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Documentation of Automatic Liquid Injection Water Isotope Calibration-tool (ALWIC-tool)

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1 Introduction to ALWIC-tool

ALWIC-tool is a program made to process water isotopes measurements in liquid injection mode. ALWIC-tool aims to provide an highly customisable tool while having high constraints on the user inputs to avoid as much as possible human errors. We aim this code to be suitable for a wide range of people no matter what is your knowledge on both water stable isotopes measurements or programming. We will start this documentation by a brief description of the effects occurring during measurements of water isotopes.

1.1 Memory effect

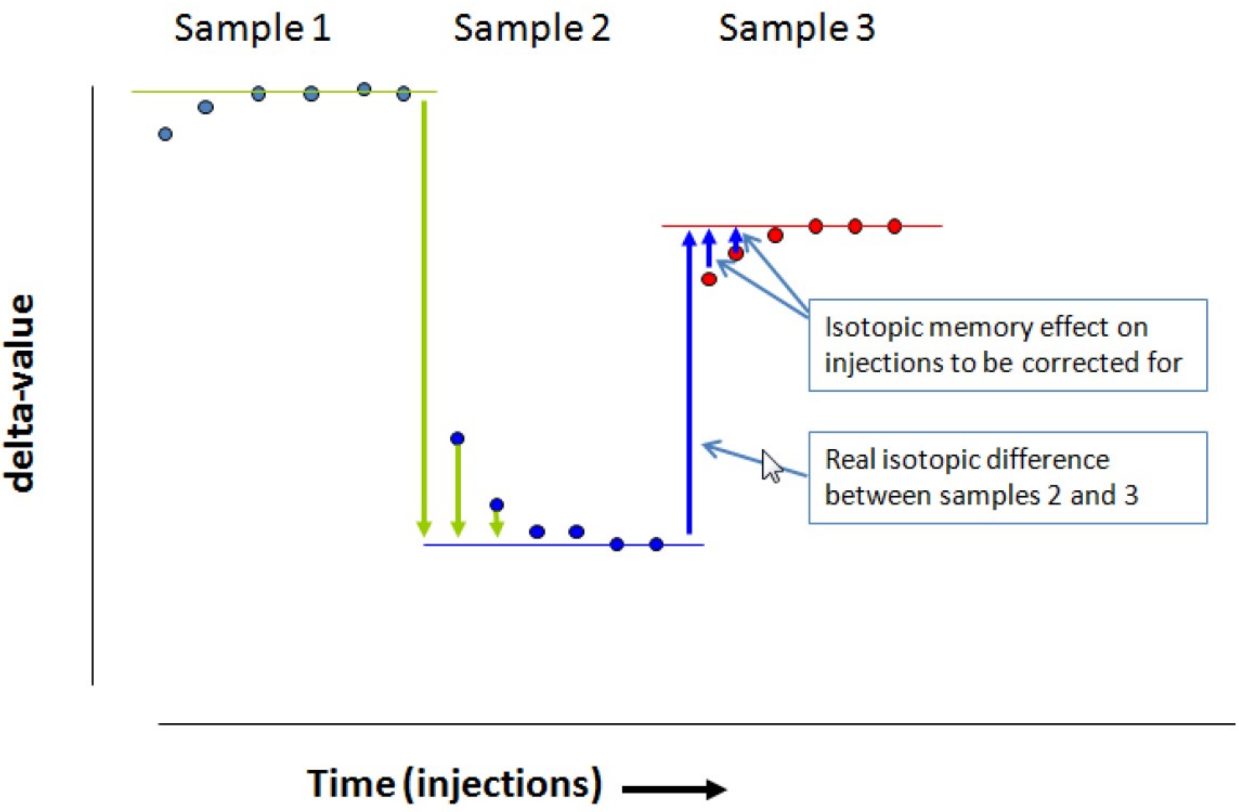

Sample 1
Sample 2
Sample 3
delta-value
Isotopic memory effect on injections to be corrected for
Real isotopic difference between samples 2 and 3
Time (injections)

Figure 1: Illustration of the memory effect, taken from the SICalib user manual (Gröning [2018])

Since the injection system of water isotopes analyser is not perfectly hydrophobic some water will stick to the walls of the system (tubing, syringe mostly) during the injection of the sample. When injecting the next sample, some of this residual water will be blown away from the injection system and will be measured along with the new sample. This effect called memory effect produce results as shown in figure 1. The first injections of one sample are influenced by the value of the previous sample and this influence decreases with the number of injection. In ALWIC-tool there are two methods implemented to correct this effect:

- The method suggested by van Geldern and Barth [2012] who proposed to evaluate the proportion of residual water in the mixing with standards and correct on samples.

- The method suggested by Gröning [2011] who proposed to evaluate the residual water through a two memory reservoir.

1.1.1 Van Geldern correction method

To evaluate the proportion of residual water, a constrained non-linear optimisation is applied on standards' injections. This only means to adjust the memory coefficients (i.e. the proportion of water at each injection) to minimize the standard deviation of all the standards combined. The method used to calculate the memory coefficients is a constraint non linear optimization performed with the COBYLA algorythm (Constrained Optimization BY Linear Approximation). Details on the implementation can be found here : Scipy Community [a], Scipy Community [b].

