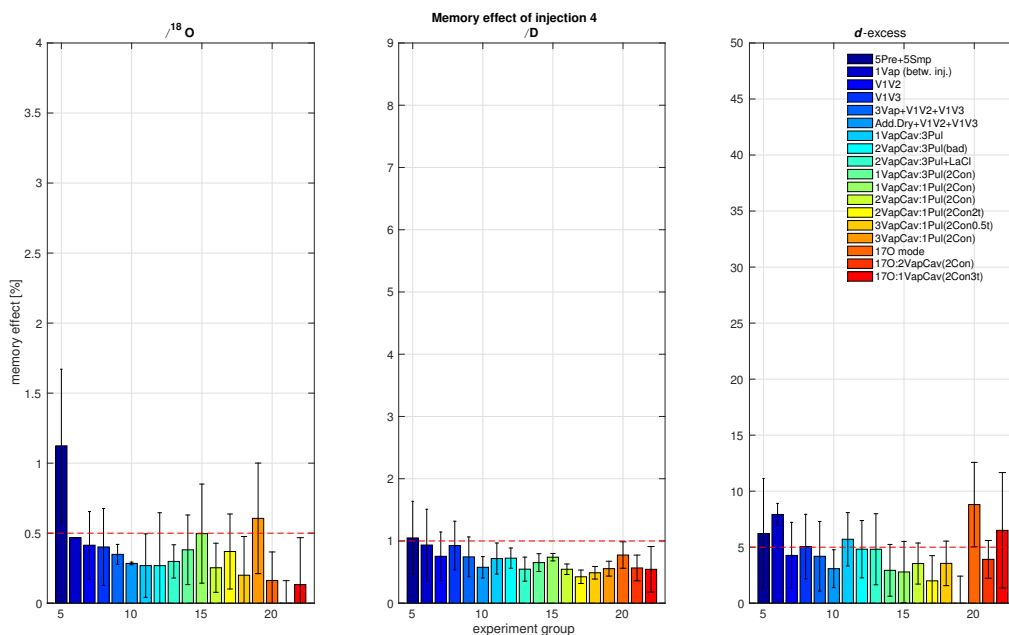
Figure 10: Evaluation of memory effect for the different tested measures: averaged memory effect of the 4th injection. Legends and y-axis scale same as in Figure 7.

8   Conclusion and recommendations

Based on the results from the various measures, the following conclusions can be drawn:

1. Cleaning syringe or vaporizer only does not reduce the memory effect significantly.

2. Cleaning including vaporizer, filter and cavity provides promising improvement.

3. The main source for the memory effect should locate in the filter and cavity, secondly in the vaporizer. The filter locates between vaporizer and cavity in order to filter the sample vapour and is probably the main source for memory effect because of its large contact surface.

4. Wet flush (i.e. cleaning with the current water sample) is more efficient than dry flush (cleaning with dry gas).

5. The impact of the wet flush is proportional to the time length it is implemented. Therefore, a balance should be considered between reducing memory effect and saving time.

6. Water is sticky. Thus the memory effect presents all along the transport path. It will be implausible to try to absolutely remove the memory effect.

There are, however, some uncertainties during the evaluation of the tested measures:

1. Uncertainty due to instrument instability. Some measurements with bad data qualities will have interference on the quantification of the memory effect. The interference will be minimized by disregarding the bad measurements before processing the quantification.

2. Uncertainty of statistics. Limited by the experiment time, each implemented measure was only repeated three times (even some of the duplicates are disregarded because of the bad data quality). Strictly saying, this will not be sufficient to quantify the impact of the measure in a statistical approach, but rather acceptable for gaining an insight.

Based on the conclusions above, the measure with 2 times of wet flushes (each wet flush 1 pulse with doubled concentration, No. 16) is chosen to be implemented for the routine sample measurement in the future. This measure takes 12 minutes in total and the first injection after the measure can reduce the

memory effect to reach about 0.8%, 1.4%, 8% for δ^{18}O, δD, d-excess, respectively, which is even better compared to those of the 3rd injection with the default method, which will instead consume 18 minutes (high precision mode: 9 minutes per injection x 2 injections). It will thus save 1 hour by measuring every 10 samples in high precision mode.

Even though the precision of the results will be much improved with two double-concentration wet flushes, it is still preferable to disregard the first 3 or 4 injections for precise results if the time consumption is allowed since memory effect still exists. 12 injections for the standard and 8 injections for the sample is currently used in FARLAB routine measurement.

