

Setup of the LIMS for Lasers Add-On tool

1. Introductory remarks

- This software tool is unsupported.
- The tool was developed in a Microsoft® Windows 10 64-bit environment with a 32-bit Office-365 version. Other versions may be functional but are not tested.
- Several functionalities use simplistic programming routines which are prone to unexpected behaviors or database inconsistencies. Note that all functions triggering a “write” action will write to the LIMS backend database immediately; there is no “undo” function.
- Whilst most of the bugs are eliminated, the software has not undergone professional and security testing.
- This software lacks entirely a sample registration facility. To add new samples and projects, use the LIMS9 or LIMS for Lasers frontends, supplied e.g., here: <https://nucleus.iaea.org/sites/ihn/Pages/Homepage.aspx> (IAEA-NUCLEUS user login required)
- This version is intended for offline use and cannot be intermingled with existing LIMS9 or LIMS for Lasers databases. The tool modifies data in the LIMS backend with the above constraints, and we caution users not to connect it to an established LIMS production backend used by others.
- The exercises and test datasets supplied were designed to work with this demo version.
- The tool computes $\Delta^{17}\text{O}$ in per meg (while in the manuscript, a ‰ annotation is used).

2. Setup

We recommend setting up the tool in a single folder. This folder needs to contain the following files:

- LIMS_Addon_FE.accdb (the interface frontend)
- LIMS_Addon_BE.accdb (the backend for additional data not storable in LIMS)
- LIMS Backend Database.accdb (the LIMS backend)
- LIMS_Addon_Config.xml (this file configures the file paths to the data tables)

The config file can be edited in Notepad or WordPad or similar applications able to read and edit plain text only. Do not use Office word processing software to edit file paths as needed. The config file must read like:

```
<?xml version="1.0" encoding="UTF-8"?>
<dataroot xmlns:od="urn:schemas-microsoft-com:officedata" generated="2022-08-
12T20:25:07">
  <tmpLocalSettings>
    <strTokenName>strLimsDbPath</strTokenName>
    <strTokenValue> c:\LIMS_Addon\LIMS Backend DB.accdb </strTokenValue>
  </tmpLocalSettings>
  <tmpLocalSettings>
    <strTokenName>strLimsAddonDbPath</strTokenName>
    <strTokenValue>c:\LIMS_Addon\LIMS_Addon_BE.accdb</strTokenValue>
  </tmpLocalSettings>
</dataroot>
```

If the file paths are not set correctly or connections are unavailable, LIMS-Addon will prompt you to specify the correct paths; otherwise, it will not start.

3. Parameterizations in addition to LIMS

3.1. “Service”

The LIMS-Addon uses the concept of a lab “service” to define the number of repetitions and acceptance criteria. For example, one service called “Dual isotope two assays” is defined as:

| Measurable | 1/#Assays* | Max. Unc. | Max. SD | σ_p |
|-----------------------|------------|-----------|---------|------------|
| $\delta^2\text{H}$ | 0.5 | | 1.6 | 0.8 |
| $\delta^{18}\text{O}$ | 0.5 | | 0.2 | 0.1 |

Note that the number of assays (*) is expressed for computational logic reasons as 1/n; hence two assays need to be annotated as 0.5; three such as 0.333 etc.

Services can also be defined including derivative parameters like deuterium excess or $\Delta^{17}\text{O}$:

| Measurable | 1/#Assays* | Max. Unc. | Max. SD | σ_p |
|-----------------------|------------|-----------|---------|------------|
| $\delta^2\text{H}$ | 0.33333 | 0.8 | 1.2 | 0.4 |
| $\delta^{18}\text{O}$ | 0.33333 | 0.09 | 0.06 | 0.03 |
| $\delta^{17}\text{O}$ | 0.33333 | 0.045 | 0.03 | 0.015 |
| d-excess | 0.33333 | 0.8 | 1.2 | 0.8 |
| $\Delta^{17}\text{O}$ | 0.33333 | | 20** | 10** |

(**) Note that the LIMS-Addon uses the per meg annotation.

The LIMS-Addon does not conduct a validation check of what has been entered.

You can define your “services” in the “Settings” menu using the GUI. Click “New service” to create a new one and set attributes through the GUI (Figure 1). The GUI window also allows associating instrument templates to a given workflow.

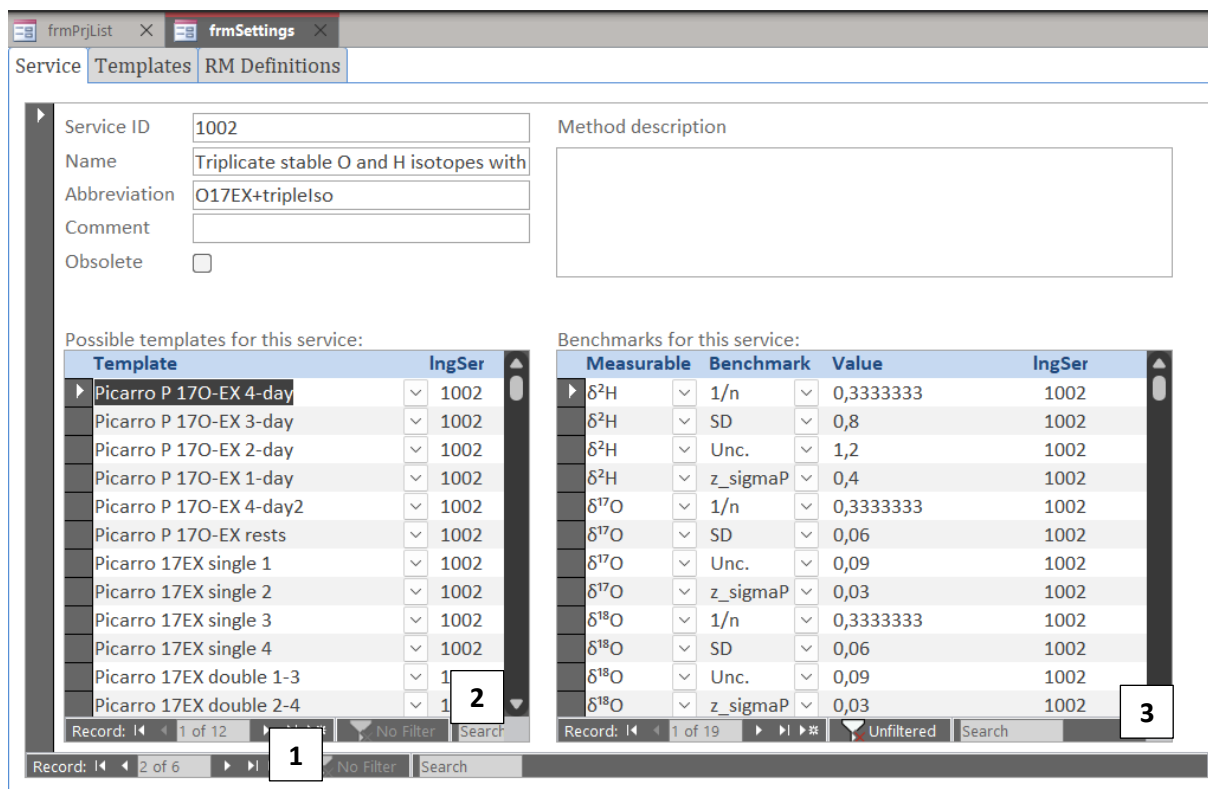


Figure 1: “Services” menu in settings: (1) click navigation buttons to go to next “service” in list; (2) go to new line (*) to link an additional template; (3) go to new line (*) to create a new benchmark criterion.

3.2. Advanced run template properties

Use the advanced run template property menu to specify features unavailable in LIMS:

- On the template level, you can specify to:
 - Randomize samples within a normalization subrange,
 - Randomize controls within a normalization subrange, and
 - How many injections by default a template uses.
- On the sample position level, you can define
 - Normalization subranges (from 1 to n; this is needed for the randomization commands)
 - The function of a sample (Unknown, control, enriched or depleted RM, drift control, linearity control or wash sample), and
 - The actual number of injections for this position. (For Picarro analysers less relevant, because this is defined in the autosampler setup.)