From these coefficients the correction of all the values can be made through the formula given in van Geldern and Barth [2012] :

$$\delta^n_{j(mc)} = \delta^n_{j(raw)} + (1 - m_j) * (\delta^n_{j(raw)} - \delta^{n-1}_t) \tag{1}$$

where :

- $\delta^n_{j(mc)}$ is the memory corrected value of the j^{th} injection of the n^{th} sample,
- m_j is the memory coefficient of the j^{th} injection
- δ^{n-1}_j is the true isotopic value of the previous sample.

1.1.2 Gröning correction method

The method is subdivided into two steps :

- First, there is the single factor calculation which calculates an approximation using the last three injection to correct the current injection.
- Then, an exponential where the parameters are set manually (Will be set to automatic if it's possible) is used to correct more accurately each injection.

Gröning's method is based on two successive correction. The first one assumes a single memory reservoir with "a constant relative memory decrease with time" (Gröning [2018]). The second one assumes two memory reservoir represented by two exponential laws combined to represent their interactions.

The first part is all done automatically. It's based on the evaluation of the memory contribution f for each pair of samples with the following formula :

$$f = \frac{a_j}{a_{j-1}} = \frac{true_j - meas_j}{true_j - true_{j-1}}$$

j refer to the sample number and starts at the second sample.

To take into account of the last three samples f is reduced :

$$f = f * (1 - f - f * f)$$

Then a mean of all f is done excluding the ones with two little difference in a_i (a_i should be more than 0.4 ‰ for $\delta^{18}O$, 4 ‰ for δD and 0.4 ‰ for $\delta^{17}O$) and the f negative (physically impossible).

Finally the first correction is applied with the following equation :

$$\delta_i^{first\ correction} = \delta_i^{raw} + f * (\delta_i^{raw} - \delta_{i-1}^{raw}) + f^2 * (\delta_i^{raw} - \delta_{i-2}^{raw}) + f^3 * (\delta_i^{raw} - \delta_{i-3}^{raw}) \tag{2}$$

Then to start the second correction, a percentage is calculated based on the following formula :

$$corr1 = \frac{\delta_i^{first\ correction} - true_j}{true_{j-1} - true_j} * 100$$

This percentage is then adjusted with the exponential parameters, alpha, beta and balance. These parameters are specific to each instruments.

$$corr = corr1 * (balance * e^{(-\alpha*(i-1))} + (1 - balance) * e^{(-\beta*(i-1))}$$

Finally this correction term is applied to the data :

$$\delta_{mc} = \delta_i^{first\ correction} - corr * (\frac{true_{j-1}}{true_j} * 100) \tag{3}$$

1.2 Calibration

The calibration is done by measuring standards with the instruments and comparing their values to the values measured by references

The values are then corrected again with the standards. The memory corrected standards (all except the first one which is used as a rinsing one) can be used to create a calibration curve. The calibration curve is evaluated with the scipy linear regression function (Scipy Community [c]).

2 How to install ALWIC-tool ?

2.1 Download from github

In order to download ALWIC you can click here. This will download a zip file with all the modules. If you are familiar with github you can clone the project with the following command :

```
git clone (repo_link) <local directory>
```

2.2 Install ALWIC-tool with Anaconda

The first recommendation is to create a new environment to avoid any conflicts of the installed packages with your previous configuration. In Anaconda a new environment is created in the Anaconda prompt with the following command :

```
conda create -n environment_name
```

Then the environment is activated with the command :

```
activate environment_name
```

To install necessary packages for ALWIC-tool open a prompt window and navigate into the directory where you downloaded ALWIC-tool. Then run the following command :

```
conda env update -n environment_name -f requirements.yaml
```

After this you can open the file called GUI_main.py in Spyder and run it.

