LIMS for Lasers 2015

Laboratory Information Management System for Stable Hydrogen and Oxygen Isotopes in Water Samples by Laser Spectrometry

User Manual

Revision v 2.1
LIMS for Lasers v10.083
18 April 2016

Foreword

Measurement of the stable isotopes of hydrogen and oxygen (δ^2H, δ^{18}O, δ^{17}O) in environmental water samples by laser spectrometers is a cost-effective analytical method for hydrologic and environmental studies around the world for analysis of relatively clean water samples.[1] Measurement of δ values by laser spectrometers usually provide accurate results, but where samples contain interfering volatile organic molecules, or where data are required for legal purposes, results should be verified by isotope-ratio mass spectrometry (IRMS).[2]

Liquid water isotope laser spectrometers from Los Gatos Research* and Picarro Inc.* are easy to operate; but, incorporation into routine laboratory operations is not as easy owing to extensive CSV data processing required by the operator. Some users developed complex data processing spreadsheets; however, spreadsheets present a serious challenge to maintaining long-term QA/QC or laboratory audits. None of the manufactures provide data processing software that can meet all of these data processing needs.

7 Critical Data Processing Steps

There are seven key data processing steps required for obtaining accurate and precise water long-term isotopic data using laser spectrometers, which are altogether difficult to achieve by using spreadsheets:

- Eliminate "bad" samples or injections based on H_2O concentrations due to syringe or septa underperformance
- Determine δ amount dependence on H_2O amount and apply corrections, as required
- Ignore the first 3–4 injections of each sample to reduce between-sample memory
- Determine and apply a residual memory carryover correction algorithm
- Correct for linear or non-linear instrumental drift
- Normalization of all data to the VSMOW/SLAP scales
- Track QA/QC, on a per analysis basis and over the long-term

Laboratory Information Management System (LIMS) for Lasers 2015 automates these 7 steps and eliminates entirely the need for spreadsheets. *LIMS for Lasers 2015* uses systematic templates for samples and measurement standard analyses based on Identical Treatment principles. Templates contain multiple occurrences of standards to quantify memory and drift, to correct for H_2O amount, and to normalize results to the VSMOW–SLAP scale. Control standards track long-term QA/QC and laboratory performance.

LIMS for Lasers 2015 furthermore manages all client and project data for laser instruments. Laser performance is monitored with control standards by δ^2H vs. δ^{18}O cross plots and time series plots. The automated processing features improve accuracy and precision, and they help to reduce user mistakes and errors.

This document describes how users can implement *LIMS for Lasers 2015* for Los Gatos Research and Picarro instruments into their daily laboratory operations. To facilitate use of *LIMS for Lasers 2015*, this document contains links to the latest software repository. In this document the terms reference and standard are used interchangeably.

A summary of the performance benefits of using *LIMS for Lasers 2015* is found in this publication:[3]

Coplen, T. B., & Wassenaar, L.I. (2015). LIMS for Lasers 2015 for achieving long-term accuracy and precision of δ^2H, $\delta^{17}O$, and $\delta^{18}O$ of waters using laser absorption spectrometry. Rapid Communications in Mass Spectrometry 29(22): 2122–2130. http://dx.doi.org/10.1002/rcm.7372

The *LIMS for Lasers 2015* User Manual was written by Leonard I. Wassenaar and Tyler B. Coplen. Persons involved in extensively testing *LIMS for Lasers 2015* on a day-to-day basis were Stefan Terzer, Cedric Douence and Liliana Poeltenstein at the IAEA. Feedback and comments from Yesha Shreshta, Lauren Brandes, and Haiping Qi at the USGS helped to improve *LIMS for Lasers 2015* and the user manual.

*Currently, OA-ICOS laser instrumentation is sold by Los Gatos Research Inc. (www.lgrinc.com) and CRDS laser instrumentation is sold by Picarro Inc. (www.picarro.com). Any use of trade, firm, or product names in this manual is for descriptive purposes only and does not imply endorsement by the International Atomic Energy Agency or the U. S. Government.

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1 Introduction to LIMS for Lasers 2015

1.1 What is LIMS for Lasers 2015?

LIMS for Lasers 2015 is a Laboratory Information Management System (LIMS) for Los Gatos Research off-axis integrated cavity output (OA-ICOS) and Picarro cavity ring-down (CRDS) laser absorption spectrometers used for the purposes of δ^2H and δ^{18}O (and optionally δ^{17}O) assays of liquid water samples in hydrological and environmental studies. *LIMS for Lasers 2015* provides a convenient Windows environment to manage clients, projects, samples and instrumental data. *LIMS for Lasers 2015* can also be used on an Apple Mac using Boot Camp or a Windows Virtual PC.

Features

- Full client, project and sample management and reporting system
- Laser sample analysis and laboratory standard calibration templates
- Syringe performance pre-screening graph
- Color-coded outlier detection and automated error flagging
- Corrections for variations in δ values with relative water concentrations
- Automated between-sample memory corrections
- Automated instrumental drift correction
- Automated normalization of data to the VSMOW-SLAP scales
- Track My Lab QA/QC for instrument and laboratory assessment audit
- Excel client sample submission templates

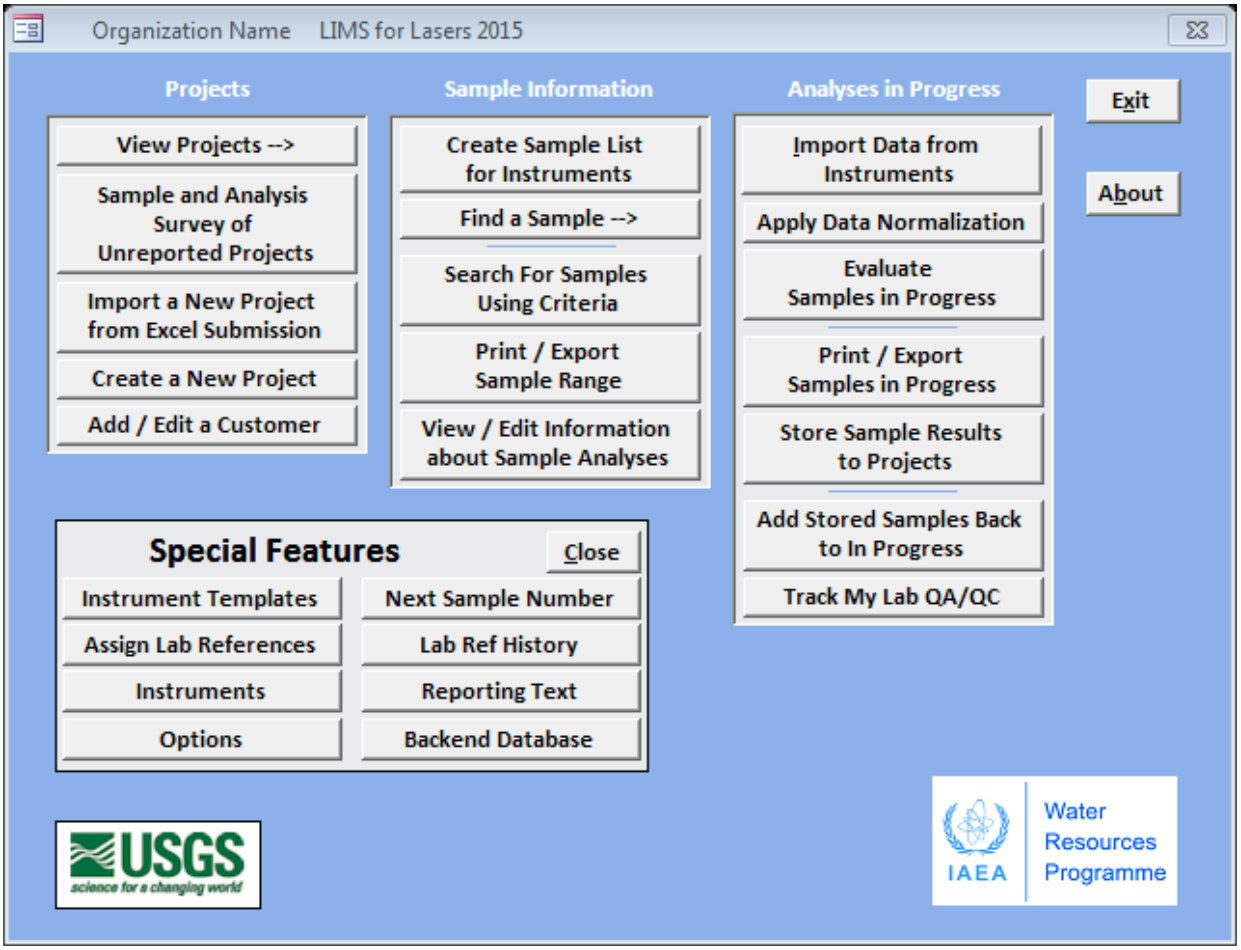
Benefits

- Increased productivity by eliminating complex spreadsheets
- Improved long-term performance through standardized approaches
- Reduction of laboratory errors in client and data management
- Fully compatible with *LIMS for Light Stable Isotopes v.9x* for IRMS

LIMS for Lasers 2015 is built upon the 32-bit MS Access code of *LIMS for Light Stable Isotopes* [4], and it can be used concurrently on an existing *v.9* backend database. *LIMS for Light Stable Isotopes* is a mature software application developed and maintained by T.B. Coplen at the U.S. Geological Survey (USGS) in Reston, Virginia, USA. *LIMS for Lasers 2015* is the result of a collaborative effort between the IAEA Isotope Hydrology Laboratory (IHL) and the Reston Stable Isotope Laboratory (RSIL) of the U.S. Geological Survey (USGS), and is provided at no cost to users.

2 LIMS for Lasers 2015 at a Glance

2.1 LIMS for Lasers 2015 at a Glance



The user interface of *LIMS for Lasers 2015*.

Projects

- View projects, print reports, and export data to Excel
- Inspect sample queue
- Import project data from Excel forms
- Create new projects
- Add new clients

Special Features

- Add/edit laser instruments
- Add / edit laboratory standards
- Backup and customize the database
- Design analysis templates

Sample Information

- Create sample lists that can be imported into Los Gatos Research or Picarro instruments
- Search, view, print and edit specific client samples

Analyses in Progress

- Import data output files from Los Gatos Research or Picarro instruments
- Automatically determine and apply memory correction and drift corrections
- Normalize results to VSMOW-SLAP scale
- Evaluate results and track laboratory QA/QC
- Store final accepted results for reporting

2.2 Routine Sample Autorun Checklist

After *LIMS for Lasers 2015* is installed, this procedural checklist provides a quick overview of routine isotopic analysis of water samples:

A. Projects Column

1. Ensure the Customer is added to *LIMS for Lasers 2015* (Chp. 6.1).
2. Create a new Project for the customer, either manually entering sample information or importing from an Excel file (Chp. 6.3, 6.4).
3. Add customer Project(s) samples to a laser Analysis Template queue (Chp. 8.8, 8.9).

B. Sample Information Column

4. Create an autorun Sample List for the laser instrument and copy to USB flash drive (Chp. 9.1, 10.1).

C. In the Laboratory

5. Pipette project sample waters and laboratory standards into labelled 2-mL vials.
6. Arrange samples and laboratory standard vials in correct trays and positions (Chp. 8.3).

D. On the Laser Instrument

7. Copy the Sample List file to the laser instrument from USB flash drive (Chp.9, 10).
8. Analyse sample on the Sample List on Los Gatos Research or Picarro laser instrument.
9. Copy the completed autorun data output file to a USB flash drive.

E. Analysis in Progress Column

10. Import Data from Instruments – use default or custom corrections (Chp. 11).
11. Apply Data Normalization (Chp. 12.1).
12. Evaluate Analyses in Progress (Chp. 12.3).
13. Store Final Accepted Results to Projects (Chp. 12.5).
14. Track My Lab QA/QC to assess overall performance (Chp. 12.7).

F. Projects Column

15. View Projects – Reporting Results to customer (Chp. 13.1).

3 Computer & Software Requirements

3.1 Computer & Software Requirements

Required

- Windows PC with USB or LAN connection to a laser instrument. *LIMS for Lasers 2015* can be used on an Apple computer using windows Boot Camp or virtual Windows PC.
- Microsoft Access 2007/2010/2013/2016 (32-bit only) for Windows 7/8.1/10 (32/64-bit).
- *LIMS for Lasers 2015* frontend (*v.10.083* or later).
- A new or existing LIMS backend database for current LIMS users.
- A new or existing LIMS folder location for the backend database (network or PC).
- An Example Client Sample submission Excel spreadsheet or an Alternative sample submission Excel workbook (available only from the USGS Web site).

LIMS for Lasers 2015 software is composed of 3 components

- The *LIMS for Lasers 2015* (*v10.083),* or later, frontend user interface.
- A *LIMS for Lasers 2015* backend database.
- An Excel client sample submission template.

The latest software can be downloaded cost-free from the IAEA or USGS Web sites:

http://www-naweb.iaea.org/napc/ih/IHS_resources_sampling.html#lims
http://isotopes.usgs.gov/research/topics/lims.html

Optional

- A network connection to the laser instrument(s)
- A backup disk (network or external storage location)

Security Settings

LIMS for Lasers 2015 requires enabling macros. You may require administrator rights to change these settings. Enable MS Access to run all macros under |Trust Center| Trust Center Settings | Macro Settings | *Enable all macros*.

Setting up Trusted Locations

LIMS for Lasers requires Trusted Locations in Microsoft Access. For example, assume C:\LIMS is the database location. We will need to add this directory to Trusted Locations in MS Access:

Access 2010/13: File Tab | Options | Trust Center | Trust Center Settings |Trusted Locations | Add new location | Path: C:\LIMS, Check box: Subfolders are trusted, click “OK”

Access 2007: Office Button | Access Options | Trust Center | Trust Center Settings | Trusted Locations | Add new location | Path: C:\LIMS, Check box: Subfolders are trusted, click “OK”.

Note: Some IT policies may not allow using the Windows Desktop as a trusted location.

4 Starting with LIMS for Lasers 2015

4.1 Setup LIMS for Lasers 2015 - New Laboratory

1. Create a *LIMS for Lasers 2015* folder on any hard drive on your PC for the user interface, backend database and backups (e.g. C:\LIMS). The LIMS folder should be located on a dedicated computer or on a reliable (and preferably fast) mapped network drive.

    a. C:\LIMS\Backend
    b. C:\LIMS\Frontend
    c. C:\LIMS\Backup

2. Ensure Microsoft Access 2007/10/13/16 (32-bit only) is installed. Ensure MS Access has C:\LIMS and subfolders added as Trusted Locations (see previous chapter).

3. Download and extract an *unopened* version of the latest *LIMS for Lasers 2015 front-end* interface (e.g. LIMS for Lasers 2015 10.083.zip) into C:\LIMS\Frontend.

4. Download and extract an *unopened* instrument-specific *backend* for new laboratories (e.g. LIMS Backend for Picarro.zip) into C:\LIMS\Backend.

5. Consider renaming the LIMS backend database to something more descriptive of your laboratory, such as “My Laboratory LIMS Backend.accdb”.

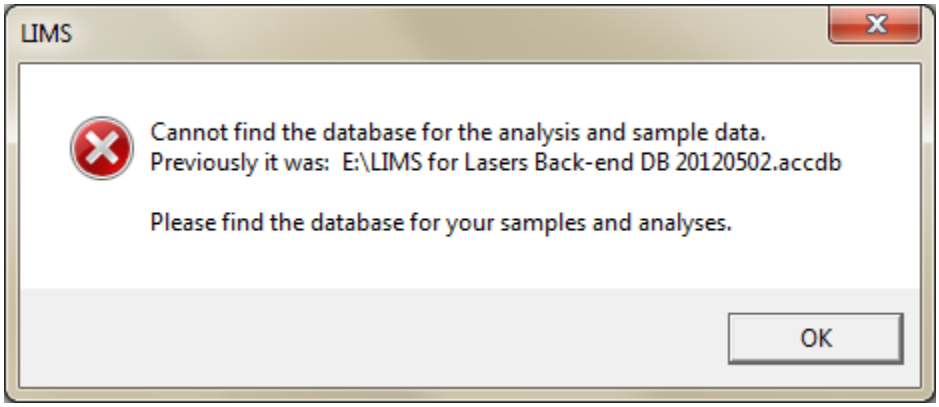
6. Keep backup copies of the original unopened ZIP files for safekeeping.

7. In the Frontend folder, open the file “LIMS for Lasers 2015 10.083.accdb”, or later version. You may also create a Windows shortcut to this file on your desktop for easy access.

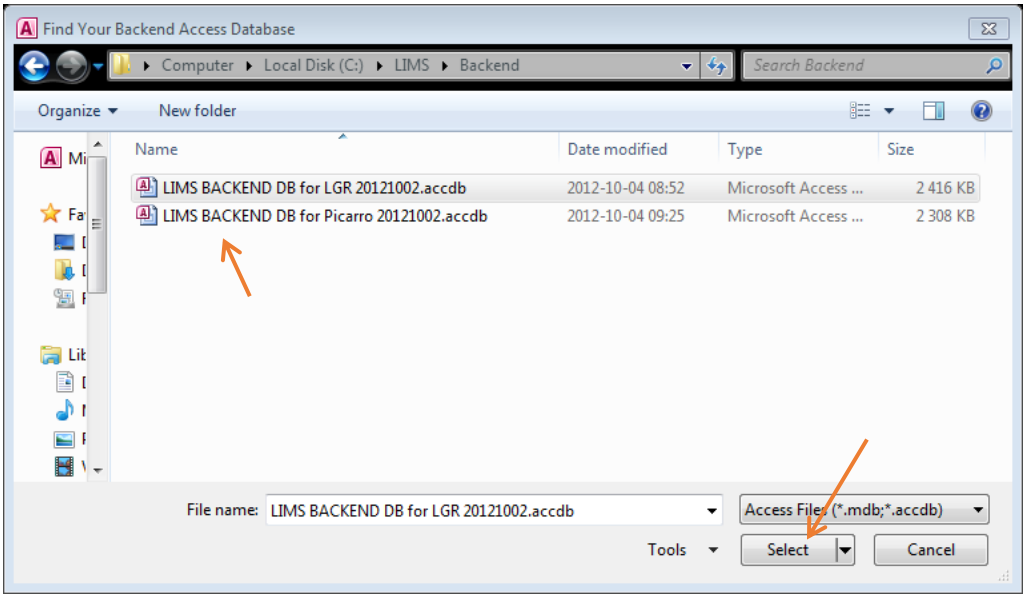
8. If you encounter this security warning, then “Trusted Locations” were not set up properly - see previous section:

9. Click “Open” (a warning will not appear if Trusted Locations are correctly set).

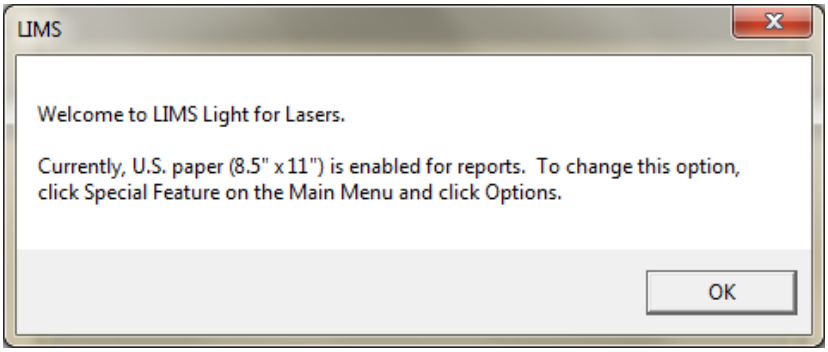
10. *LIMS for Lasers 2015* will ask for the location of the “Back-end” database.



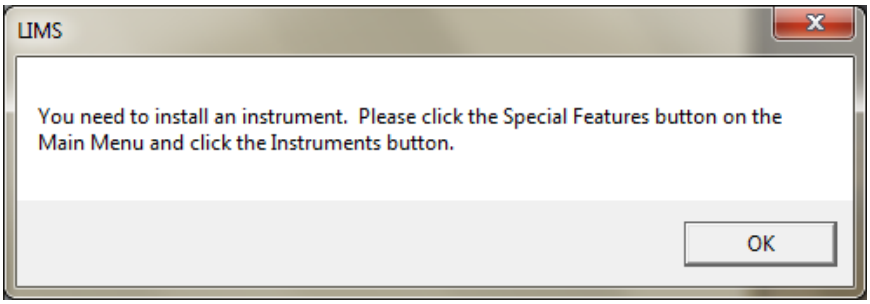
11. Click “OK”, and use the file dialog to navigate to C:\LIMS\Backend and “Select” the new Picarro or Los Gatos Research, or the newly renamed backend file that you copied previously in Step 4 or 5.



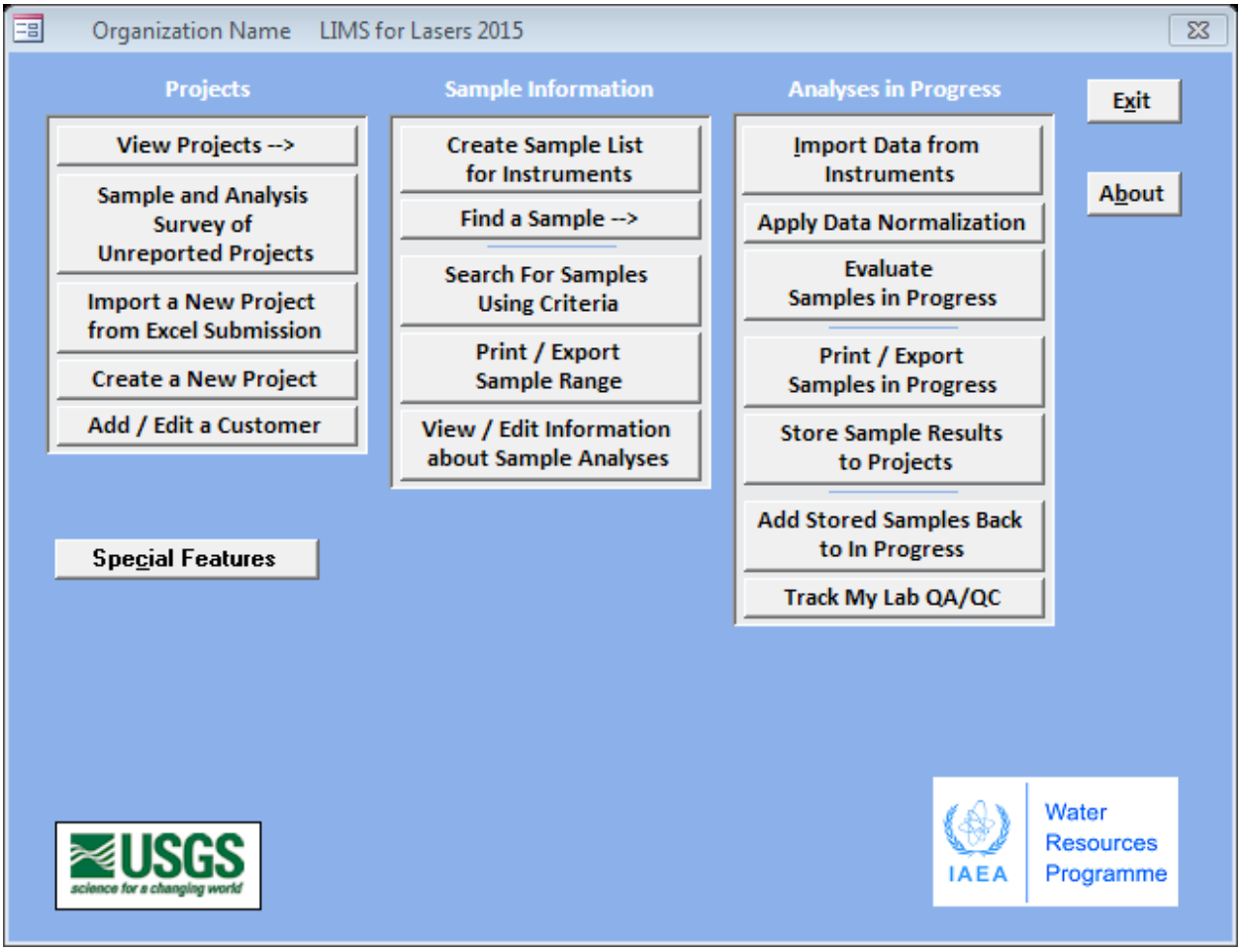
12. Next, a Welcome message appears, Click OK (a security warning pops up if Trusted Locations were not setup), click “Select”:



13. A reminder may appear, indicating a laser instrument may need to be installed into your laboratory database. Click “OK”. Another reminder about setting up daily backups will appear, Click “OK” again.



14. *LIMS for Lasers 2015* is now successfully installed. This should be your screen upon start up:



LIMS for Lasers 2015 Main Page.

Registering for Support

It is a good idea to register *LIMS for Lasers 2015* by emailing tbcoplen@usgs.gov. Registration ensures you will be informed about important updates. Similarly, user suggestions for improvements to *LIMS for Lasers 2015*, reporting bugs, and suggested improvements to the user manual are always appreciated.

Note: For European and other international users, the Windows Regional Settings in the computer Control Panel may have either a point or a comma as the decimal separator. *LIMS for Lasers 2015* will function properly with either choice; figures in this document were created with a point as the decimal separator.

4.2 Upgrading from LIMS for Lasers 2012

For laboratories using the original *LIMS for Lasers* (e.g. <v.10.69) from 2012*,* follow the same procedure for a new laboratory (above), but use the existing *LIMS for Lasers* backend database file. A *LIMS for Lasers 2015* restart will be required. The existing backend database remains unaffected.

4.3 Set up LIMS for Lasers 2015 in a v.9 Laboratory

For laboratories using *LIMS for Light Stable Isotopes v.9x*, follow the same procedure for a new laboratory (above), but use the existing LIMS v.9x backend directory. Some warnings do not apply. In step 11, select the existing LIMS (*v*.9x) backend database. A *LIMS for Lasers 2015* restart will be required.

Note: When using a *v*.9x backend database, only the medium "W" (e.g. water δ^{18}O, δ^{17}O and δ^{2}H) and laser instruments will be visible to the user. This is intentional: no isotope-ratio mass spectrometers (IRMS) or any other isotopic media (e.g. C->carbonates, S->sulfur, etc.) will be visible, *even though they are still present in the backend database*. The δ^{2}H and δ^{18}O results of water samples analysed by IRMS will also be shown in *LIMS for Lasers 2015*, and they can be evaluated with any δ values from a laser instrument. There is no danger to the backend database, and all *v*.9x preferences are retained. You can seamlessly switch back and forth between *LIMS for Light Stable Isotopes* and *LIMS for Lasers 2015*. Laboratory staff using only laser instruments, for example, may prefer to only use *LIMS for Lasers 2015* because of all of its new features.

Note: When new water isotope projects are added using v.9x, upon start up *LIMS for Lasers 2015* will alert the user that a project was created using *LIMS for Light Stable Isotopes v.9x.* This notice is informational only.

4.4 Quick-Start Backend Database

In subsequent chapters of the manual, we describe how to use *LIMS for Lasers 2015*, add new laser instruments, design and create new analysis templates, measure and normalize data and report results. This information should be reviewed in order to fully understand the software.

To get new users running quickly, we provided separate "ready-made" *LIMS for Lasers 2015* backend data bases and analysis templates for Los Gatos Research and for Picarro water

isotope laser instruments. These are downloadable (see Chapter 3.1) backend databases that assume:

- The Picarro instrument software has identification prefix “P” (default).
- The Los Gatos Research instrument software has identification prefix “L” (default).
- Uses a 10-, 20-, or 30-sample template with USGS lab standards.
- Local laboratory measurement and control standards assigned values are provided by and *must be edited by the user* – these are initially set to null values, or USGS laboratory isotopic reference waters are used.

For Los Gatos Research users:

1. Download the Los Gatos Research *LIMS for Lasers 2015* backend data base from the link provided above.
2. Review Chapters 4–8 to customize *LIMS for Lasers 2015*, and to edit or add your local measurement standards and create analysis templates.
3. Then, go to Chapter 8.9 to get started with samples to be measured.

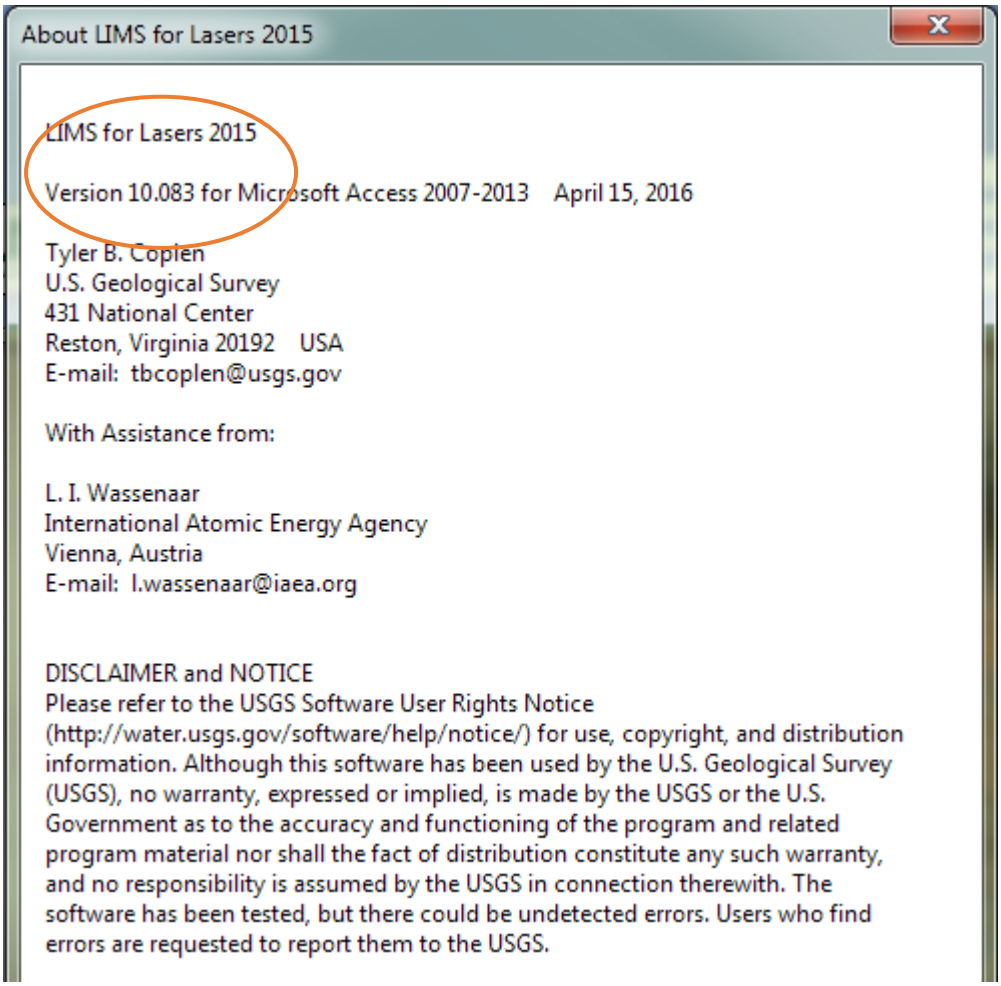
For Picarro users:

1. Download the Picarro *LIMS for Lasers 2015* new backend data base from the link provided above.
2. Review Chapters 4–8 to customize *LIMS for Lasers 2015*, to edit or add your local measurement standards and create analysis templates.
3. The go to Chapter 8.8 to get started with samples to be measured.

4.5 Check LIMS for Lasers Version

LIMS for Lasers software is continually updated based on user feedback. Updates are posted at the Web links given above. To determine which *LIMS for Lasers* version you are using, click the "About" menu on the main page (see below).

To update *LIMS for Lasers*, download the new zip file and extract the user interface. Follow Step 3, and then Step 7 in Section 4.1. If you created a Windows desktop "shortcut" to the frontend interface folder, be sure to update the shortcut to the newer version.



4.6 Customize Laboratory Settings

Prior to adding laser instrument(s) to *LIMS for Lasers 2015*, you should make your own laboratory customizations (location, laboratory name, paper size, printers, etc.). These customizations create a new file in the LIMS directory named "LM9PREFS.ACCDB", which retains your laboratory details. Depending upon the computer settings, the file extension .ACCDB may not be visible.

The "Preferences" file must reside in the same directory as the LIMS front-end file. If the LM9PREFS file is mistakenly deleted, your customizations will be lost and LIMS will revert to default values if you install an updated *LIMS for Lasers 2015* front-end. However, if you move the front-end interface to a new folder and forget to move LM9PREFS.ACCDB, *LIMS for Lasers 2015* will create another preferences file with your custom laboratory settings.

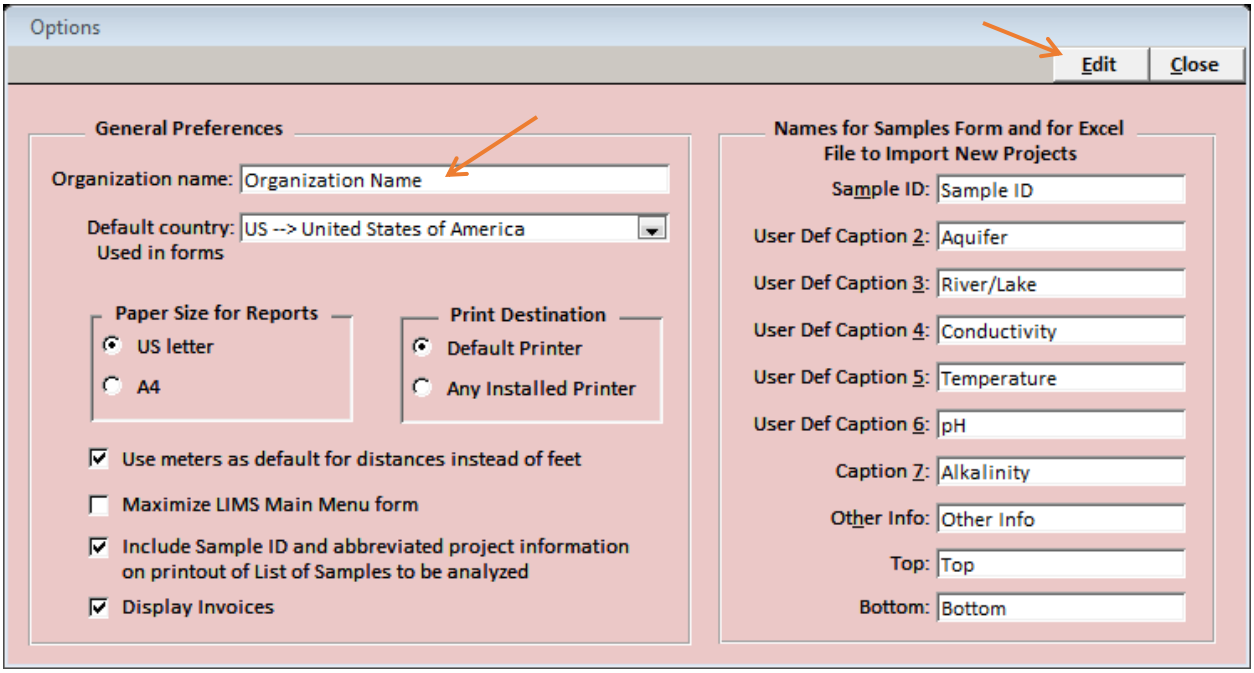
To protect against mistaken entries and deletions, all editable forms in *LIMS for Lasers 2015* require the user to click on the **"Edit"** button at the top of the screen before edits can be made. This may be confusing at first –remember it is for your protection! Think "**Click Edit**" - and it will become a routine habit.

On the Main Page - Click "Special Features" / Options. Click "Edit" (the control now changes to "Save").

- Enter your Organization Name; select your Country and printer paper size.
- Choosing "Any Installed Printer" will bring up a Windows Printer Dialog box instead of immediately printing to the default Windows printer.
- Maximize LIMS forces a full entry page on your display. Invoicing features are optional - enable or disable as desired.
- Sample ID and abbreviated project info adds more detail to the printouts of sample lists, as various laboratories prefer more or fewer levels of detail on their reports.

The customizable user-defined options on the right side are fully discussed in Chapter 6.5. The invoicing capability is discussed in Chapter 13.3.