When creating a new template, it is mandatory to

1. Create a new template using LIMS
2. Populate its positions either in the LIMS GUI or by uploading them from a spreadsheet. Mind the page/slot order.
3. Change to the LIMS-Addon GUI and define the additional properties (see window below).

Note: When changing a template; this has to be done through LIMS first to maintain compatibility. The LIMS-Addon has no viewer capable of editing the LIMS backend tables themselves. In this case, perform the edits in LIMS, and in the third step, use either the “Clean up additional info” or “Delete all additional info”: The former deletes only superfluous positions. The latter deletes all additional

information, and you can set those instructions again. Figure 2 shows a screenshot of the GUI. The menu further allows associating the template with one or more services.

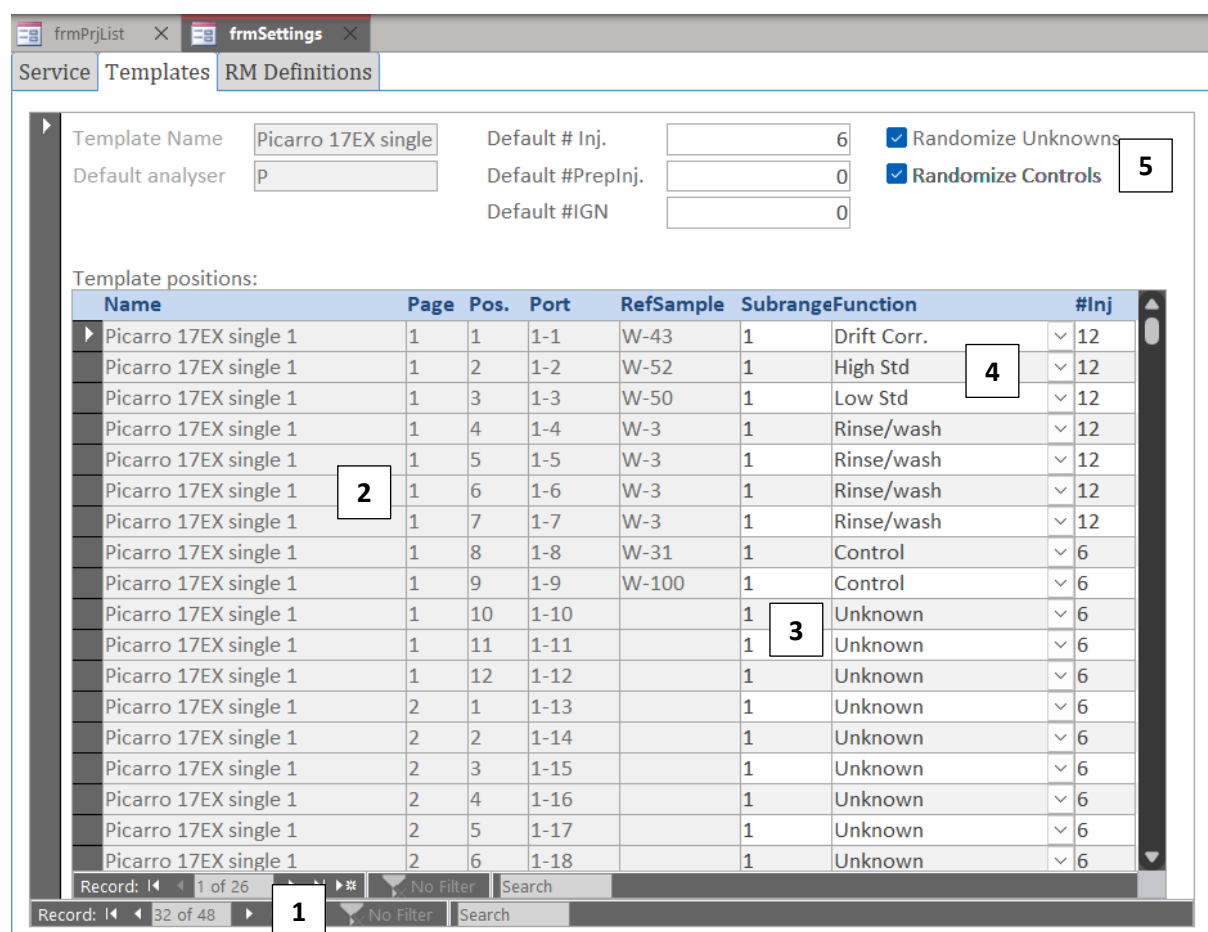


Figure 2: Additional template properties in the settings menu. (1) use navigation buttons to move to next template. (2) greyed-out properties are to be set in LIMS for Lasers. (3) specify subranges if your run design includes multiple. (4) specify sample function. (5) click checkboxes to randomize unknowns and/or controls across a subrange. Note that the sequence is governed by the autosampler control; hence wash positions 4-7 may not come to use.

3.3. RM definitions

The RM definitions module was foreseen to be able to assign revised values of the same RM to the unknowns analysed in the run concerned. This feature was intended with a view to a possibly changing RM definition for $\delta^{17}\text{O}$ because SLAP2 is provisional. In its current state, the LIMS-Addon fetches the most recent non-expired definition of an RM. It is possible to assign reference values to normalization anchors and controls, and also to δ values themselves but also to the derivative parameters deuterium excess and $\Delta^{17}\text{O}$. Figure 3 shows a screenshot of the GUI window.

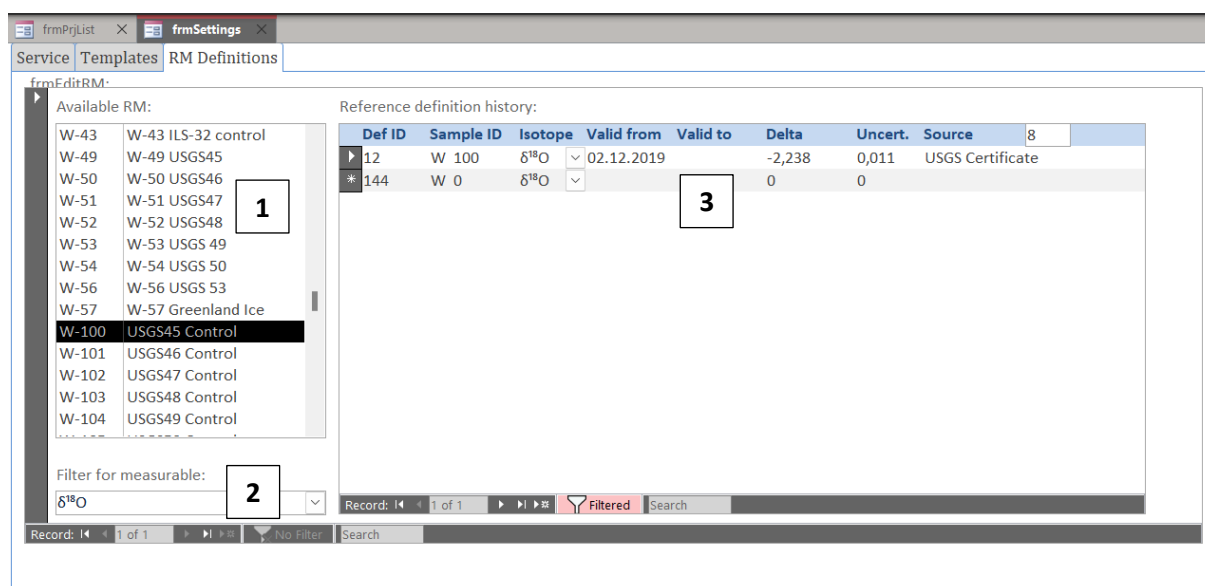


Figure 3: RM Definitions menu in the settings menu. (1) select RM to define, (2) filter for isotope or derivable, (3) type in line with (*) to add a new definition, or in the corresponding line to edit an existing one.

4. Handling projects and samples

4.1. Projects' list and filters

The main project window allows a user to filter for some LIMS core and expanded attributes. Text-based filter criteria always select for where the search string is contained. The filter menu also includes lookup-based selection criteria, such as filtering for a certain service, or a project status. After making selections, click on "apply filters". A double-click on a line in the project list opens the project properties (Figure 4).