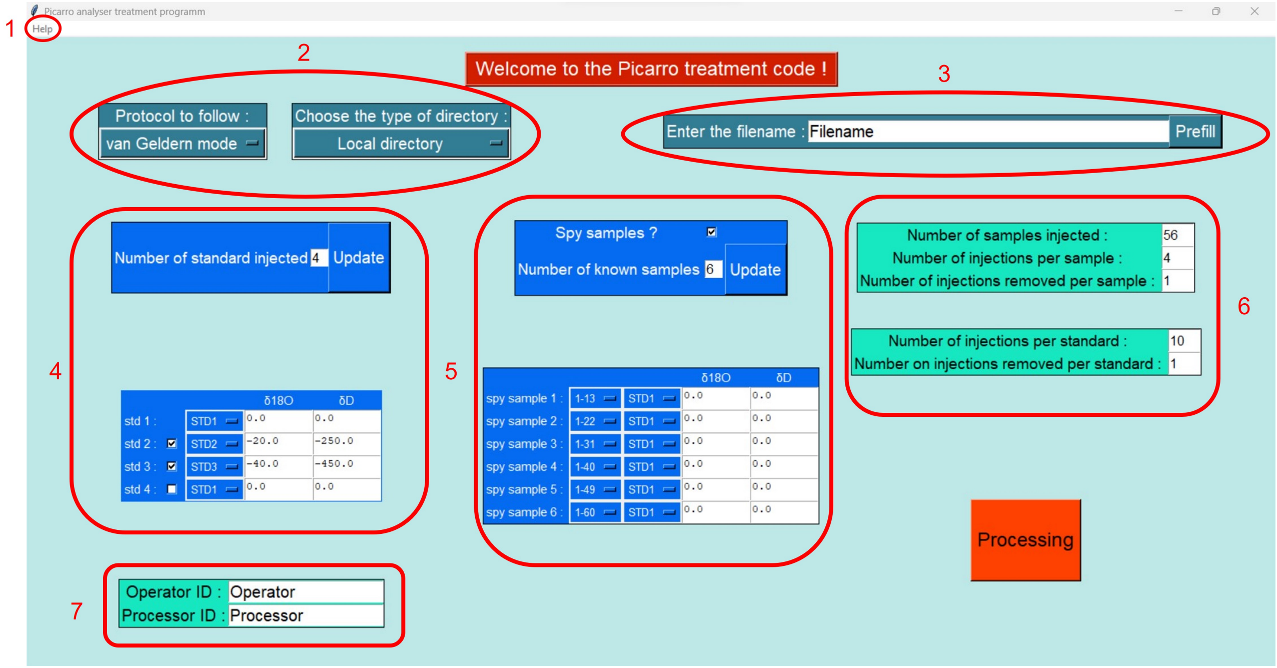
2.3 Install ALWIC-tool with another Python distribution

You will need to install the packages included in the requirements.txt file. This file is included in the file you downloaded. The method to install it is yours, depending on your IDE but the command to install all the required packages is :

```
pip install requirements.txt
```

Then you can run the GUI_main.py file and start processing.

3 How to make a run ?


Picarro analyser treatment programm
Help
1
2
3
4
5
6
7
Welcome to the Picarro treatment code !
Prefill
Update
Update
Processing

Protocol to follow : van Geldern mode

Choose the type of directory : Local directory

Enter the filename : Filename

Number of standard injected 4

			δ18O	δD
std 1 :		STD1	0.0	0.0
std 2 :	☑	STD2	-20.0	-250.0
std 3 :	☑	STD3	-40.0	-450.0
std 4 :	□	STD1	0.0	0.0

Spy samples ? ☑

Number of known samples 6

			δ18O	δD
spy sample 1 :	1-13	STD1	0.0	0.0
spy sample 2 :	1-22	STD1	0.0	0.0
spy sample 3 :	1-31	STD1	0.0	0.0
spy sample 4 :	1-40	STD1	0.0	0.0
spy sample 5 :	1-49	STD1	0.0	0.0
spy sample 6 :	1-60	STD1	0.0	0.0

Number of samples injected : 56
Number of injections per sample : 4
Number of injections removed per sample : 1

Number of injections per standard : 10
Number on injections removed per standard : 1

Operator ID : Operator
Processor ID : Processor

Figure 2: Screenshot of the interface of ALWIC-tool

Here will be described how to run ALWIC-tool. The details of the options presented here are further discussed in section 5.

After starting a run a first page appears similar to the figure 2. There are different parts on this page numbered from 1 to 7 :

- 1 : Help links, they will redirect either directly to this document, either to the github page of ALWIC-tool.

- 2 : Here you will choose which method to correct the memory effect. You also have to choose if you want to correct the $\delta^{17}O$ as well. On the second box you need to chose from you want to extract the file (see section 6.2 for how to set-up a drive account).

- 3 : Here you have to write the filename without extension. If you chose the local directory option on the previous point this will be already filled. Once you done this you can use the prefill function to prefill the points 4, 5 and almost all of 6. To be able to do the prefill the file must be customized before the measurements (more information on this on section 5.4).