Outlooks: Instrument parts (vaporizer, filter) may be coated to be 'anti-water' so that less water molecules would remain on the contact surface.

A Memory effect for δ^{17}O and ^{17}O-excess

The memory tests during liquid injections have also been carried out on ^{17}O mode of Picarro (No. 20-22). ^{17}O mode on Picarro allows outputs of δ^{18}O, δD, δ^{17}O, and ^{17}O-excess at the same time. However, the outputs of δ^{18}O and δD are different (drifted towards more negative: about -0.5‰ for δ^{18}O and -3‰ for δD) compared to those on ÂźâAÿO mode. The results of the memory test for δ^{18}O and δD on ^{17}O mode have been included in the main part of the report above. ^{17}O-excess, analogous to d-excess, is defined as the surplus of ^{17}O caused by non-equilibrium processes and is interpreted as a direct proxy for humidity conditions of the moisture origin (Barkan and Luz 2007).

Figure 11-16 show the results of the memory tests on ^{17}O mode. The value of ^{17}O-excess turned out to have a much bigger standard deviation relative to the value itself. And both δ^{17}O and ^{17}O-excess have big variations through the run. Thus it is difficult to identify the memory effect for these two proxies. Nevertheless, compared to the default setup (indicated in blue color in Figure 11-16), the two tested measures (indicated in red and green color in Figure 11-16) reduces the memory effect for δ^{17}O and ^{17}O-excess in an overall similar way as it does for δ^{18}O, δD, and d-excess.

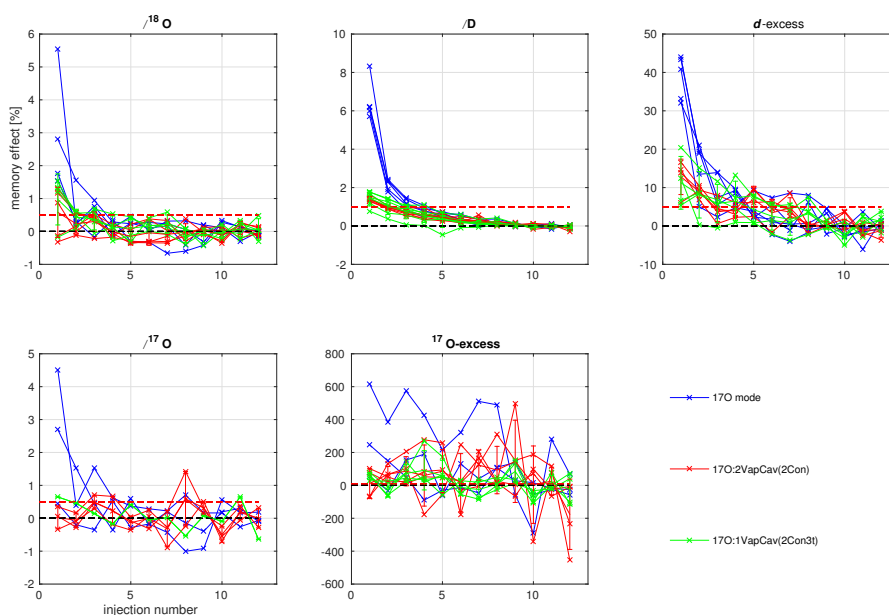Figure 11: Evaluation of memory effect for the tested measures on ^{17}O mode: the averaged memory effect for each group of measures. The groups are indicated by lines in color and standard deviation by bars. Red dashed lines indicate the thresholds for detecting memory affected injections.
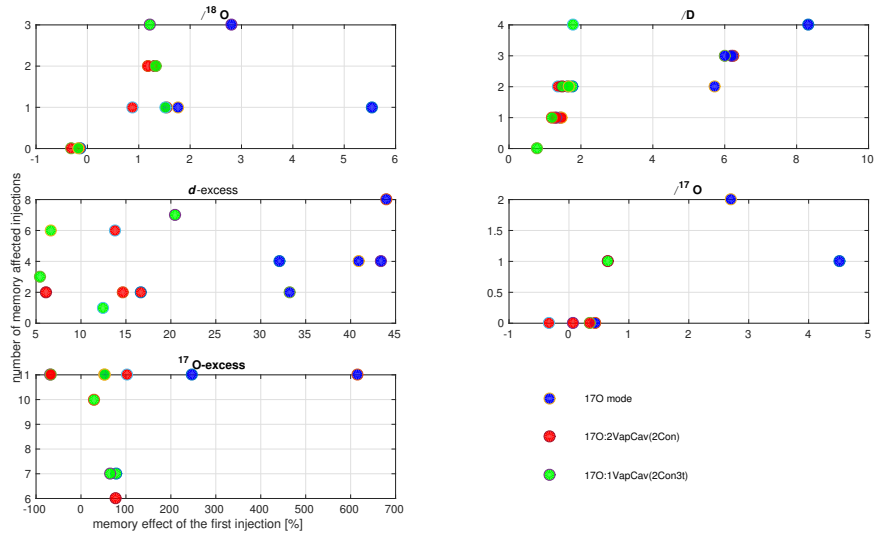
Figure 12: Evaluation of memory effect for the tested measures on ^{17}O mode:: 2D plot. The tests are indicated in solid circles with colors.
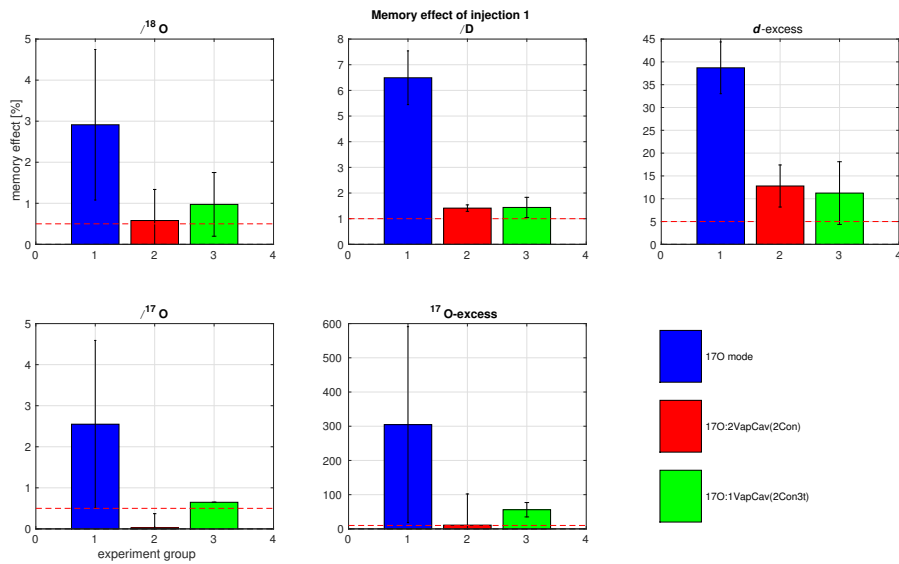