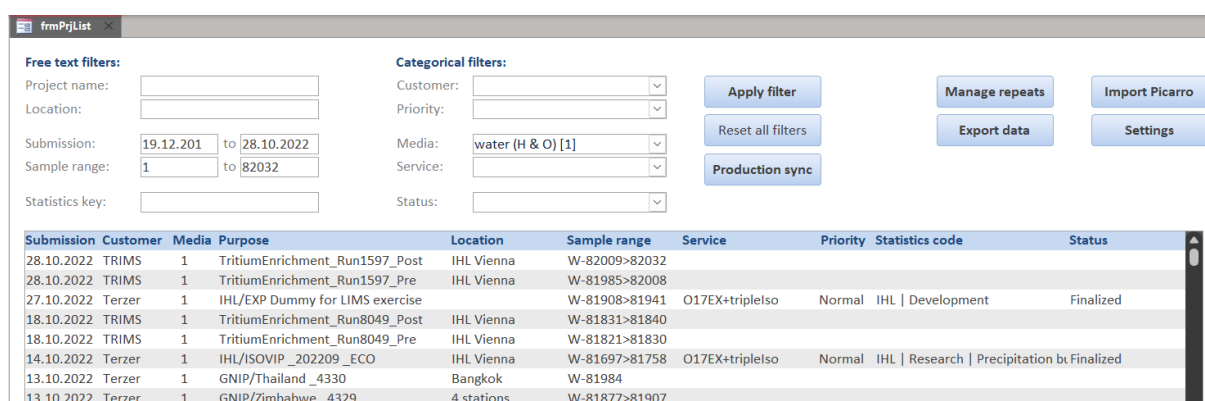


Figure 4: Project main menu

4.2. Additional project properties

An essential step in the LIMS-Addon work is to assign the additional project and sample attributes to an existing LIMS project (Figure 5). To initiate this process, click on the project dropdown list (it has only one entry here) and confirm the message following. This function is necessary to also zero the project and sample statuses. Once this is initiated, you can set the workflow, statistics, priority, etc.

settings. All sample and project statuses can be recalculated by pressing the “Validate statuses” button. (Note: At the current stage of LIMS-Addon, it is necessary to conduct this step manually.)

frmPrjList x frmProjectSampleMgr

Pick: IHL/ISOVIP_202209_ECO 4583

validate statuses with Results to LIMS

Project properties Analytical overview Sample properties Analyses & Results Reports Archive

LIMS project properties

Project ID: 4583
Analyses Range: 81697 > 81758
Customer ID: Terzer
Media Code: 1
Purpose: IHL/ISOVIP_202209_ECO
Location: IHL Vienna
Submission: 14.10.2022
Reported:
Date stamp: 14.10.2022 07:25:19
Comments:

LIMS-Addon project properties

Project ID: 4583
Service: O17EX+tripleIso
Priority: Normal
Statistics Code: IHL | Research | Precipitation bulk
Created at: 17.10.2022 07:18:06
Created by: TERZER-WASSMUTH Stefan
Modified at:
Modified by:

LIMS companion projects

Project ID: 4583
Main project:
Companion prj: 4584
Date stamp: 14.10.2022 07:25:32

Project and samples' status

| | intStatus | dtmCreateDate | strLastName |
|---|-----------|---------------|---------------------|
| ▶ | 4583 | Finalized | 03.11.2022 11:08:27 |
| | 4583 | In Progress | 19.10.2022 07:37:47 |
| | 4583 | Pending | 17.10.2022 07:18:06 |
| | 4583 | In Progress | 14.10.2022 07:31:51 |

| Status | Samples |
|--------|---------|
| 255 | 61 |
| 258 | 1 |

Figure 5: Additional project properties menu. (1) click on the project name in the drop-down list to create the additional properties' record. (2) set additional attributes. (3) sample statuses (255=finalized for 61 samples). (4) click “validate statuses” to recalculate the project's and samples' statuses. (5) status history of the project.

4.3. Sample properties: Status and Tags

Click on the “Samples” tab to edit samples' additional properties:

- You can cancel samples' analyses (Note: This action cannot be undone through the addon GUI.) – this sets their status to “Cancelled” and they will not be considered for further analysis. You can use the complex multi-select function (Ctrl+Shift+click) to select any combination of samples for this action.
- You can assign tags to samples, e.g., when samples from a common area span over several LIMS projects but you wish to query across them. It is possible to assign multiple tags to a sample, but also you can choose multiple samples (again through complex multi-select) for the same tag. Tags do not have a dictionary (lookup) in the background, but the dropdown selection allows to reuse tags used before (Figure 6).

The screenshot shows the 'frmProjectSampleMgr' application window. At the top, there's a 'Pick:' dropdown set to 'IHL/ISOVIP_202209_ECO' and a text field with '4583'. Buttons for 'validate statuses' and 'Push Results to LIMS' are on the right. Below is a tabbed interface with 'Project properties', 'Analytical overview', 'Sample properties', 'Analyses & Results', 'Reports', and 'Archive'. The 'Sample properties' tab is active, showing a form for sample details like 'str_FieldID', 'Date/Time Stamp', and various Delta and Comment fields. On the left, there are sections for 'Available samples' (a list of sample IDs and codes), 'Samples on templates' (a table with 'Template' and 'Rep.' columns), 'Samples in runs' (a table with 'Run/Instr.', 'SeqNo', and 'Tray/vial' columns), and 'Sample status' (a table with 'intStatus' and 'dtmCreateDate' columns). At the bottom, there are buttons for 'Cancel analysis' and 'Add tag', and a 'Sample Tags' section.

Available samples:

| | |
|---------|-------------|
| W-81697 | AM/2022/001 |
| W-81698 | AM/2022/002 |
| W-81699 | AM/2022/003 |
| W-81700 | AM/2022/004 |
| W-81701 | AM/2022/005 |
| W-81702 | AM/2022/006 |
| W-81703 | AM/2022/007 |

Samples on templates:

| Template | Rep. |
|----------|------|
| | |

Samples in runs:

| Run/Instr. | SeqNo | Tray/vial |
|------------|-------|-----------|
| ECW Q | 23 | 1-23 |
| CWMQCC Q | 12 | 1-33 |

Sample status:

| intStatus | dtmCreateDate |
|-------------|---------------------|
| Finalized | 20.10.2022 11:41:59 |
| Pending | 17.10.2022 07:18:06 |
| In Progress | 14.10.2022 07:31:50 |

Sample properties form:

str_FieldID: AM/2022/001
Date/Time Stamp: 14.10.2022 07:25:19
str_Other:
Low Delta:
High Delta:
Comment (Low Del):
Comment (High Del):
Low Procedure Cod:
High Procedure Cod:
Site Name:
State Code:
Site Number:
Country Code:
Field Office:
Latitude:
Phone #:
Longitude:
Project Chief:
Date/Time Collecti: 07.07.2022
ASR Field Sample ID:
Date/Time Collecti:
Elevation (feet):

Buttons: Cancel analysis, Add tag

Sample Tags:

Figure 6: Additional sample properties. (1) list of samples in the project, (2) sample's LIMS properties, (3) sample status history, (4) click to cancel (takes it out of "in progress", (5) click to add tags, (6) tags assigned to this sample.

4.4. Analyses and results; assigning samples to templates

The LIMS-Addon has an evaluation menu that works on the project and run level (i.e., the same menu serves at two different steps of the post-processing). The menu displays the current measurement results and benchmarks them against a service's performance criteria:

- The checkbox "only show pending" shows samples that are not yet finalized (be it for not meeting the repetition/uncertainty targets or for not yet having been set to finalized).
- The "cancel" buttons set all (selected) samples' status to "canceled".
- The "finalize" buttons set all (selected) samples' status to "finalized". The "finalize selected" button also allows overriding if the specifications are not met.
- The "repeat" buttons place all (selected) samples onto the template specified in the dropdown menu. Only those templates that are available for a given service are shown in the list.
- The lower part of the menu shows individual analyses. If you wish to (un-)ignore assays, click the pencil next to the "IGN" checkbox.
- See also chapter 5.7 for further information.