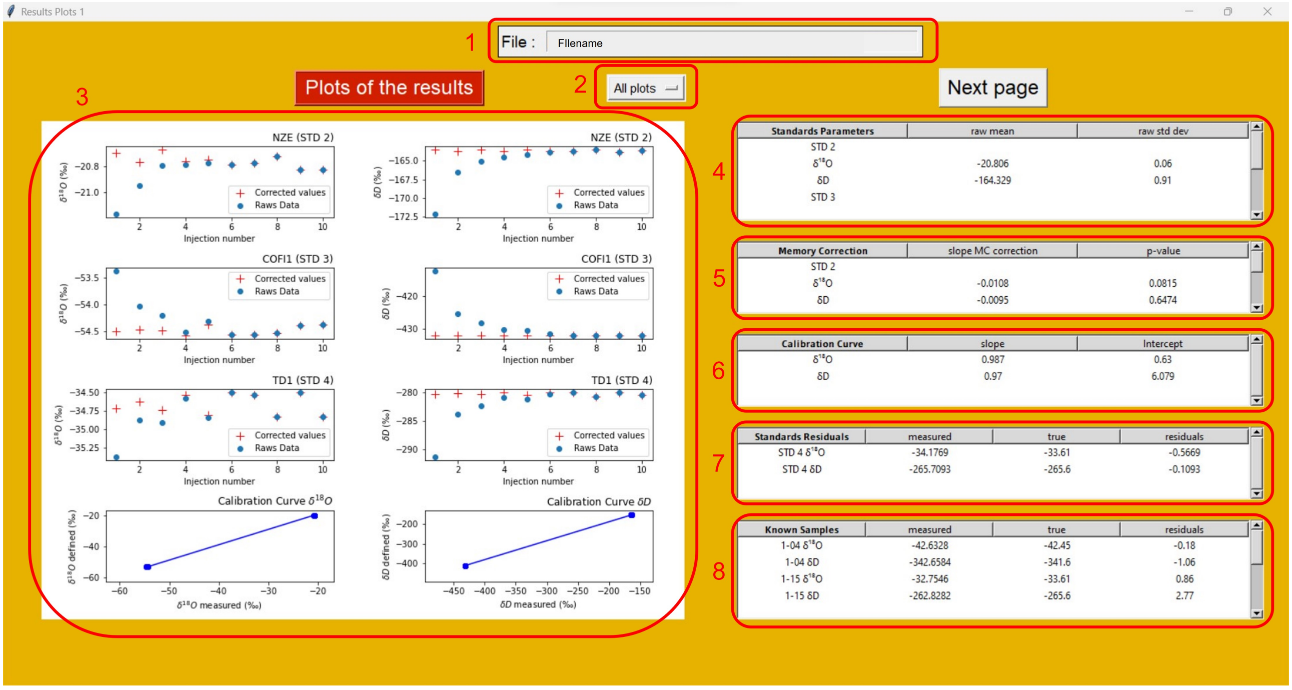
- 4 : Here you first need to enter the number of standard injected at the beginning of the sequence with a maximum of 6 (This can be increased on the code, see section 6.5 to do it, add here the references to the changes on the code). Then click on the update button. A table will appear where you will be able to modify only two things : the tick-boxes and the names of standards. The tick-boxes control which standards are used for the calibration (on means the standard is used for calibration). The names of the standards are controlling the true values of these standards. The values are set in a different file before running ALWIC-tool, see section 6.4 to know how to modify this file.

- 5 : Here is an optional part to fill. If you don't have any known samples in your run you can go to the next point. Else, you need to check the little tick-box and enter the number of known samples you have over the run with again a maximum of 6 known samples which can also be modified on the code, see section 6.5 for more information. Also if you're using a quality control standards you can include it here. Before clicking the update button make sure that the filename is filled because the update button will need your file to display the table. On this table you need to indicate the port where you placed these known samples. And in the in the same way as the last point you need to set-up the true values by changing the names. To modify the file controlling this you can look at section 6.4.

- 6 : Here you just have to enter a certain numbers of parameters of the run which are in order : The number of samples (with the known samples !!) injected on all the run, the number of injections per sample (must be constant along the run), the number of injections you want to remove to calculate the mean and standard deviation on each sample, the number of injection for each standard (must be the same for all standards) and the number of injections you want to remove to calculate the mean and standard deviation on each standard, see section 4 for more details on those calculations.

- 7 : Here is an optional part. You can indicate who ran the measurements and who is processing the data.

When all the steps have been made you can click on Processing. The memory correction process will start and show the first result page.



Standards Parameters	raw mean	raw std dev
STD 2		
$\delta^{18}O$	-20.806	0.06
δD	-164.329	0.91
STD 3		

Memory Correction	slope MC correction	p-value
STD 2		
$\delta^{18}O$	-0.0108	0.0815
δD	-0.0095	0.6474

Calibration Curve	slope	Intercept
$\delta^{18}O$	0.987	0.63
δD	0.97	6.079

Standards Residuals	measured	true	residuals
STD 4 $\delta^{18}O$	-34.1769	-33.61	-0.5669
STD 4 δD	-265.7093	-265.6	-0.1093

Known Samples	measured	true	residuals
1-04 $\delta^{18}O$	-42.6328	-42.45	-0.18
1-04 δD	-342.6584	-341.6	-1.06
1-15 $\delta^{18}O$	-32.7546	-33.61	0.86
1-15 δD	-262.8282	-265.6	2.77

Figure 3: Screenshot of the first page of results of ALWIC-tool

4 Output of ALWIC-tool

If you choose the van Geldern method to do the memory correction, a temporary window will appear before doing the calculation. This window allows you to remove either one standard if you have multiple injections with issues or you can also remove one injection (but not more) of all the standards' injections. This tool should be used carefully and only in the case of really outliers. It should not be used to improve the memory correction !

To start the processing click on next page. The window will be destroyed and the corrections will be made.

4.1 New windows

When the processing button is pressed and all the calculation made a new window appears. It looks like fig. 3. The parameters of the correction are shown on this page.