Figure 13: Evaluation of memory effect for the tested measures on ^{17}O mode: averaged memory effect of the 1st injection. The measures are indicated in coloured histograms and standard deviation in bars. Red dashed lines indicate the thresholds for detecting memory affected injections.
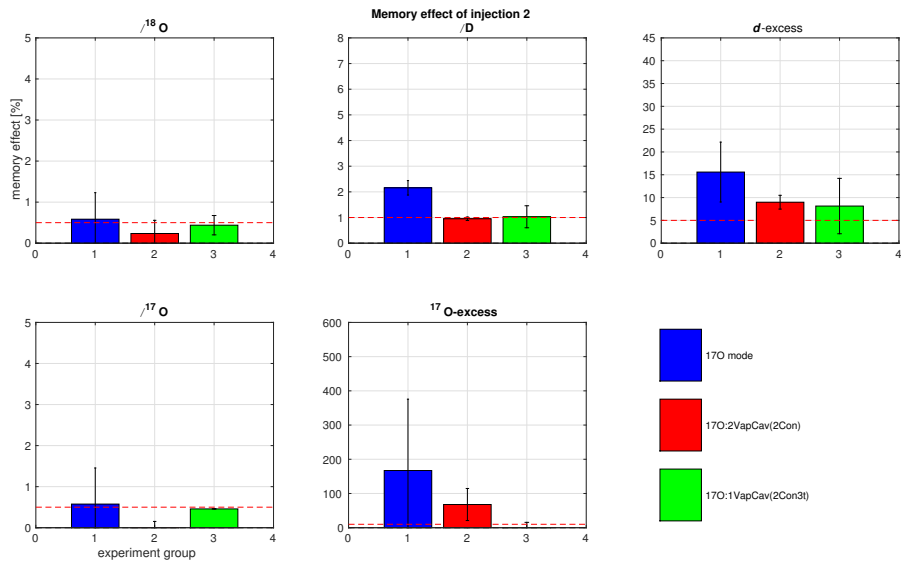
Figure 14: Evaluation of memory effect for the tested measures on ^{17}O mode: averaged memory effect of the 2nd injection. Legends and y-axis scale same as in Figure 13.
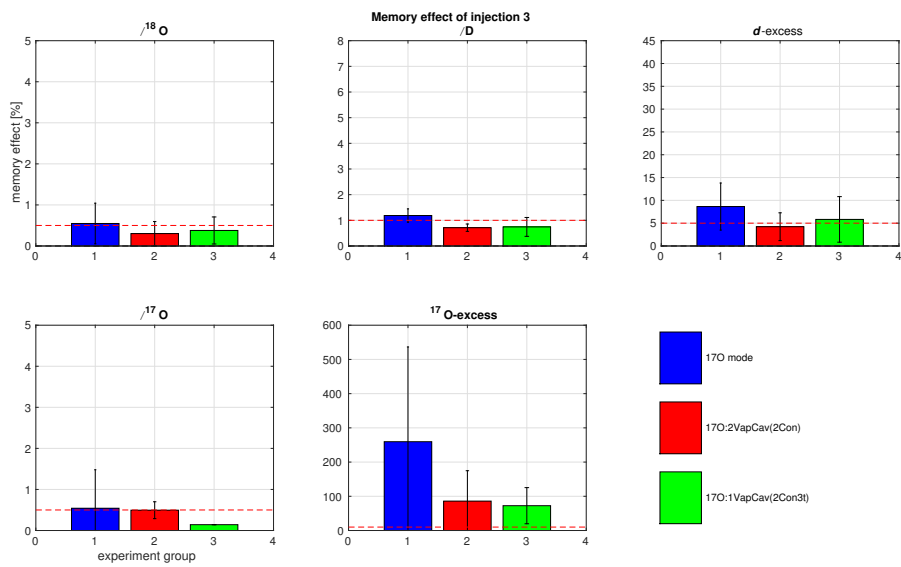