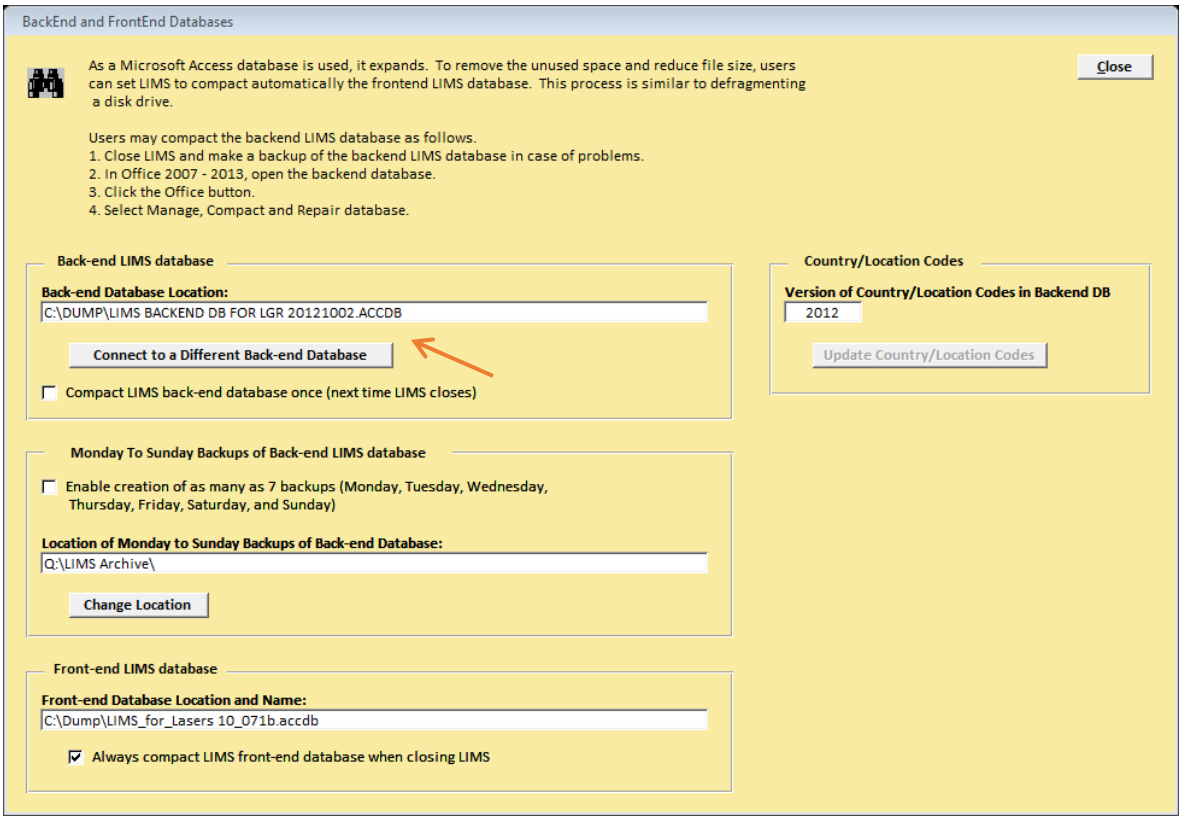
When done, click "Save", and Close, and Close again to return to the Main Page.


Options
Edit
Close
General Preferences
Organization name:
Organization Name
Default country:
Used in forms
US --> United States of America
Paper Size for Reports
US letter
A4
Print Destination
Default Printer
Any Installed Printer
Use meters as default for distances instead of feet
Maximize LIMS Main Menu form
Include Sample ID and abbreviated project information on printout of List of Samples to be analyzed
Display Invoices
Names for Samples Form and for Excel File to Import New Projects
Sample ID:
Sample ID
User Def Caption 2:
Aquifer
User Def Caption 3:
River/Lake
User Def Caption 4:
Conductivity
User Def Caption 5:
Temperature
User Def Caption 6:
pH
Caption 7:
Alkalinity
Other Info:
Other Info
Top:
Top
Bottom:
Bottom

4.7 LIMS for Lasers 2015 Backend Database Locations

It is a good idea to ensure your *LIMS for Lasers 2015* backend and backup location is set up permanently, and that it is routinely backed up.

1. Click on “Special Features”.
2. Click on “Backend Database” – the following screen opens:



3. The “Backend Database location will reveal the location assigned above. If not, click “Connect to a Different Backend Database” and navigate to the target backend LIMS database folder.
4. The compacting option forces a compression – you will be reminded when the database expands to occasionally compact it.
5. Enable (or disable) backups, and specify the location. LIMS uses a 7-day back-up cycle (e.g. Monday is replaced the following Monday). This gives you 1 week of back-up protection.

Note: Backups are only made when *LIMS for Lasers 2015* closes. *These are NOT unattended or automatic backups.* Users are strongly encouraged to use other regular forms of automated or offsite backup (network, DVD, USB flash drive, cloud etc.).

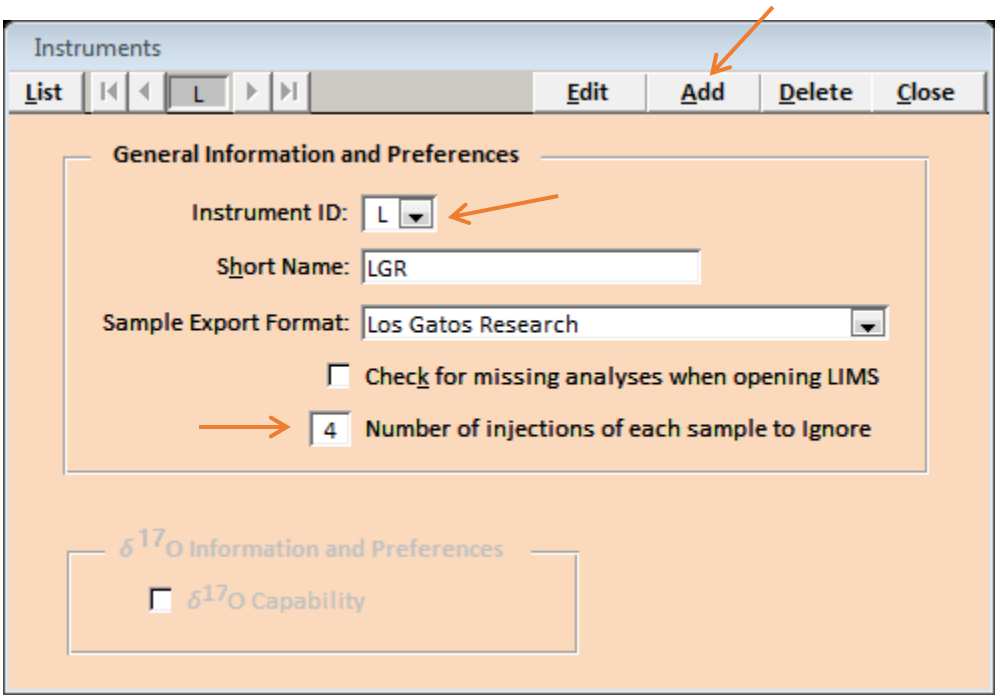
5 Add New Laser Instruments

5.1 Add Los Gatos Research DLT-100 Series Laser Instruments

To view, install or remove 2007–2013 Los Gatos Research DLT-100/24D series water isotope laser instruments(s) in *LIMS for Lasers 2015*:

1. Click “Special Features”.
2. Click “Instruments” to view.

In the screen below, click “Add”.



Example: older generation Los Gatos Research DLT-100 series water isotope instruments.

3. Select or enter “L” in the Code box.
4. Enter a short descriptive name for the Los Gatos Research instrument.
5. On the “Sample Export Format” pick list, choose “Los Gatos Research”.

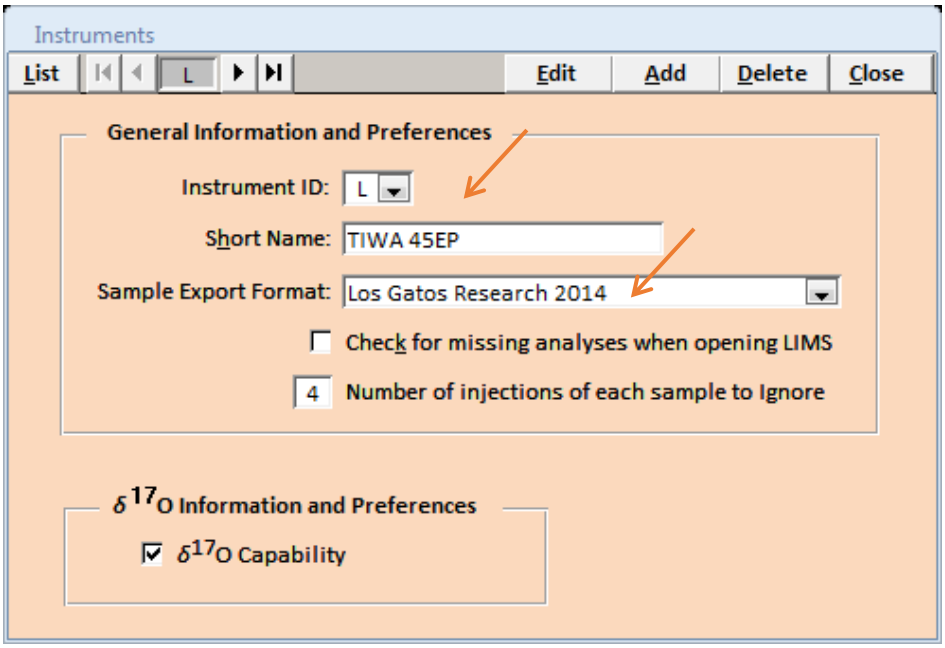
To remove a Los Gatos Research instrument, click on “Delete”.

If isotopic analyses for the instrument have already been imported into *LIMS for Lasers 2015*, the instrument cannot be deleted.

5.2 Add Los Gatos Research IWA-35EP or TIWA-45EP Series Laser Instruments

To view, install or remove newer (2014-present) Los Gatos Research IWA-35EP or TIWA 45-EP instruments(s) in *LIMS for Lasers 2015*:

1. Open *LIMS for Lasers 2015.*
2. Click "Special Features".
3. Click "Instruments" to view.
4. Click "Add". Then, edit as below.



Example: Newer Los Gatos Research TIWA 45 EP water isotope instruments.

5. Select or enter "L" in the Code box (note: this letter can be changed on the instrument and should match the prefix on the instrument output file).
6. Enter a short descriptive name for the Los Gatos Research instrument.
7. On the "Sample Export Format" pick list, choose "Los Gatos Research 2014".
8. Optionally, if the instrument has δ^{17}O capability, check that box.
9. Click "Save", then Click on "List" - the new Los Gatos Research instrument should appear here.

To remove a Los Gatos Research instrument, click "Delete".

If analyses for an LGR instrument have already been imported into *LIMS for Lasers 2015*, the instrument cannot be deleted.

Number of Injections

For best results on Los Gatos Research instruments, we recommend a total of 9 injections per sample and recommend ignoring the first 4 injections (as set on the instrument configuration). See discussion on templates for rationale for ignoring injections and other options (Chapter 8.2).

The number of ignored injections is *instrument specific* and must be less than the total number of sample injections as defined in the "Analysis Template".

Instrument Prefix

The instrument ID Prefix "L" is a pre-set default on all new Los Gatos Research instruments. For laboratories having two or more Los Gatos Research instruments, the ID code must be unique for each instrument (L, M, N…).

- On older DLT-100/24D instruments (first generation LGR software), changing the instrument prefix requires access to the LINUX shell on the Los Gatos Research instrument and a minor edit to an instrument INI file. Contact Los Gatos Research for instructions on how to change the default instrument Prefix ID on older instruments.

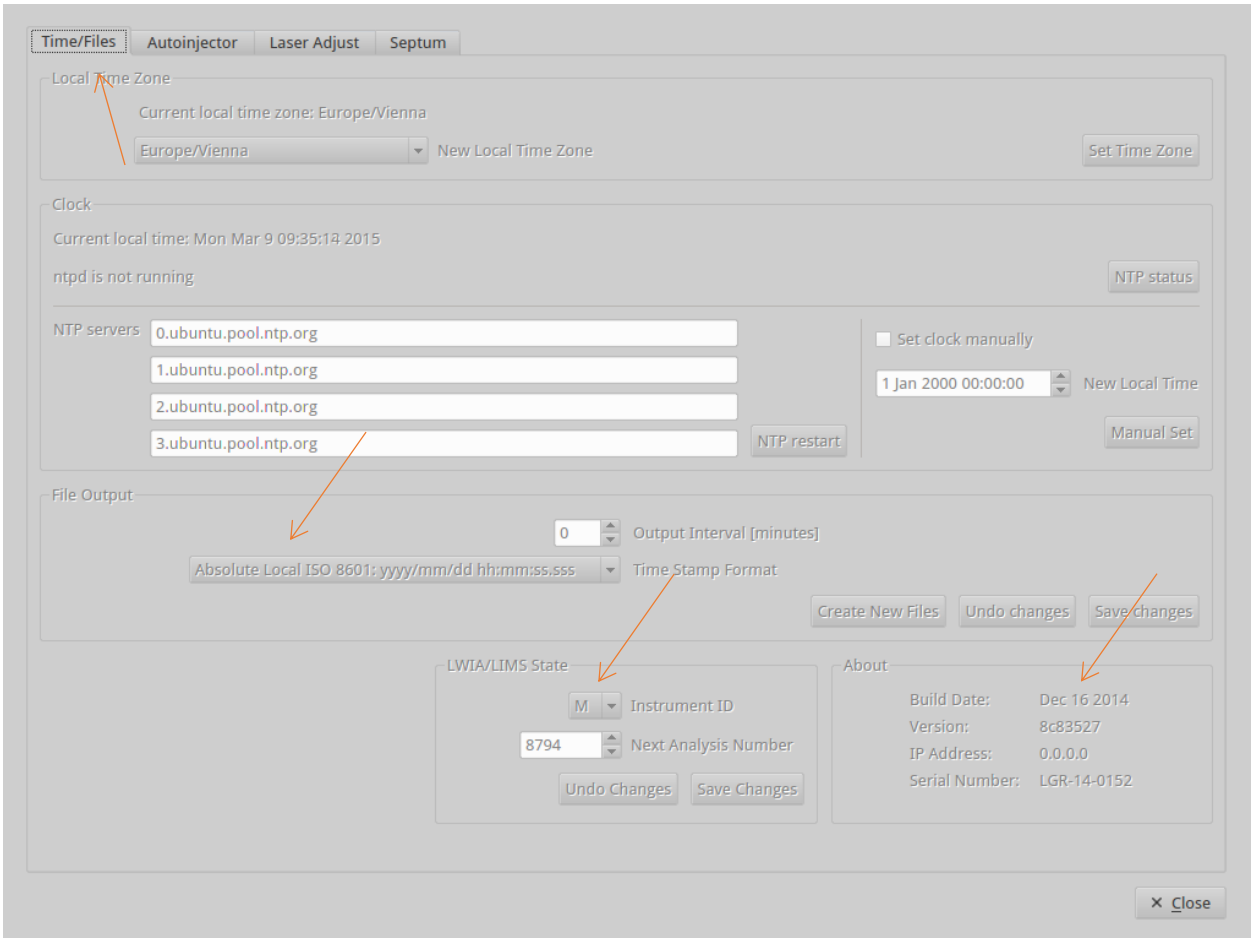
- On new LIWA/TIWA -35/45EP instruments (new software, 2014-present), the instrument prefix can easily be changed in the instrument Settings panel (see the Los Gatos Research LWIA/TIWA user manual and picture on next page).

LIMS Button is greyed on your Los Gatos Instrument?

- Some early LIWA/TIWA -35/45EP instruments shipped without LIMS capability implemented. You may see no button or a greyed out LIMS button on the main screen.
- To correct this, a firmware update is required from Los Gatos Research that can be installed by the user in about 10–15 minutes. The required firmware build should be checked on the instrument, under the Setup -> Time/Files tab. At the lower right check the software build date (see Figure next page). It should be:
    - Build Aug 6, 2015 or later, for dual-isotope instruments
    - Build Dec 16, 2014 or later, for triple-isotope instruments

Required Date Format for LIMS Output

- The required date format for LIMS is "Absolute Local ISO 8601". Check under Setup -> Time/Files tab to change to correct setting. (see figure on next page)



Changing the Los Gatos Research instrument ID prefix and date format in the Time/Files tab.

Caution: If you have multiple laser instruments, be sure they do not have the same Instrument ID letter! *LIMS for Lasers 2015* tracks sample data from each Instrument via the instrument Prefix ID.

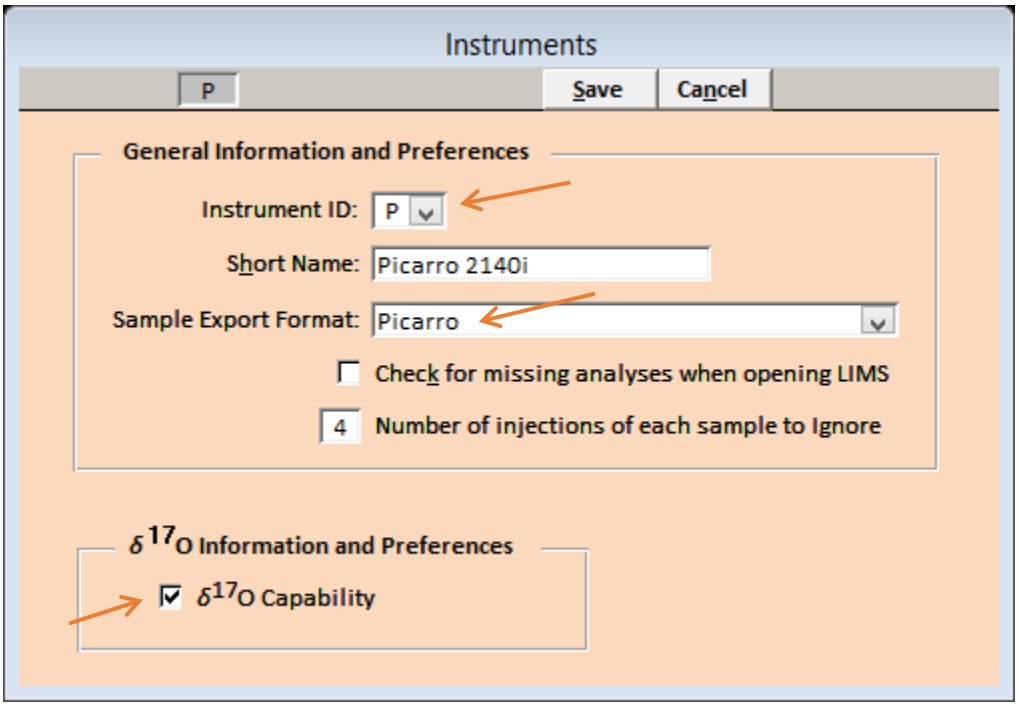
Caution*:* If you return your instrument for repair and Los Gatos Research replaces the hard drive, please check to ensure that Los Gatos Research resets the prefix letter and analysis number to the values on the instrument at the time you returned it for repair.

5.3 Add Picarro Instruments

To view, install or remove a Picarro (11xx-2xxx generations) laser instrument in *LIMS for Lasers 2015*:

1. Open *LIMS for Lasers 2015.*
2. Click "Special Features".
3. Click "Instruments" to view.

In the screen below, click "Add".



4. Enter "P" in the Code box.
5. Enter a short descriptive name for the Picarro instrument.
6. From the "Analysis import format" pull down menu, select Picarro. If the Picarro instrument is a 2140i or later with δ^{17}O capability, check the δ^{17}O box.
7. Click "Save", then Click on "List" - the new Picarro instrument should appear here.

For best results on Picarro, we recommend a total of 8 injections per sample and recommend ignoring the first 4 injections (shown above). See discussion on templates for rationale for ignoring injections and other options (Chapter 8.2).

To remove a Picarro instrument, click on "Delete".

If analyses for a Picarro instrument have already been imported into *LIMS for Lasers 2015*, the instrument cannot be deleted.

Number of Injections

The number of ignored injections is *instrument specific.* The total number of injections for each water sample vial on Picarro instruments is set up on the PAL handheld device (e.g. 11xx Series) or on the G2000 Autosampler Configurator Software (e.g. 21xx Series).

Instrument Prefix

The ID prefix "P" is coded in the Picarro Coordinator INI software. For laboratories having two or more Picarro instruments this code must be unique for each instrument (e.g. P, Q, T). This will require manually editing the correct Coordinator.ini file(s) using NotePad++ and simply changing the "Instrument prefix" header to the chosen letter.

Note: There are several Coordinator INI files for each method (e.g. High Precision, High Throughput, ^{17}O in N_2, etc.). You may therefore be required to change the instrument prefix in several INI files if using several modes. It is not a difficult task; please contact Picarro support for detailed instructions on changing the default instrument prefix ID on your specific instrument configuration.

Caution: If you have multiple laser instruments, be sure they do not have the same instrument ID letter! *LIMS for Lasers 2015* tracks sample data from each Instrument via its unique Prefix ID.

Caution: If you return your instrument to Picarro for repair and they replace the hard drive, ensure that Picarro sets the correct prefix letter and analysis number to those values that were on the instrument when you returned it for repair.

6 Customers, Projects and Samples

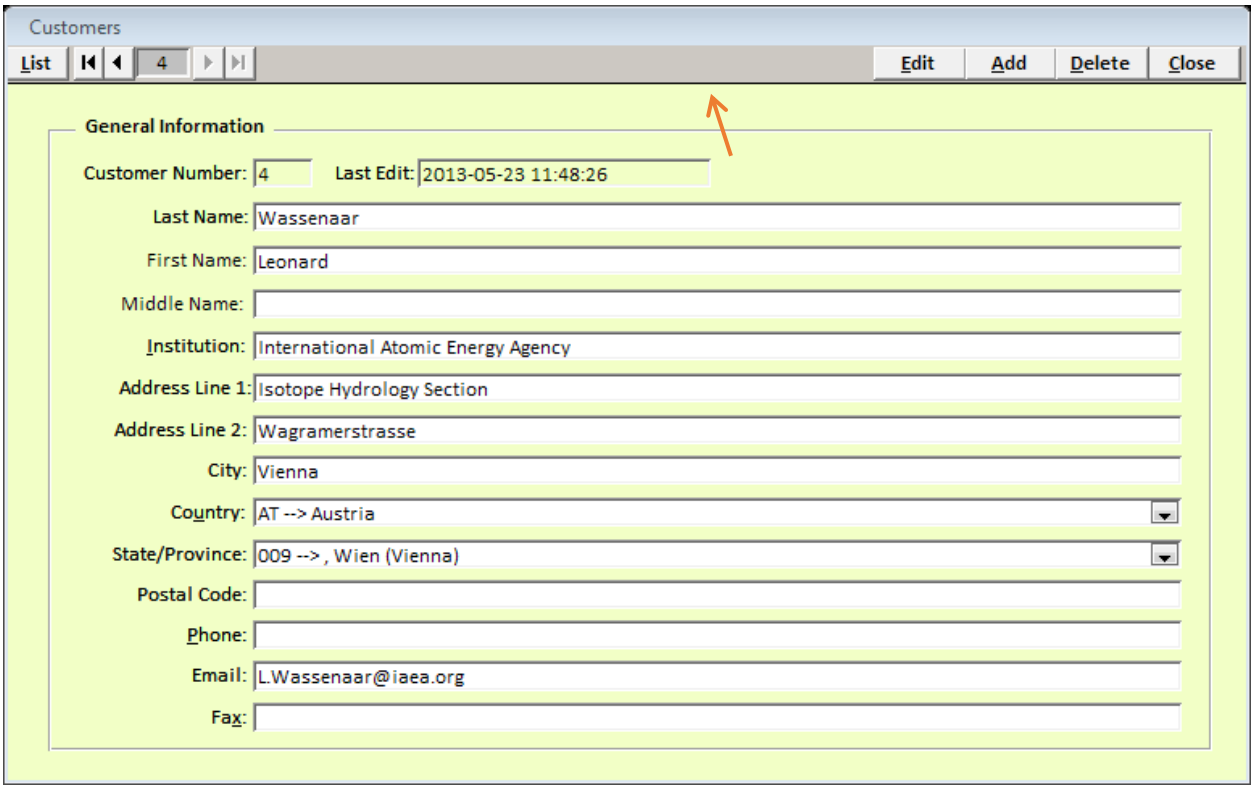
6.1 Add and Edit Customers

Before water isotope samples can be analysed and reported using *LIMS for Lasers 2015,* they must be associated with a "Customer" (or a client) and their "Project". A Customer is typically the person responsible for sample submission and to whom stable isotopic results will be reported. A customer can be laboratory and technical staff. *LIMS for Lasers 2015* keeps track of all laboratory customers and the information associated with their data.

A customer list can be pre-populated with clients, or customers may be added individually over time. Always ensure a customer exists before attempting to create new projects. Pay attention to correct spelling and avoid duplicating the same customer name (e.g. Bill Smith, William Smith).

To add a new Customer:

1. On the LIMS Main Page, Click "Add/Edit a Customer" in the Projects column.
2. Click "Add".
3. Enter a Last Name, First Name, and other optional contact and address information.
4. Click "Save", then Click "List" to see your current list of customers.
5. To remove a Customer, click on "Delete".



The *minimum information* required is *Last Name* and *First Name*; all other fields are optional. Customer information can be updated later on by choosing client name from the "List" menu and clicking "Edit". The clients "Reference" and "Test" are pre-set entries that can be used for running laboratory tests or calibration samples or standards.

Note: A customer cannot be deleted if their project already has stored isotope data.

6.2 Add Projects and Samples

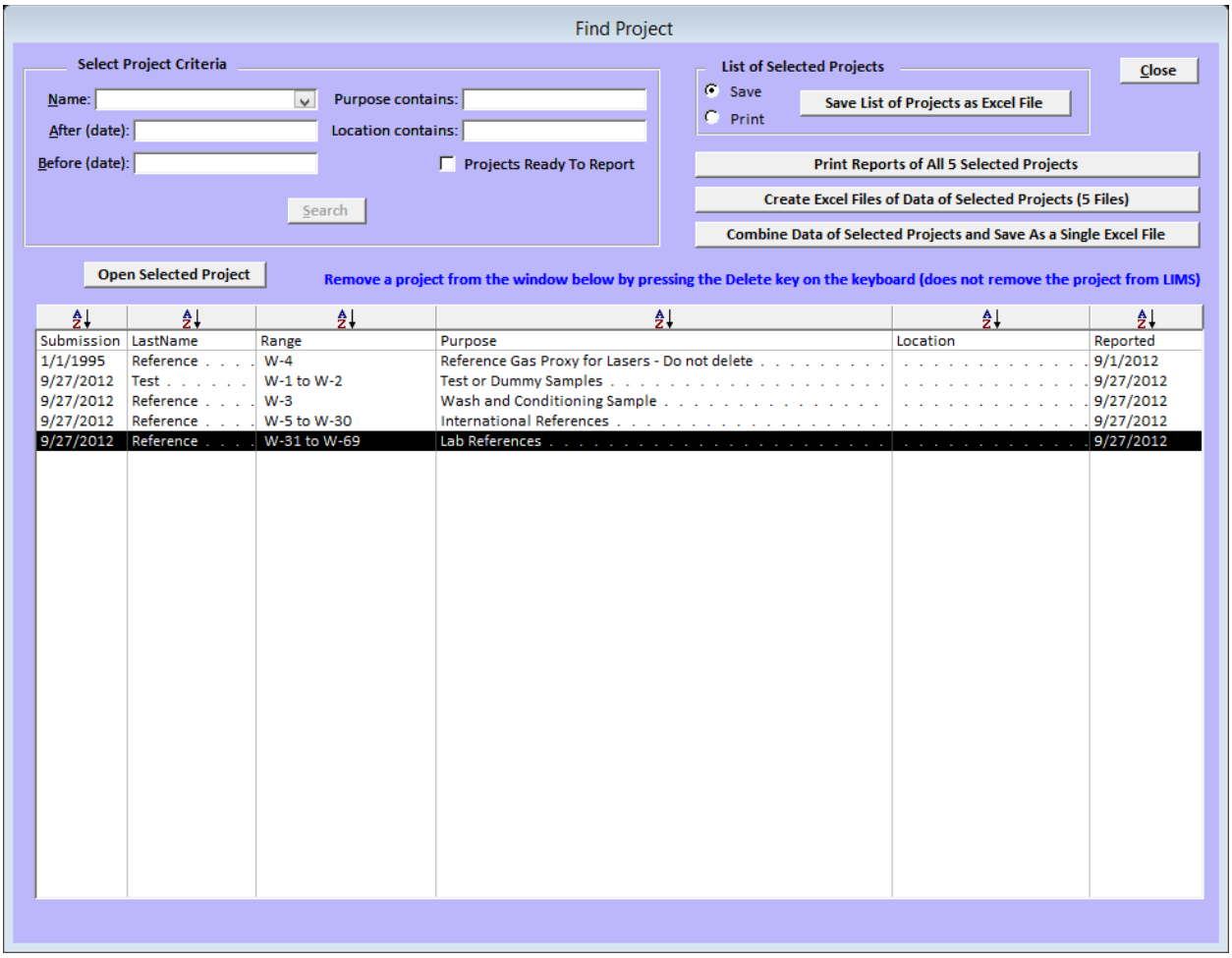
A Project is defined as one set of water samples submitted by one customer for the analysis of δ^2H and δ^{18}O/δ^{17}O for a particular purpose and/or from a specific location (e.g. Project Name, Location).

LIMS for Lasers 2015 comes pre-populated with projects for international primary measurement standards (e.g. VSMOW2, SLAP2) and for your own laboratory standards. A test project is also included - typically used for dummy or pre-conditioning samples. These projects should not be deleted. Your laboratory measurement standards and tests waters can be added and edited within these dedicated Projects.

New customer Projects are created in one of two ways:

- Manually entering a customer and all of the sample information
- Automatically importing a customer's samples using an Excel submission template

The second option may be preferable since it contains information supplied by the customer and typically accompanies the water samples arriving at the laboratory. Importing project information from an Excel template is preferred because it ensures no typographic errors are made by laboratory staff (see Excel Submission Templates).



The Projects Summary Page.

Searching for Projects

As projects accumulate in the database over time, *LIMS for Lasers 2015* includes powerful searching capabilities for quickly locating client projects and data. One can search for projects using a combination of full and partial information criteria by:

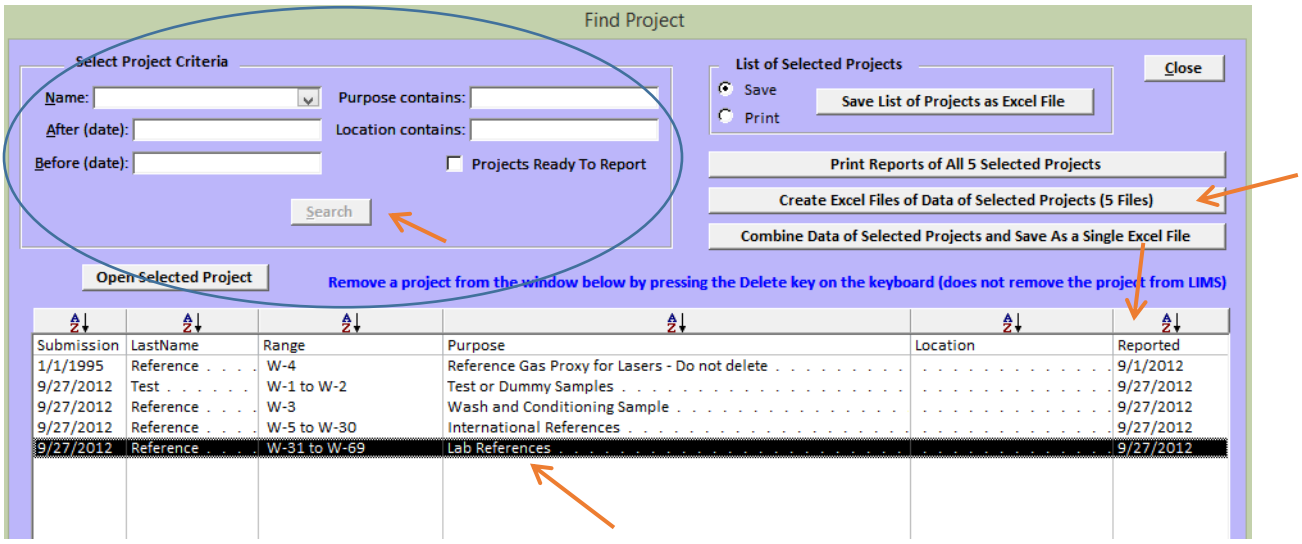
- Customer Name
- Purpose: that contains specified text, such as Leakage
- Before and/or after dates
- Completed or uncompleted projects
- Project Location; contains the specified location text, such as Texas

Sorting Projects

Quick sorting of Projects can be accomplished by clicking on the desired header, like Submission Date, Lastname, ID Range, Purpose Location or date submitted or reported.

Reporting and Exporting Projects

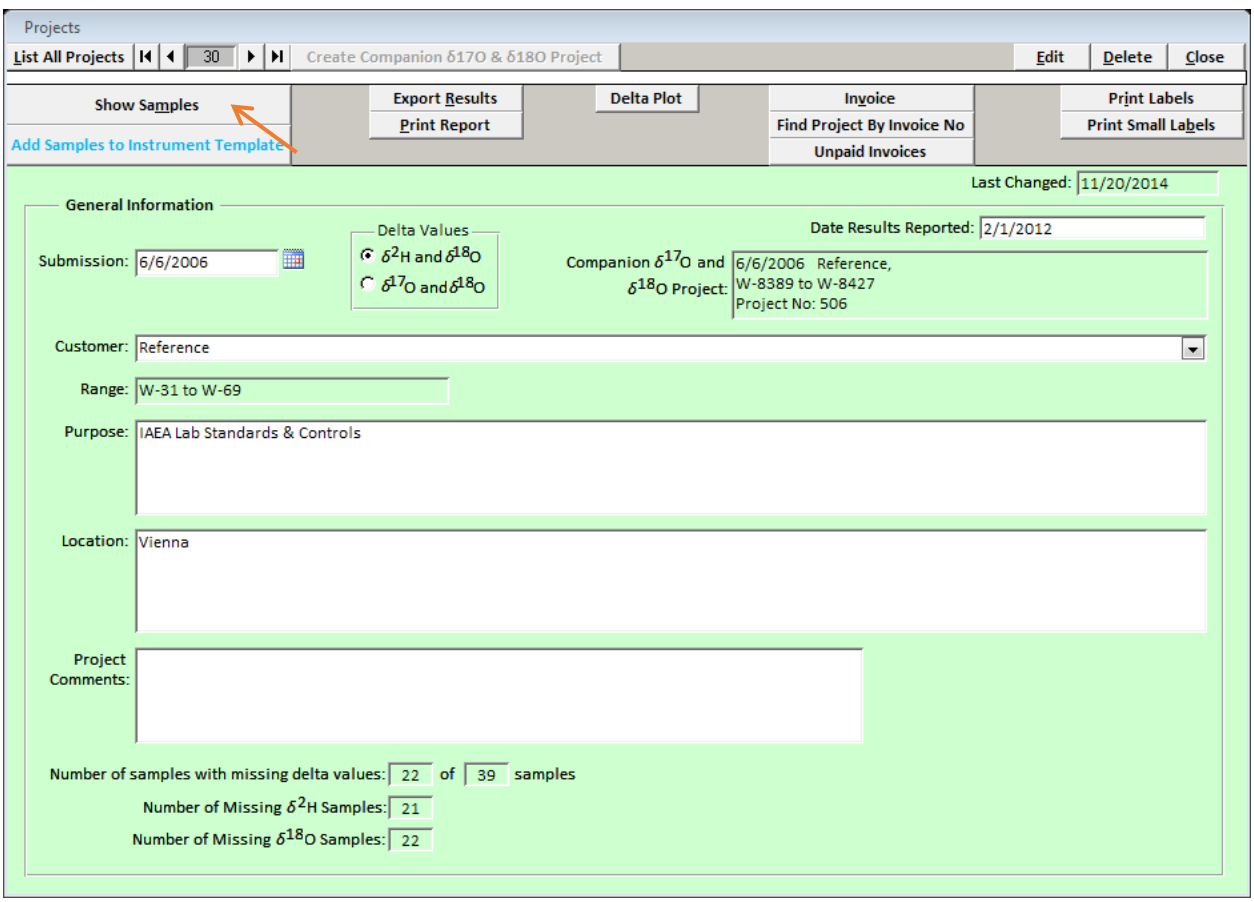
Searching, exporting, and combining multiple projects into a single report or single or combined Excel file is done on the Project overview page. Summary lists of all, searched or sorted laboratory projects may be printed or saved to Excel files. This feature provides a quick way to search, acquire, and summarize laboratory productivity information for annual reports, for example (e.g. how many samples and projects the lab completed in 2015).