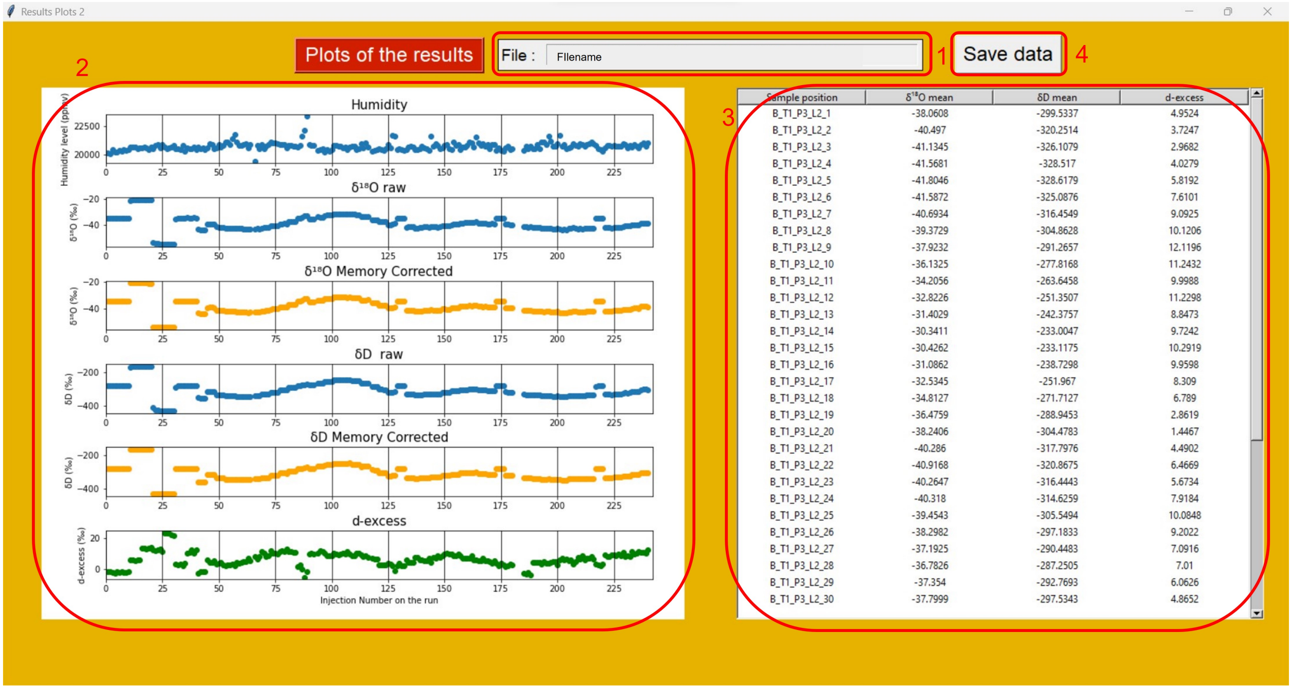
As previously this page is composed of different parts from 1 to 8 :

- 1 : Here it is a reminder of the filename. It may become really useful when you start to correct several files in a row.
- 2 : When this is set to all plots the page looks like the figure 3. But if you choose an another plot the tables on the right will be overwritten to put a zoom on the plot you selected. To view again the tables, select all plots.
- 3 : You have here a summary of the correction. For each standard and isotope you will have one plot with the raw data and the memory corrected data (before calibration).These plots are auto-scaled in y so be careful before trying to compare them. At the bottom you will have the calibration curves. These plots have the same scale for the two axis.

- 4 : Here you will find the mean and standard deviation of all the standards and isotopes. The mean and standard deviation are calculated on the values you choose not to reject on the previous page. These values are calculated on the raw values.
- 5 : This table will be different according to the memory correction method you use. If you used the van Geldern method, it shows the slope of the memory corrected values and its p-value. If you used the Gröning method, it will show you the mean single factor and alpha, beta and the balance term for each isotope.

  Note : Be very very careful with the p-values, it is calculated on a very limited number of values and p-value is a probability not a statistic (Wikipedia Contributors). If you are not aware enough of what are the limits do not use it !
- 6 : Here you will find the parameters of the calibration curves i.e. slope and intercept.
- 7 : This table is optional it will only show up if you don't use all the standards to show the residuals on the standard not used for calibration. The residuals are always defined by $residuals = measured - true$.
- 8 : Also an optional table. It will show up if you have known samples in your run. Again it will show the residuals of the known samples. The residuals are always defined by $residuals = measured - true$.

By clicking on next page you will not close the first page of results and will open the second page of results (figure 4). On this page the results shown are the samples values. Again there are several parts on this page from 1 to 4.