Project properties Analytical overview Sample properties Analyses & Results Reports Archive

validate statuses Push Results to LIMS

Pick: IHL/ISOVIP_202209_ECO 4583

LIMS project properties

Available samples: W-81697

| | |
|---------|-------------|
| W-81697 | AM/2022/001 |
| W-81698 | AM/2022/002 |
| W-81699 | AM/2022/003 |
| W-81700 | AM/2022/004 |
| W-81701 | AM/2022/005 |
| W-81702 | AM/2022/006 |
| W-81703 | AM/2022/007 |

here some sample and or project properties

Previous O18: -999 H2: -999 DEX: -999 Select template: Picarro 17EX single 1

sfrmResults:

| Measured | | | | Benchmark | | | |
|-------------------|---|------------|-------|-----------|---|------|------|
| Meas. | n | finalValue | Unc. | SD | n | Unc. | SD |
| δ ² H | 3 | -28,16 | 0,47 | 0,24 | 3 | 1,2 | 0,8 |
| δ ¹⁷ O | 3 | -2,42 | 0,013 | 0,021 | 3 | 0,09 | 0,06 |
| δ ¹⁸ O | 3 | -4,613 | 0,019 | 0,026 | 3 | 0,09 | 0,06 |
| d | 3 | 8,7 | 0,5 | 0,1 | 3 | 1,2 | 0,8 |
| Δ ¹⁷ O | 3 | 19 | 17 | 8 | 3 | | 20 |

☐ Only show pending

Cancel sel. Push to LIMS

Repeat sel. Repeat all

Finalize sel. Finalize all

Show:
☐ Analyses (classical LIMS style)
☒ Results (LIMS2020 style)

Analyses: δ²H ☒ Ignore all measurables Args: prj/4583/

| Analysis Date | Analysis | Peak | Error | IGN | penult. δ | blank Corr. | Hourly Corr. | Exp.Coeff. | Add.Corr. | final δ |
|---------------------|----------|------|-------|--------------------------|-----------|-------------|--------------|------------|-----------|-----------------|
| 15.10.2022 03:41:34 | Q-13623 | | | <input type="checkbox"/> | | | | | | -28,014 ± 0,817 |
| 16.10.2022 21:24:01 | Q-13665 | | | <input type="checkbox"/> | | | | | | -28,029 ± 0,817 |
| 18.10.2022 12:09:21 | Q-13700 | | | <input type="checkbox"/> | | | | | | -28,436 ± 0,815 |

Figure 7: Results evaluation window.

5. Importing CRDS analyses

5.1. Step 1: Import dialogue box

Import an instrument run

Instrument and file

Instrument: P - Picarro 2140 Paula

File name: D:\OneDrive\Stable Isotope Analysis\Picarro\Picarro P 202209-

☒ fix leading ☒ Treat consecutive standards as one

DIW ☐ Load list comes from LTG

File format: Picarro triple isotope

Handling staff and comments

Preparation: A.N. Employee ☒ and all following steps

Analysis: A.N. Employee

Post-process.: A.N. Employee

Comments:

Cancel Import

Figure 8: Picarro data import main screen.

In this dialogue, the user must specify:

- the file path, instruments, the user in charge of the post-processing and
- the file format (Picarro dual- or triple isotope),
- and whether consecutive standard vials are treated as one sequence – the latter ensures compatibility with LIMS for Lasers which requires two vials per standard at the usual number of injections, while LIMS-Addon uses one single vial each with twice the number of injections)

5.2. Step 2: Define normalization subranges

Display data

☐ All injections

☒ Means per analysis

Unc Method

new method

Here maybe a concentration chart

Normalization blocks:

| Block | From | To | Hi STD | LowSTD |
|-------|------|----|-------------|-------------|
| 1 | 1 | 22 | W-52 USGS48 | W-50 USGS46 |
| 2 | 23 | 45 | W-52 USGS48 | W-50 USGS46 |

Reset range markers

Cancel

Next

Imported data:

| Line | BlockSeq | Port | Inj | Analysis | Sample | Sample Name | H ₂ O | δ ¹⁷ O | δ ¹⁸ O | δ ² H | |
|------|----------|------|---------|----------|------------------|-------------|------------------|-------------------|-------------------|------------------|--|
| 2 | 23 | 1-02 | P-31780 | W-52 | W-52 USGS48 | 21 350 ± 12 | 0,954 ± 0,031 | -0,781 ± 0,055 | -1,99 ± 1,21 | | |
| 2 | 24 | 1-03 | P-31781 | W-50 | W-50 USGS46 | 21 371 ± 21 | -14,417 ± 0,198 | -29,403 ± 0,367 | -240,07 ± 6,24 | | |
| 2 | 25 | 1-28 | P-31782 | W-1 | --- | ± | ± | ± | ± | | |
| 2 | 26 | 1-29 | P-31783 | W-81941 | Tap Water Sample | 21 353 ± 39 | -3,995 ± 0,136 | -10,035 ± 0,256 | -81,35 ± 3,81 | | |
| 2 | 27 | 1-30 | P-31784 | W-81913 | OH-30 A | 21 430 ± 59 | -4,049 ± 0,017 | -10,140 ± 0,014 | -80,29 ± 0,10 | | |
| 2 | 28 | 1-31 | P-31785 | W-81939 | WICO 04 C | 21 390 ± 43 | 2,746 ± 0,115 | 2,657 ± 0,215 | 2,45 ± 2,87 | | |
| 2 | 29 | 1-32 | P-31786 | W-81911 | OH-28 A | 21 346 ± 90 | -3,779 ± 0,111 | -6,568 ± 0,158 | -48,55 ± 1,73 | | |
| 2 | 30 | 1-33 | P-31787 | W-81910 | OH-27 A | 21 350 ± 42 | -11,639 ± 0,141 | -24,192 ± 0,307 | -192,95 ± 4,94 | | |
| 2 | 31 | 1-34 | P-31788 | W-81917 | WICO 04 A | 21 384 ± 27 | 2,696 ± 0,237 | 2,536 ± 0,446 | 0,11 ± 6,58 | | |
| 2 | 32 | 1-35 | P-31789 | W-81927 | WICO 03 B | 21 404 ± 67 | -9,967 ± 0,193 | -21,141 ± 0,376 | -169,72 ± 5,82 | | |

Figure 9: Step 1: Definition of normalization subranges and specification of high and low RMs.

- The user can toggle between all injections displayed, or only means (note – means of the raw data)
- By clicking on the ➔ button, a new normalization subrange is established, going from the analysis clicked on to the end, whereby clicking on a later sample redefines the end of the previous subrange. In the example above, we clicked positions 1 (getting first 1-68), then 24 (creating 1-23, 24-68) and then 46 (getting 1-23, 24-45 and 46-68).
- In case of a mistake, the whole range marking is nullified by clicking the “Reset range markers” button and starting over.
- For each subrange, the high and the low standards are chosen, in our case USGS48 as high standard and USGS46 as low standard.
- The user can ignore individual injections or a whole sample by clicking the “ignore” checkbox to the right of the δ²H column.
- When done with settings, click “next” to move to the next step: Memory correction.

5.3. Step 3: Memory correction

This current version supports one memory correction method, which is a modified version of the van Geldern and Barth (2011) calculations but ignoring the first injection.