Project Information

A Project is opened by selecting and double-clicking a highlighted project in the View Projects page. The lower part of the view pane displays a summary of mandatory and optional information about the project, including:

- The Submission date when the samples arrived or were logged (required)
- The Customer name (required)
- Purpose - a descriptive, searchable field (optional)
- Location - a descriptive, searchable field (optional)
- Range (W-XX numbers are automatically assigned by LIMS)
- Comment field for other relevant project information (optional)
- Total number of samples, and type and number of samples to be completed
- The date when final results were reported to the Customer



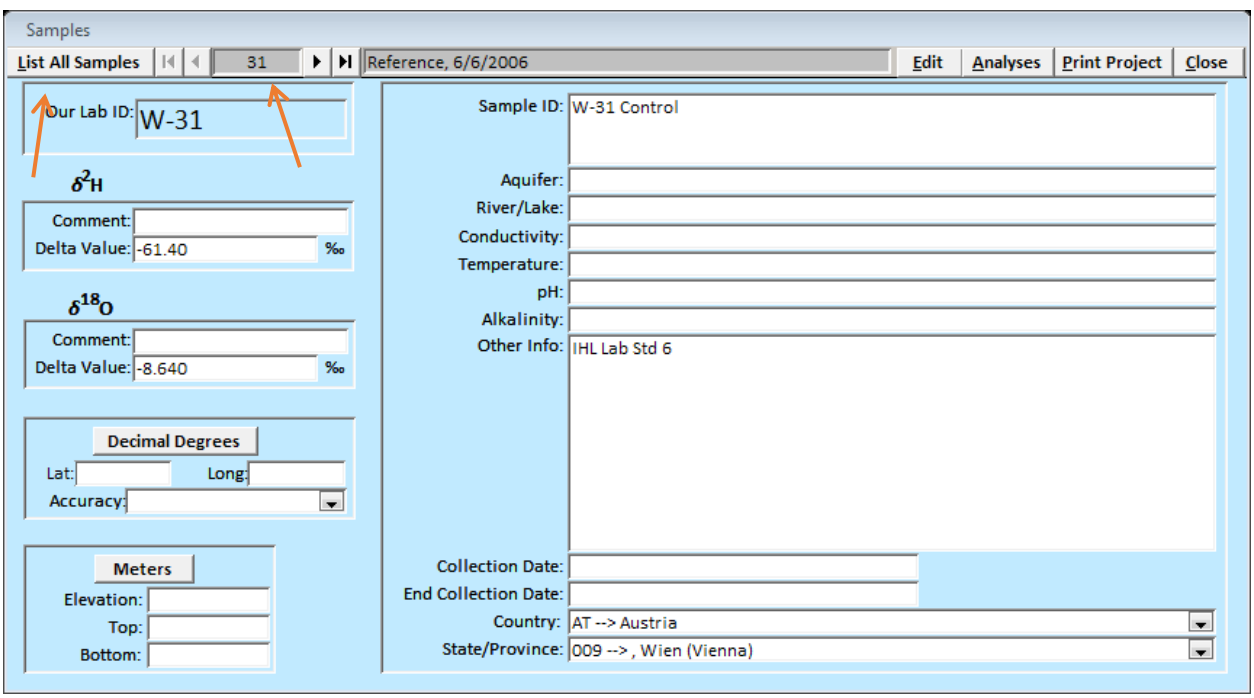
The upper part of the project pane (grey buttons) display several action items that apply to the opened Project. These include:

- Editing and viewing individual sample details in Show Project Samples
- Adding Samples to an Instrument Template (in blue)
- Creating / Showing the Companion Project for $\delta^{17}O$ (optional)
- Printing sample or laser-vial labels
- Printing a copy of the project report for the customer
- Graphing a $\delta^{2}H$ vs. $\delta^{18}O$ cross plot of the results (Delta Plot)
- Exporting results to an Excel spreadsheet
- Invoicing features (optional)
- Deleting a Project – click the "Delete" button –this action can only be performed if no analyses were imported into *LIMS for Lasers 2015*

The above information can be edited by clicking the "Edit "button on the top of the window.

Samples and Analyses

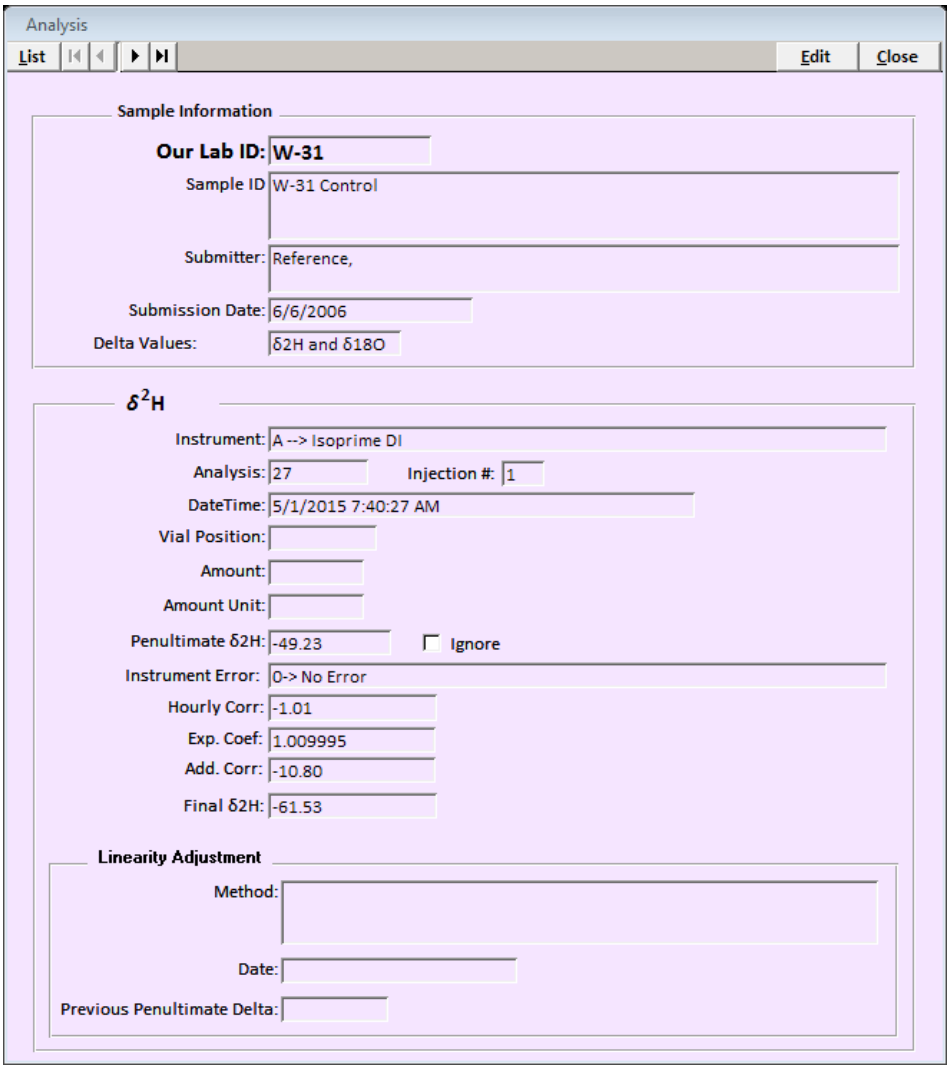
Clicking on the "Show Samples" button opens up more information about each sample in the Project. Navigation through samples is performed by using the arrow buttons, the "List All Samples" button, both at the top left of the Window, or the scroll wheel of the mouse.



On the Samples page information about the sample is summarized that includes:

- The sample Our Lab ID (a W-number assigned by LIMS).
- The sample $\delta^{2}H$ and $\delta^{18}O$/ $\delta^{17}O$ results, if evaluated and stored.
- Various optional customer supplied information about the specific sample.

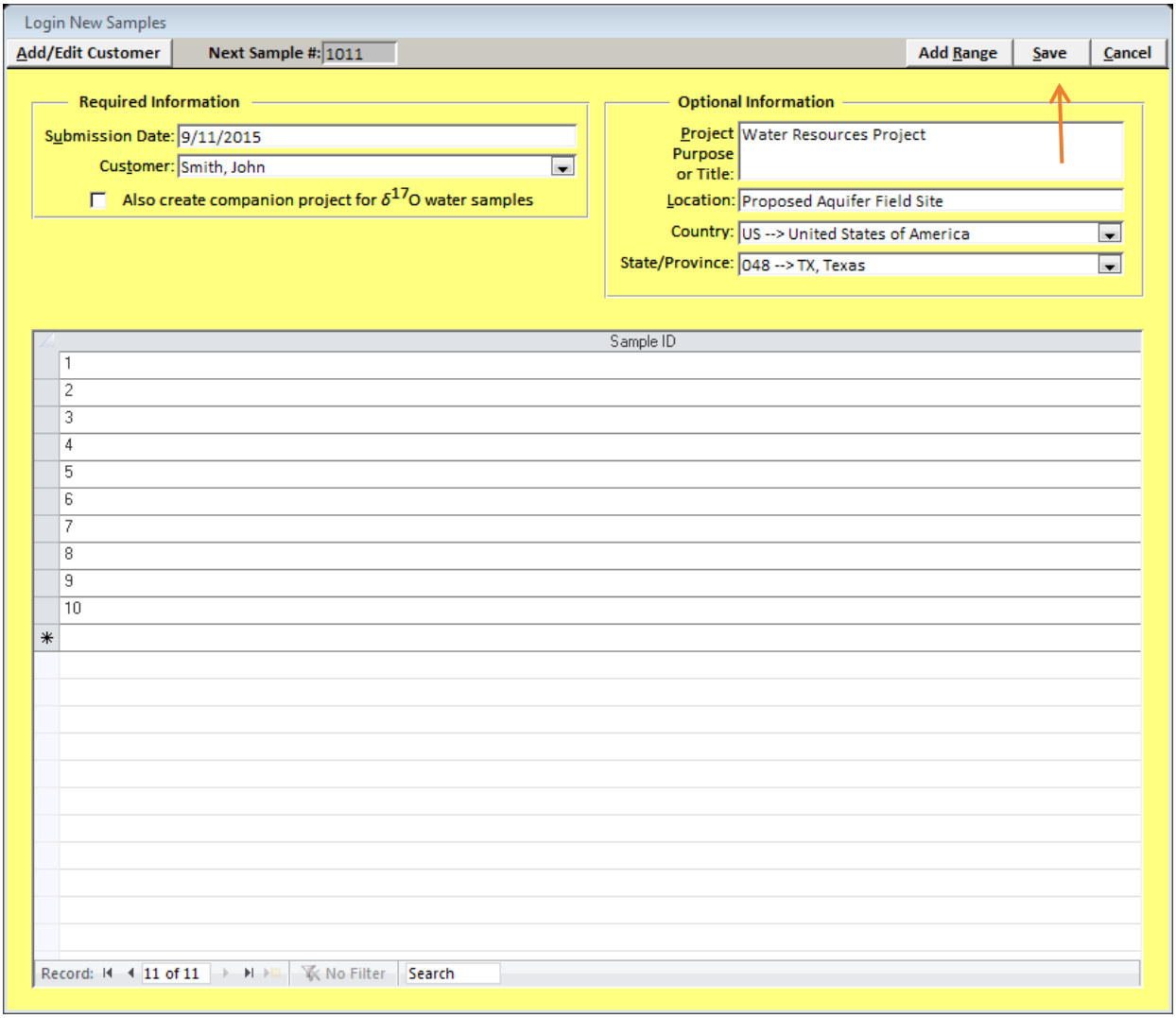
Clicking on the “Analyses” button opens a new window that gives more detailed information about each isotopic analyses of one sample, including date analysed, the instrument used, method, etc. This window will only open if sample analyses have been completed.



6.3 Manually Create a New Project

Manual $\delta^{18}O$ and $\delta^{2}H$ Project creation and typographical entry of samples is illustrated using an example. John Smith (a previously added Customer) has submitted 10 water samples from a proposed aquifer site in Texas for a water resources project. The sample bottles arriving in the laboratory were labelled “1” through “10”.

1. On the Main Page, Click “Create a New Project”.
2. Click “Submission Date” – use the calendar icon to select a date or click “Today”.
3. Choose “Smith, John” from the Customer menu.
4. Type “Water Resource Project” in Project Purpose or Title field.
5. For Location – enter “Proposed Aquifer Field Site”.
6. Choose “US” from country pull down menu.
7. In the Sample ID list, enter the sample names (1 to 10), using one sample per line.
8. If $\delta^{17}O$ were required, check the appropriate box for a companion project.
9. When completed, click “Save” (top right).
10. A dialog box confirms that you want to create a new project containing 10 new water samples with LIMS assigned ID ranging from W-1001 to W1010. Click Yes.
11. The new Project is completed and is now visible in the “View Projects” tab.

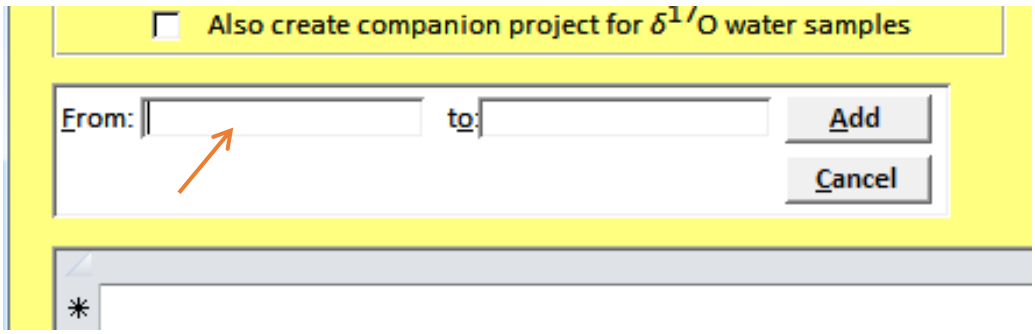


The *minimum* information required is a Submission Date, Customer, and Sample ID. Optional Information can be updated or added later. Note: Sample names must be unique, any duplicate names should be recoded (e.g. Sample1, Sample1a, Sample1b, etc.).

The "Add Range" Option

Project entry can be partly automated using the "Add Range" button located on the top right of the Login New Samples page (see previous figure). Add Range automatically inserts a range of named samples with, for example, incremental numbering.

Clicking on "Add Range" button opens a new "From:" and "To:" field in the white box below Required Information area:



The format of the From and To fields requires that both entries have the same nonnumeric prefix if there is a nonnumeric prefix. To create a δ^{17}O companion project, check the box here.

Correct Range Entry Format

Example: From: IAEA 001 To: IAEA 200
Automatically adds 200 samples of consecutively numbered samples

Example From: IAEA 4.011 To: IAEA 4.210
Automatically adds 200 consecutively numbered samples

Example From: IAEA200 To: IAEA1
Automatically adds 200 consecutively numbered samples, in decreasing value

Incorrect Range Entry Format (Results in Range Error)

Example: From: Test1 to: Testsample200 (non-numeric prefix different)

Important Note About Projects and New Samples
Once a Project has been created, one cannot later on add new samples into the Project. Be sure to have all samples in hand before creating a Project, or otherwise create several projects over time (client multiple projects are easily combined for single file export – see Section 13.2).

6.4 Create a δ^{17}O Project

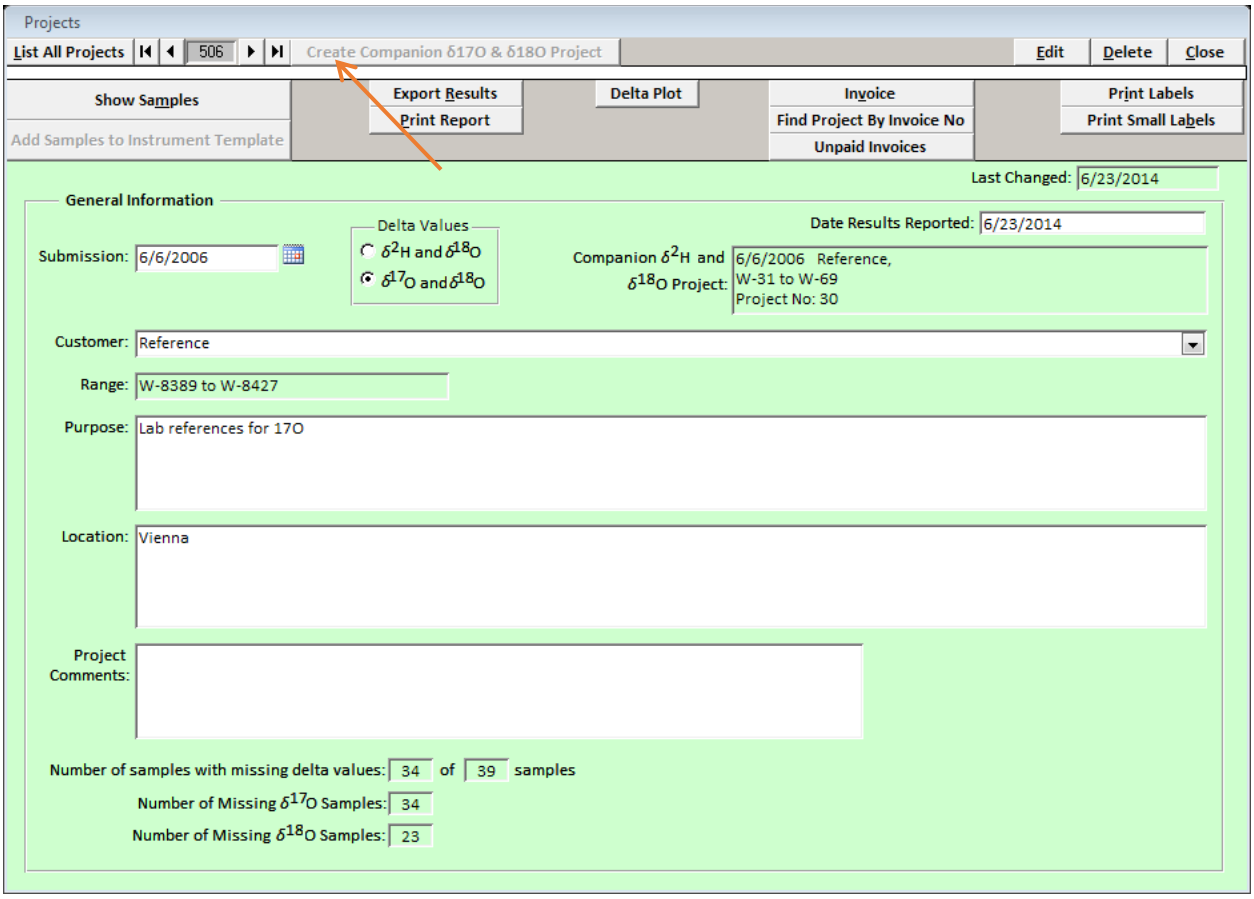
Some water isotope laser instruments can be purchased with δ^{17}O measurement capability. These instruments currently include the Los Gatos Research TIWA 45-EP and the Picarro L2140i models.

If your laser has δ^{17}O capability, it can be enabled in *LIMS for Lasers 2015* as described in Chapter 5.2 for the Los Gatos Research instrument and Chapter 5.3 for the Picarro instrument. To avoid any confusion between dual and triple water isotope lasers or projects, a Complimentary Project must be created for δ^{17}O.

Caution: Specialized templates are required to achieve the "<30–50 per meg" uncertainties required for δ^{17}O and ^{17}O-excess data interpretations. Achieving this high level of precision requires many more injections than routine δ^{2}H and δ^{18}O analyses. Measurement of δ^{17}O is therefore considered to be a distinctive analytical activity, and it is thereby treated separately in *LIMS for Lasers 2015*.

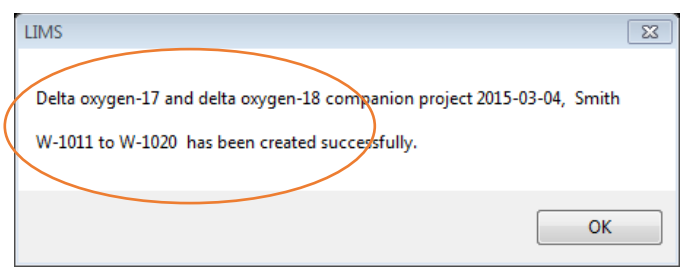
First, create the water isotope Project for δ^{2}H and δ^{18}O, as described in Sections 6.3 above and 6.5 below.

1. Open the δ^{2}H and δ^{18}O Project that also requires δ^{17}O assays.
2. At the top of the Project δ^{2}H and δ^{18}O window, click "Create Companion δ^{17}O and δ^{18}O Project"



3. A confirmation message will appear; click "OK". Note: A new W- range is created for the δ^{17}O project.

Note: It is recommended that a δ^{17}O Project, if required, be created at the same time as the δ^{2}H and δ^{18}O project. In this way, the Our Lab ID numbers are adjacent to each other for easier sample and project identification.



Submission: 3/4/2015 Smith, John W-1001 to W-1010 3/4/2015

Purpose: Johns Test Waters for LAS

Location: El Paso aquifer

Sample ID:	Collection Date	Our Lab ID	δ^2H_{VSMOW}, in ‰ Value	Comment	$\delta^{18}O_{VSMOW}$, in ‰ Value	Comment
Sample1		W-1001				
Sample2		W-1002				
Sample3		W-1003				
Sample4		W-1004				
Sample5		W-1005				
Sample6		W-1006				
Sample7		W-1007				
Sample8		W-1008				
Sample9		W-1009				
Sample10		W-1010				

Example $\delta^{18}O$ and δ^2H project printed from the LIMS Project Page (no completed samples).

Submission: 3/4/2015 Smith, John W-1011 to W-1020 3/4/2015

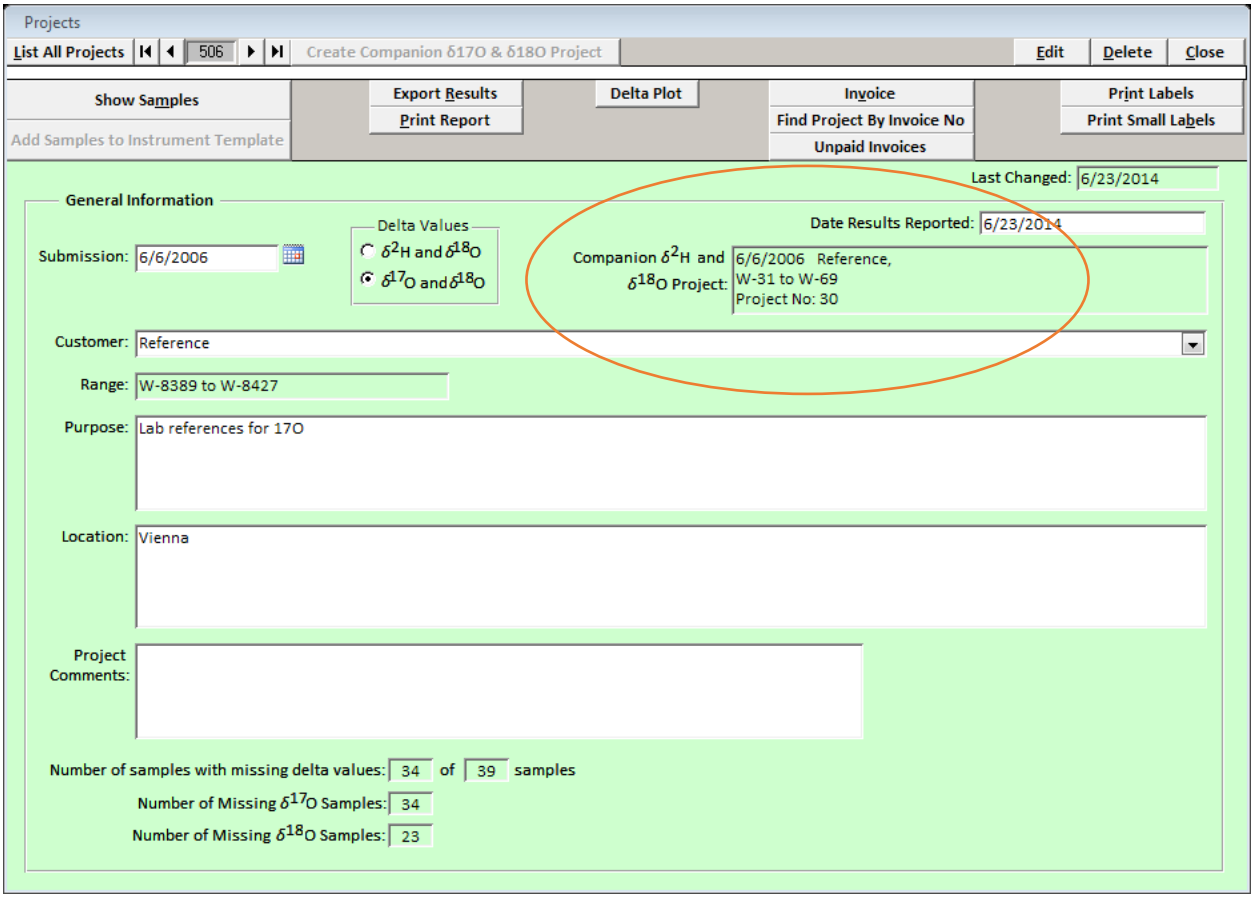
Purpose: Johns Test Waters for LAS

Location: El Paso aquifer

Sample ID:	Collection Date	Our Lab ID	$\delta^{17/16}O_{VSMOW}$, in ‰ Value	Comment	$\delta^{18}O_{VSMOW}$, in ‰ Value	Comment
Sample1		W-1011				
Sample2		W-1012				
Sample3		W-1013				
Sample4		W-1014				
Sample5		W-1015				
Sample6		W-1016				
Sample7		W-1017				
Sample8		W-1018				
Sample9		W-1019				
Sample10		W-1020				

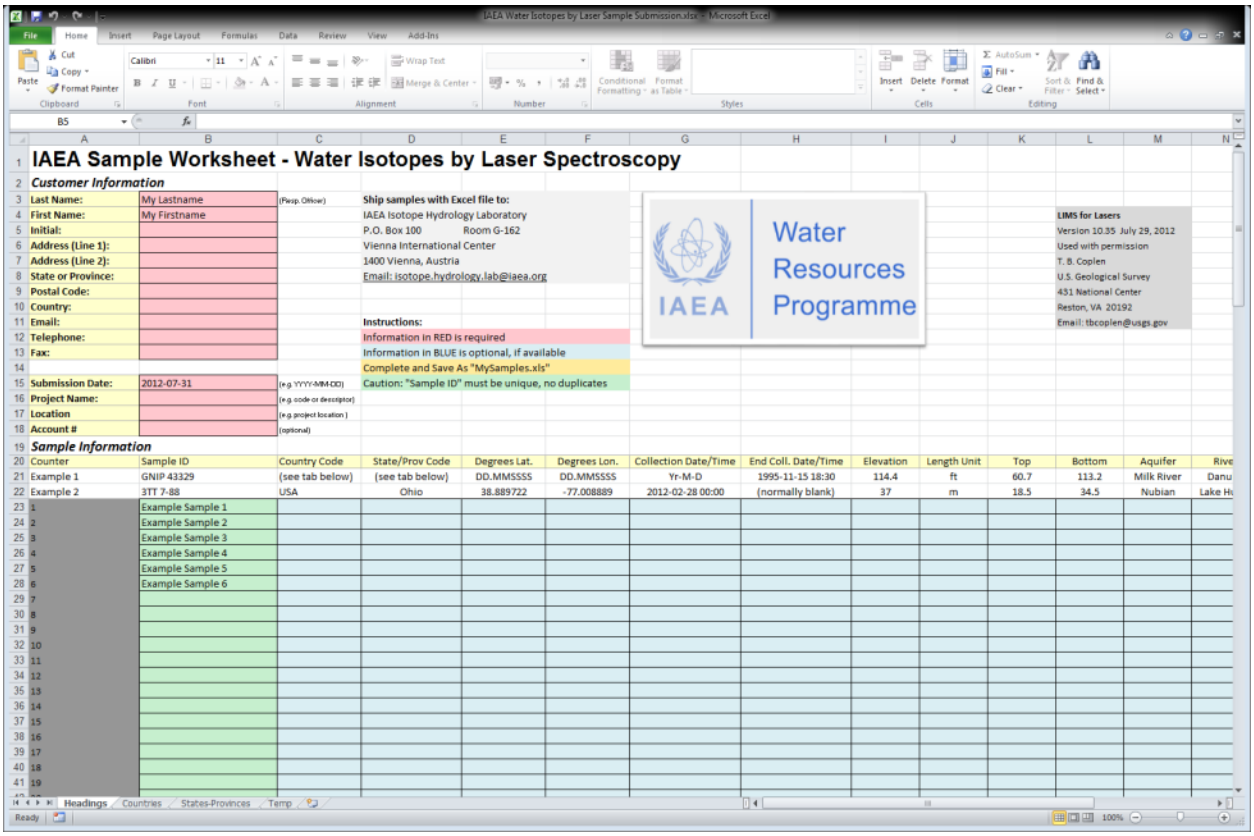
Example $\delta^{17}O$ companion project from the LIMS Project Page (no completed samples).

Keeping track of $\delta^{17}O$ Companion Projects is done from the main page of each Project. For example, for the previously created project, the Project panel displays the Our Lab ID range of the companion project. The $\delta^{18}O$ values are automatically updated from the δ^2H and $\delta^{18}O$ project.


Projects
List All Projects
506
Create Companion δ17O & δ18O Project
Edit
Delete
Close
Show Samples
Add Samples to Instrument Template
Export Results
Print Report
Delta Plot
Invoice
Find Project By Invoice No
Unpaid Invoices
Print Labels
Print Small Labels
Last Changed: 6/23/2014
General Information
Date Results Reported: 6/23/2014
Submission: 6/6/2006
Delta Values
δ2H and δ18O
δ17O and δ18O
Companion δ2H and δ18O Project:
6/6/2006 Reference,
W-31 to W-69
Project No: 30
Customer: Reference
Range: W-8389 to W-8427
Purpose: Lab references for 17O
Location: Vienna
Project Comments:
Number of samples with missing delta values: 34 of 39 samples
Number of Missing δ17O Samples: 34
Number of Missing δ18O Samples: 23

6.5 Import a New Project using Excel

A convenient way to make a new Project is to import an Excel file containing information provided by the Customer. Having clients complete and provide sample names and details and submitting an Excel file (by email or CD) along with the water samples saves time and eliminates transcription errors. User-editable sample submission templates are available from the IAEA and USGS Web sites (Chapter 3.1). The latest IAEA Excel water sample submission file is shown here as an example:



IAEA Sample Worksheet - Water Isotopes by Laser Spectroscopy

Customer Information

Last Name:	My Lastname	(Pwsp. Office)
First Name:	My Firstname	
Initial:		
Address (Line 1):		
Address (Line 2):		
State or Province:		
Postal Code:		
Country:		
Email:		
Telephone:		
Fax:		
Submission Date:	2012-07-31	(e.g. YYYY-MM-DD)
Project Name:		(e.g. code or descriptor)
Location		(e.g. project location)
Account #		(optional)

Ship samples with Excel file to:
IAEA Isotope Hydrology Laboratory
P.O. Box 100 Room G-162
Vienna International Center
1400 Vienna, Austria
Email: isotope.hydrology.lab@iaea.org

Instructions:
Information in RED is required
Information in BLUE is optional, if available
Complete and Save As "MySamples.xls"
Caution: "Sample ID" must be unique, no duplicates

IAEA Water Resources Programme

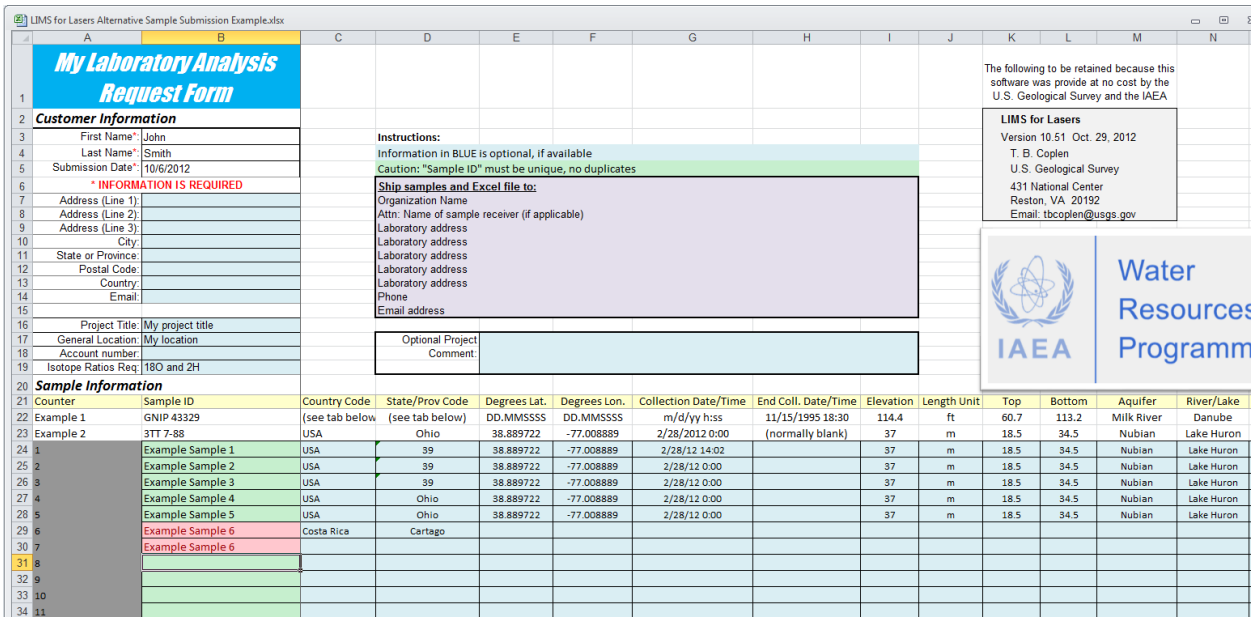
LIMS for Lasers
Version 10.35 July 29, 2012
Used with permission
T. B. Coplen
U.S. Geological Survey
431 National Center
Reston, VA 20192
Email: tbcoplen@usgs.gov

Sample Information

Counter	Sample ID	Country Code	State/Prov Code	Degrees Lat.	Degrees Lon.	Collection Date/Time	End Coll. Date/Time	Elevation	Length Unit	Top	Bottom	Aquifer	Rive
Example 1	GNIP 43329	(see tab below)	(see tab below)	DD.MMSSSS	DD.MMSSSS	Yr-M-D	1995-11-15 18:30	114.4	ft	60.7	113.2	Milk River	Danu
Example 2	3TT 7-88	USA	Ohio	38.889722	-77.008889	2012-02-28 00:00	(normally blank)	37	m	18.5	34.5	Nubian	Lake H
1	Example Sample 1												
2	Example Sample 2												
3	Example Sample 3												
4	Example Sample 4												
5	Example Sample 5												
6	Example Sample 6												
7													
8													
9													
10													
11													
12													
13													
14													
15													
16													
17													
18													
19													

An alternative sample submission (shown below) is available from [http://isotopes.usgs.gov/research/topics/lims.html.](http://isotopes.usgs.gov/research/topics/lims.html)

Both incorporate conditional formatting in order to identify samples with duplicate names (see the two magenta cells in the spreadsheet below). Both Excel templated from IAEA and USGS can be easily modified to your own laboratory needs.