Sample position	δ^{18}O mean	δD mean	d-excess
B_T1_P3_L2_1	-38.0608	-299.5337	4.9524
B_T1_P3_L2_2	-40.497	-320.2514	3.7247
B_T1_P3_L2_3	-41.1345	-326.1079	2.9682
B_T1_P3_L2_4	-41.5681	-328.517	4.0279
B_T1_P3_L2_5	-41.8046	-328.6179	5.8192
B_T1_P3_L2_6	-41.5872	-325.0876	7.6101
B_T1_P3_L2_7	-40.6934	-316.4549	9.0925
B_T1_P3_L2_8	-39.3729	-304.8628	10.1206
B_T1_P3_L2_9	-37.9232	-291.2657	12.1196
B_T1_P3_L2_10	-36.1325	-277.8168	11.2432
B_T1_P3_L2_11	-34.2056	-263.6458	9.9988
B_T1_P3_L2_12	-32.8226	-251.3507	11.2298
B_T1_P3_L2_13	-31.4029	-242.3757	8.8473
B_T1_P3_L2_14	-30.3411	-233.0047	9.7242
B_T1_P3_L2_15	-30.4262	-233.1175	10.2919
B_T1_P3_L2_16	-31.0862	-238.7298	9.9598
B_T1_P3_L2_17	-32.5345	-251.967	8.309
B_T1_P3_L2_18	-34.8127	-271.7127	6.789
B_T1_P3_L2_19	-36.4759	-288.9453	2.8619
B_T1_P3_L2_20	-38.2406	-304.4783	1.4467
B_T1_P3_L2_21	-40.286	-317.7976	4.4902
B_T1_P3_L2_22	-40.9168	-320.8675	6.4669
B_T1_P3_L2_23	-40.2647	-316.4443	5.6734
B_T1_P3_L2_24	-40.318	-314.6259	7.9184
B_T1_P3_L2_25	-39.4543	-305.5494	10.0848
B_T1_P3_L2_26	-38.2982	-297.1833	9.2022
B_T1_P3_L2_27	-37.1925	-290.4483	7.0916
B_T1_P3_L2_28	-36.7826	-287.2505	7.01
B_T1_P3_L2_29	-37.354	-292.7693	6.0626
B_T1_P3_L2_30	-37.7999	-297.5343	4.8652

Figure 4: Screenshot of the second page of results of ALWIC-tool

- 1 : Same as previous page, a reminder of the filename.

- 2 : This part shows several plots against the injection number.
- 3 : This table shows every mean sample (the mean being calculated by removing the number injection set at the beginning of the post-processing).
- 4 : This allows to save the data in different files (next section will describe it). You will be asked for the folder where you want to save the date. A pop-up window will appear after saving.

4.2 Saved Results

There are up to 4 files after each processing.

- 1. The first file to be saved is called your_filename_final_file. It contains the input file with some columns added which are the memory corrected values as well as the calibrated values and some flags (more on it on section 6.1).
- 2. The second file to be saved is called your_filename_std_parameters. It contains a lot of information about the run like starting and ending time, parameters of the correction, the standard deviation of the humidity (detrended) along the run, names of people who ran the file and processed the data, the correction method and the mean and standard deviation of all standards.
- 3. The third file to be saved is called your_filename_spl_results. It contains the name of each sample as well as the mean and standard deviation of the last injections (the one you didn't choose to remove).
- 4. The last file to be saved is called your_filename_control_samples_results and is optional. It is only saved when you have spy samples in your run. It contains the position of each control samples with their measured values, true values and residuals.

5 Options of treatment

ALWIC-tool offers numerous options to process your data. They are described in the sections below.

5.1 Using google drive

Google drive can be used to store measured files and treated files. ALWIC-tool has a module allowing it to communicate with google drive. It uses the google API (Application Programming Interface) which allows two machines to communicate in this case ALWIC-tool and google drive. To do so the google account ha to be set-up, it is described in section 6.2.

5.2 $\delta^{17}O$ mode

When measuring $\delta^{17}O$ this column is corrected and a new column for 17O-excess is calculated. The 17O-excess column is calculated with the following formula according to Luz and Barkan [2005]:

$$\Delta^{17}O = \ln(\delta^{17}O + 1) - 0.528 * \ln(\delta^{18}O + 1) \tag{4}$$

5.3 Control samples

In order to look at the short term drift and to evaluate the performance of the run, "spy samples" can be added to the run. They are standards measured as samples (with the same number of injection and corrected in the same way as samples). It is then possible to evaluate the residuals along the run and the change of these residuals to identify potential issues.

5.4 Prefill

ALWIC-tool has a function to evaluate parameters directly from the file and to prefill it for the user. The filename needs to be filled and the following parameters are evaluated when it is possible : number of standards, True values of the standards, injection per standards (must be constant along one run), number of samples, injection per sample (must be constant along one run), if there are spy samples, if yes the port of each spy sample, the values of the spy samples.

Note : in order to prefill the true values of standards and spy sample the names of standards in the measurements files have to match with one standard name in the std_values.csv file (see section 6.4)

The set-up of this function is described in section 6.3.

6 Miscellaneous

6.1 Flags

There are three flags in total. One is saved in the spl_results file. It indicates a standard deviation of each sample higher than the threshold (By default, the thresholds are fixed to 0.06‰ for $\delta^{18}O$, 0.21‰ for δD and 0.1‰ for $\delta^{17}O$. See section 6.5 to know how to change these values).

The two other flags are saved in the final_file. One is for the humidity level, if the humidity for one injection higher than 23000 ppmv or lower than 17000 a flag will be raised.

The other flag indicates if an injection has been corrected or not. There are three possible values : 0, the value hasn't been corrected either because it's the first standard either because there is NaN somewhere. 1, the value has been corrected. 2, the value has not been corrected and the final value has been replaced by the raw value. This has been set-up for the case where the last injection of a sample is missing the next sample can't be corrected by any method. Instead of losing the value of this sample the raw values are used and the user is informed of this with a pop-up window when the second page of results is opened.