Memory correction type
sVGB-1

Memory coefficients for block: 1

| Inj. | mc $\delta^{17}\text{O}$ | mc $\delta^{18}\text{O}$ | mc $\delta^2\text{H}$ |
|------|--------------------------|--------------------------|-----------------------|
| 1 | 0,9567 \pm 0,0247 | 0,9552 \pm 0,0143 | 0,9089 \pm 0,0042 |
| 2 | 0,9903 \pm 0,0248 | 0,9890 \pm 0,0139 | 0,9749 \pm 0,0044 |
| 3 | 0,9950 \pm 0,0247 | 0,9943 \pm 0,0142 | 0,9865 \pm 0,0040 |
| 4 | 0,9935 \pm 0,0233 | 0,9948 \pm 0,0134 | 0,9911 \pm 0,0038 |
| 5 | 0,9975 \pm 0,0240 | 0,9968 \pm 0,0136 | 0,9937 \pm 0,0037 |
| 6 | 0,9977 \pm 0,0242 | 0,9976 \pm 0,0136 | 0,9951 \pm 0,0035 |
| 7 | 0,9994 \pm 0,0242 | 0,9987 \pm 0,0134 | 0,9966 \pm 0,0035 |
| 8 | 0,9986 \pm 0,0244 | 0,9985 \pm 0,0138 | 0,9975 \pm 0,0035 |
| 9 | 0,9994 \pm 0,0246 | 0,9995 \pm 0,0133 | 0,9980 \pm 0,0034 |

Here maybe a memory curve chart

compute memory

Drift Corr

sfrmMemCorrData:

| Block | Pos | Line | Analysis | Inj | W-ID | IG | Sample Name | memCorr $\delta^{17}\text{O}$ | memCorr $\delta^{18}\text{O}$ | memCorr $\delta^2\text{H}$ |
|-------|-----|------|----------|-----|------|-------------------------------------|-------------|-------------------------------|-------------------------------|----------------------------|
| 1 | 1 | 1 | 31758 | 1 | W-3 | <input checked="" type="checkbox"/> | DIW Wash | \pm | \pm | \pm |
| 1 | 1 | 2 | 31758 | 2 | W-3 | <input type="checkbox"/> | DIW Wash | -3,469 \pm 0,193 | -8,975 \pm 0,183 | -79,06 \pm 0,34 |
| 1 | 1 | 3 | 31758 | 3 | W-3 | <input type="checkbox"/> | DIW Wash | -3,358 \pm 0,195 | -8,788 \pm 0,179 | -77,17 \pm 0,33 |
| 1 | 1 | 4 | 31758 | 4 | W-3 | <input type="checkbox"/> | DIW Wash | -3,321 \pm 0,172 | -8,756 \pm 0,186 | -76,75 \pm 0,33 |
| 1 | 1 | 5 | 31758 | 5 | W-3 | <input type="checkbox"/> | DIW Wash | -3,368 \pm 0,181 | -8,807 \pm 0,185 | -76,57 \pm 0,33 |
| 1 | 1 | 6 | 31758 | 6 | W-3 | <input type="checkbox"/> | DIW Wash | -3,343 \pm 0,173 | -8,766 \pm 0,186 | -76,45 \pm 0,35 |
| 1 | 1 | 7 | 31758 | 7 | W-3 | <input type="checkbox"/> | DIW Wash | -3,381 \pm 0,191 | -8,801 \pm 0,198 | -76,35 \pm 0,37 |
| 1 | 1 | 8 | 31758 | 8 | W-3 | <input type="checkbox"/> | DIW Wash | -3,343 \pm 0,186 | -8,755 \pm 0,175 | -76,39 \pm 0,30 |
| 1 | 1 | 9 | 31758 | 9 | W-3 | <input type="checkbox"/> | DIW Wash | -3,327 \pm 0,189 | -8,766 \pm 0,204 | -76,34 \pm 0,34 |
| 1 | 1 | 10 | 31758 | 10 | W-3 | <input type="checkbox"/> | DIW Wash | -3,345 \pm 0,201 | -8,771 \pm 0,195 | -76,26 \pm 0,36 |
| 1 | 1 | 11 | 31758 | 11 | W-3 | <input type="checkbox"/> | DIW Wash | -3,359 \pm 0,185 | -8,773 \pm 0,175 | -76,22 \pm 0,37 |
| 1 | 1 | 12 | 31758 | 12 | W-3 | <input type="checkbox"/> | DIW Wash | -3,323 \pm 0,197 | -8,763 \pm 0,199 | -76,27 \pm 0,33 |
| 1 | 1 | 13 | 31758 | 13 | W-3 | <input type="checkbox"/> | DIW Wash | -3,345 \pm 0,189 | -8,760 \pm 0,189 | -76,13 \pm 0,34 |
| 1 | 2 | 14 | 31759 | 1 | W-52 | <input checked="" type="checkbox"/> | W-52 USGS48 | 0,937 \pm 0,176 | -0,762 \pm 0,172 | -1,88 \pm 0,39 |
| 1 | 2 | 15 | 31759 | 2 | W-52 | <input type="checkbox"/> | W-52 USGS48 | 0,975 \pm 0,194 | -0,703 \pm 0,190 | -1,29 \pm 0,36 |

Record: 1 of 307 No Filter Search

Figure 10: Memory coefficient determination and run computation.

- For each block, the memory coefficients from high to low standard are calculated.
- Click “compute memory” to apply the memory coefficients and proceed to the drift correction menu.

5.4. Step 4: Drift correction

While both van Geldern and Barth (2011) and Pierchala et al. (2019) recommend a drift correction based on interspersed samples of deionized water, this step was skipped in the processing after ca. 3 months. Nevertheless, the LIMS-Addon program can do a drift correction on high and low standards, on dedicated drift samples or no correction.

Step 4: Instrumental drift correction

Select drift correction

Drift corrections can be performed on the normalization anchors (High and Low STDs) or dedicated drift samples. Choose "no correction" to skip this step. You can select for each isotope and normalization block, or use the "use for all" option to apply one setting for all.

Use for all:

W-52 USGS48

| Block | fr./to | Drift sample | $\delta^{17}\text{O}$ | Slope | Slp.Err. | R ² | Drift sample | $\delta^{18}\text{O}$ | Slope | Slp.Err. | R ² | Drift sample | $\delta^2\text{H}$ | Slope | Slp.Err. | R ² |
|-------|--------|--------------|-----------------------|----------|----------|----------------|--------------|-----------------------|---------|----------|----------------|--------------|--------------------|---------|----------|----------------|
| 1 | 1 | 22 | W-52 USGS48 | 0,00001 | 0,00000 | 1,000 | W-52 USGS48 | -0,00015 | 0,00000 | 1,000 | | W-52 USGS48 | -0,00083 | 0,00000 | 1,000 | |
| 2 | 23 | 45 | W-52 USGS48 | -0,00001 | 0,00000 | 1,000 | W-52 USGS48 | 0,00002 | 0,00000 | 1,000 | | W-52 USGS48 | 0,00083 | 0,00000 | 1,000 | |

Show drift-corrected data

☐ Individual injections ☒ Averaged data

| Block | Seq. | Line | Analysis ID | Inj | Sample ID | Sample Name | $\delta^{17}\text{O}$ | u $\delta^{17}\text{O}$ | $\delta^{18}\text{O}$ | u $\delta^{18}\text{O}$ | $\delta^2\text{H}$ | u $\delta^2\text{H}$ |
|-------|------|------|-------------|-----|-----------|----------------|-----------------------|-------------------------|-----------------------|-------------------------|--------------------|----------------------|
| 1 | 1 | 7,5 | 31758 | 12 | W-3 | DIW Wash | -3,357 | 0,040 | -8,789 | 0,061 | -76,66 | 0,81 |
| 1 | 2 | 20 | 31759 | 11 | W-52 | W-52 USGS48 | 0,964 | 0,016 | -0,735 | 0,018 | -1,27 | 0,07 |
| 1 | 3 | 32 | 31760 | 11 | W-50 | W-50 USGS46 | -14,521 | 0,000 | -29,592 | 0,001 | -243,33 | 0,04 |
| 1 | 4 | 41 | 31761 | 5 | W-81932 | OH-27 C | -11,765 | 0,015 | -24,449 | 0,011 | -196,89 | 0,07 |
| 1 | 5 | 47 | 31762 | 5 | W-81925 | WICO 01 B | -3,848 | 0,013 | -9,731 | 0,010 | -79,82 | 0,05 |
| 1 | 6 | 53 | 31763 | 5 | W-81936 | WICO 01 C | -3,855 | 0,019 | -9,745 | 0,022 | -80,01 | 0,12 |
| 1 | 7 | 59 | 31764 | 5 | W-81940 | WICO 07 C | -3,368 | 0,015 | 7,443 | 0,018 | 57,75 | 0,05 |
| 1 | 8 | 65 | 31765 | 5 | W-81923 | OH-29 B | 1,590 | 0,013 | 0,473 | 0,007 | 2,55 | 0,14 |
| 1 | 9 | 71 | 31766 | 5 | W-100 | USGS45 Control | 0,938 | 0,009 | -0,739 | 0,013 | -9,69 | 0,07 |
| 1 | 10 | 77 | 31767 | 5 | W-81908 | OH-25 A | -7,256 | 0,026 | -16,090 | 0,020 | -132,75 | 0,02 |

Cancel

Next: VSMOW-SLAP normalization

Figure 11: Drift correction

- By using the combo box on top, one drift sample can be specified for the whole run and all isotopes.
- For finer details, any subrange's drift can be set individually.
- If there is no closing bracket (or adjacent opening bracket), no drift can be calculated for a subrange.
- LIMS-Addon displays "function samples" in different colours: standards in blue, controls in green, drift samples in purple.
- After making all settings, click "VSMOW-SLAP normalization" to complete the last step of the post-processing.