LIMS for Lasers Alternative Sample Submission Example.xlsx

My Laboratory Analysis Request Form

The following to be retained because this software was provide at no cost by the U.S. Geological Survey and the IAEA

LIMS for Lasers
Version 10.51 Oct. 29, 2012
T. B. Coplen
U.S. Geological Survey
431 National Center
Reston, VA 20192
Email: tbcoplen@usgs.gov

Customer Information

First Name*:	John
Last Name*:	Smith
Submission Date*:	10/6/2012
* INFORMATION IS REQUIRED	
Address (Line 1):	
Address (Line 2):	
Address (Line 3):	
City:	
State or Province:	
Postal Code:	
Country:	
Email:	
Project Title:	My project title
General Location:	My location
Account number:	
Isotope Ratios Req:	18O and 2H

Instructions:
Information in BLUE is optional, if available
Caution: "Sample ID" must be unique, no duplicates

Ship samples and Excel file to:
Organization Name
Attn: Name of sample receiver (if applicable)
Laboratory address
Laboratory address
Laboratory address
Laboratory address
Laboratory address
Phone
Email address

Optional Project Comment:

IAEA Water Resources Programm

Sample Information

Counter	Sample ID	Country Code	State/Prov Code	Degrees Lat.	Degrees Lon.	Collection Date/Time	End Coll. Date/Time	Elevation	Length Unit	Top	Bottom	Aquifer	River/Lake
Example 1	GNIP 43329	(see tab below	(see tab below)	DD.MMSSSS	DD.MMSSSS	m/d/yy h:ss	11/15/1995 18:30	114.4	ft	60.7	113.2	Milk River	Danube
Example 2	3TT 7-88	USA	Ohio	38.889722	-77.008889	2/28/2012 0:00	(normally blank)	37	m	18.5	34.5	Nubian	Lake Huron
1	Example Sample 1	USA	39	38.889722	-77.008889	2/28/12 14:02		37	m	18.5	34.5	Nubian	Lake Huron
2	Example Sample 2	USA	39	38.889722	-77.008889	2/28/12 0:00		37	m	18.5	34.5	Nubian	Lake Huron
3	Example Sample 3	USA	39	38.889722	-77.008889	2/28/12 0:00		37	m	18.5	34.5	Nubian	Lake Huron
4	Example Sample 4	USA	Ohio	38.889722	-77.008889	2/28/12 0:00		37	m	18.5	34.5	Nubian	Lake Huron
5	Example Sample 5	USA	Ohio	38.889722	-77.008889	2/28/12 0:00		37	m	18.5	34.5	Nubian	Lake Huron
6	Example Sample 6	Costa Rica	Cartago										
7	Example Sample 6												
8													
9													
10													
11													

To Import and Create a New Project using an Excel Template

1. On the LIMS Main Page, click “Import a New Project from Excel Submission” under the Projects heading.
2. In the Windows filename dialog box, locate and double click on the Excel sample submission file to be imported.
3. A confirmation dialog will indicate how many samples and the range of new “W” Laboratory ID numbers to be assigned to the samples. Click “OK”.
4. A dialog will ask if you also want to create a companion ^{17}O project (Y/N as needed).
5. The New Project will appear under “View Projects”.

Reminder*:* Before importing, be sure the Customer name was added and the first and last names *match exactly* those in the Excel file (see Chapter 6.1).

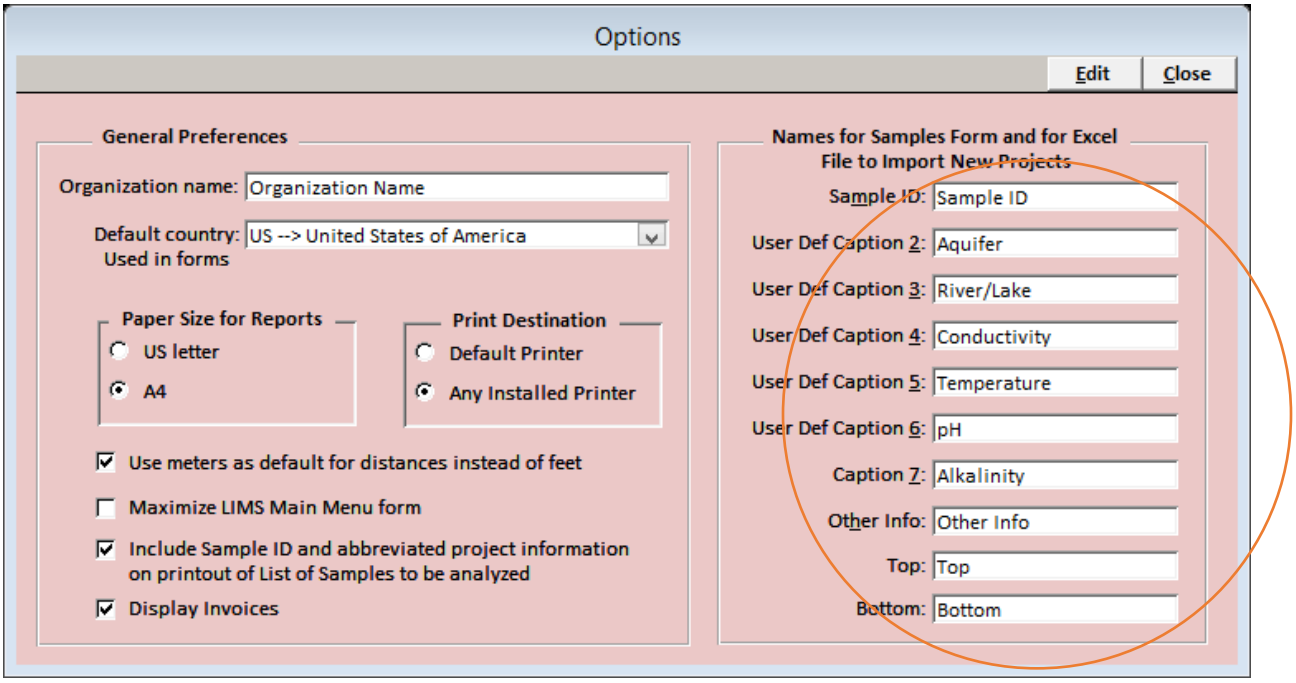
6.6 Customize Excel Submission Forms

A useful way to import new Projects is to deploy customized Excel sample submission templates to your customers.

Editable "unprotected" *LIMS for Lasers* Excel Submission templates are available from the links in Chapter 3.1. These Excel files may be edited and changed to construct your own laboratory information needs and graphics.

Any data field customizations made to the provided Excel templates will also require editing *LIMS for Lasers 2015* optional sample information. This is due to the fact that the field names in the Excel template must have a corresponding field name in *LIMS for Lasers 2015*.

On the Main page, click "Special Features", and click the "Options" button. On the right panel there is a list of User Definable Captions that can be changed and used in the Excel file.

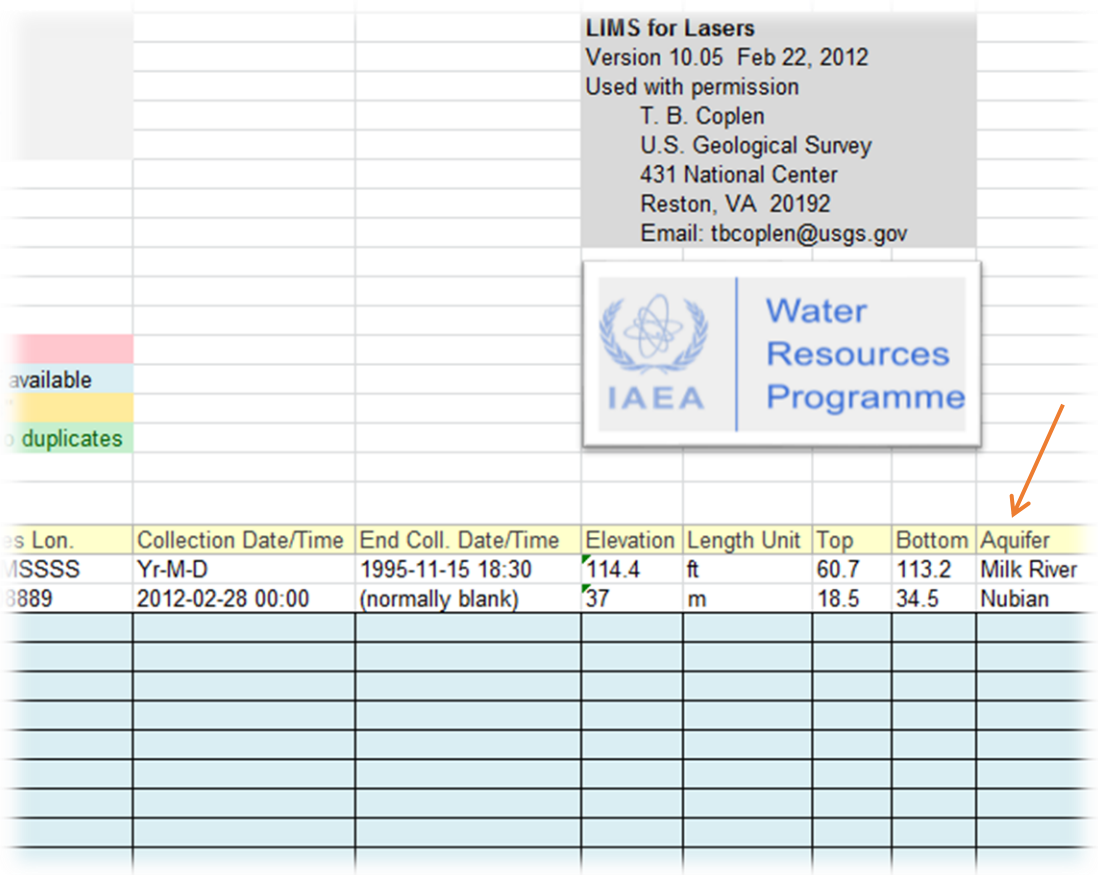


To change any of the field names (e.g. Aquifer, Conductivity, pH, etc.) to your own preferences, click "Edit" and change the fields. For example, "Aquifer" might be changed to "Site Name".

Not all field names are required. *LIMS for Lasers 2015* requires only Sample ID in this custom list. If you do not need Caption 7 (e.g. Alkalinity), then delete Alkalinity from the Caption 7 textbox and delete the Alkalinity column from the Excel template. Once all required edits are made, click "Save" and "Close". LIMS will expect matching headers in the customized Excel import file.

Changing Headers in the Excel Submission Template

Open the “unprotected” Excel Submission template and locate the corresponding optional field(s) names to be changed. In this example, the header “Aquifer” can be replaced with “Site Name”:



Important: Be sure the headers in the worksheet correspond *exactly* to those in the *LIMS for Lasers 2015* options fields or the import will fail. For optional fields left blank in *LIMS for Lasers 2015*, delete the corresponding column from the submission spreadsheet.

Caution! Repeatedly changing LIMS field header names is strongly discouraged. Give clear thought to what information is required by your laboratory, and stick with it.

Note: The *LIMS for Lasers 2015* permission insignia shown above must be retained on import spreadsheets for legal purposes because this software is provided by the U.S. Geological Survey and the IAEA at no cost and the spreadsheets may not import.

Protect the Sample Submission Template

Experience has shown that Excel sample submission templates are invariably altered by customers (e.g. customers may try to delete or add columns, paste incorrect cell formats, paste to a new spreadsheet, etc.), all of which can cause import failure in *LIMS for Lasers 2015*.

For this reason, the final submission worksheet should be "protected" to allow customers to only fill out those fields required by the laboratory. While Excel cell protection is not fool-proof, your laboratory should provide explicit instruction for use.

To help protect your Laboratory Sample Submission Excel spreadsheet:

1. In Excel 2007/10, Click on the "Review" Tab.
2. Click on "Protect Sheet" – enter a new password (and record it).
3. Save the file, distribute to Customers.
4. Now clients can add their information to the sample data fields required by LIMS. All other fields are locked against editing, unless the password is disabled.

6.7 Tips for Successful Excel Submission Templates

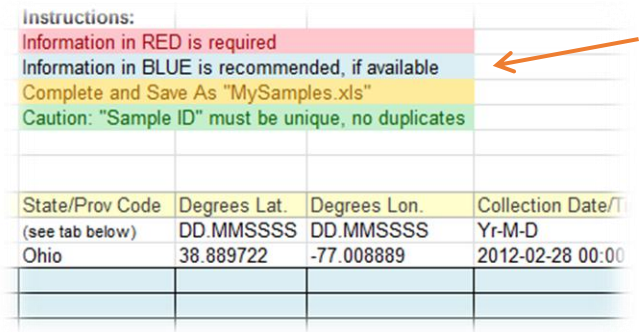
Based on our experience with hundreds of clients, here are a few tips for successful use of Excel sample submission forms:

In the Laboratory

- Download one of the provided unprotected Excel template to add/edit your required data (contact information, address, add your laboratory logo, etc.).
- Ensure changed optional fields in Excel *exactly* match those in your LIMS "Options".
- Protect your distributable Excel Submission Template with a password.
- Test your new Excel import file with dummy data to ensure that the imports work correctly.
- **Never** combine different customers' samples into a single project – this will be confusing.

For your Customers

- Email protected Excel Submission forms to your customers, or post on your Web site.
- Recommend that customers keep a copy of the original Excel template for future samples.
- Customers should complete their information and "Save As" using a descriptive filename.
- The Excel Submission Template should accompany the water samples (on CD/USB stick or by email).
- A printed hard copy of the Excel submission along with the water samples is useful.
- The *minimum information* required is: Lastname, Firstname, Submission Date, and Sample IDs.



Note to LIMS v.9 users: *LIMS for Lasers 2015* does not require any media codes – samples are automatically assigned to Media Code 1 (water δ^2H and δ^{18}O) and Media Code 1017 for δ^{17}O).

6.8 Print Sample and Vial Labels

Printing Large Sample Bottle Labels

LIMS for Lasers 2015 can print large labels (Avery or equivalent) that may be attached to incoming water sample bottles. This will allow laboratory staff to organize and easily locate the water samples.

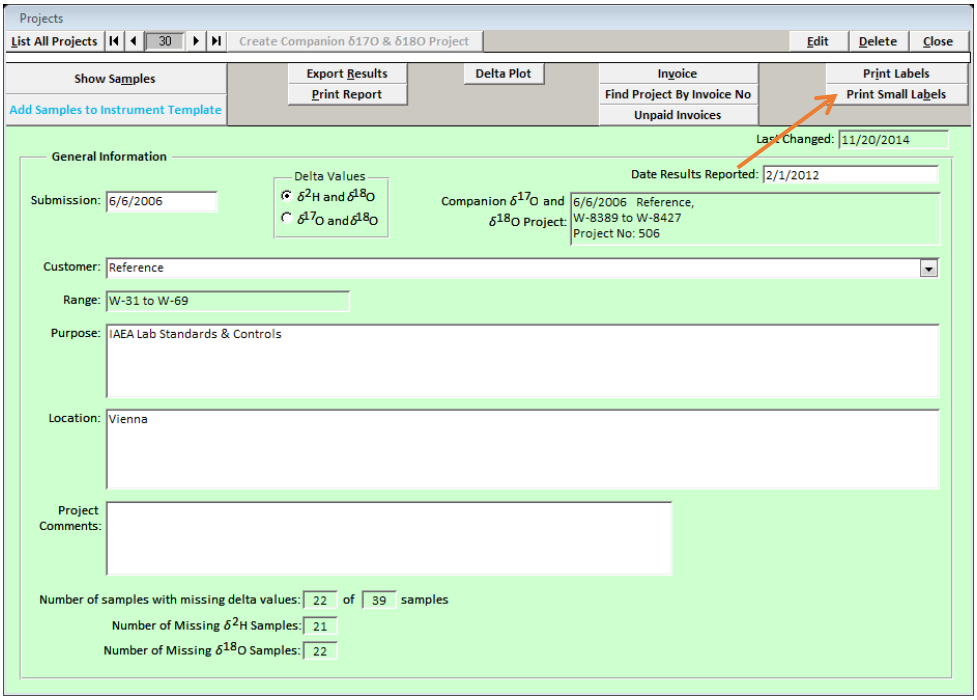
1. In a Customer Project, click “Print Labels”, and then click “Yes”.
2. The default number of labels printed is 1 (select 2 or more in case of sample splits).
3. Ensure the printer has the correct size 30 or 21 large label laser printer sheets inserted (respectively, Avery 5260 Letter Size or Avery L7160 A4 Size, or equivalent). The label sheet size should match the paper size set in LIMS Options (Letter / A4). Click “Print”.
4. Affix the large sample labels to the correct customer sample bottles.

Print Small Labels for Laser Sample Vials

LIMS for Lasers 2015 can also print small labels to be affixed to the 2-mL sample vials used on the laser instrument auto sampler.

1. In the Project window, click on Print Small Labels, and click “Yes”.
2. The default number of labels per sample printed is 1 (select 2 for two-vial assays).
3. Ensure the printer has 80 or 84 small labels per sheet (respectively, Avery 5267 for Letter Size or Avery L7656 for A4, or equivalent) inserted. Click “Print”.
4. Affix the sample label to the appropriate sample vial (alternately, W numbers can simply be written on the side of the vials using a permanent marker).

Tip: It may be easier to write the sample ID on small laser vials with a permanent marker.



W-1001 Sample1	**W-1002** Sample2	**W-1003** Sample3	**W-1004** Sample4
W-1005 Sample5	**W-1006** Sample6	**W-1007** Sample7	**W-1008** Sample8
W-1009 Sample9	**W-1010** Sample10		

Example sheet printout of small Avery labels.

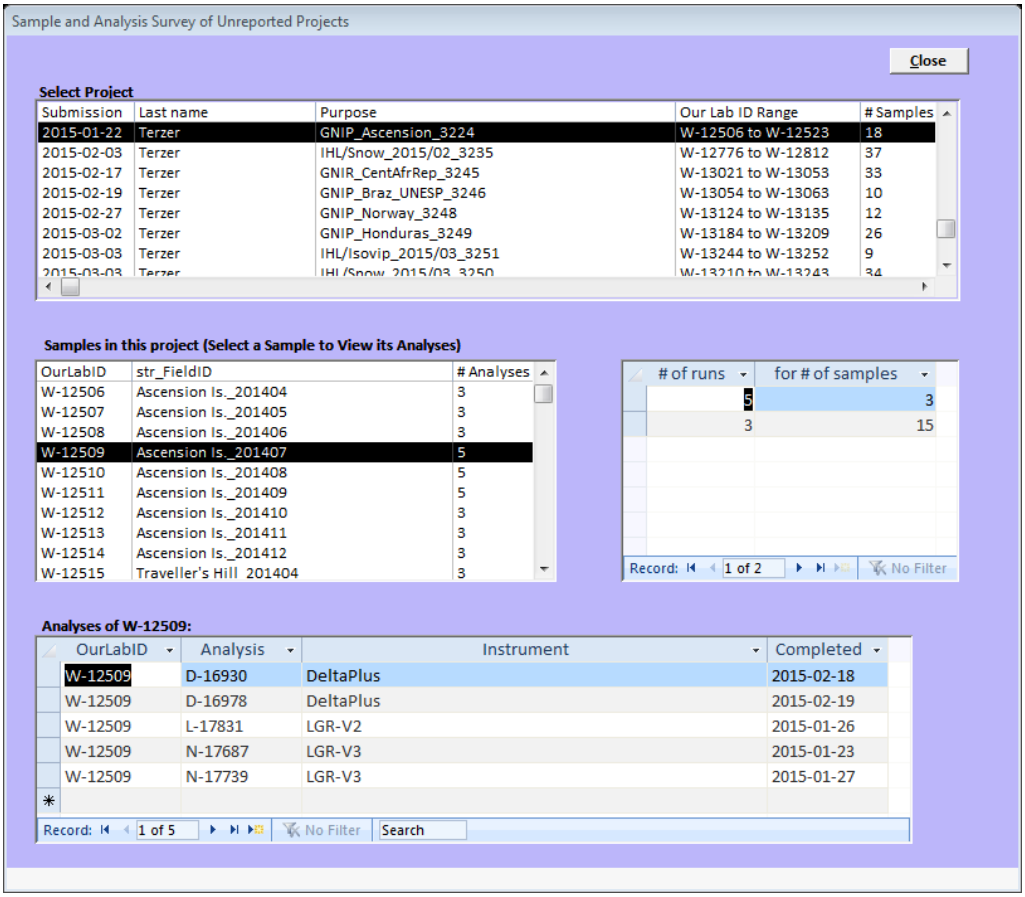
Example: Laser instrument 2-mL vial with small Avery label attached.

6.9 Survey of Unreported Projects

For laboratories that analyse samples with multiple instruments (e.g. lasers, mass spectrometers), it's easy to lose track of incomplete analyses, on which instruments samples were measured, or how many times samples were replicated.

LIMS for Lasers 2015 allows the analyst to quickly identify outstanding samples and identify whether replicates are needed. On the main page, click "Sample and Analysis Survey of Unreported Projects". In the window that opens (see below), a list of unreported Projects is displayed (e.g. not analysed, partially completed, or not stored). The middle and lower panels reveal a list of samples in the project, how often each sample has been analysed (e.g. if lab has an analyse-twice policy), and on which instruments samples have been analysed.

In the example below, we see sample W-12509 was measured 5 times (bottommost panel) on three different instruments (prefix L, N, D). We see in the middle-right panel that of 18 samples in the project, 15 samples were analysed 3 times and 3 samples were analysed 5 times.



Example screen of Survey of Unreported Projects

7 Isotopic Measurement Standards

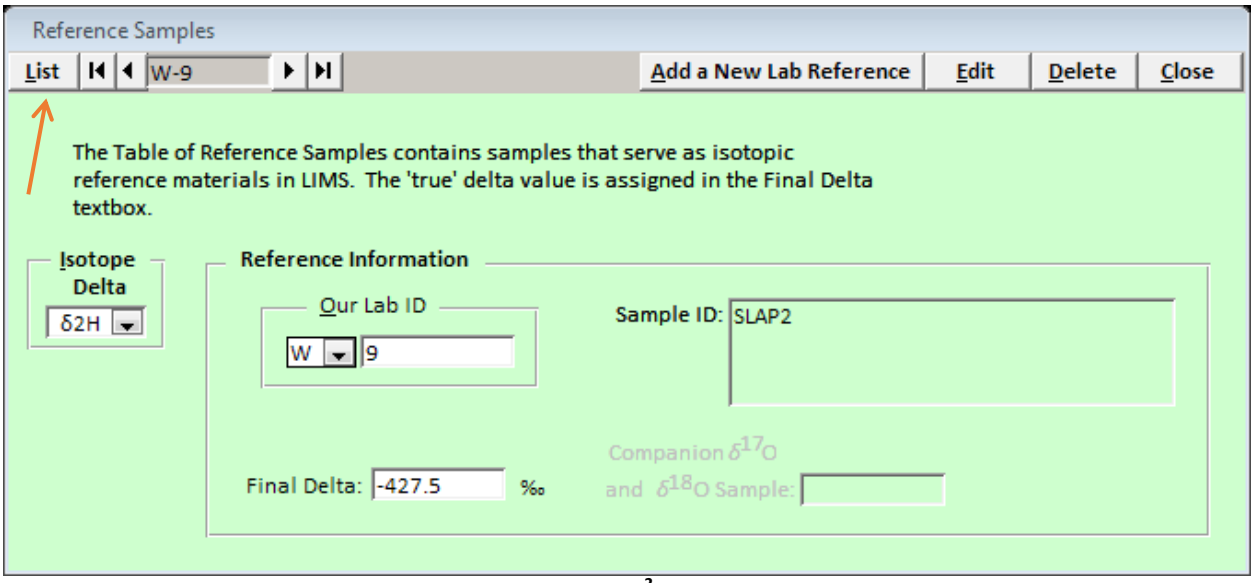
7.1 Primary and Laboratory Isotopic Standards

LIMS for Lasers 2015 is provided with pre-defined Projects for international primary standards and for daily use laboratory measurement standards that are used for normalizing the analytical results of routine water samples.

Primary Reference Materials (VSMOW/2, SLAP/2)

To view the table of assigned values for international measurement standards:

1. On the LIMS Main Page open "Special Features"
2. Click "Assign Lab References"
3. Click "List" (top left) to see δ values of international measurement standards

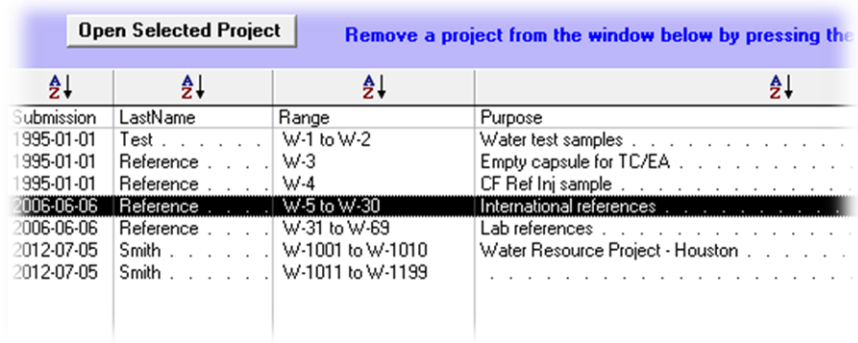


Example: SLAP2 has a Laboratory ID "W-9" and assigned δ^2H value of –427.5 ‰

Note that *LIMS for Lasers 2015* follows recommendations of the Système International d'Unités, the SI (known in English as the International System of Units). When % or ‰ are used, a space separates the number and the symbol ‰ (see section 5.3.7 of the 8th SI brochure)[5]. Thus, the assigned δ^2H value of SLAP2 is -427.5 ‰.

Note that the international measurement standards are located in Project "International References" and the default Customer name is "Reference". There are 25 placeholders for current and future international primary reference waters (W-5 to W-30).

Note: The δ^{17}O values are currently not assigned to any primary standards because this is an outstanding scientific issue. Adding δ^{17}O will require the user to create a Companion Project for their Primary Standards Project (see Chapter 6.4).



Submission	LastName	Range	Purpose
1995-01-01	Test	W-1 to W-2	Water test samples
1995-01-01	Reference	W-3	Empty capsule for TC/EA
1995-01-01	Reference	W-4	CF Ref Inj sample
2006-06-06	Reference	W-5 to W-30	International references
2006-06-06	Reference	W-31 to W-69	Lab references
2012-07-05	Smith	W-1001 to W-1010	Water Resource Project - Houston
2012-07-05	Smith	W-1011 to W-1199	

7.2 Add and Edit Standards and Control Standards

Daily-use laboratory standards (or in-house lab standards) are used to normalize measured δ values of samples to the VSMOW-SLAP scales for final reporting [6]. The onus is on each laboratory to obtain and maintain appropriate laboratory measurement standards, and to ensure they are routinely calibrated against the VSMOW/2-SLAP/2 international measurement scales (See Appendices for Sources and Templates for Daily-use standards).

LIMS for Lasers 2015 is provided with over 35 placeholders for new user-supplied laboratory measurement standards in a Project called "Lab References" whose Customer is "Reference". Laboratory standards have pre-assigned LIMS Laboratory ID numbers ranging from W-31 to W-69 (see previous Figure). Your laboratory can edit or add new lab standards to this project.

Be aware that the default version of *LIMS for Lasers 2015* does not have any δ values assigned to the lab measurement standard placeholders in the Table of References. To assign known δ values, one must edit the laboratory standard names and then add their δ values to the *LIMS for Lasers 2015* Table of References.

For example, we can edit a new High and a Low δ-value laboratory standard and add a control standard into the Table of References. These have the following known δ values (relative to VSMOW):

High Standard	δ^{18}O = –0.07 ‰	δ^{2}H = –4.1 ‰	δ^{17}O = -0.2
Low Standard	δ^{18}O = –24.76 ‰	δ^{2}H = –189.2 ‰	δ^{17}O = -14.2
Control	δ^{18}O = –999 ‰	δ^{2}H = not assigned	

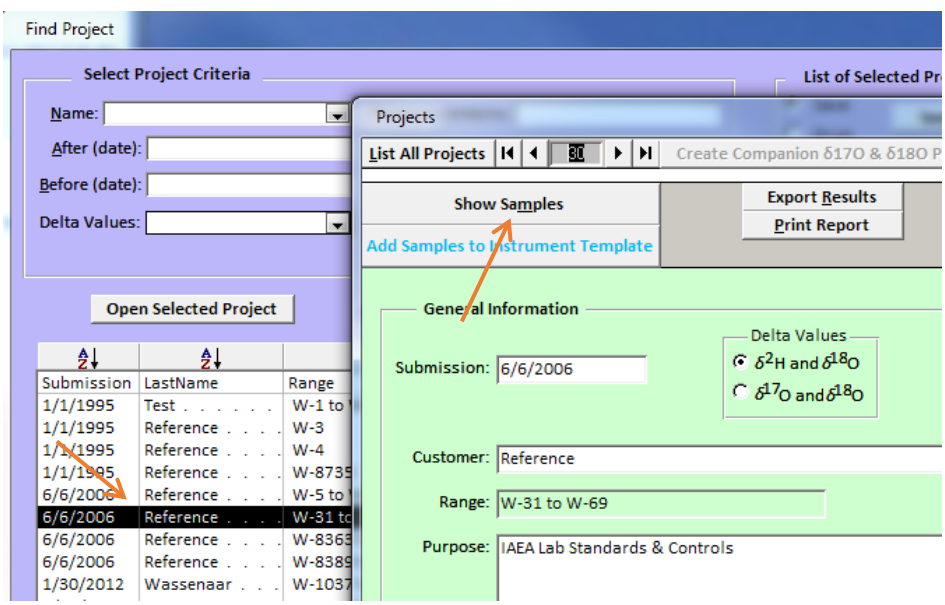
Note: The control standard is assigned a δ^{18}O value of –999 ‰, which acts as a flag to denote the δ^{18}O of this standard is null. It should not be assigned any δ^{2}H value. Because the control standard is null, *LIMS for Lasers 2015* will not use it in any normalization when it is included in analysis runs, although the user will be able to monitor the results. The δ value of the control standard does not matter, although control standards with δ^{2}H and δ^{18}O values between the

High and Low measurement standards are preferable. The purpose of a control standard(s) will be to track laboratory QA/QC over time.

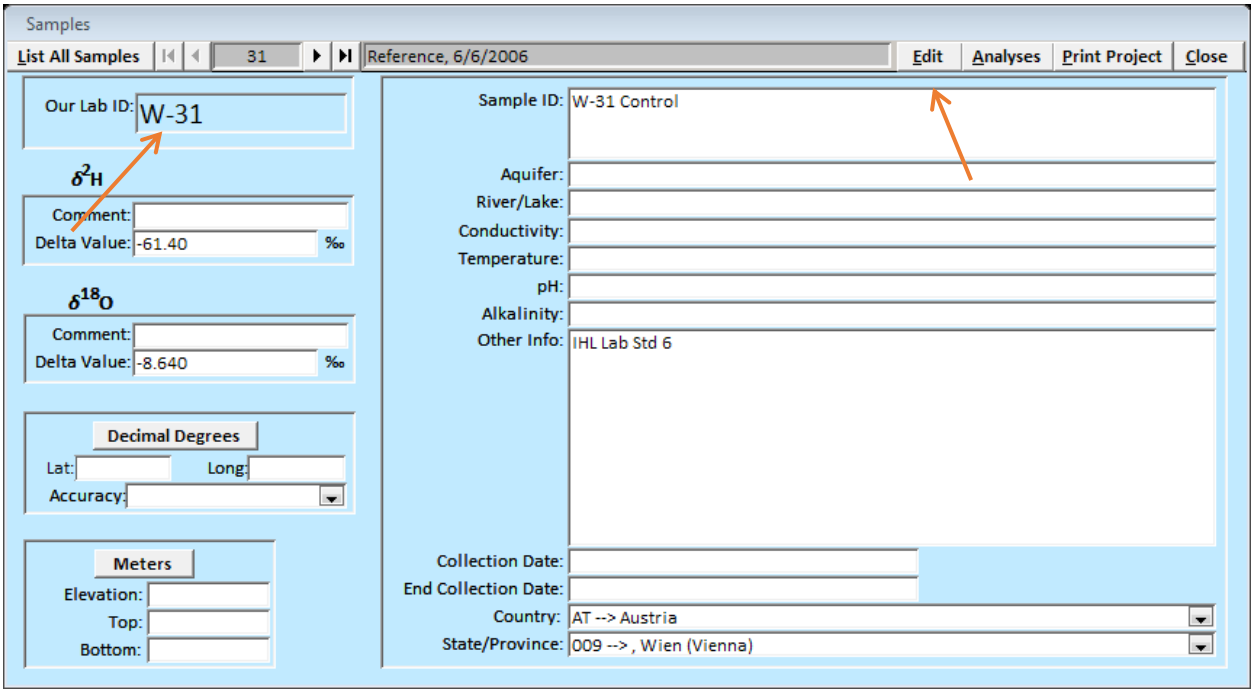
First, in this example, we need to edit and rename three “pre-assigned placeholders” for the lab standards and the control standard to their actual names or Sample IDs, as listed above.

Here we assign the name “High Standard” to W-31, “Low Standard” to W-32, and “Control” to W-33.

1. On the LIMS Main Page, Click “View Projects”.
2. Double click on the Project called “Lab References”.
3. Click on “Show Project Samples”.
4. The first sample in the Project opens; in this case, it happens to be W-31.
5. Click the “Edit” button.
6. The Sample ID field is now highlighted – delete and replace “My laboratory ref 1” with “High Standard”, but leave all other entries alone (do not enter δ values!).
7. Click “Save”.
8. Click again on the “List All Samples” button and choose W-32 from the pull down menu.
9. Click “Edit”, delete and replace “My laboratory ref 2” with “Low Standard”.
10. Click “Save”.
11. Click again on the “List All Samples” button and choose W-33 from the pull down menu.
12. Click “Edit”, delete and replace “My laboratory ref 3” with “Control”.
13. Click “Save”. The renaming of these three samples is completed.
14. Click “Close” to return to the LIMS Main Page.



Project “References” with Laboratory IDs W-31 through W-69 for IAEA lab standards.



Entry information for sample W-31 to be edited to "My Laboratory Standard 1".

Note: To create a Project for δ^{17}O values for laboratory measurement standards, you must first create a companion lab standard Project (see Chapter 6.4). The W numbers of the δ^{17}O lab standard Project will differ from those in the δ^{18}O and δ^{2}H Project. See example:

Submission	LastName	Range	Purpose
1995-01-01	Reference	W-4	Reference Gas Proxy for Lasers - Do not delete
2012-09-27	Test	W-1 to W-2	Test or Dummy Samples
2012-09-27	Reference	W-3	Wash and Conditioning Sample
2012-09-27	Reference	W-5 to W-30	International References
2012-09-27	Reference	W-31 to W-69	Lab References
2012-09-27	Reference	W-70 to W-108	Lab References for 17O
2015-03-04	Smith	W-1001 to W-1010	Johns Test Waters for LAS

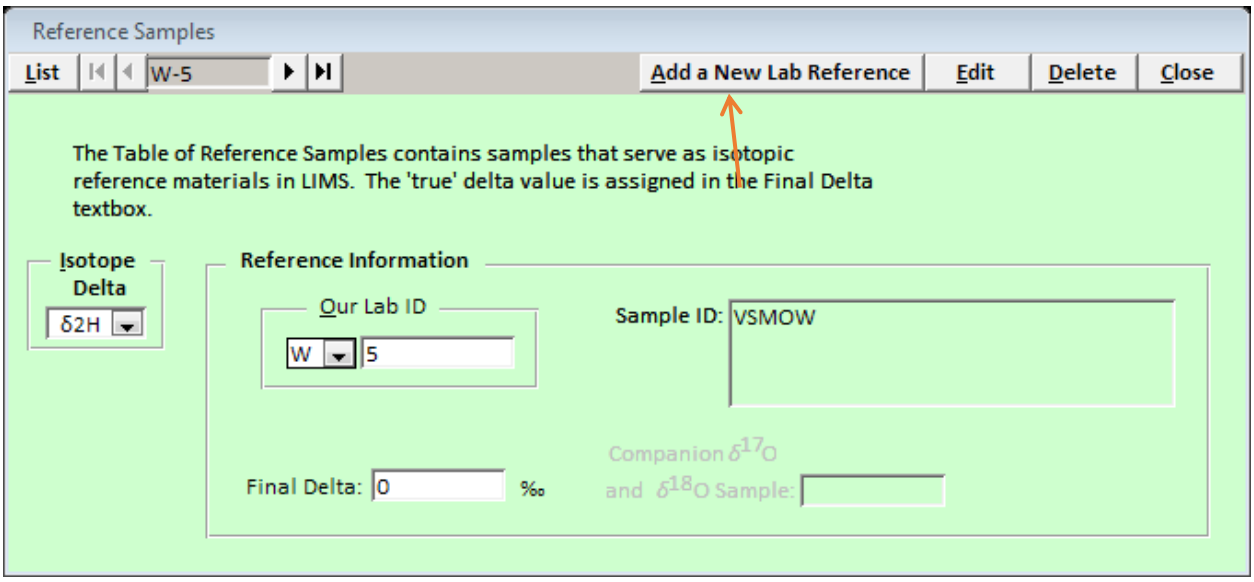
7.3 Assign δ Values to Laboratory Standards

One must assign known δ values to the laboratory measurement standards and add a special LIMS flag to demark the control standard. There is currently no uncertainty assignable to lab standards.