6.2 Set-up a google account to interact with ALWIC-tool

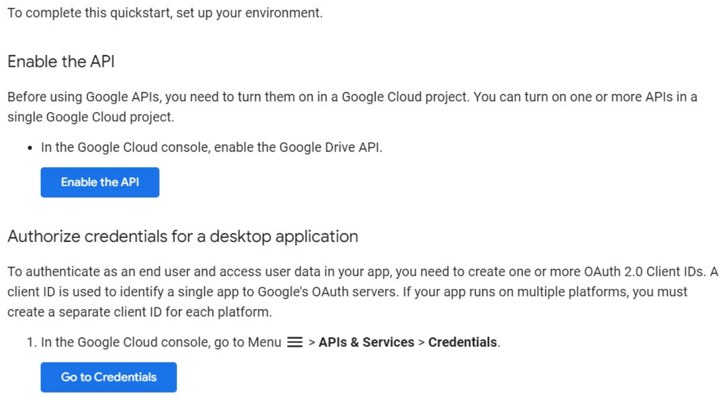
Setting-up the link between ALWIC-tool and a google account is a tedious task but once it's done, it can be a very powerful tool to work remotely or with co-workers.

The first thing to do is to create a google account. It is probably a good idea to use an account only dedicated to this task since the account will be set-up in a developer mode.

In google drive two folders have to be created : one for the raw files named raws_data (the name does not matter since the search from ALWIC-tool will look into the entire drive for the file), one for the treated files named Treated_data (the name can be changed on the code, see section 6.5). The files can be anywhere in the drive, the only requirements is to not have other folders with the same name.

Now, the google account will be set-up to use the google API. Before starting this be sure to be logged in with the account which will be set-up. If you have a different default account the solution is to log-out and then reconnect with the account you want to set-up in first. This will automatically change the default account.

The first thing to do is to enable the API. This can be done on the following link : `https://developers.google.com/drive/api/v3/quickstart/python`. When scrolling down you will see something similar to the figure 5. Click on Enable the API.



To complete this quickstart, set up your environment.

Enable the API

Before using Google APIs, you need to turn them on in a Google Cloud project. You can turn on one or more APIs in a single Google Cloud project.

- In the Google Cloud console, enable the Google Drive API.

Authorize credentials for a desktop application

To authenticate as an end user and access user data in your app, you need to create one or more OAuth 2.0 Client IDs. A client ID is used to identify a single app to Google's OAuth servers. If your app runs on multiple platforms, you must create a separate client ID for each platform.

1. In the Google Cloud console, go to Menu ☰ > **APIs & Services** > **Credentials**.

Figure 5: Box to click on to start the set-up

This will open a new window which is your google cloud console. The first thing to do is to create a new project. You chose a name and then enable the API. Then you can go back to the cloud console by clicking on Google cloud on top left of your window. Then on your left you have a panel You will have to select the credentials in API and services as shown in figure 6.

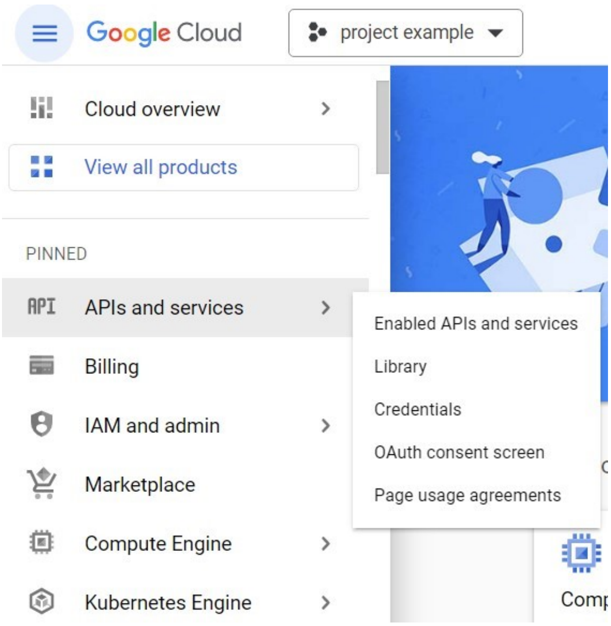


Figure 6: left panel where to find the credential control page

Then in order to create the credentials, you will have to click on create credentials and chose the API key. Then wait and close the pop up window. Then click again on create credentials and this time chose the OAuth ID. Then click on configure consent screen. Chose the user type Extern. Then, fill the App name, the user support name and the developer contact information. Skip the scope page. On the next page there the test users. You can fill up to 100 google account. Here you will fill every email which will use ALWIC-tool. This can of course be modified later. And then you can ho back to the dashboard. And click again on create crendentaials and chose again OAuth ID. Chose Desktop App as application type and then create. When the pop-up window appears download the .json file and rename it client_code.json. You will need to move file into the app folder. If these informations are not clear enough you can refer to the video available with the code or on github. It is entitled :

6.3 Set-up the prefill function

In order to use the prefill function the sample descriptor file has to be set up before the measurements. If you already use it to mark your samples name you only need to add one more column with title Identifier 2 and for vial indicate if it is a standard by putting STD, a sample by putting SAMPLE or control sample by putting SPY. The code is sensitive to upper-case be careful.

If you never used the sample descriptor, there is a file example in the example_files folder you just need to adjust it to your run.

When the Identifier 2 column is filled with STD, SAMPLE and SPY the prefill function is fully functional.