5.5. Step 5: Normalization to the VSMOW-SLAP range

Step 5: Normalization to VSMOW-SLAP

Normalize:

☒ ... for one block
 ☐ ... over adjacent brackets

Choose whether to use only the standards in the block or average them with those of the following block. The table shows the normalization slopes and intercepts for all three isotopes:

| Rng | FromTo | Standards | | $\delta^{17}\text{O}$ | | | | $\delta^{18}\text{O}$ | | | | $\delta^2\text{H}$ | | | |
|-----|--------|-----------|------|-----------------------|--------|-----------|--------|-----------------------|--------|-----------|--------|--------------------|--------|-----------|--------|
| | | High | Low | Slope | uSlope | Intercept | uInt. | Slope | uSlope | Intercept | uInt. | Slope | uSlope | Intercept | uInt. |
| 1 | 1 22 | W-52 | W-50 | 0,9493 | 0,0053 | -2,0646 | 0,0969 | 0,9556 | 0,0030 | -1,5217 | 0,1104 | 0,9659 | 0,0034 | -0,7653 | 1,0987 |
| 2 | 23 45 | W-52 | W-50 | 0,9500 | 0,0046 | -2,0694 | 0,0896 | 0,9568 | 0,0027 | -1,4950 | 0,1043 | 0,9666 | 0,0034 | -0,5110 | 1,0979 |

Cancel

Run QA/QC

Show data

☐ Individual injections
 ☒ Means of analyses

| Block | Seq. | Line | Analysis ID | Inj | Sample ID | Sample Name | $\delta^{17}\text{O}$ | u $\delta^{17}\text{O}$ | $\delta^{18}\text{O}$ | u $\delta^{18}\text{O}$ | $\delta^2\text{H}$ | u $\delta^2\text{H}$ | DEX | u DEX | O17-EX | u O17-EX |
|-------|------|------|-------------|-----|-----------|----------------|-----------------------|-------------------------|-----------------------|-------------------------|--------------------|----------------------|------|-------|--------|----------|
| 1 | 1 | 7,5 | 31758 | 12 | W-3 | DIW Wash | -5,251 | 0,016 | -9,921 | 0,023 | -74,81 | 0,56 | 4,6 | 0,6 | -1 | 20 |
| 1 | 2 | 20 | 31759 | 11 | W-52 | W-52 USGS48 | -1,150 | 0,022 | -2,224 | 0,032 | -2,00 | 0,81 | 15,8 | 0,8 | 25 | 28 |
| 1 | 3 | 32 | 31760 | 11 | W-50 | W-50 USGS46 | -15,850 | 0,005 | -29,800 | 0,005 | -235,79 | 0,02 | 2,6 | 0,0 | -3 | 6 |
| 1 | 4 | 41 | 31761 | 5 | W-81932 | OH-27 C | -13,233 | 0,006 | -24,886 | 0,008 | -190,93 | 0,18 | 8,2 | 0,2 | -15 | 8 |
| 1 | 5 | 47 | 31762 | 5 | W-81925 | WICO 01 B | -5,717 | 0,018 | -10,820 | 0,025 | -77,86 | 0,62 | 8,7 | 0,7 | 11 | 22 |
| 1 | 6 | 53 | 31763 | 5 | W-81936 | WICO 01 C | -5,724 | 0,018 | -10,834 | 0,025 | -78,04 | 0,62 | 8,6 | 0,7 | 11 | 22 |
| 1 | 7 | 59 | 31764 | 5 | W-81940 | WICO 07 C | -5,262 | 0,018 | 5,591 | 0,047 | 55,01 | 1,14 | 10,3 | 1,2 | -8220 | 31 |
| 1 | 8 | 65 | 31765 | 5 | W-81923 | OH-29 B | -0,555 | 0,027 | -1,070 | 0,038 | 1,70 | 0,93 | 10,3 | 1,0 | 10 | 33 |
| 1 | 9 | 71 | 31766 | 5 | W-100 | USGS45 Control | -1,174 | 0,025 | -2,228 | 0,037 | -10,13 | 0,89 | 7,7 | 0,9 | 3 | 32 |
| 1 | 10 | 77 | 31767 | 5 | W-81908 | OH-25 A | -8,953 | 0,012 | -16,898 | 0,018 | -128,99 | 0,42 | 6,2 | 0,4 | 5 | 15 |
| 1 | 11 | 83 | 31768 | 5 | W-31 | W-31 Control | -4,545 | 0,020 | -8,623 | 0,028 | -60,63 | 0,69 | 8,4 | 0,7 | 17 | 25 |

Figure 12: VSMOW-SLAP normalization

- The user has the option to normalize based on the starting bracket only (default) or using opening and closing bracket (mathematically a mean of the two).
- LIMS-Addon displays the normalization slopes and intercepts for each subrange in the top window.
- In the bottom window, the normalized data are displayed (with the same colour coding as shown before).
- By clicking “Run QA/QC” the user moves to the final step of the run evaluation.

5.6. Step 6: Run QA/QC

In this window, the user can evaluate subranges based on the controls included. LIMS-AddOn uses z- and ζ -scores against the controls' known values to validate the goodness of the run. For $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ analysis, the thresholds specified in the service (cf. chapter 3.1) were used.

List of controls in this run:

| Block | Analysis | Sample ID & Name | Bias | | | | | z-Score | | | | ζ -Score | | | |
|-------|----------|----------------------|-----------------------|-----------------------|--------------------|-----|-----------------------|-----------------------|-----------------------|--------------------|-----------------------|-----------------------|-----------------------|--------------------|-----------------------|
| | | | $\delta^{17}\text{O}$ | $\delta^{18}\text{O}$ | $\delta^2\text{H}$ | DEX | $\Delta^{17}\text{O}$ | $\delta^{17}\text{O}$ | $\delta^{18}\text{O}$ | $\delta^2\text{H}$ | $\Delta^{17}\text{O}$ | $\delta^{17}\text{O}$ | $\delta^{18}\text{O}$ | $\delta^2\text{H}$ | $\Delta^{17}\text{O}$ |
| 1 | P-31766 | W-100 USGS45 Control | 0,016 | 0,010 | 0,17 | 0,1 | -9 | 0,53 | 0,34 | 0,43 | -0,91 | 0,41 | 0,26 | 0,18 | -0,28 |
| 1 | P-31768 | W-31 W-31 Control | 0,015 | 0,027 | 0,47 | 0,3 | 2 | 0,50 | 0,92 | 1,18 | 0,22 | 0,54 | 0,67 | 0,45 | 0,08 |
| 2 | P-31790 | W-31 W-31 Control | 0,013 | 0,030 | 0,27 | 0,0 | -2 | 0,42 | 1,01 | 0,68 | -0,18 | 0,45 | 0,74 | 0,26 | -0,07 |
| 2 | P-31799 | W-100 USGS45 Control | 0,039 | 0,026 | 0,25 | 0,0 | 6 | 1,30 | 0,85 | 0,63 | 0,57 | 0,99 | 0,67 | 0,26 | 0,18 |