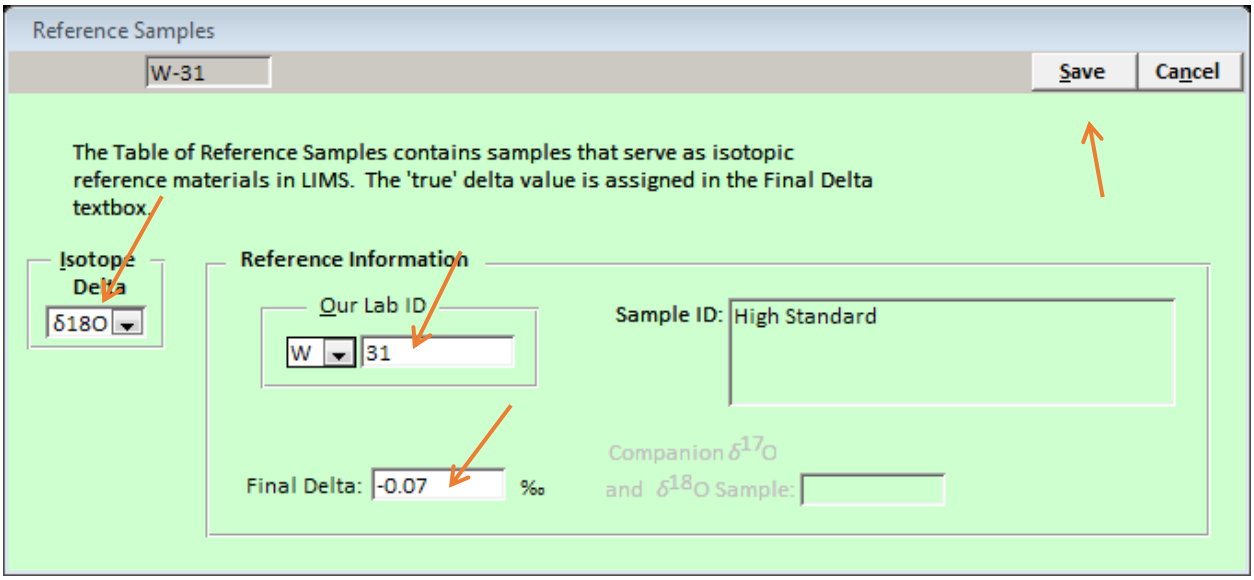
1. On the LIMS Main Page, open "Special Features"
2. Click "Assign Lab References"

To Add High Laboratory Standard δ^{18}O, δ^{2}H and δ^{17}O Values

3. To add the High δ^{18}O value lab standard, click "Add a New Lab Reference".



4. Click the pull down menu under "Isotope Delta", choose **"δ^{18}O".**
5. In "Our Lab ID" field, enter W "31". "High Standard" should appear in the "Sample ID" field.
6. In the "Final Delta" field, enter its assigned value, here –0.07 ‰ for δ^{18}O as listed on page 49.
7. Click "Save".



8. Next, add the known or assigned δ^2H value; click on "Add a New Lab Reference".
9. Click the pull down menu under "Isotope Delta" and choose **"δ^2H".**
10. In the "Our Lab ID field, enter W "31". "High Standard" will appear in "Sample ID" field.
11. In the "Final Delta" field, enter its assigned value, here –4.1 ‰ for the δ^2H that is listed above.
12. Click "Save".
13. To add the known or assigned δ^{17}O value, click on "Add a New Lab Reference".
14. Click the pull down menu under "Isotope Delta" and choose **"δ^{17}O"**.
15. In the "Our Lab ID field, enter W "70". "High Standard" will appear in the "Sample ID" field.
16. In the "Final Delta" field, enter its assigned value, here –0.2 ‰ for δ^{17}O that is listed above.

To Add Low Laboratory Standard δ^{18}O, δ^2H and δ^{17}O Values

17. To add the Low Standard, repeat steps 3 to 12 above, instead use W-32 "Low Standard" with the values for δ^{18}O and δ^2H (δ^{18}O = –24.76 ‰, δ^2H = –189.2 ‰, δ^{17}O = –14.2 ‰ (W-71) as shown above).

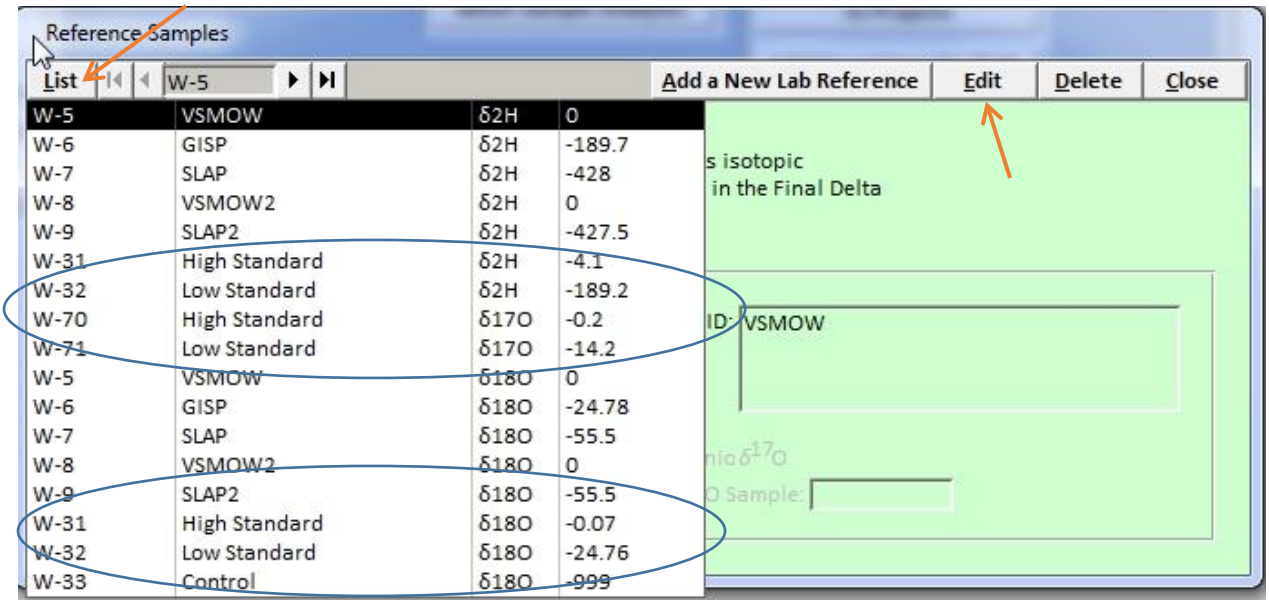
To Add a Control Standard

18. Repeat steps 3 to 7, instead using sample W-33 "Control"
19. Enter the ^{18}O value of –999 ‰ (**remember:** do not add any δ^2H or δ^{17}O values to control standards)
20. Click "Save"
21. Click "Close"

To review the newly edited list of your primary and laboratory standards and their assigned δ values, in Special Features click on “Assign Lab References”, and then click the “List” button on the upper left.

The figure below shows international measurement standards, the newly added laboratory standards and control standard, sorted by element and their corresponding “W” Our Lab ID numbers.

If you need to change assigned δ values of primary or laboratory standards, highlight the specific standard and isotope delta to be changed in the list and click “Edit”. Then, enter the new δ value in the Final Delta field and click “Save”.



Example of the newly added daily use measurement standards and a control.

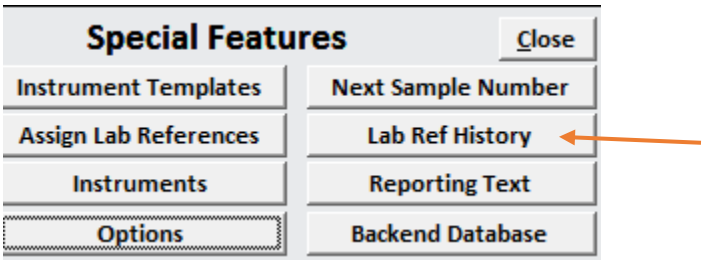
IMPORTANT NOTE ABOUT ASSIGNED LAB STANDARD VALUES

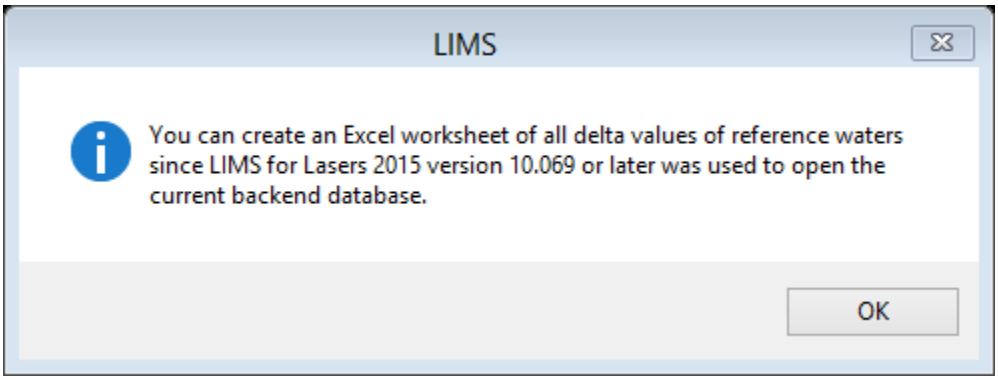
Newly edited laboratory standard δ values affect *only future results that have not yet been normalized or stored*. Previously normalized stored results are *not* changed retroactively; they retain the normalization parameters and assigned δ values that were used at the time of data processing. All prior data normalizations are protected.

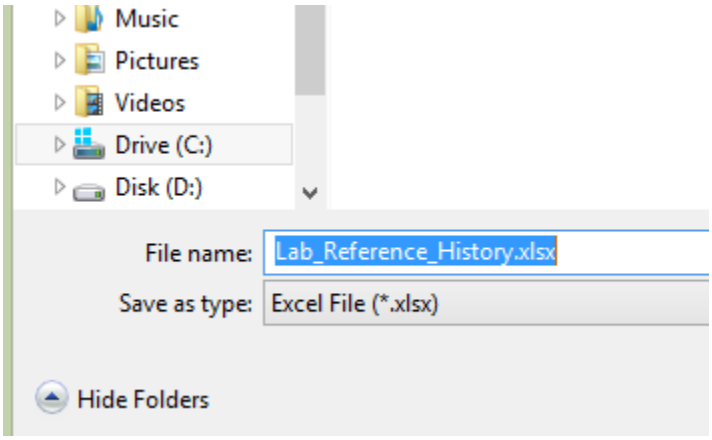
7.4 Track Laboratory Standards over Time

A record of any changes made to primary and laboratory standard δ values are recorded in *LIMS for Lasers 2015* for long term laboratory tracking purposes.

1. Click “Special Features”
2. Click “Lab Ref History” button
3. An Excel file of the full history of reference δ values assigned to calibration and primary standards is created and saved.







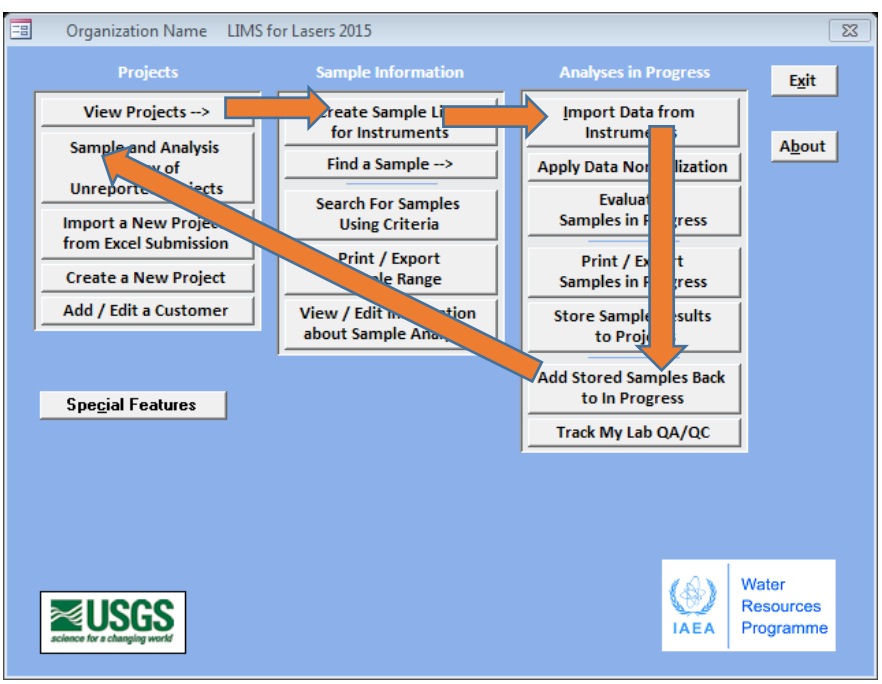
8 Sample Analysis Templates

8.1 Sample Analysis in LIMS for Lasers 2015

Since we have learned to add Customers and their Project and Samples into *LIMS for Lasers 2015*, we can prepare and analyse water samples on a laser instrument through the use of instrument Analysis Templates (also referred to as sample lists, queues, or sequence run files).

Analysing samples in *LIMS for Lasers 2015* follows a 9-Step procedure:

1. Add samples to an instrument *Analysis Template* (or queue).
2. Create and print a list for sample preparation (e.g. filling sample vials) and transferring the sequence to the Los Gatos Research or Picarro data acquisition and control software via USB flash drive.
3. Measure unknown samples at least twice (on a Los Gatos Research or Picarro) and importing the isotopic data into *LIMS for Lasers 2015.*
4. Optionally correct for H_2O amount dependence.
5. Correct imported results for between-sample memory and/or instrumental drift.
6. Normalize samples to the VSMOW-SLAP scales using measurement standards.
7. Evaluate and accept final results, tracking control-standard performance.
8. Check and store accepted mean final results of two or more sample repeats.
9. Report final mean results to the Customer in hard copy or Excel file.



Routine work flow path in LIMS for Lasers 2015.

8.2 The Importance of Analysis Templates

LIMS for Lasers 2015 is provided with sample analysis templates designed to obtain high quality results, check for problematic analyses based on the sample water yield, correct for δ dependency on H_2O concentrations, correct between-sample memory, check and correct for instrumental drift, and normalize the results of the unknown samples to the VSMOW-SLAP scale using calibrated laboratory standards. A control standard monitors results for long-term laser performance for QA/QC purposes. Users can create their own custom templates.

Systematic analysis templates founded upon Identical Treatment principles [7] are well-known to give the best results. Further, systematic templates make it easy for the analyst to identify problems when changes in routine analysis patterns are observed.

In *LIMS for Lasers 2015,* we recommend an 8/9-injection-ignore-4 template as a starting point for all laser instruments for $\delta^{18}O$ and $\delta^{2}H$. Users can experiment with templates to optimize performance for their own needs, or they can improve sample throughput by experimenting with fewer injections and ignored injections (e.g. 6 injections-ignore 3). Analysis templates are fully customizable to user preferences.

The recommendations in this manual are intentionally conservative to provide the best possible $\delta^{18}O$ and $\delta^{2}H$ results from all generations of laser instruments. Instrument templates for $\delta^{17}O$ are considerably more complex than routine $\delta^{18}O$ and $\delta^{2}H$ templates and analyses, and they require multiple vials with 30–50 or more injections.

Why We Need Systematic Analysis Templates

There are two hardware features that constrain the length of a laser autorun template:

- Injection port septum failure. Septa will leak or fail after 300 to 800 injections, depending on the brand and the quality (standard vs. high performance).

- Syringe failure. Microliter syringes can fail between a dozen injections to over 2000 injections. Generally, high dissolved solids (TDS) content water samples result in faster syringe failure from salt build-up in the syringe barrel.

As a result, laser autoruns should total no more than 300–800 injections, after which the septum must be changed. The syringe should be checked for signs of failure or jamming. Syringe degradation is usually manifested by decreased or variable H_2O yield on laser instruments, in contrast with new performance.

There are three instrumental factors that impact the quality of laser isotope analyses:

- Between-sample memory – this is residual contamination from prior sample water molecules still in the laser cavity and/or transfer lines between adjacent samples. Larger δ differences between samples will have a larger impact.

- Dependency of δ values on H_2O amount injected. Variable H_2O amounts, for example from underperforming syringes or leaky septa, lead to high isotopic variance on most laser instruments.

- Instrumental drift. Early generation laser instruments, or new instruments insufficiently warmed, exhibit linear drift over the course of an autorun [8].

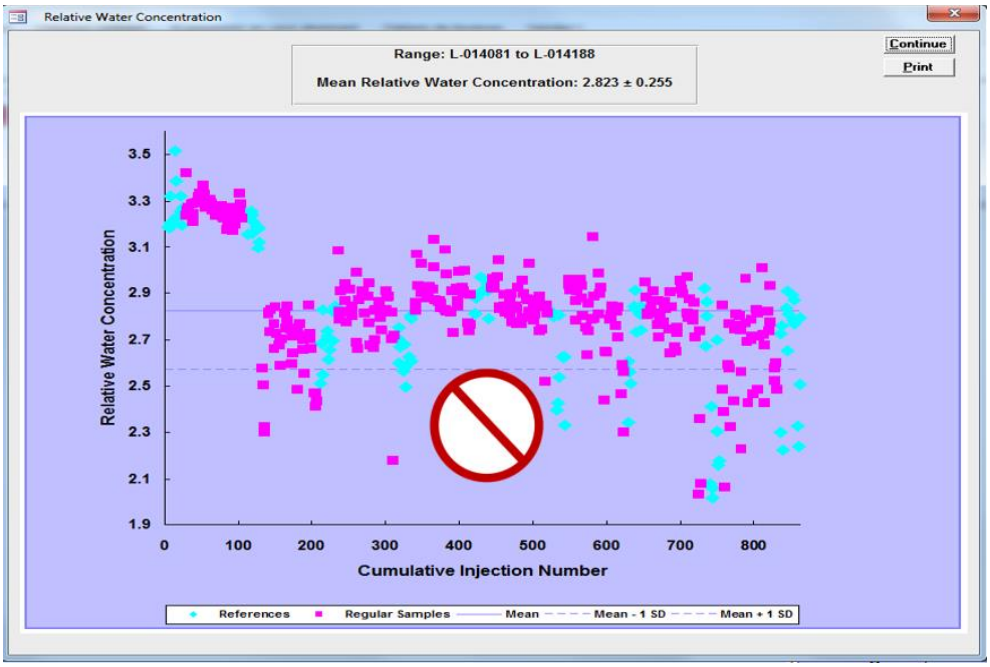
Whereas the physical constraints of septa and syringes require routine instrument maintenance as described in the user manuals from each supplier, *LIMS for Lasers 2015* helps out by identifying and correcting for these issues, as described below.

Screening Tools for Poor Performance, Instrument Errors, and High Variance

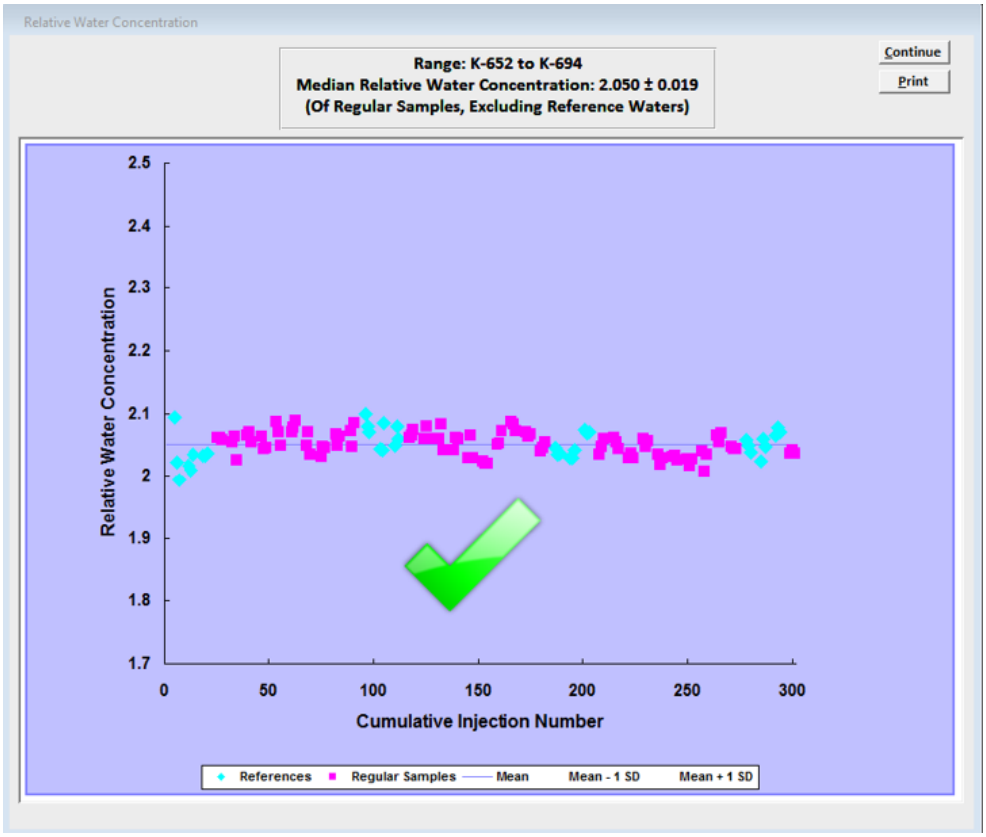
The frequent failure of syringes or septa usually results in low or highly variable H_2O yields in the laser cavity or pressure errors reported by the instrument software. Laser instruments often exhibit a strong response of δ values on cavity water vapour amount; therefore, precise and highly consistent water injections are crucial. While hardware failure like a stuck or broken syringe may be obvious, less obvious are somewhat poor injections or slightly variable yields when vials are insufficiently or over-filled or the syringe is nearly under-performing. Locating poor injections among comma-separated (CSV) lines in Excel is very difficult.

To check for poor injections, imported data files are pre-screened by *LIMS for Lasers 2015* to graphically show if H_2O yields were consistent across the run. A graphical cross plot of water yield by injection number is presented to the analyst after data import. The plot shows individual sample and standard injections relative to 85 % of the mean H_2O yield. Results falling outside this limit are flagged and their sample IDs are displayed; a warning that the run may be compromised by syringe failure is provided. This gives the analyst a chance to review and check the instrument hardware or reanalyse the samples *before* erroneous results are imported.

Below are examples of *LIMS for Laser 2015* initial data import screenings that illustrate poor syringe performance and/or septa leakage and good syringe performance:



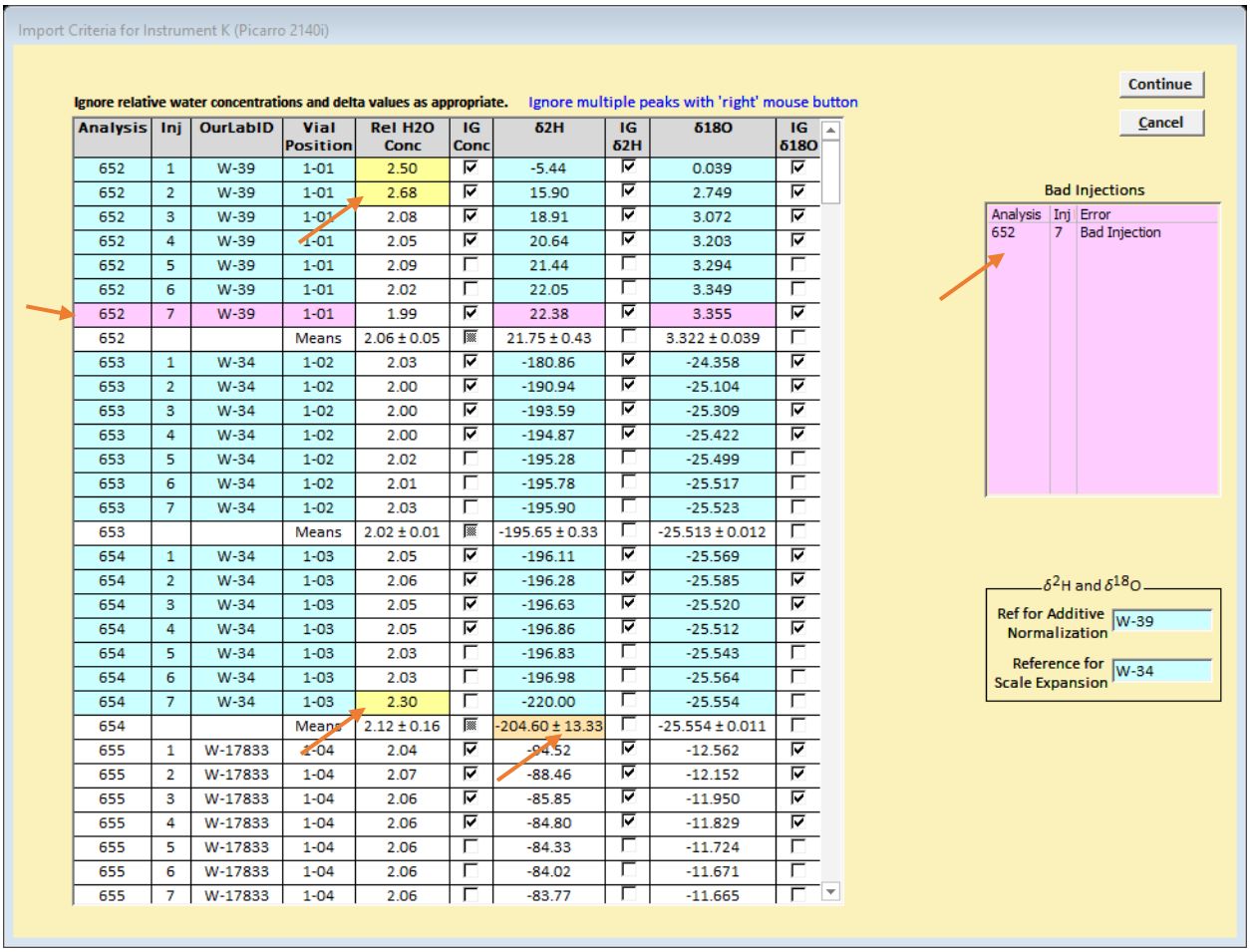
Bad Syringe Performance: A large H_2O drop from a septa leak is followed by high H_2O variance. Blue symbols are the laboratory standards; red symbols are samples.



Good Syringe Performance. Symbol colours are as above.

To further assist with data screening prior to importing and processing, a summary tabulation of measured δ data is presented after the H_2O amount vs injection plot. In this tabulation, shown below, several features help to further screen and eliminate bad data:

- The first 4 injections are automatically ignored (IG); as user specified
- Injections yielding instrumental errors, coloured purple, are automatically ignored. The error coming from the laser instrument is given to the right
- Samples with H_2O concentration beyond 85 % of the mean are coloured yellow, they are not automatically ignored unless they are located within the first 4 injections
- Measured δ results for any vial having mean standard deviations beyond ±0.2 and ±1.5 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively, for each vial are coloured orange
- Laboratory standards are coloured blue for easy recognition. Samples are white.



Analysis	Inj	OurLabID	Vial Position	Rel H2O Conc	IG Conc	δ2H	IG δ2H	δ18O	IG δ18O
652	1	W-39	1-01	2.50	☑	-5.44	☑	0.039	☑
652	2	W-39	1-01	2.68	☑	15.90	☑	2.749	☑
652	3	W-39	1-01	2.08	☑	18.91	☑	3.072	☑
652	4	W-39	1-01	2.05	☑	20.64	☑	3.203	☑
652	5	W-39	1-01	2.09	☐	21.44	☐	3.294	☐
652	6	W-39	1-01	2.02	☐	22.05	☐	3.349	☐
652	7	W-39	1-01	1.99	☑	22.38	☑	3.355	☑
652			Means	2.06 ± 0.05	▩	21.75 ± 0.43	☐	3.322 ± 0.039	☐
653	1	W-34	1-02	2.03	☑	-180.86	☑	-24.358	☑
653	2	W-34	1-02	2.00	☑	-190.94	☑	-25.104	☑
653	3	W-34	1-02	2.00	☑	-193.59	☑	-25.309	☑
653	4	W-34	1-02	2.00	☑	-194.87	☑	-25.422	☑
653	5	W-34	1-02	2.02	☐	-195.28	☐	-25.499	☐
653	6	W-34	1-02	2.01	☐	-195.78	☐	-25.517	☐
653	7	W-34	1-02	2.03	☐	-195.90	☐	-25.523	☐
653			Means	2.02 ± 0.01	▩	-195.65 ± 0.33	☐	-25.513 ± 0.012	☐
654	1	W-34	1-03	2.05	☑	-196.11	☑	-25.569	☑
654	2	W-34	1-03	2.06	☑	-196.28	☑	-25.585	☑
654	3	W-34	1-03	2.05	☑	-196.63	☑	-25.520	☑
654	4	W-34	1-03	2.05	☑	-196.86	☑	-25.512	☑
654	5	W-34	1-03	2.03	☐	-196.83	☐	-25.543	☐
654	6	W-34	1-03	2.03	☐	-196.98	☐	-25.564	☐
654	7	W-34	1-03	2.30	☐	-220.00	☐	-25.554	☐
654			Means	2.12 ± 0.16	▩	-204.60 ± 13.33	☐	-25.554 ± 0.011	☐
655	1	W-17833	1-04	2.04	☑	-94.52	☑	-12.562	☑
655	2	W-17833	1-04	2.07	☑	-88.46	☑	-12.152	☑
655	3	W-17833	1-04	2.06	☑	-85.85	☑	-11.950	☑
655	4	W-17833	1-04	2.06	☑	-84.80	☑	-11.829	☑
655	5	W-17833	1-04	2.06	☐	-84.33	☐	-11.724	☐
655	6	W-17833	1-04	2.06	☐	-84.02	☐	-11.671	☐
655	7	W-17833	1-04	2.06	☐	-83.77	☐	-11.665	☐

In the example, the 7th injection of Analysis 654 should be ignored by the analyst before continuing. The screening tools are useful to visually locate and remove occasional bad data. **Note:** A poor performing run with many errors or colour flags cannot be reliably fixed here and should never be imported, instead reanalysed with a properly functioning laser instrument.

Between-Sample Memory

Between-sample memory in *LIMS for Lasers* 2015 is quantified using two local measurement standard pairs that differ greatly in their δ values (by at least 40 ‰ and 5 ‰ for δ^2H and δ^{18}O, respectively) and are sequentially spaced multiple times throughout the autorun. A measurement standard with a substantially different δ value is followed by two successive vials of the second standard in order to calculate between-sample memory. The memory corrections for standard sets in the autorun are averaged, and they are applied to all samples in the autorun. LIMS calculates between-sample memory using "non-ignored" injections of sample and standards.

The advantage of this approach is that memory corrections are calculated using the mean of repeating groupings of two references with widely separated δ values throughout the entire autorun, and not inconsistently amongst pairs of differing samples having large or small differences in δ values. Further, it does not matter how many injections are ignored because the between-sample memory correction is quantified and follows Identical Treatment principles. The determined mean between-sample memory correction is applied to *all* samples analysed regardless of their measured δ values. As a matter of good practice, we recommend ignoring the first 3–4 injections, which should result in lower between-sample memory (usually < 1–2 %). See Chapter 11 for details on the calculations.

Adjustment for Variation in δ with Water Concentration

Studies have shown the δ-value dependence of each isotopologue species is often strongly correlated to concentration of water vapour in the laser cavity. This concentration dependence affords an opportunity to improve isotopic results by purposely adjusting H_2O injection amounts using a targeted laboratory standard (e.g. using 800, 1000 and 1200 µL triplets) placed at the beginning of each run. This will allow *LIMS for Lasers 2015* to determine H_2O concentration correction algorithms for each δ value.

A H_2O concentration adjustment algorithm, provided it is robust, can be applied to all sample injections to normalize measured δ values to a constant water injection amount. Depending on the instrument, a concentration adjustment may result in marked improvement in the isotopic results for one or more isotopologues and can help to smooth out, for example, the effects of variable syringe injection performance.

Note: See Appendix 3 on how to set up optional Adjustments for δ with Relative Water Concentration. Although this option cannot be used on early Los Gatos Research instruments to purposely vary H_2O injection amounts, the *LIMS for Lasers 2015* H_2O concentration adjustment algorithm can be used on these instruments and can substantially improve results.

Instrumental Drift

Temporal instrumental drift in *LIMS for Lasers 2015* is quantified using a least squares regression of analysis time versus one or more measurement standards that occur throughout the autorun. The drift correction (reported in ‰ per hour) is determined and applied to all samples. However, laser instrumental drift is not often linear over long autoruns (>2–3 hours), and instrumental drift may be inconsistent among laboratory standards within an autorun (one standard drifts positively, the other negatively). Therefore, this regression often gives poor statistical confidence (e.g. low R^2 values).

Regardless, *LIMS for Lasers 2015* gives users the option to check for singular linear instrumental drift using one or more laboratory standards. One measure of confidence of whether to apply a linear drift correction is when drift is strongly linear (e.g. R^2 >0.6) and occurring in the same direction (e.g. all drift positively) for two or more measurement standards. Only then can a linear drift correction be applied with confidence. While instrument drift correction is optional, the use of "bracketed data normalization" (default setting) is generally found to give better results.

8.3 Systematic Analysis Templates

The following sections show example analysis templates for Los Gatos Research and Picarro instruments used in *LIMS for Lasers 2015*. These templates were designed to be robust and were tested to produce the best possible results for all generations of laser instruments. Further, they were optimized to obtain accurate determinations of between-sample memory, optionally quantify instrumental drift, and to apply bracketed standard and sample data normalization.

These example *LIMS for Lasers 2015* analysis templates are illustrated in table format and sequential sample vial analysis layout for both Los Gatos Research and Picarro instruments, followed by individual sections on setting up and using analysis templates for each instrument.

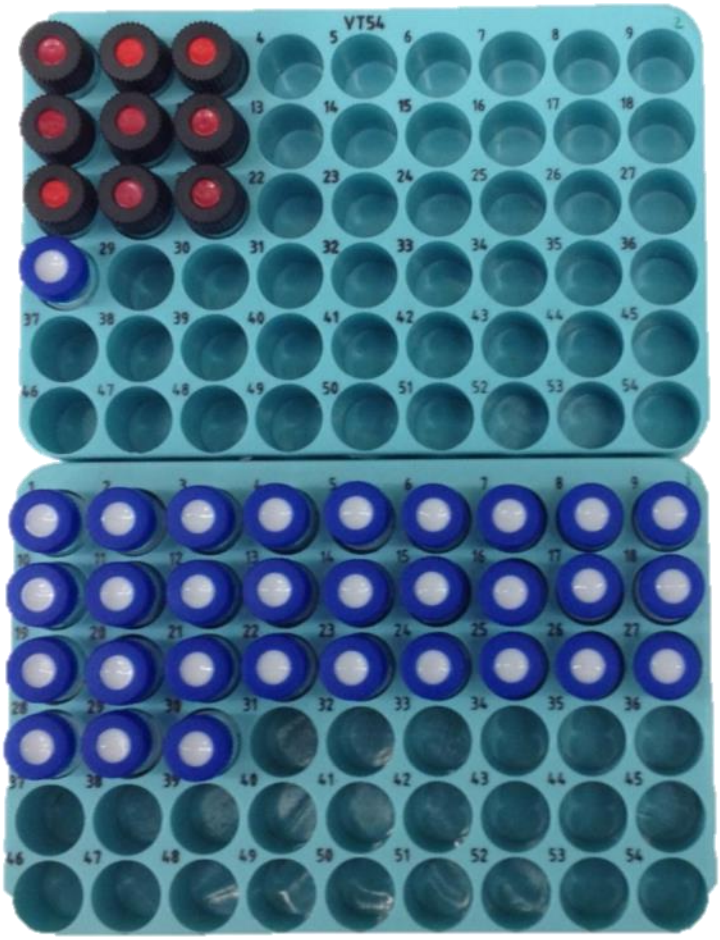
Notably, users are free to design their own analyses templates, and these examples serve as a suggestion to get started. Several 10-, 20- and 30-sample Excel template designs for Picarro or Los Gatos research are found in the Appendices and on the Web site, and they are included in new instrument backend downloads.