Figure 15: Evaluation of memory effect for the tested measures on ^{17}O mode: averaged memory effect of the 3rd injection. Legends and y-axis scale same as in Figure 13.

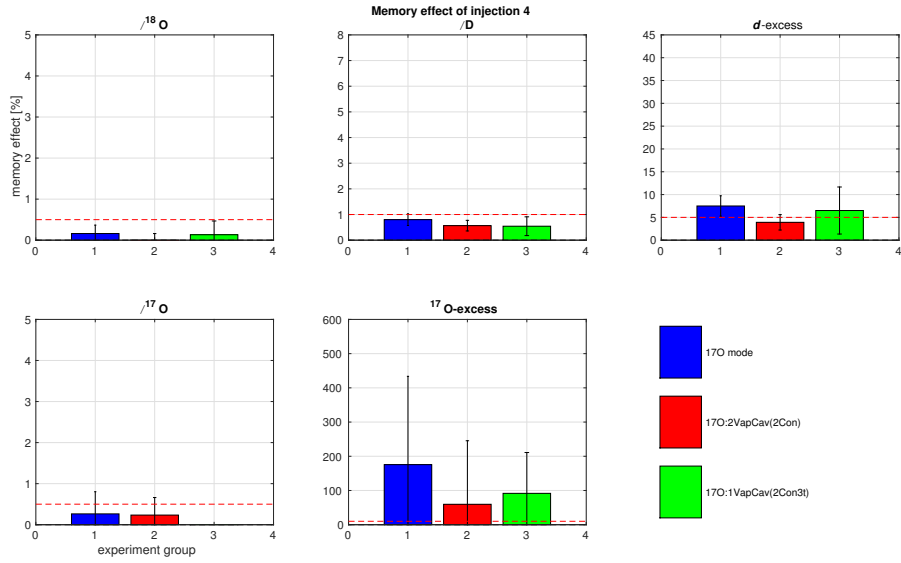Figure 16: Evaluation of memory effect for the tested measures on ^{17}O mode: averaged memory effect of the 4th injection. Legends and y-axis scale same as in Figure 13.

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