Control summary per normalization block and acceptance:

| Block | Pos.Range | Acc. | mean z Score | | | | mean ζ Score | | | | red flags | | | | Acceptance? | |
|-------|-----------|-------------------------------------|-----------------------|-----------------------|--------------------|-----------------------|------------------------|-----------------------|--------------------|-----------------------|-----------------------|-----------------------|--------------------|-----------------------|----------------|-------------------------------------|
| | | | $\delta^{17}\text{O}$ | $\delta^{18}\text{O}$ | $\delta^2\text{H}$ | $\Delta^{17}\text{O}$ | $\delta^{17}\text{O}$ | $\delta^{18}\text{O}$ | $\delta^2\text{H}$ | $\Delta^{17}\text{O}$ | $\delta^{17}\text{O}$ | $\delta^{18}\text{O}$ | $\delta^2\text{H}$ | $\Delta^{17}\text{O}$ | Recommendation | |
| 1 | 1 > 22 | <input checked="" type="checkbox"/> | 0,52 | 0,63 | 0,81 | 0,57 | 0,47 | 0,46 | 0,31 | 0,18 | 0 | 0 | 0 | 0 | Accept | <input checked="" type="checkbox"/> |
| 2 | 23 > 45 | <input checked="" type="checkbox"/> | 0,86 | 0,93 | 0,66 | 0,37 | 0,72 | 0,70 | 0,26 | 0,12 | 0 | 0 | 0 | 0 | Accept | <input checked="" type="checkbox"/> |

Cancel

Save run

Figure 13: QA/QC check

- All acceptable values are in green, questionable in yellow and unacceptable controls are in orange.
- Based on the z and ζ -scores, LIMS-AddOn determines a recommendation to accept or reject a subrange and its samples. If no control is included, a subrange is rejected by default.
- The user can manually override acceptance (e.g., if it becomes clear that the control vial itself has been compromised); however, there is also the option to un-ignore individual analyses in step 7. This is however a practice to be used with extreme caution!

5.7. Step 7/8: Evaluate the results

LIMS-Addon allows evaluation of all samples of a run, but also the samples' project.

Available samples:

| | |
|---------|-----------|
| W-81910 | OH-27 A |
| W-81911 | OH-28 A |
| W-81912 | OH-29 A |
| W-81913 | OH-30 A |
| W-81914 | WICO 01 A |
| W-81915 | WICO 02 A |
| W-81916 | WICO 03 A |

Show:

☐ Analyses (classical LIMS style)

☒ Results (LIMS2020 style)

here some sample and or project properties

Previous O18: H2: DEX: Select template:

sfrmResults:

| Measured | | | | Benchmark | | | |
|-----------------------|---|------------|-------|-----------|---|------|------|
| Meas. | n | finalValue | Unc. | SD | n | Unc. | SD |
| $\delta^2\text{H}$ | 3 | -77,99 | 0,36 | 0,25 | 3 | 1,2 | 0,8 |
| $\delta^{17}\text{O}$ | 3 | -5,928 | 0,01 | 0,016 | 3 | 0,09 | 0,06 |
| $\delta^{18}\text{O}$ | 3 | -11,196 | 0,015 | 0,009 | 3 | 0,09 | 0,06 |
| d | 3 | 11,6 | 0,4 | 0,2 | 3 | 1,2 | 0,8 |
| $\Delta^{17}\text{O}$ | 3 | 0 | 13 | 18 | 3 | | 20 |

☐ Only show pending

Cancel sel. Push to LIMS

Repeat sel. Repeat all

Finalize sel. Finalize all

Analyses: ☒ Ignore all measurables

Args

| Analysis Date | Analysis | Peak | Error | IGN | penult. δ | blank Corr. | Hourly Corr. | Exp. Coef. | Add. Corr. | final δ |
|---------------------|----------|------|-------|--------------------------|-----------|-------------|--------------|------------|------------|-----------------|
| 29.10.2022 03:05:52 | Q-13916 | | | <input type="checkbox"/> | | | | | | -77,84 ± 0,624 |
| 29.10.2022 17:35:37 | P-31784 | | | <input type="checkbox"/> | | | | | | -78,274 ± 0,619 |
| 31.10.2022 01:14:23 | Q-13962 | | | <input type="checkbox"/> | | | | | | -77,858 ± 0,621 |

Record: 14 1 of 3 Filtered Search

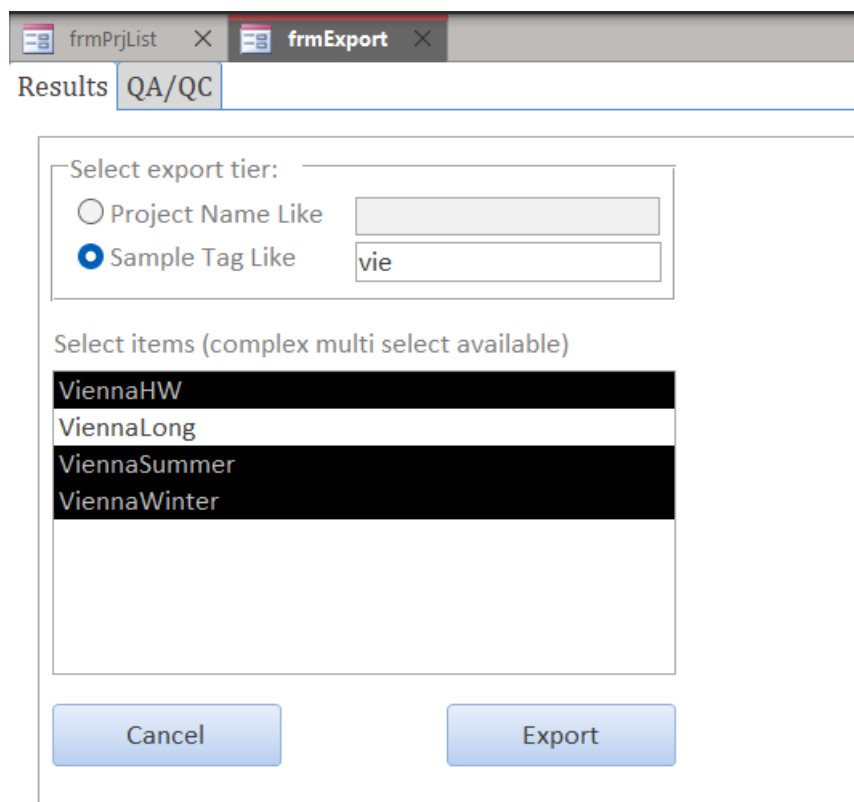
Figure 14: Analysis results evaluation per sample

- In the top left list box, the user selects a sample of the run or project.
- The centre top window shows the current and previous (from LIMS) measurements.
 - Results are shown against the benchmark previously specified for an “analytical service” and are red when violating the benchmark and green if passing.
 - For example, the sample shown meets the $\delta^{17}\text{O}$ criteria for propagated uncertainty ($0.082 < 0.09$), repeatability ($\text{SD } 0.021 < 0.06$) but fails the number of repetitions ($2 \text{ done} < 3 \text{ needed}$). Had the requirements been to repeat only twice, it would have passed.
- In the bottom window, the analyses are displayed. The user can ignore analyses manually – it is best to keep the “ignore all measurables” option checked, so that ignoring one measured parameter ignores all.
- In the upper right area, actions can be set:
 - A Picarro template for repeats can be selected.
 - The samples displayed can be constrained to those pending.
 - The user can cancel a sample (e.g., if the repeated run is far off the initial value)
 - The user can book the selected sample (or all in the samples' list) onto a template to repeat it.
 - The user can set all samples matching the benchmark criteria to “finalized”, or only one (setting one individual sample also allows to override if the criteria are not met).

6. Export functions

6.1. Export results

The export menu allows the user to export data by LIMS project, or by tag across projects, to a Microsoft® Excel spreadsheet. You can access it from the main screen by clicking the “export” button. The LIMS-Addon software will prompt you for a filename /-location.



The screenshot shows the LIMS-Addon software interface. At the top, there are two tabs: 'frmPrjList' and 'frmExport'. The 'frmExport' tab is active. Below the tabs, there is a 'Results' section with a dropdown menu showing 'QA/QC'. Below this, there is a 'Select export tier:' section with two radio buttons: 'Project Name Like' and 'Sample Tag Like'. The 'Sample Tag Like' radio button is selected. To the right of the radio buttons is a text input field containing the text 'vie'. Below this, there is a 'Select items (complex multi select available)' section. This section contains a list of tags: 'ViennaHW', 'ViennaLong', 'ViennaSummer', and 'ViennaWinter'. The tags 'ViennaHW', 'ViennaSummer', and 'ViennaWinter' are highlighted in black, indicating they are selected. At the bottom of the dialog, there are two buttons: 'Cancel' and 'Export'.