Table 1. Example 30-sample Analysis Template for Los Gatos Research Instruments. Unknown samples are arranged sequentially in positions 1–30 of Tray 1 (front tray) in the Combi-PAL auto sampler. Laboratory standards, control standards, and conditioning samples are arranged in Tray 3 (rear tray), each in their own row. The recommended analysis procedure is 9 injections per sample, ignoring the first 4. This template contains 61 rows of 9 injections each which total 549 individual injections. Run Order is the sequence order in which samples are analysed. Injection amount is controlled in the Los Gatos instrument software.

Sample	Vial Pos	Run Order	LIMS for Lasers 2015 Function
Deionized Water	3-28	1	Instrument Conditioning
Deionized Water	3-28	2	Instrument Conditioning
High δ Standard	3-10	3	Between-Sample Memory
Low δ Standard	3-1	4	Between-Sample Memory
Low δ Standard	3-2	5	Bracketed Normalization
Sample 1	1-1	6	Unknown Sample
Sample 2	1-2	7	Unknown Sample
Sample 3	1-3	8	Unknown Sample
Sample 4	1-4	9	Unknown Sample
Sample 5	1-5	10	Unknown Sample
Control Standard	3-19	11	QA/QC
Low δ Standard	3-3	12	Between-Sample Memory
High δ Standard	3-11	13	Between-Sample Memory
High δ Standard	3-12	14	Bracketed Normalization
Sample 6	1-6	15	Unknown Sample
Sample 7	1-7	16	Unknown Sample
Sample 8	1-8	17	Unknown Sample
Sample 9	1-9	18	Unknown Sample
Sample 10	1-10	19	Unknown Sample
Control Standard	3-20	20	QA/QC
High δ Standard	3-10	21	Between-Sample Memory
Low δ Standard	3-1	22	Between-Sample Memory
Low δ Standard	3-2	23	Bracketed Normalization
Sample 11	1-11	24	Unknown Sample
Sample 12	1-12	25	Unknown Sample
Sample 13	1-13	26	Unknown Sample
Sample 14	1-14	27	Unknown Sample
Sample 15	1-15	28	Unknown Sample
Control Standard	3-21	29	QA/QC
Low δ Standard	3-3	30	Between-Sample Memory
High δ Standard	3-11	31	Between-Sample Memory

High δ Standard	3-12	32	Bracketed Normalization
Sample 16	1-16	33	Unknown Sample
Sample 17	1-17	34	Unknown Sample
Sample 18	1-18	35	Unknown Sample
Sample 19	1-19	36	Unknown Sample
Sample 20	1-20	37	Unknown Sample
Control Standard	3-19	38	QA/QC
High δ Standard	3-10	39	Between-Sample Memory
Low δ Standard	3-1	40	Between-Sample Memory
Low δ Standard	3-2	41	Bracketed Normalization
Sample 21	1-21	42	Unknown Sample
Sample 22	1-22	43	Unknown Sample
Sample 23	1-23	44	Unknown Sample
Sample 24	1-24	45	Unknown Sample
Sample 25	1-25	46	Unknown Sample
Control Standard	3-20	47	QA/QC
Low δ Standard	3-3	48	Between-Sample Memory
High δ Standard	3-11	49	Between-Sample Memory
High δ Standard	3-12	50	Bracketed Normalization
Sample 26	1-26	51	Unknown Sample
Sample 27	1-27	52	Unknown Sample
Sample 28	1-28	53	Unknown Sample
Sample 29	1-29	54	Unknown Sample
Sample 30	1-30	55	Unknown Sample
Control Standard	3-21	56	QA/QC
High δ Standard	3-10	57	Between-Sample Memory
Low δ Standard	3-1	58	Between-Sample Memory
Low δ Standard	3-2	59	Bracketed Normalization
Deionized Water	3-28	60	DI Wash
Deionized Water	3-28	61	DI Wash

Vial Layout for Default Los Gatos Research Analysis Template



Tray3, Row1– Low δ Standard ×3

Tray3, Row 2– High δ Standard ×3

Tray3, Row 3– Control Standard δ ×3

Tray3, Row 4– DI for wash

Tray 1– Sequential unknown samples placed from position 1 to 30

See Table 1 for descriptions

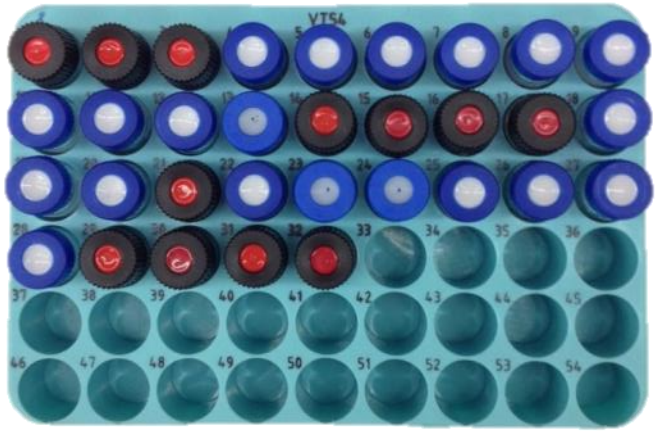
Layout of Samples on Los Gatos Research Combi-PAL Front and Rear Tray

Note: In this Los Gatos Research analysis template, the vials of each measurement and control standard contain ~1 to 1.5 mL of water. Triplicate redundancy of standards is intentional in order to avoid reliance on a single vial and to ensure best possible QA/QC. The volume of the daily laboratory standard water consumed per analysis template is 3 to 4 mL and was designed to correspond to the daily standard ampoules available to users from the USGS and IAEA (See Appendix 1).

Table 2. An Example 20-sample Analysis Template for Picarro Instruments (CTC Pal).
The samples, local measurement standards, and control standards are arranged sequentially in positions 1–32 of Tray 1. The recommended procedure is 9 injections per sample, ignoring the first 4 injections. This template contains 32 rows of 9 injections each = 288 individual injections. Analysis time using the Picarro L2130i is ~32 hours. List # is the order in which samples are analysed. It is strongly recommended that Picarro instruments are pre-conditioned with 1–2 deionized water samples immediately prior and following the autorun (using the Coordinator software). Injection amount is controlled by the CTC or G2000 autosampler.

Sample	Vial Pos	Run Order	Function
High δ Standard	1-01	1	Memory/Normalization
Low δ Standard	1-02	2	Memory/Normalization
Low δ Standard	1-03	3	Normalization
Sample 1	1-04	4	Unknown Sample
Sample 2	1-05	5	Unknown Sample
Sample 3	1-06	6	Unknown Sample
Sample 4	1-07	7	Unknown Sample
Sample 5	1-08	8	Unknown Sample
Sample 6	1-09	9	Unknown Sample
Sample 7	1-10	10	Unknown Sample
Sample 8	1-11	11	Unknown Sample
Sample 9	1-12	12	Unknown Sample
Sample 10	1-13	13	Unknown Sample
Control Standard	1-14	14	QA/QC
High δ Standard	1-15	15	Memory/Normalization
Low δ Standard	1-16	16	Memory/Normalization
Low δ Standard	1-17	17	Normalization
Sample 11	1-18	18	Unknown Sample
Sample 12	1-19	19	Unknown Sample
Sample 13	1-20	20	Unknown Sample
Control Standard	1-21	21	QA/QC
Sample 14	1-22	22	Unknown Sample
Sample 15	1-23	23	Unknown Sample
Sample 16	1-24	24	Unknown Sample
Sample 17	1-25	25	Unknown Sample
Sample 18	1-26	26	Unknown Sample
Sample 19	1-27	27	Unknown Sample
Sample 20	1-28	28	Unknown Sample
Control Standard	1-29	29	QA/QC
High δ Standard	1-30	30	Memory/Normalization
Low δ Standard	1-31	31	Memory/Normalization
Low δ Standard	1-32	32	Normalization

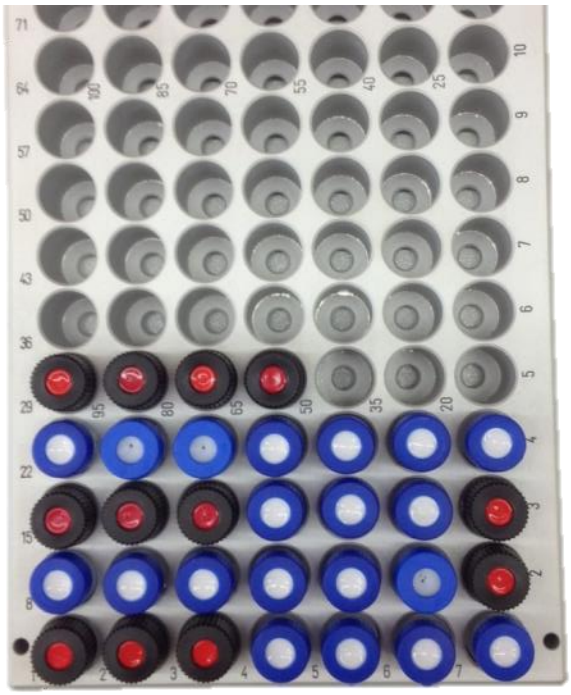
Vial Layout Example for Picarro Analysis Template



Example 20-Sample Analysis Template and vial layout, shown for Picarro Combi-PAL Autosampler.

Blue capped vials are unknown samples. Red capped vials are laboratory standards and control standards, corresponding to the layout shown in Table 2.

Above: Front Tray of Picarro Combi-PAL Liquid Autosampler



Example 20-Sample Analysis Template and vial layout, shown for Picarro G-2000 Autosampler.

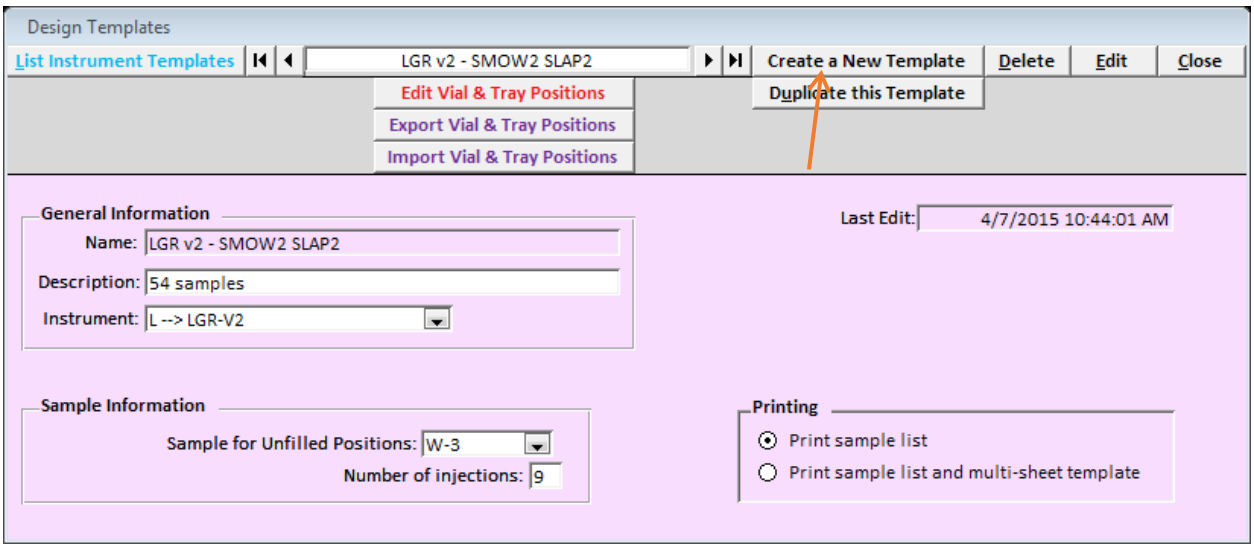
Blue capped vials are samples. Red capped vials are laboratory standards and control standards, corresponding to the layout shown in Table 2.

(See Appendix 1 for an alternate layout)

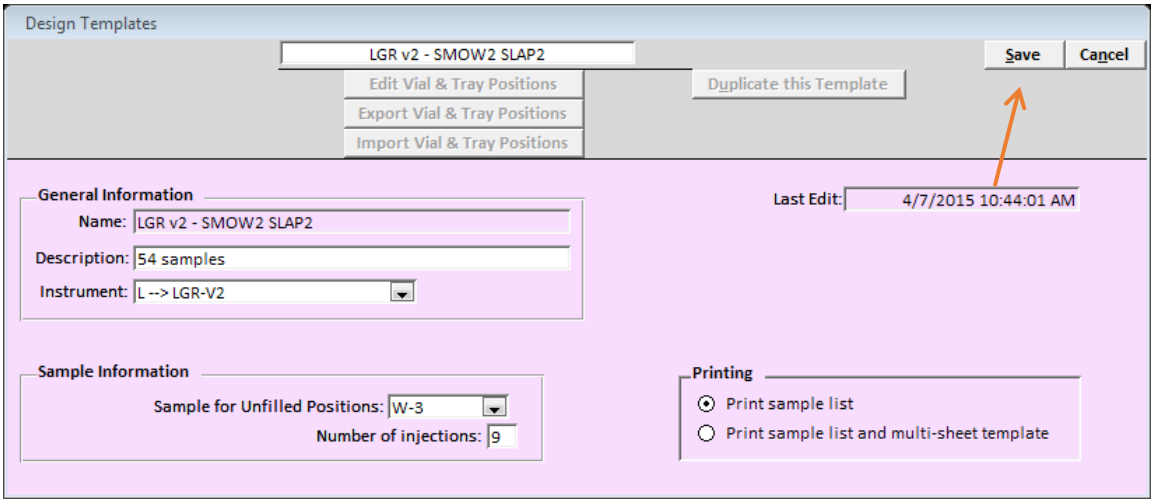
Above: Tray of the Picarro G-2000 Series Liquid Autosampler

8.4 Create a Los Gatos Research 30-Sample Template

1. From the LIMS Main Page, open “Special Features”
2. Click on “Instrument Templates”
3. Click on “Create a New Template”

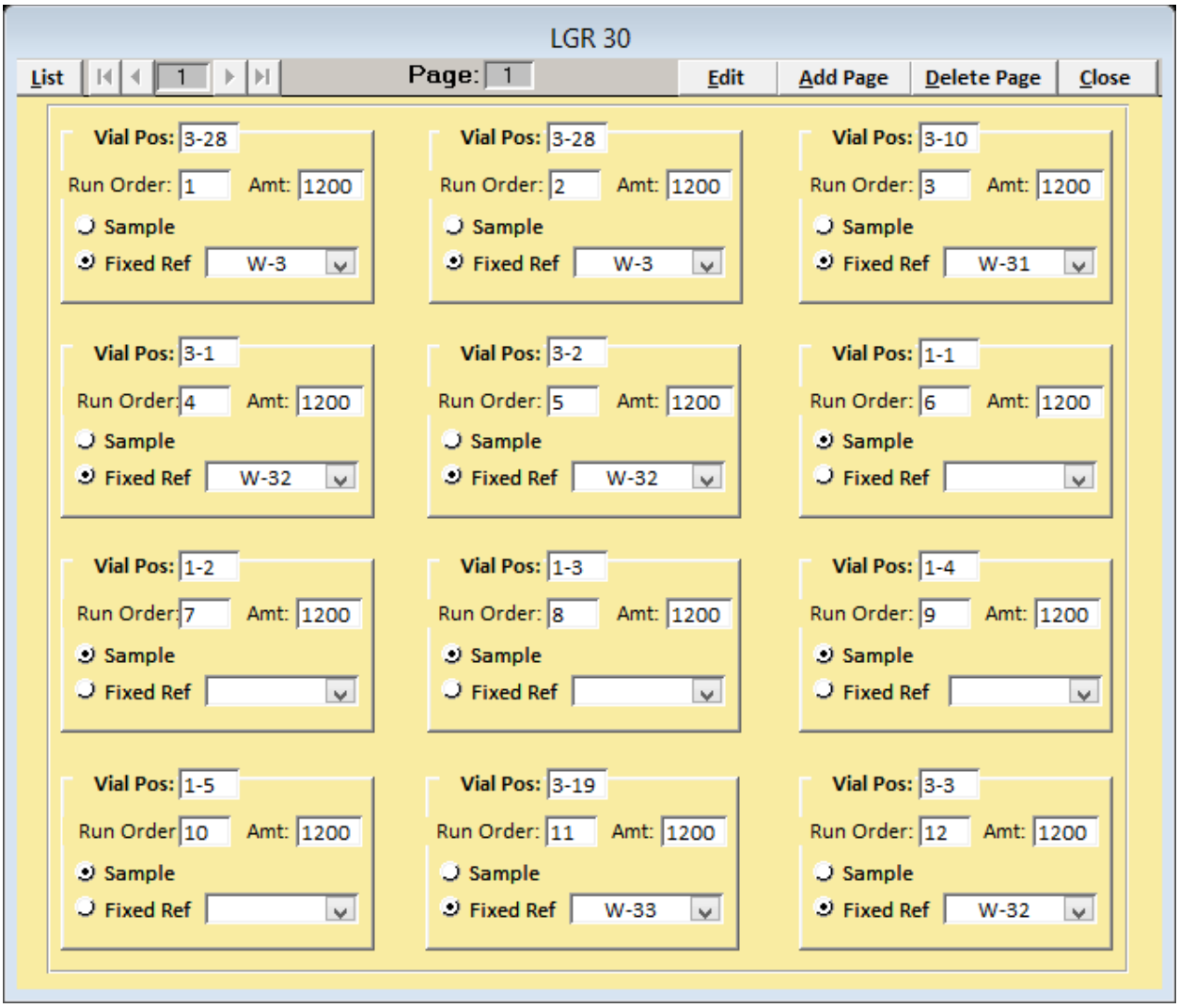


4. Under “Name”, enter a relevant description (e.g. Los Gatos Research 30 Samples).
5. Under Description – add relevant additional details (e.g. which Standards used).
6. Under Instrument, choose “L” or appropriate letter for the Los Gatos Research laser.
7. The “Sample for Unfilled Positions” defaults to W-1 (a dummy sample). This dummy is used, for example, when only 20 samples are added to a 30-position template. This field cannot be left blank.
8. Number of injections per sample, leave set to 9.
9. Click “Save”.
10. Once saved, the “Name” field cannot be edited; only the description and other fields can be edited. The template can be deleted and re-created in case of a mistake.



Creating a Los Gatos Research Sample Analysis Templates using Template Pages.

The analysis sequence for measurement standards, control standards and the client samples can be set up by clicking the "Edit Vial and Tray Positions" button. A Page template for 12 samples will appear. Click Edit to complete (completed example below reflects lines 1–12 in Table 1):



Vial Pos = vial position of a sample in the tray of the liquid autosampler. For example, 1-1 means Tray 1 Position 1, whereas, 3-7 indicates Tray 3 Position 7.

Run Order = The numbered order in which samples are analysed, e.g. 1,2,3…. 30. (unique)

Amt = H_2O Injection volume amount in nL (e.g. 400 up to 1200 nL for LGR). *The amount field is only available to IWA-35d/TIWA-45EP systems, not DLT-100 series.* If this field is left blank, the injection volume is controlled using the instrument setup panel.

Sample = Choose this button to denote an unknown sample.

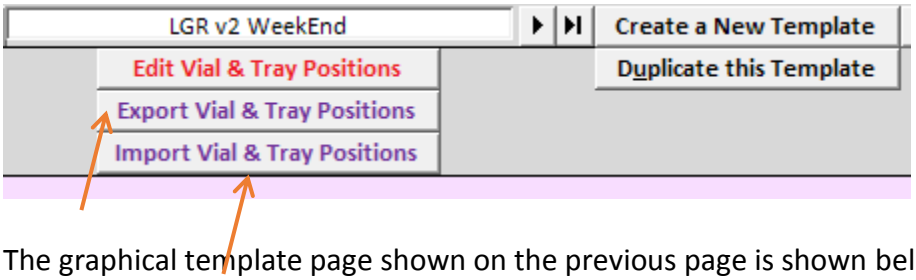
Fixed Ref = Use the drop down box to select a lab standard, control standard or wash sample.

Add Page /Delete Page = add more pages to increase the template length. Always delete pages starting from the last page.

Using Excel to Design and Import or Export Templates

It is more convenient to design analysis templates in Excel and then import them into *LIMS for Lasers 2015*. The autofill and copy-paste features of Excel make it easy to quickly design and import a new analysis template into *LIMS for Lasers 2015*.

Export Vial and Tray Positions: export the selected analysis template to an Excel file.
Import Vial and Tray Positions: imports the Excel analysis template into *LIMS for Lasers 2015*. The template will be visible, and it can be edited using the normal Page editing mode shown. above.



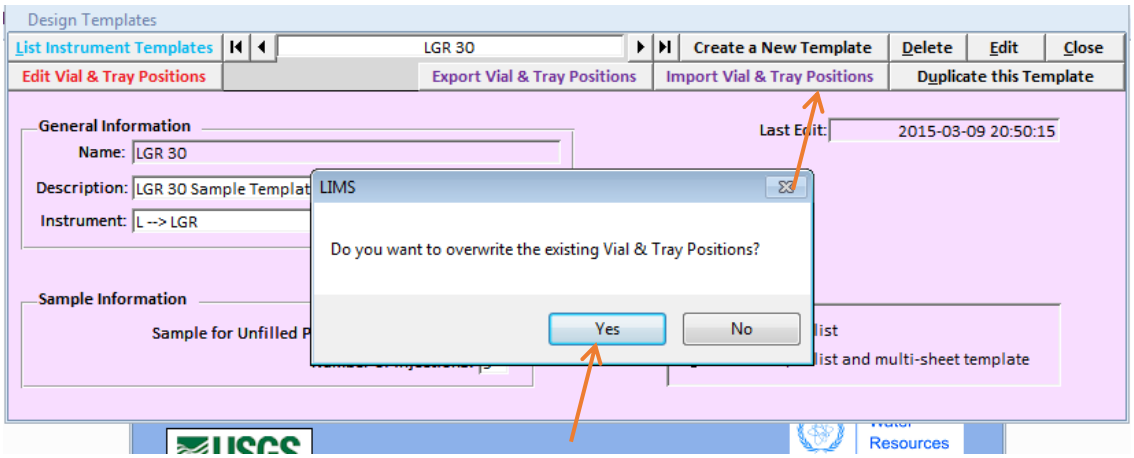
The graphical template page shown on the previous page is shown below using Excel. The spreadsheet headers must be exactly as shown for importing purposes.

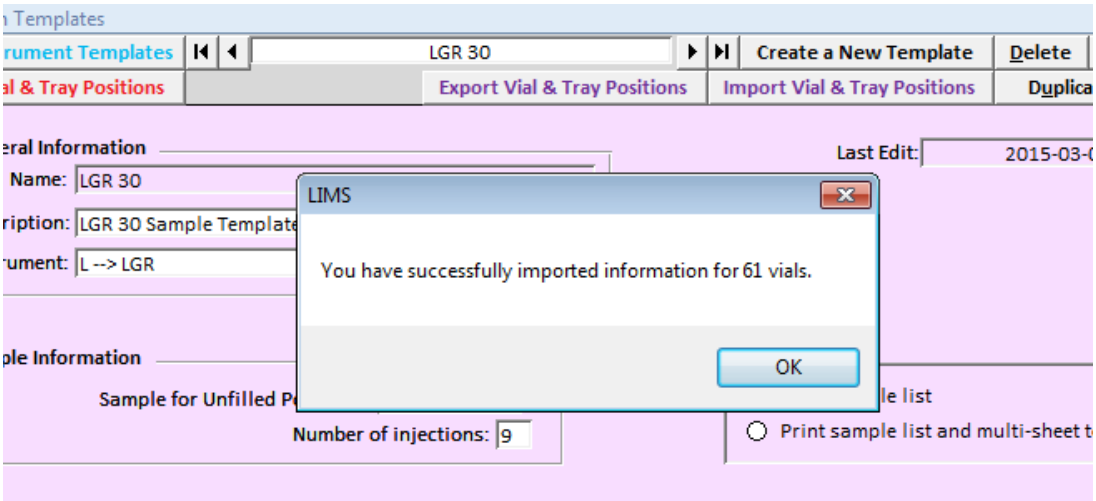
	A	B	C	D	E	F	G
	LIMS_List_No	Tray_Position	Ref_OurLabID	Page	Page_Position	Amount	
	1	3-28	W-3	1	1	1200	
	2	3-28	W-3	1	2	1200	
	3	3-10	W-31	1	3	1200	
	4	3-1	W-32	1	4	1200	
	5	3-2	W-32	1	5	1200	
	6	1-1		1	6	1200	
	7	1-2		1	7	1200	
	8	1-3		1	8	1200	
0	9	1-4		1	9	1200	
1	10	1-5		1	10	1200	
2	11	3-19	W-33	1	11	1200	
3	12	3-3	W-32	1	12	1200	
4							

Import Template from Excel

1. To import a template from Excel, click “Import Vial and Tray Positions” button
2. Select the Excel File template

3. Click “Yes” (if mistakes were made, a descriptive error will be displayed)
4. If a previous template has already been made, confirm that it will be overwritten



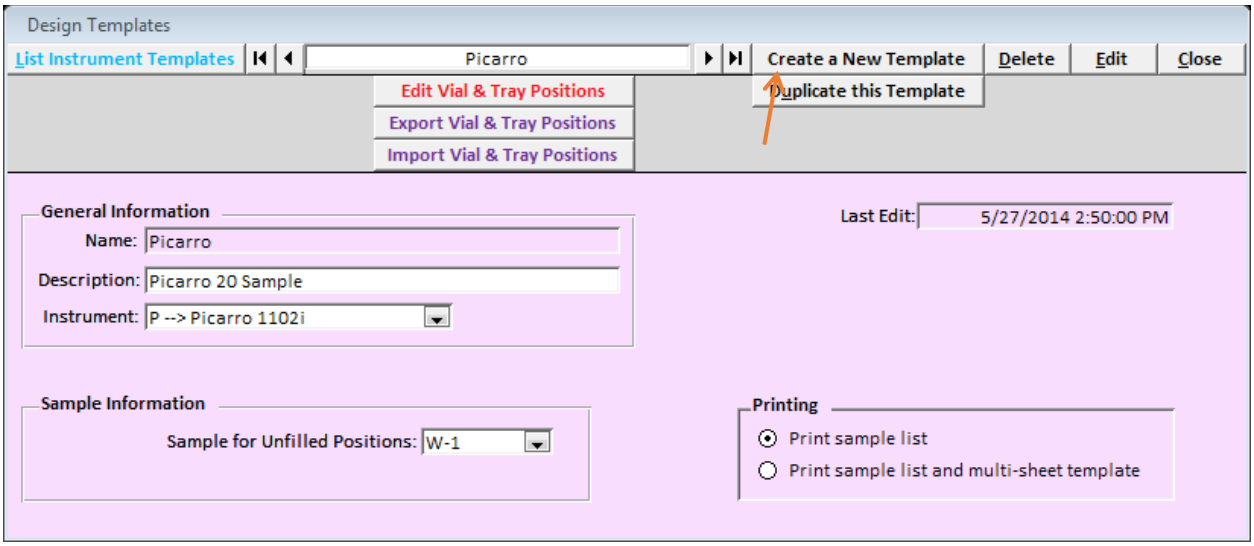


Tip: One useful feature of the Design Template page is the “Duplicate” button. For example, suppose you want 60-, 30-, and 10-sample Los Gatos Research Analysis templates. Start by constructing the largest (60-position) template, duplicate it, and then edit it by deleting pages to obtain a smaller sample template. For the default LGR template, however, this will also require you to recreate the pages of references and controls that follow the unknown samples. Fortunately, good performing analytical templates, once created, need rarely be changed.

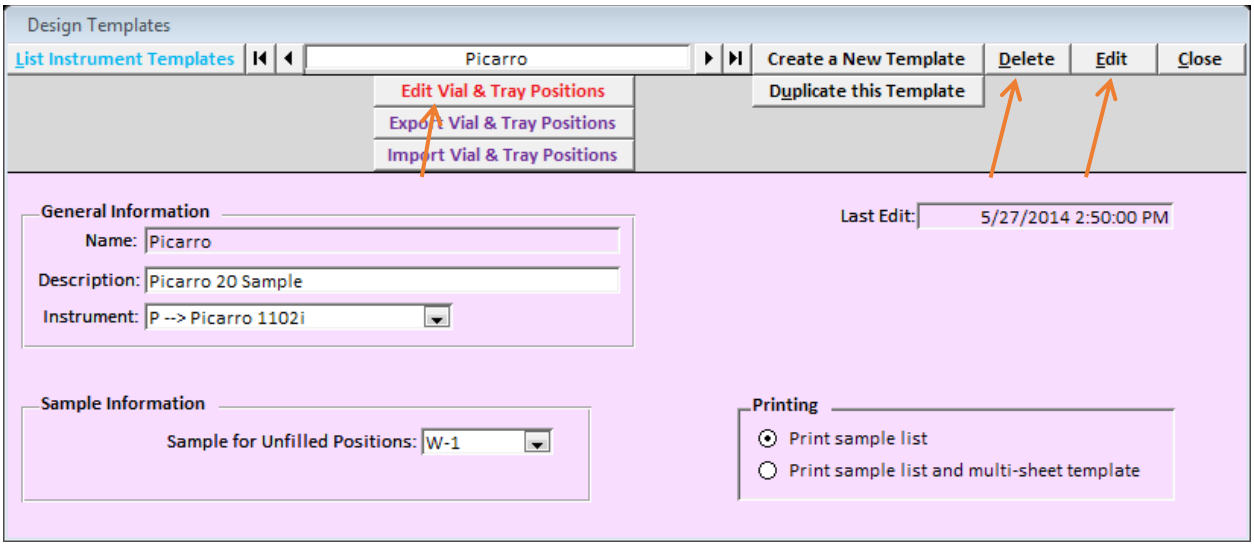
Caution! It is easy mistakenly overwrite an existing Analysis Template. Be sure to first duplicate and rename an existing editable template *before* making and saving changes to it.

8.5 Create a Picarro 20-Sample Analysis Template

1. From the Main Page, open “Special Features”
2. Click on “Analysis Templates”
3. Click on “Create a New Template”



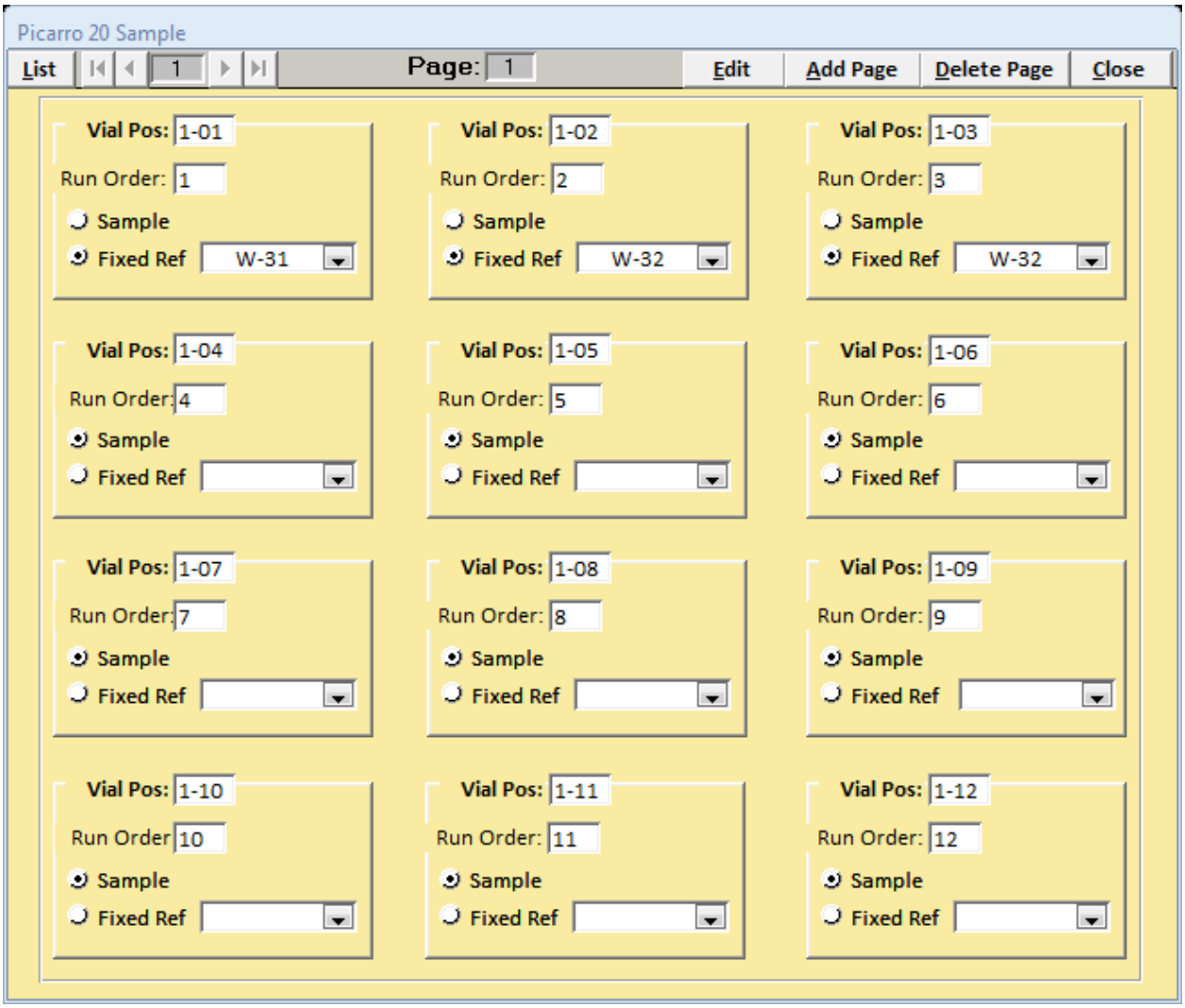
4. Under “Name”, enter a short description (e.g. Picarro 20 Sample)
5. Under Description – add descriptive template details
6. Under Instrument, choose “P” for Picarro
7. The “Sample for Unfilled Positions” defaults to W-1 (a dummy sample). This dummy is used in the case, for example, where only 10 samples are added to a 20-position template. This field cannot be left blank.



8. Click “Save”.
9. Once saved, the template “Name” cannot be edited; only the description and lower fields can be edited. The template may be deleted or edited if a mistake was made, as shown below.

Editing a Picarro Sample Analysis Templates using Pages

The sequence of analysis for measurement standards, control standards and the client samples can be set up by clicking the “Edit Vial and Tray Positions” button. A blank page for 12 samples will appear. Click Edit to complete (completed example below reflects lines 1–12 in Table 2):

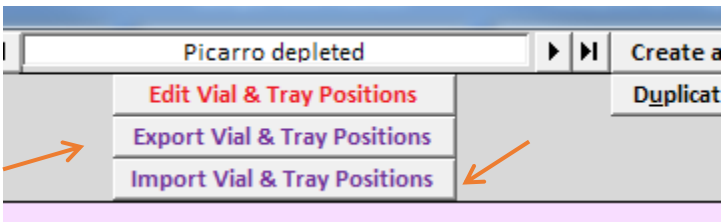


Vial Pos = vial position of a sample in the tray of the liquid autosampler. For example, 1-1 means Tray 1 Position 1, whereas, 3-7 indicates Tray 3 Position 7.
Run Order = Numbered order in which samples are analysed (1,2,3…. 30)
Sample = Choose this button to place an unknown sample

Fixed Ref = Use the drop down box to select a lab standard, control standard or wash sample
Add /Delete Page - add more pages to increase the template length. Always delete pages starting from the last page.

Using Excel to Design and Import or Export Analysis Templates

It may be more convenient to design analysis templates in Excel and import them into *LIMS for Lasers 2015*. The autofill and copy-paste features of Excel make it easy to quickly design and then import a new analysis template into *LIMS for Lasers 2015*.