6.4 Standards true values

The standards values are stored in a separate file which must be closed when the code is running. The file is located in the File folder in the app folder. It is named std_values.csv. There are five columns in the file, the first one is the description and can be used to add some annotation on the standards. The second column is the short name, this is the name which will be displayed on screen so be careful to have meaningful names in this column. The last three columns are the values for each isotopes expressed in ‰.

6.5 Changes in the code

- How to increase the number of standard and control sample possible in the tables ?

  This requires some modifications. In the GUI_main.py there are the functions called define_table and define_known_sample_table. In these function you need to follow all the comments. If you want to add standards you will also need to change a few things in the change_table_outliers_page; function which is also in the GUI_main below the others functions.

- How to change the defaults options when you have several modes ?

  At the end of the GUI_main.py file there is the definition of all the elements of GUI. If you want to change the default protocol, you will need to look at the definition of panned window 2. Changing the default folder to look for to local directory is not recommended at all because of the construction of the code.

- How to change the default values for the flag in sample result ?

  In the file save_results.py in the function save_sample_results_file you can change the thresholds.

- How to change the default extension for saved file ?

  At the beginning of the of the save_results.py file, there is a variable called save_extension which can be modified.

- How to change the Treated_data name for google drive ?

  In the file called google_api in the function upload_files there is a parameters query which is set by default to Treated_data this can be changed.

Any other changes in the code can cause some unexpected side-effects. It is highly recommended to contact me via gitub (by opening an issue : (https://docs.github.com/en/issues/tracking-your-work-with-issues/creating-an-issue) or by creating a pull request if you want to add a feature or fix something in the code (https://docs.github.com/en/pull-requests/collaborating-with-pull-requests/proposing-changes-to-your-work-with-pull-requests/creating-a-pull-request). It is also possible to send me an email but I can not guarantee I will answer you.

7 Future developments

7.1 Executable file

An executable version will be deployed soon. It will allows people to run the code without having to install any python on their machine. Stay tuned !!

7.2 Other instruments

For now, only Picarro's files can be treated with ALWIC-tool but in the future it will be expanded to other instruments which are doing measurements of water isotopes in liquid injection mode.

7.3 Report

A pdf or html document to summarize the result of each processing could be considered but for now it is too much time consuming, I will think about it only if people ask for it.

7.4 Uncertainty

This is definitely something that should be implemented in ALWIC-tool. However this requires a lot of time which I will not have soon. If anyone is untested in doing it it will be a pleasure to help.

7.5 Drift correction

In agreement with Hans Christian Steen Larsen, we decided to not put a short-term drift correction because we don't think it is necessary especially with the new generation of Picarro which are more stable over time. Again if a lot of people ask for it, I will consider adding this feature.

8 Licence

9 Acknowledgment

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10 References

Manfred Gröning. *SICalib User Manual (Stable Isotope Calibration for routine δ-scale measurements)*. Terrestrial Environment Laboratory, International Atomic Energy Agency, Vienna, Austria, 2.16j edition, May 2018. `https://nucleus.iaea.org/sites/ReferenceMaterials/Shared%20Documents/Publications/TechnicalNotes/TELTechNote01_SICalibUserManual.pdf`.

Robert van Geldern and Johannes A.C. Barth. Optimization of instrument setup and post-run corrections for oxygen and hydrogen stable isotope measurements of water by isotope ratio infrared spectroscopy (iris). *Limnology and Oceanography: Methods*, 10(12):1024–1036, 2012. doi: https://doi.org/10.4319/lom.2012.10.1024. URL `https://aslopubs.onlinelibrary.wiley.com/doi/abs/10.4319/lom.2012.10.1024`.

Manfred Gröning. Improved water δ2h and δ18o calibration and calculation of measurement uncertainty using a simple software tool. *Rapid Communications in Mass Spectrometry*, 25(19):2711–2720, 2011. doi: https://doi.org/10.1002/rcm.5074. URL `https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/abs/10.1002/rcm.5074`.

Scipy Community. Scipy minimize tutorials. https://docs.scipy.org/doc//scipy/tutorial/optimize.html#constrained-minimization-of-multivariate-scalar-functions-mini a. Accessed on 15/12/2022.

Scipy Community. Scipy minimize documentation. https://docs.scipy.org/doc/scipy/reference/generated/scipy.optimize.minimize.html?highlight=minimize, b. Accessed on 15/12/2022.

Scipy Community. Scipy linear regression documentation. https://docs.scipy.org/doc/scipy-1.9.3/reference/generated/scipy.stats.linregress.html#scipy.stats.linregress, c. Accessed on 15/12/2022.

Wikipedia Contributors. p-value. https://en.wikipedia.org/wiki/P-value. Accessed on 31/01/2023.

Boaz Luz and Eugeni Barkan. The isotopic ratios 17o/16o and 18o/16o in molecular oxygen and their significance in biogeochemistry. *Geochimica et Cosmochimica Acta*, 69(5):1099–1110, 2005. ISSN 0016-7037. doi: https://doi.org/10.1016/j.gca.2004.09.001. URL https://www.sciencedirect.com/science/article/pii/S001670370400660X.