Figure 15: Available tags filtered for those containing “Vie”, then using Ctrl+Shift+Click to select all samples with the tags “ViennaHW”, “ViennaSummer”, “ViennaWinter” for export.

6.2. Export QA/QC

The QA/QC menu exports the quality control record (separated by control sample ID, analysis date, and instrument) to a Microsoft® Excel spreadsheet. The LIMS-Addon software will prompt you for a filename /-location (Figure 16).

Select control data for QA/QC:

Use extended multi select for list boxes

Controls:

| | |
|-------|----------------|
| W-6 | GISP control |
| W-11 | GRESF |
| W-31 | W-31 Control |
| W-40 | W-40 VOSTOK |
| W-100 | USGS45 Control |
| W-101 | USGS46 Control |
| W-102 | USGS47 Control |
| W-103 | USGS48 Control |
| W-104 | USGS49 Control |
| W-105 | USGS50 Control |
| W-106 | USGS53 Control |

Isotope:

| | |
|------|-----------------------|
| 2 | $\delta^2\text{H}$ |
| 7 | $\delta^{17}\text{O}$ |
| 8 | $\delta^{18}\text{O}$ |
| 1001 | d |

Date from

23.01.2020

Date to

03.11.2022

Include ignored

☐

Instrument:

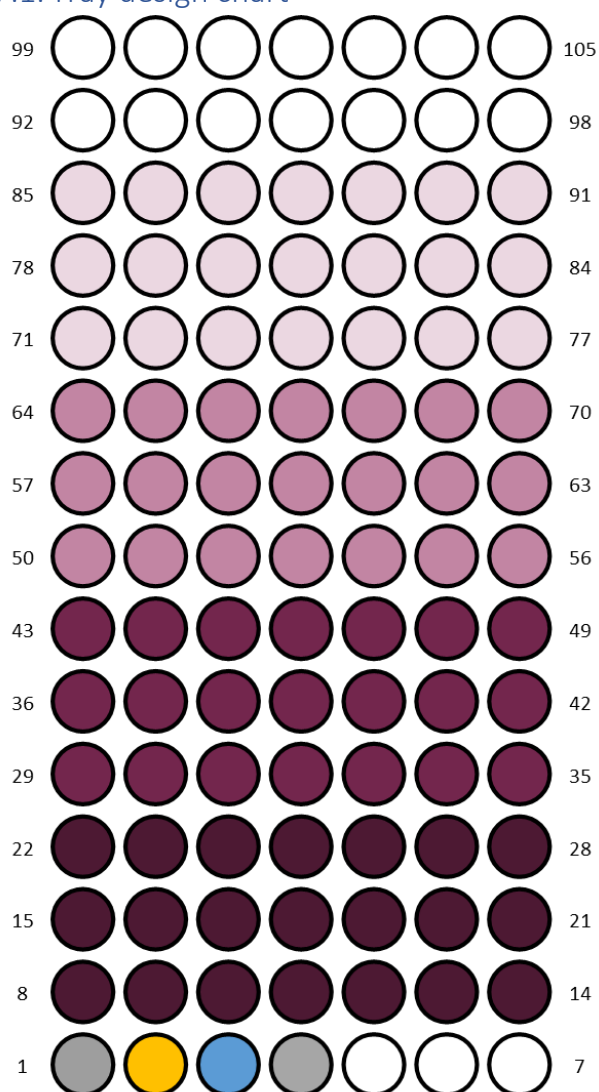
| | |
|---|--------------------|
| N | LGR V4 |
| P | Picarro 2140 |
| Q | Picarro 2130i+ Que |
| R | Radiocarbon |

[Export](#)

Figure 16: Export facility for QA/QC data. Example exports all available results for W-31 $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ results measured on Picarro analyzers P and Q.

7. Additional figures

7.1. Tray design chart



| | |
|---------|--------------------------|
| Rinse | Samples+Controls Block 1 |
| Hi Std | Samples+Controls Block 2 |
| Low Std | Samples+Controls Block 3 |
| Empty | Samples+Controls Block 4 |

Figure 17: Liquid autosampler tray layout sequence for multi-day triple-isotope runs. The rinse sample at position 4 is optional.

7.2. STD06 QA/QC charts

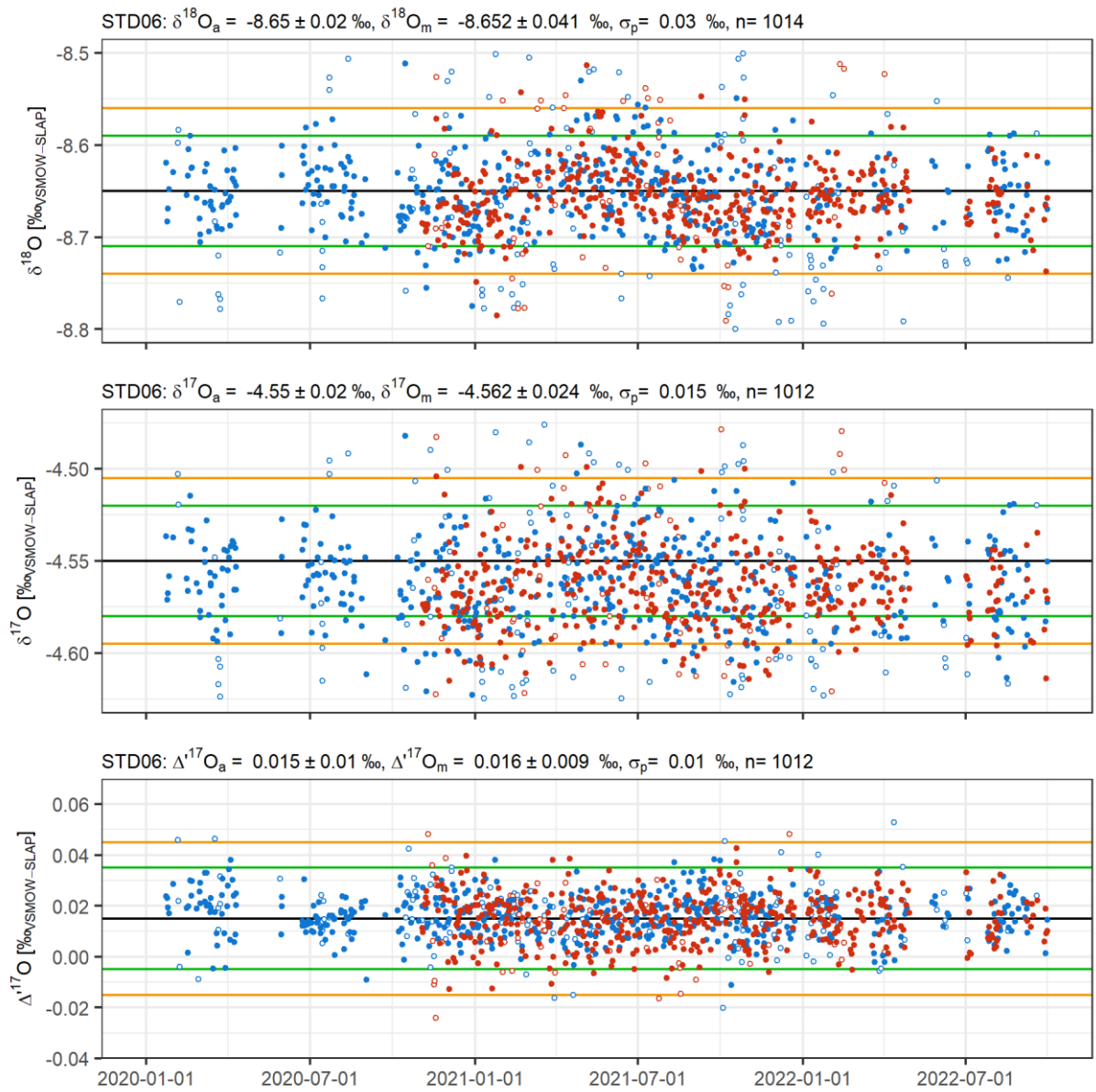


Figure 18: Protocol QA/QC chart of the control standard STD06. δ_a is assigned value; δ_m measured value; σ_p accuracy benchmark ($2\sigma_p$ and $3\sigma_p$ denoted by green and orange lines)