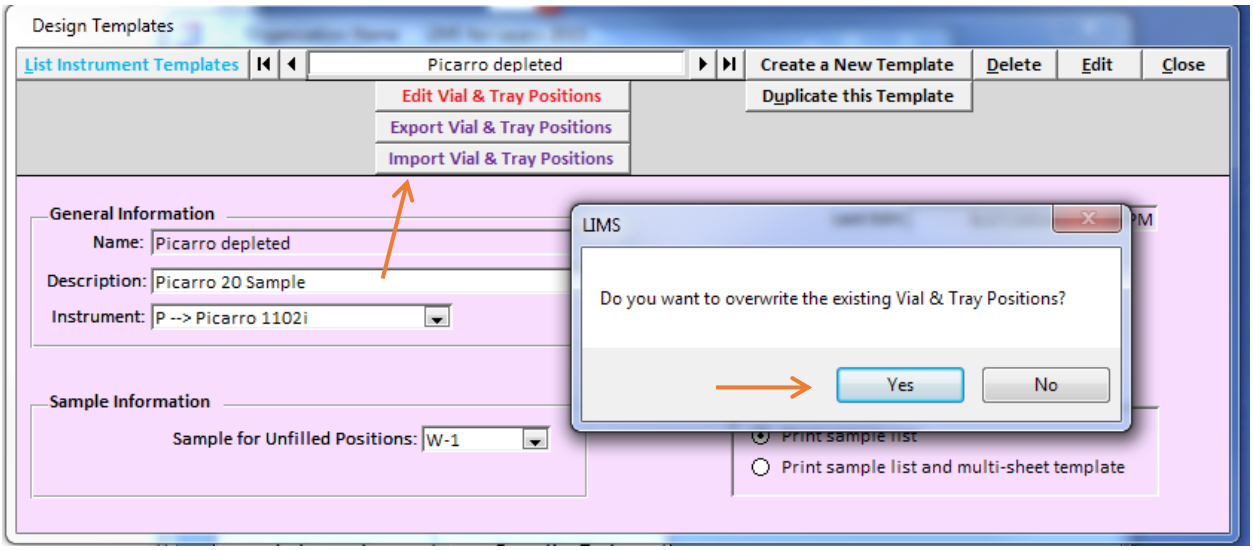
The graphical template page shown on the previous page is shown below in Excel. The spreadsheet headers must be exactly as shown for importing purposes.

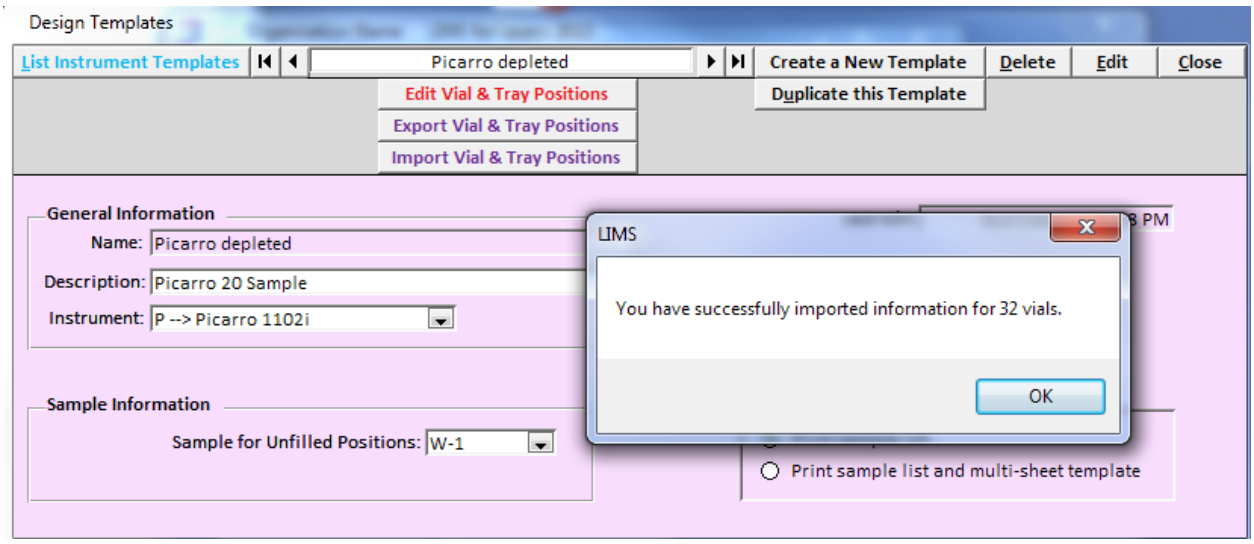
A1 | LIMS_List_No

	A	B	C	D	E
1	LIMS_List_No	Tray_Position	Ref_OurLabID	Page	Page_Position
2	1	1-01	W-31	1	1
3	2	1-02	W-32	1	2
4	3	1-03	W-32	1	3
5	4	1-04		1	4
6	5	1-05		1	5
7	6	1-06		1	6
8	7	1-07		1	7
9	8	1-08		1	8
10	9	1-09		1	9
11	10	1-10		1	10
12	11	1-11		1	11
13	12	1-12		1	12
14					

Export Vial and Tray Positions: export the selected analysis template to an Excel file.
Import Vial and Tray Positions: imports the Excel analysis template into *LIMS for Lasers 2015*. The template will be visible and can be edited using the normal Page editing mode shown above.

1. To import a template from Excel, click “Import Vial and Tray Positions”.
2. Select the Excel File template.
3. Click “Yes” (if mistakes were made, a descriptive error is displayed).
4. If a previous template has been made, confirm it will be overwritten.



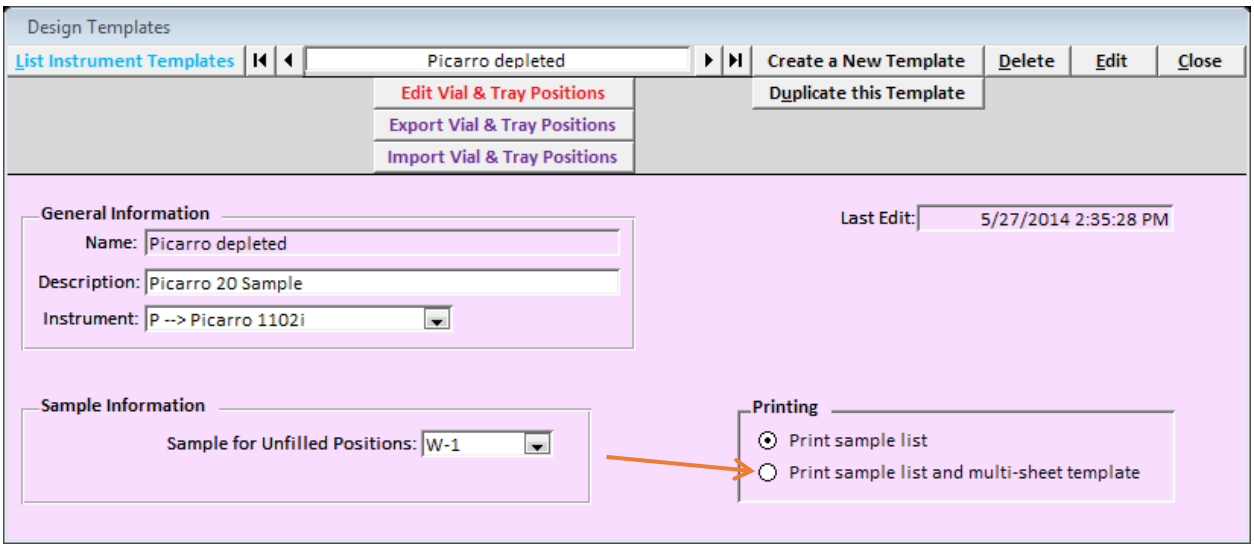


Tip: One useful feature of the Design Template page is the “Duplicate” button. For example, suppose you desire 60-, 30-, and 10-sample Picarro Analysis templates. Start by constructing the largest (60-position) template, duplicate it, and edit it by deleting the higher pages to obtain a smaller sample template. For the default Picarro template, however, this will also require you to recreate the pages of references and control standards that follow the unknown samples. Fortunately, good performing analytical templates, once created need rarely be changed.

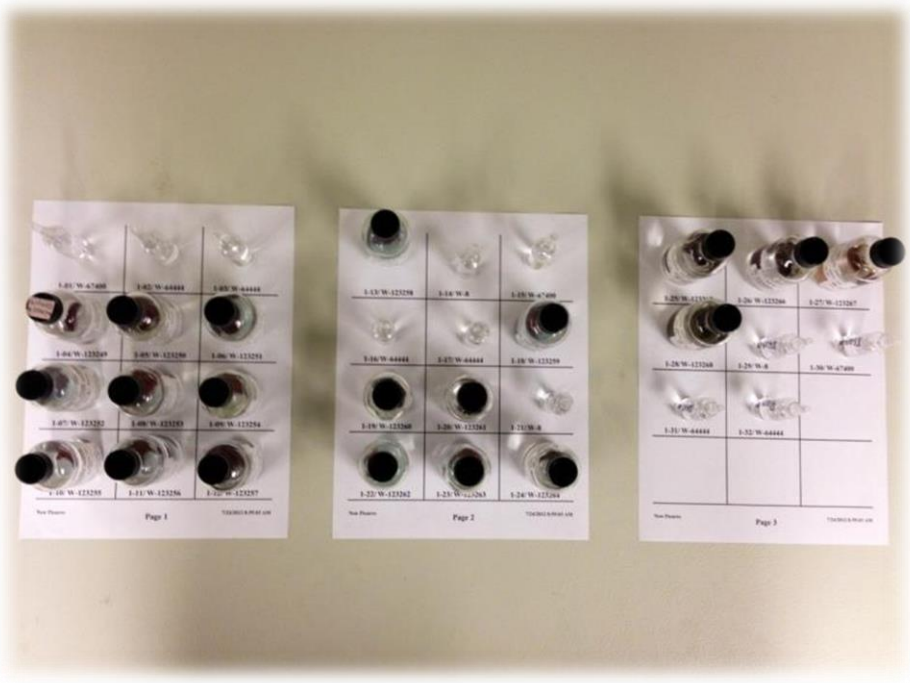
Caution! It is easy mistakenly overwrite an existing Analysis Template. Be sure to first duplicate and rename an existing editable template *before* making and saving changes to it.

8.6 Multi-sheet Sample Layout Printouts

The hands-on organization of water sample bottles and the vials in relation to the laser Analysis Template may be aided by using a multi-sheet template printout. This option prints a hard copy of the sequence layout corresponding to the Analysis Template, and it helps staff organize the samples and vials on the laboratory bench, typically the day before the samples are analysed. In this manner, a second staff person can confirm that the correct sample has been put in the correct vial location on the multi-sheet template printout, improving laboratory quality.



Enabling this option results in the standard one-page sample sequence summary, with additional multi-sheet sample templates, as illustrated below. The 20-sample layout in the photo below illustrates a template with the corresponding samples and standards to be dispensed into laser vials.

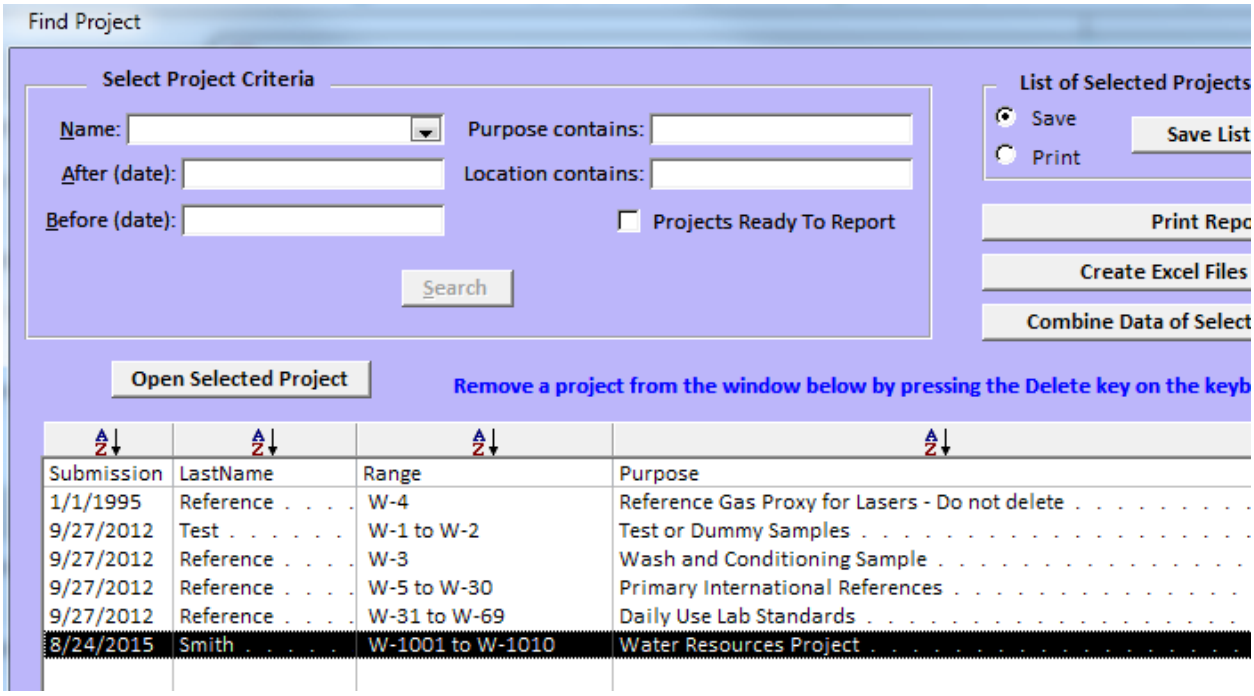


LIMS printed multi-sheet template for sample organization.

8.7 Add Samples to Analysis Templates

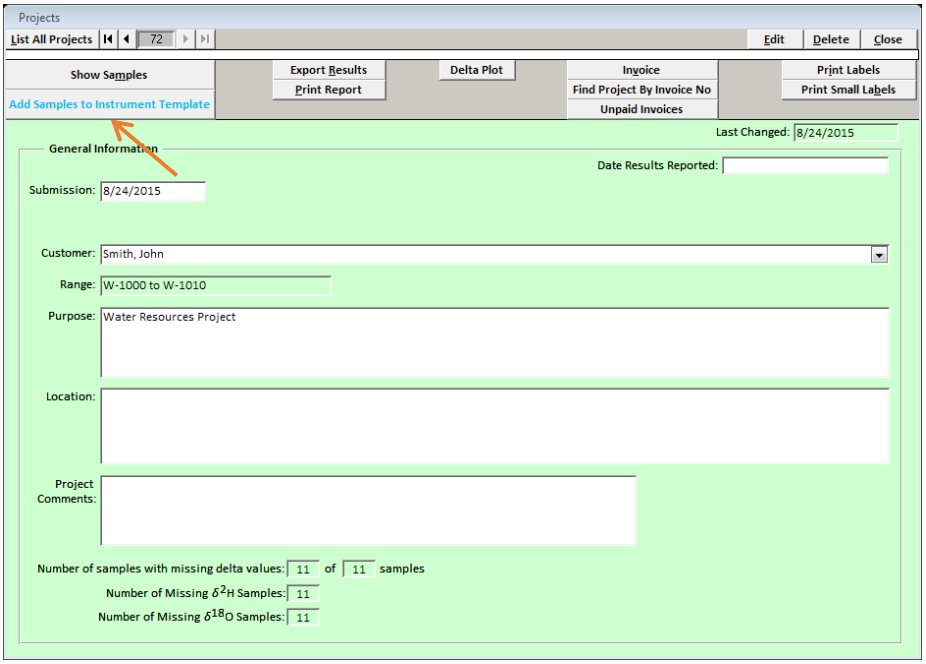
To add samples to an analysis template, a Customer and their Project samples must already exist in *LIMS for Lasers 2015* (see Chapter 6.1).

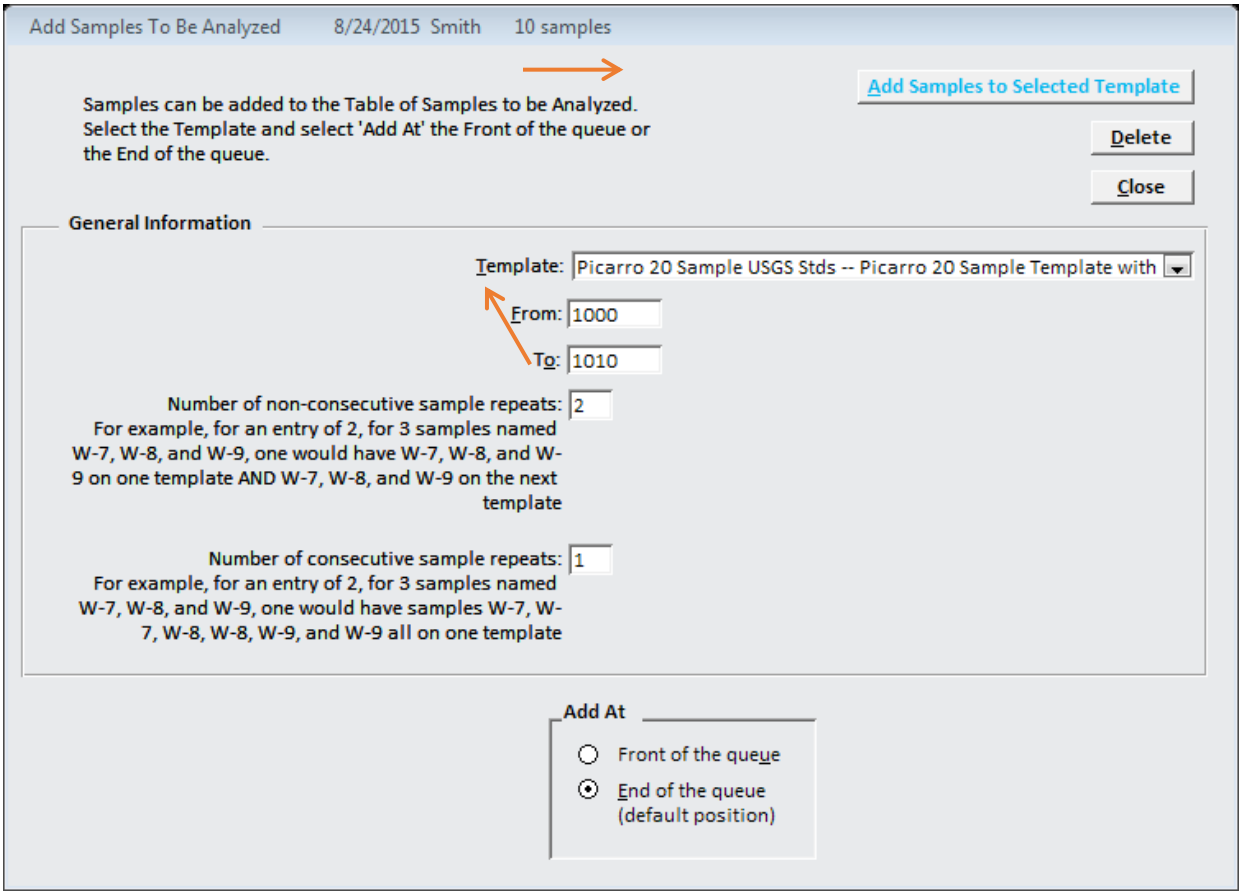
For illustrative purposes, we will analyse a Project containing water samples from John Smith (see Chapter 6). Smith submitted 10 water samples to be analysed on a Picarro and a Los Gatos Research instrument. The δ^{18}O and δ^{2}H values of samples span those of the Our Lab ID range of W-1001 to W-1010 (below).



8.8 Add Samples to a Picarro Analyser Queue

1. Open Smiths "Water Resource Project" from the Project page by double clicking it.
2. Click "Add Samples to Instrument Template".

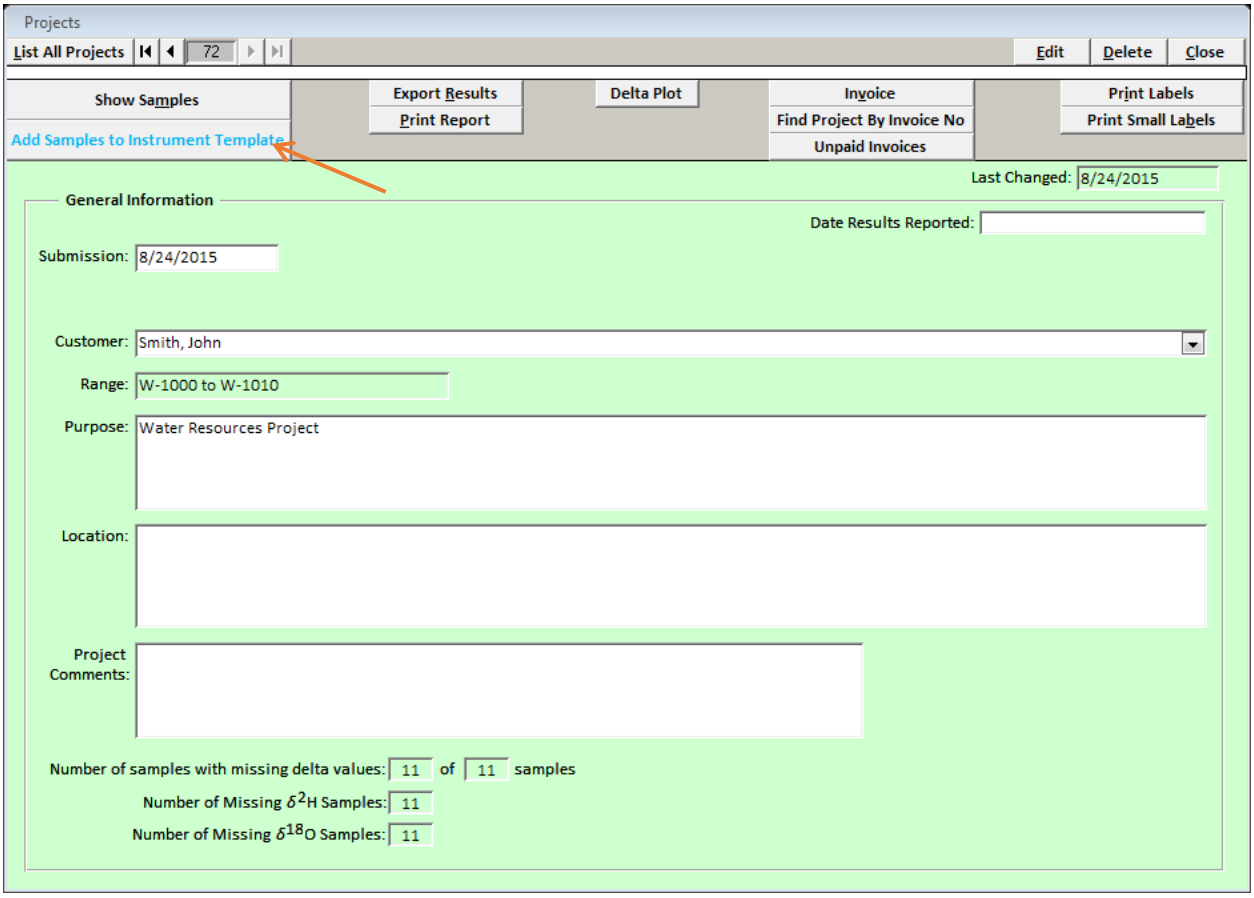




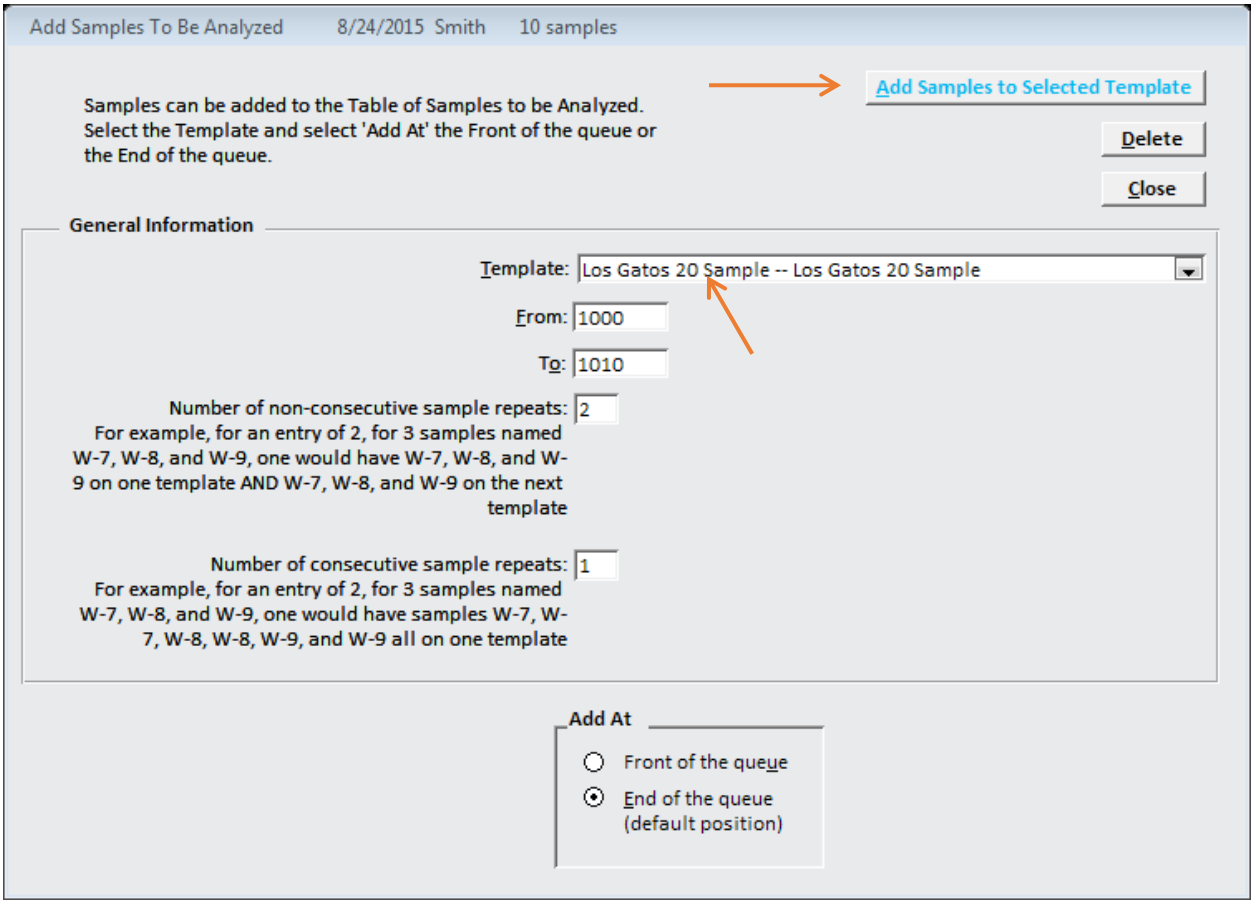
3. From the “Template” pull down, choose “Picarro 20 Sample” and then click on the “Add Samples to Selected Template” button on the top right.
4. The samples are now added to the Picarro 20-sample analysis queue.

8.9 Add Samples to Los Gatos Research Analyser Queue

1. Open “Water Resource Project” from the Project page by double clicking it.
2. Click on “Add Samples to Instrument Template” on the upper left.



1. From the “Template” pull down, choose “Los Gatos Research 30 Samples...” and then click on the “Add Samples to Selected Template” button on the top right.
2. The samples are now added to the 30-sample Los Gatos Research analysis template.



Remember: LIMS analysis templates are unique for each single instrument.

8.10 The Add Sample Options

There are several useful features on the "Add Samples to be Analysed" pages above to consider before clicking "Add" samples to the queue button:

"From" and "To" Boxes

The "From and To" option boxes confirm the Lab ID range of the samples to be added to the queue. By default, all of the samples in the customer project are proposed to be added to the queue–samples of John Smith from W-1001 to W-1010.

However, if one wanted to select only the first five of Mr Smith's samples, one could enter "1005" in the "To" box.

If one wanted to measure only the last five samples of his Project, one could enter From 1006 To 1010.

Number of Non-consecutive Repeats (Default Setting = 2)

The Number of Non-consecutive Repeats is normally set to "2". This means the laboratory will analyse Mr. Smith's samples *twice using 2 different vials on that analysis template*, and preferably on different days. For example, for a small 3-sample (1,2,3) project:

Setting = 1	Sample Queue: 1,2,3
Setting = 2	Sample Queue: 1,2,3,1,2,3
Setting = 4	Sample Queue: 1,2,3,1,2,3,1,2,3,1,2,3

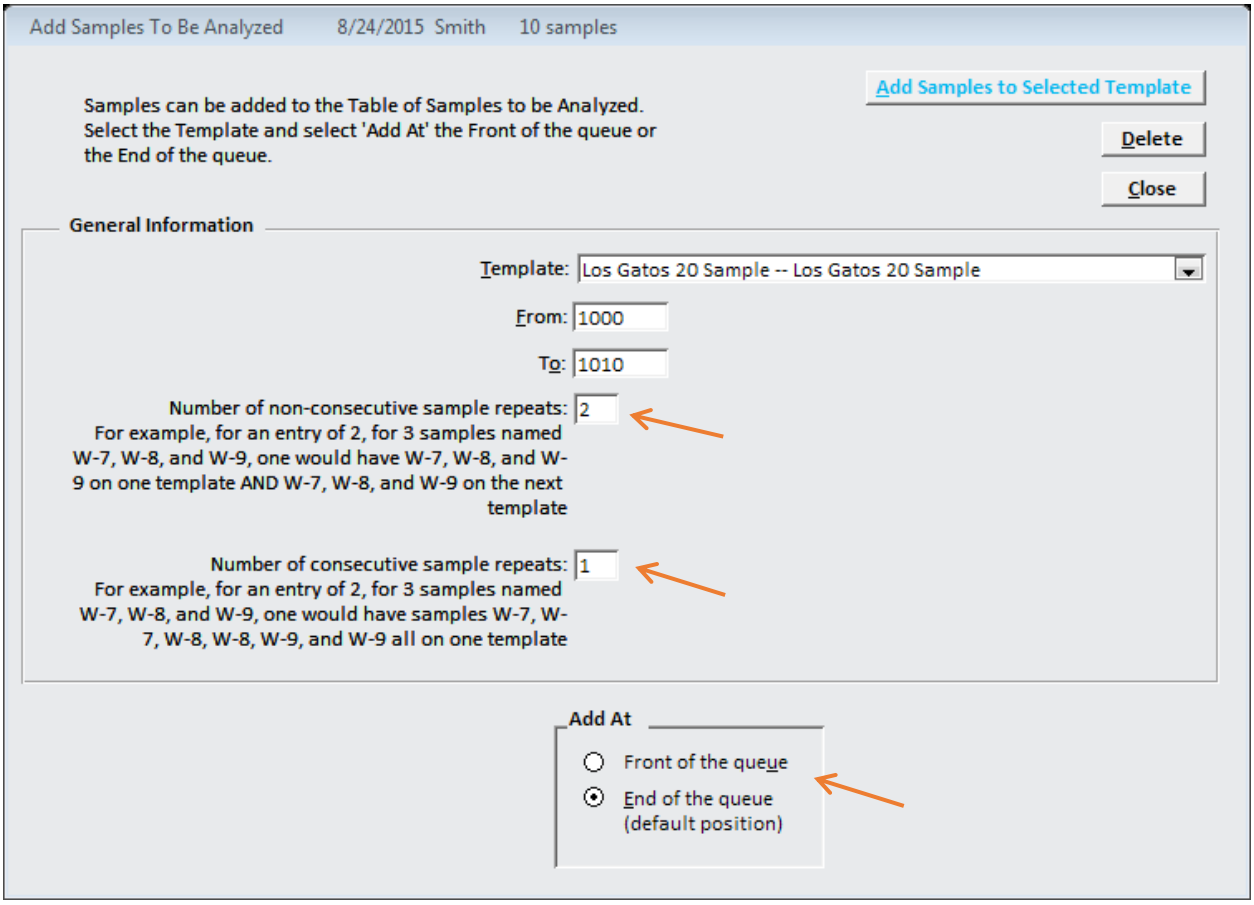
Number of Consecutive Repeats (Default Setting = 1)

Changing this to a higher value means each sample is queued into "groups", so for a small 3-sample (1,2,3) project:

Setting = 1	Sample Queue: 1,2,3
Setting = 2	Sample Queue: 1,1,2,2,3,3
Setting = 4	Sample Queue: 1,1,1,1,2,2,2,2,3,3,3,3,4,4,4,4

Using both options, setting the Consecutive *and* the Non-Consecutive Analysis options to "2" results in:

Sample Queue: 1,1,2,2,3,3,1,1,2,2,3,3



"Add At" (Default setting = end of queue)

The option to add samples to the front of a queue allows fast tracking of high priority samples ahead of those already in the queue.

For example, if one is partly through a queue and 5 urgent samples arrived, one could add the 5 samples from that urgent project to the "Front of the Queue".

If there are no unmeasured samples in the analysis queue, choosing either option yields the same result.

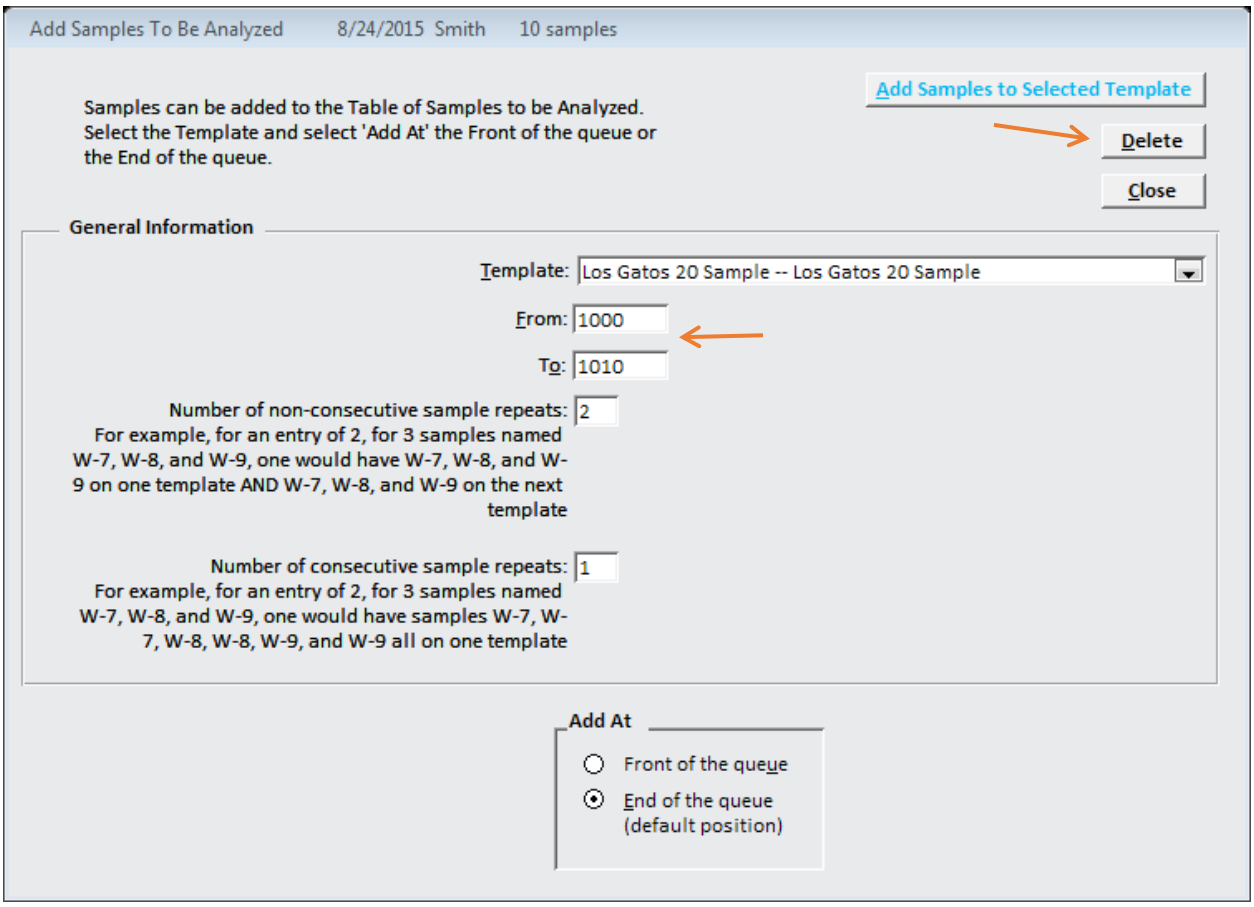
8.11 Removing Samples from a Queue

Samples added to an Analysis Template queue will continue to accumulate as they are added until all the samples have been measured and their "run flag" is set to zero, or they are deleted altogether from the queue.

There are two ways to delete samples from a current Analysis Template queue. This action may be required, for example, if one has mistakenly added samples to the wrong instrument template or one simply wishes to remove cancelled samples.

Deleting Queued Samples from the Project Page

If one added samples from an entire project to an analysis template queue, they are deleted the same way they were added. In the Project pane, click “Add Samples to Instrument Template”. The following window opens – now instead click “Delete” to remove all of the project samples from the template queue, or alternately eliminate selected samples using the “From” and “To” boxes.



One-click removal of Smith samples from the Picarro analysis queue within the Project.

Manual Removal and Editing of Queued Samples in a Template

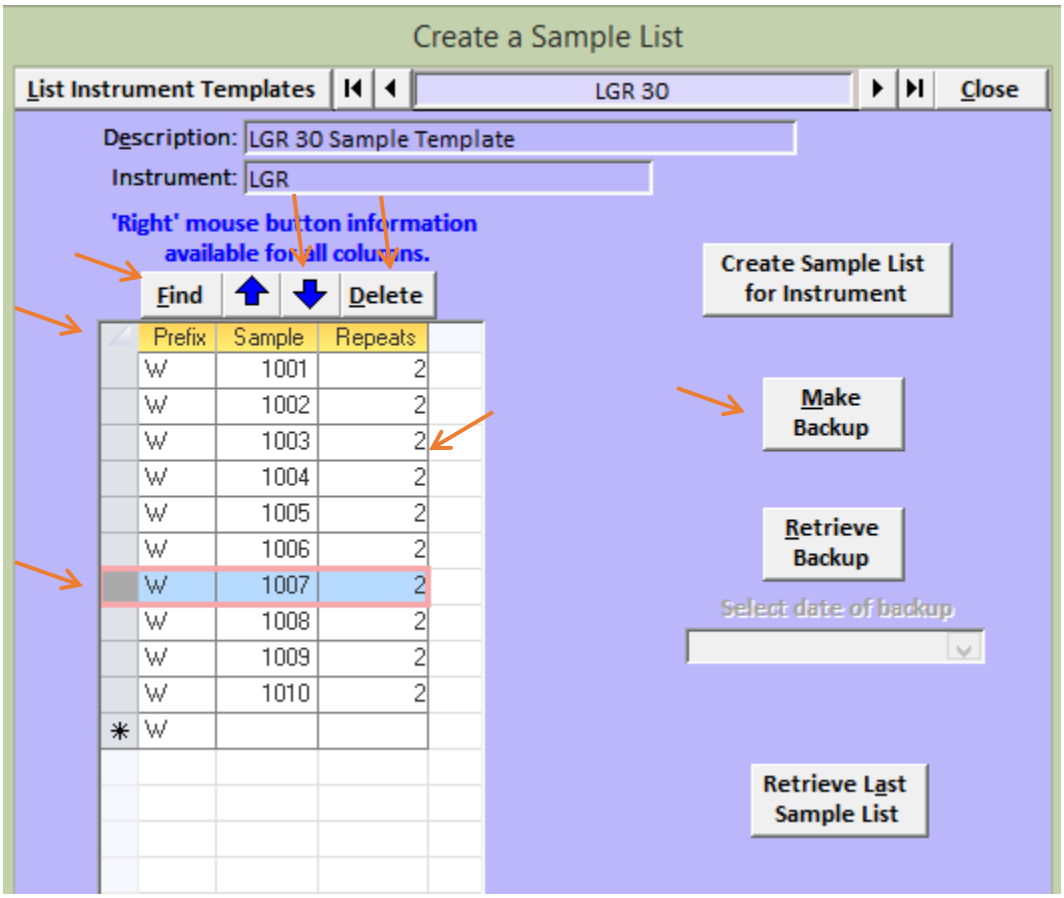
A second way to edit an analysis template queue is to do it manually:

1. On Main page, click on “Create Sample List for Instruments”.

2. From “List Instrument Templates”, choose the instrument Template queue that you wish to edit.

There are a number of manual editing options available:

- Use the “Find” button to locate a specific sample in the queue (useful for long queues).
- Move sample(s) up or down in sequence priority by highlighting and moving them using the blue arrow keys.
- Delete a sample or group of samples by highlighting the sample cells and click “Delete”.
- Manually edit the number of repeats for one or more samples (set flag from 0 to >1).
- Clear the entire queue completely by clicking top left handle to highlight all (as in Excel) and then clicking the “Delete” key on the keyboard.
- Make a backup of a queue and retrieve it (precaution in case of editing errors).
- Load the last used sample list (useful for repeating runs without having to go to the steps of adding samples from the Project page again).



LIMS for Lasers 2015 Manual Sample Queue Editing.

8.12 Repeated Samples in LIMS for Lasers 2015

LIMS for Lasers 2015 default policy is that all samples are measured twice, preferably on different days. It is good laboratory policy to perform two or more analysis repetitions of each sample (in different vials). This policy can be manually overridden (see Chapter 12.5).

The benefit of having two or more analyses of the same sample promotes good laboratory practice, helps catch vial placement errors, allows the operator to check the consistency between two or more analyses of the same sample, helps identify problematic samples (e.g. poor repeats), and allows one to compare the performance of sample repetitions with control standards in the same analysis. This approach gives realistic metrics of overall laser performance.

Note: To obtain sufficient δ^{17}O precision, some suggest at least 50 or more replicates in multiple vials are needed, compared to routine δ^{18}O and δ^{2}H analyses.

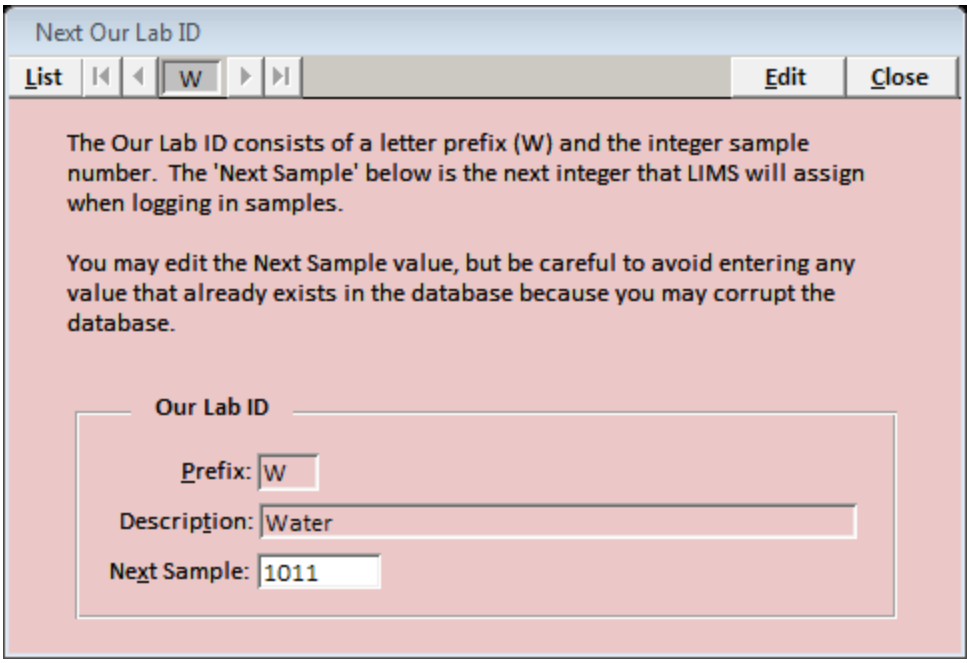
8.13 The Next Sample Number

The “Next Sample Number” button is located in the “Special Features” section. This utility allows one to specify the next Our Lab ID number assigned to newly imported samples.

While this option is rarely needed (e.g. to fix errors), it is useful for adding laboratory measurement standards and keeping them constrained within a specific “W” range. Generally, it is preferable and easier to remember measurement standards having low sequential W numbers.

For example, by default *LIMS for Lasers 2015* customer samples start at W-1001. The last default place holder for our lab standards is W-69. This means Our Lab ID numbers from W-70 to W-997 are still freely available to be assigned to new measurement standards.

Clicking on the “Next Sample Number” button reveals the next W number that will be assigned to incoming customer samples - here W-1011 is the next Our Lab ID.



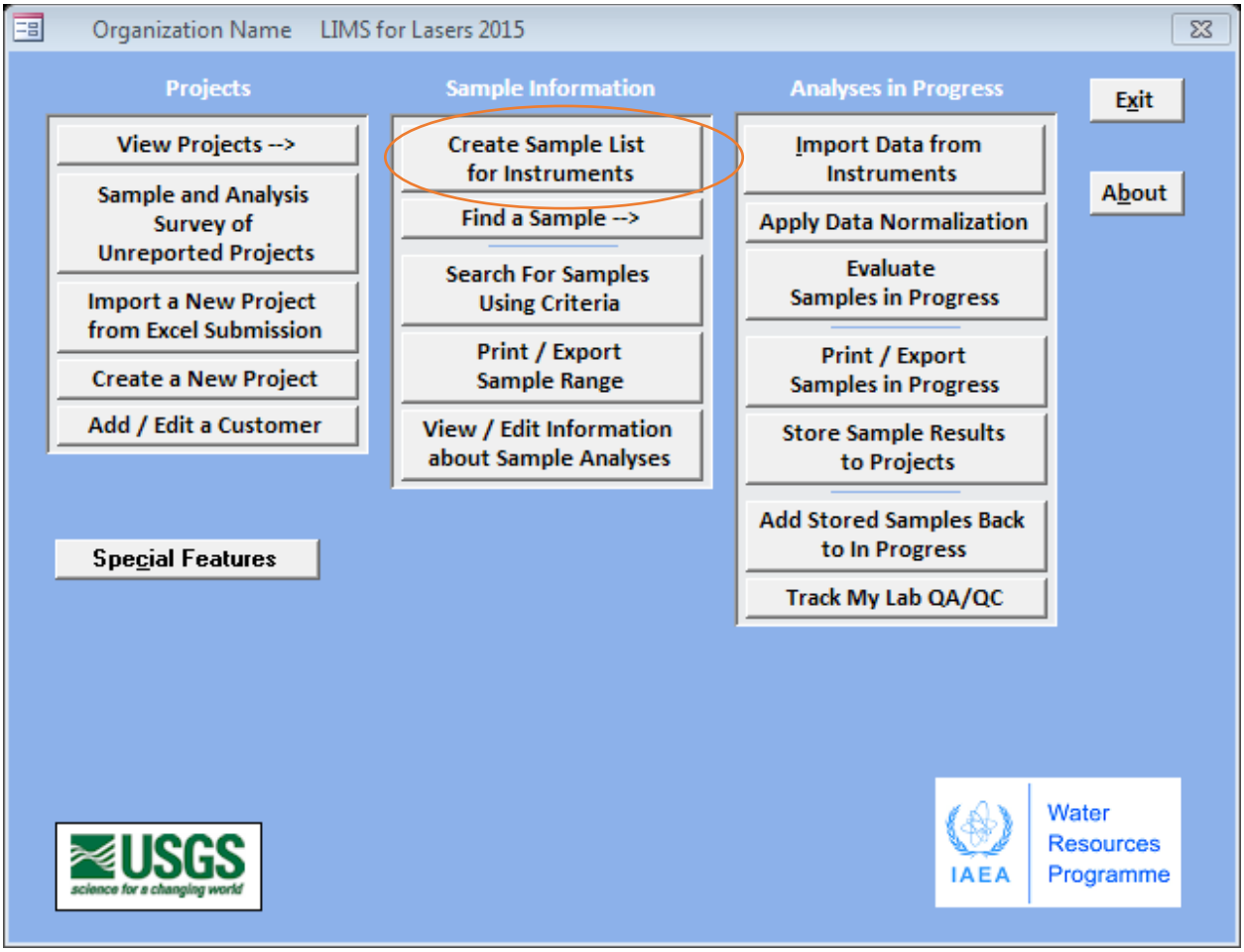
Suppose we want to add 10 new laboratory standards, but have them sequentially follow the current laboratory standards (e.g. ending at W-69). First, note the last W number shown (here it is W-1011 – the last of Smith's samples) and write it down. Click "Edit", change "Next Sample" to 70 and click "Save". Next, import the 10 new measurement standards into a new project as described in Chapter 6. They will be given Our Lab ID numbers W-70 to W-79.

Caution!: When completed, go back to Next Sample Number option, click "Edit", and change the number back to what was originally found (here W-1011). This ensures you do not attempt to overlap with any pre-existing W numbers.

9 Run Samples on a Picarro Laser

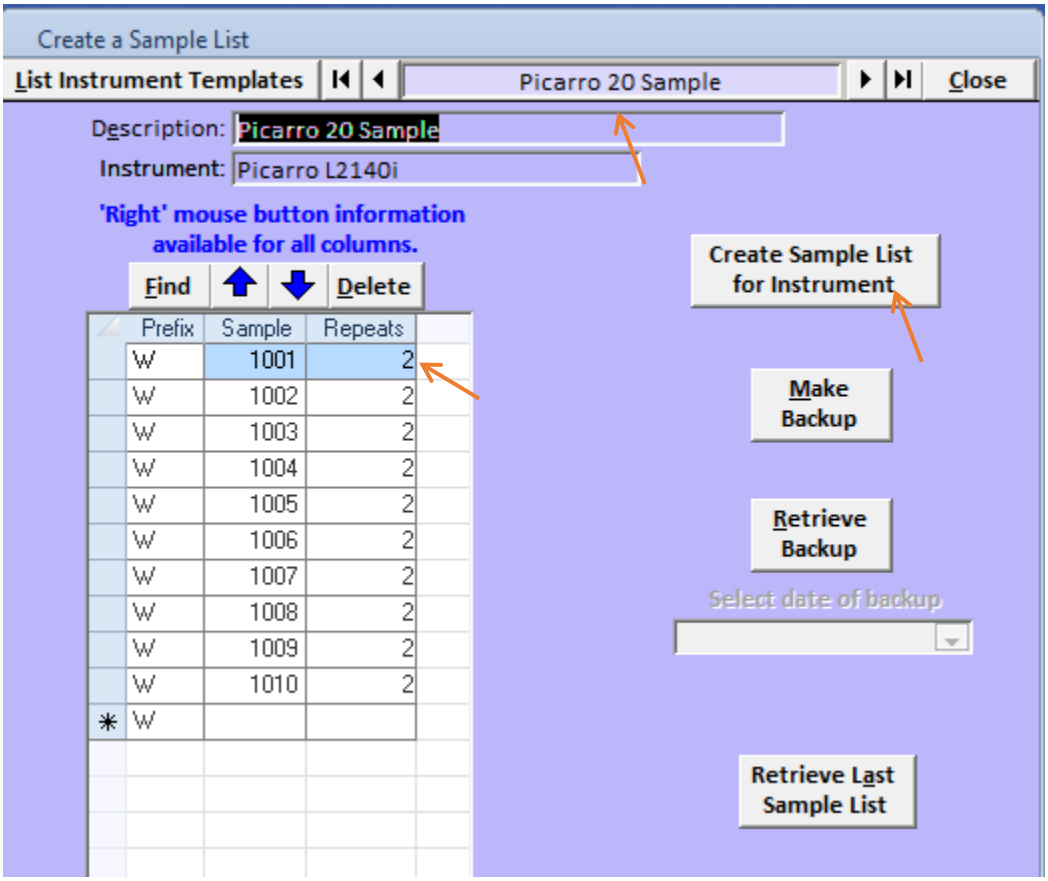
9.1 Create a Sample List for a Picarro Instrument

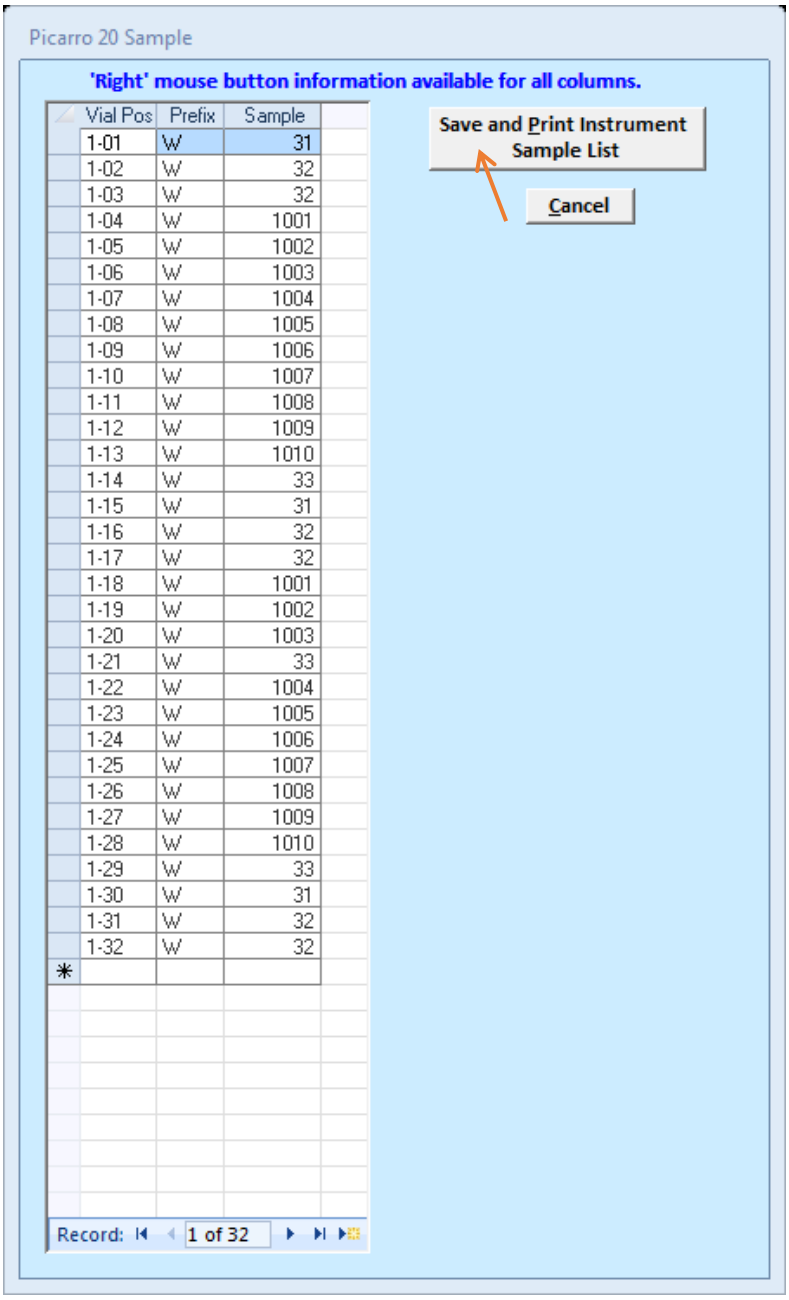
LIMS for Lasers 2015 creates Sample Lists (otherwise called sequence files or run lists) for Picarro instruments. These sample lists are transferred via a USB flash drive or network to the Picarro laser instrument for analysis. This action is performed from the "Create Sample List for Instruments" button on the Sample Information column of the LIMS Main Page.



By example, we create a sample list of Smith samples for a Picarro instrument.

1. Ensure Smith's samples were added to the Picarro queue (see Chapter 8.8).
2. On the Main LIMS Page, click "Create Sample List for Instruments".
3. Choose "List Instrument Templates" and click on "Picarro 20 Sample"; the sample queue opens.
4. Click on "Create Sample List for Instrument"; a dialog box confirms Smith's 10 samples are to be added to the current queue (twice). Click "OK".



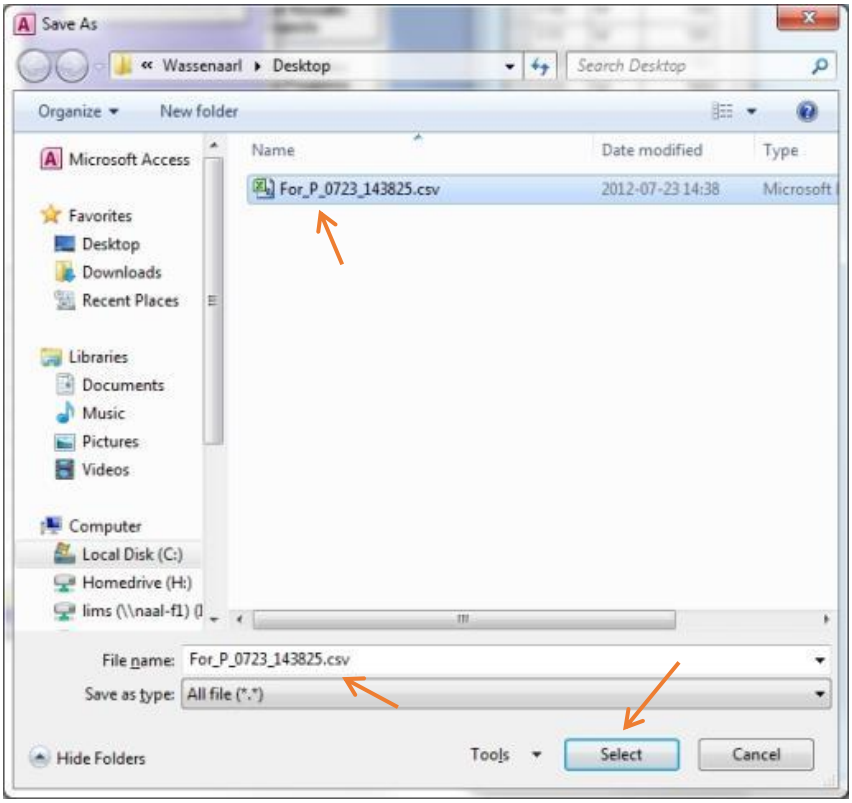


Vial Pos	Prefix	Sample
1-01	W	31
1-02	W	32
1-03	W	32
1-04	W	1001
1-05	W	1002
1-06	W	1003
1-07	W	1004
1-08	W	1005
1-09	W	1006
1-10	W	1007
1-11	W	1008
1-12	W	1009
1-13	W	1010
1-14	W	33
1-15	W	31
1-16	W	32
1-17	W	32
1-18	W	1001
1-19	W	1002
1-20	W	1003
1-21	W	33
1-22	W	1004
1-23	W	1005
1-24	W	1006
1-25	W	1007
1-26	W	1008
1-27	W	1009
1-28	W	1010
1-29	W	33
1-30	W	31
1-31	W	32
1-32	W	32

In the queue above, Smith's project (W-1001 to W-1010) is setup to be analysed twice in sequence (# of repeats = 2).

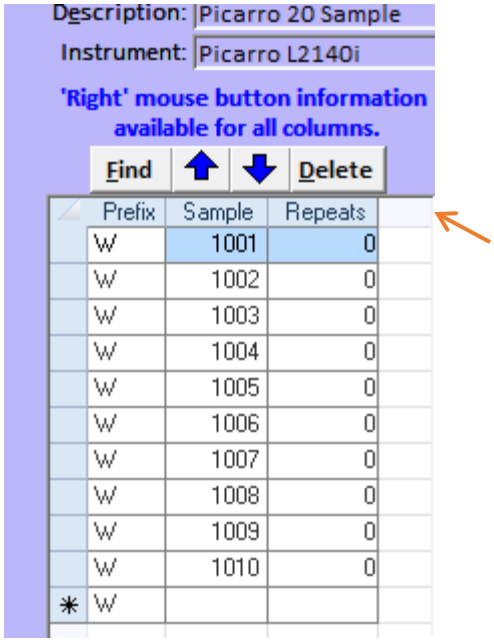
5. The analysis sequence, containing the local measurement standards and control standards assigned in the template and Smith's samples, opens (above figure).
6. Click "Save and Print Instrument Sample List".
7. A Windows dialog box opens asking where to save the sample/sequence list file. This is the CSV file that will be transferred to the Picarro instrument, and it should be saved to a USB flash drive or to a network location where the Picarro Coordinator data acquisition software can load the file.

8. Click “Select” to save the file to the desired location (e.g. USB flash drive for transfer to instrument). Note the saved file is in CSV format, and the file name is a concatenation of instrument prefix “For P” (Picarro) and the date. This file naming convention helps keep track of Picarro sample lists as they accumulate over time. Alternately, the run file may be renamed to something more descriptive, like Smith Samples.csv.



A Printer dialog box opens, asking where to print the sample run list (e.g. the default Windows printer). A one-page summary of the sample list sequence is printed.

9. After printing, the queue reopens and we see the sample “repeats” were decremented from 2 to 0 (right). This indicates that all samples have been analysed.
10. The printed list of samples to be analysed (next page) reveals the vial position and the Our Lab ID of the measurement standards, control standards, and the samples.
11. Fill the 32 sample and standard vials each with ~ 1.5 mL of sample, as per Picarro guidelines. Affix (or write) “W” number from small labels to each vial. Load the autosampler tray with the sample and measurement standard vials according to the printed sample list.



Picarro 20 Sample Samples To Be Analyzed

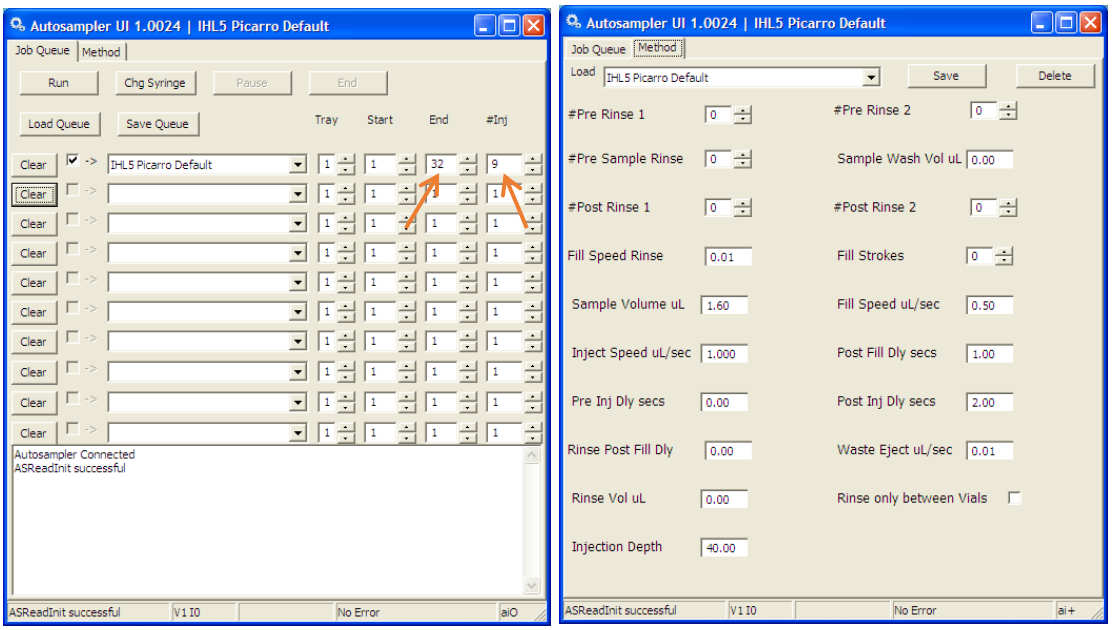
Vial Pos	Our Lab ID	Sample ID	Project	Notes	Vial Pos	Our Lab ID	Sample ID
1-01	W-31	High Standard	Refere 20120927	_____			
1-02	W-32	Low Standard	Refere 20120927	_____			
1-03	W-32	Low Standard	Refere 20120927	_____			
1-04	W-1001	Sample1	Smith 20150304	_____			
1-05	W-1002	Sample2	Smith 20150304	_____			
1-06	W-1003	Sample3	Smith 20150304	_____			
1-07	W-1004	Sample4	Smith 20150304	_____			
1-08	W-1005	Sample5	Smith 20150304	_____			
1-09	W-1006	Sample6	Smith 20150304	_____			
1-10	W-1007	Sample7	Smith 20150304	_____			
1-11	W-1008	Sample8	Smith 20150304	_____			
1-12	W-1009	Sample9	Smith 20150304	_____			
1-13	W-1010	Sample10	Smith 20150304	_____			
1-14	W-33	Control	Refere 20120927	_____			
1-15	W-31	High Standard	Refere 20120927	_____			
1-16	W-32	Low Standard	Refere 20120927	_____			
1-17	W-32	Low Standard	Refere 20120927	_____			
1-18	W-1001	Sample1	Smith 20150304	_____			
1-19	W-1002	Sample2	Smith 20150304	_____			
1-20	W-1003	Sample3	Smith 20150304	_____			
1-21	W-33	Control	Refere 20120927	_____			
1-22	W-1004	Sample4	Smith 20150304	_____			
1-23	W-1005	Sample5	Smith 20150304	_____			
1-24	W-1006	Sample6	Smith 20150304	_____			
1-25	W-1007	Sample7	Smith 20150304	_____			
1-26	W-1008	Sample8	Smith 20150304	_____			
1-27	W-1009	Sample9	Smith 20150304	_____			
1-28	W-1010	Sample10	Smith 20150304	_____			
1-29	W-33	Control	Refere 20120927	_____			
1-30	W-31	High Standard	Refere 20120927	_____			
1-31	W-32	Low Standard	Refere 20120927	_____			
1-32	W-32	Low Standard	Refere 20120927	_____			

Example Analysis template list

12. On the Picarro autosampler, the measurement standard and sample vials are set up for analysis using the layout(s) described and presented above in Table 2. Double check the printed LIMS sample run list to ensure that all vials are located in the correct positions, which will depend on which liquid autosampler model is being used.

In the figure below (left side), a Picarro G-2000 Autosampler screen is shown for the 20-sample analysis template (20 samples plus standards for a total of 32 samples). Each sample is set to be measured 9 times, as per recommendations, starting with Tray 1, Position 1. On the older Combi PAL control unit (not shown), the same analysis setup is performed using the handheld PAL unit.

Note: No pre-analysis conditioning samples or post-analysis wash samples are listed. The reason is that *the Picarro CSV data output file should contain only our LIMS sample data* and not any pre-conditioning or wash sample data. (But see Appendix 1)



Caution: Be aware that sample analyses via the Picarro Coordinator data acquisition software are independent of *LIMS for Lasers 2015*. There is no coordinated connection between the instrument and the sample file. Therefore, ensure that the number and location of analyses on the Picarro Autosampler or Combi PAL *match exactly what the LIMS Analysis Template expects*.

Finally, ensure a new Picarro Coordinator output file is created immediately before initiating the autorun to avoid importing data from previous autoruns or conditioning samples.

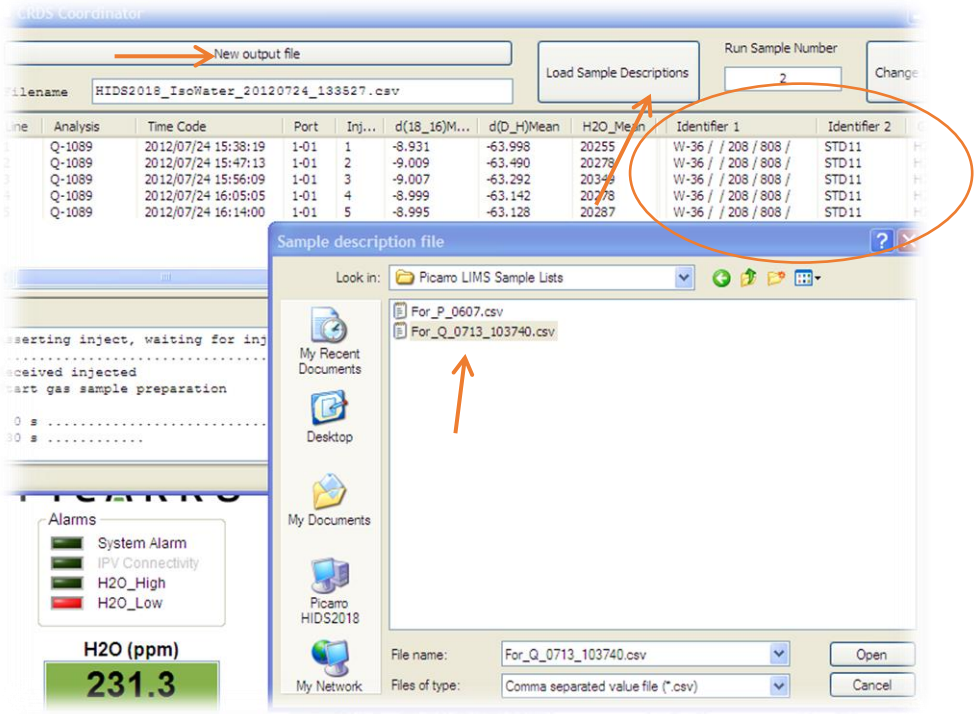
The second panel (above, right) shows the Picarro 2130i default sample injection parameters. Here a 1.6-µL injection achieves the instrumental target of a volume fraction of H_2O of 20,000 ppm. The Autosampler UI parameters shown are found on the Combi PAL controller. See the Picarro instrument user manuals for the autosampler setup details.

On all Picarro instruments, the sample data collection, integration, and processing of measured *δ* values is performed using the Coordinator data acquisition and control software. In the screenshot below, we see the first 5 injections of an autorun. The autorun output data will be saved to a filename that was created when the Picarro Coordinator software was started (e.g. HIDS2018_Isowater_201207024_133527.csv).

The LIMS sample list for Picarro instruments, created in Chapter 9.1, can be loaded into the Coordinator when one or more lines of analyses results are reported in the Coordinator window. The *LIMS for Lasers 2015* sample list can be loaded from the USB flash drive or via a network connection.

Adding the LIMS Sample List to Picarro Coordinator

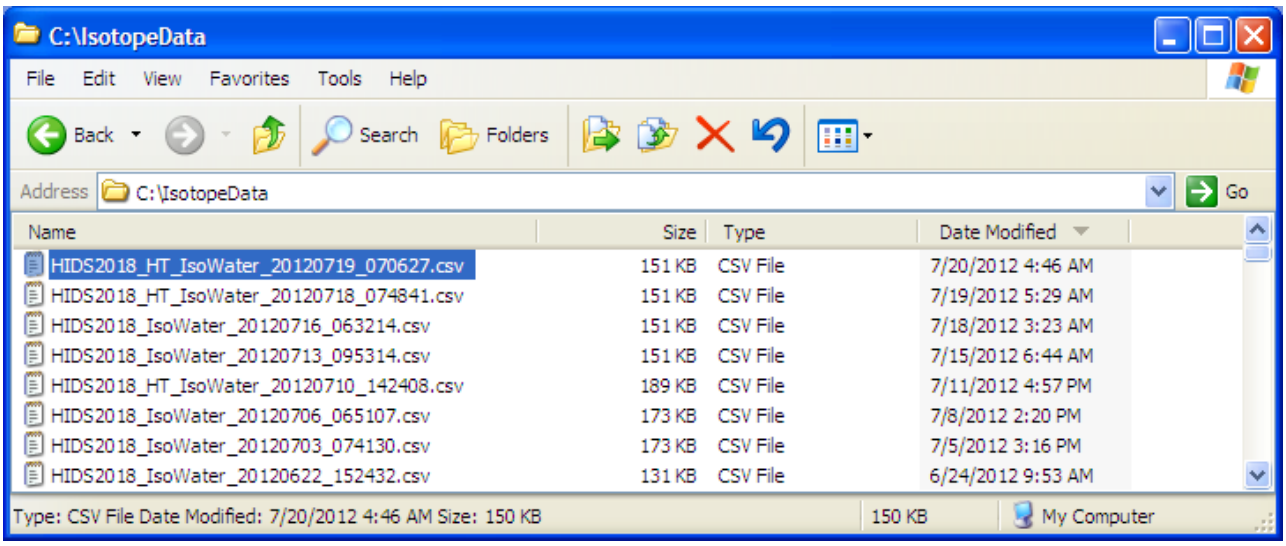
1. Start the Picarro analysis autorun and wait for one or more sample's isotopic results to appear in the Coordinator window (and before the autorun ends); this may take a few minutes following the first sample injection.
2. Next, in Picarro Coordinator, click "Load Sample Descriptions" button.
3. Locate the LIMS-generated sample list, here denoted "For_Q_0713_103740.csv" (here a second Picarro instrument Prefix was "Q" instead of the default "P").
4. The information from the LIMS file will now populate fields "Identifier 1" and "Identifier 2", and it will correspond to those samples and standards being analysed.
5. Allow the analysis autorun to finish (30+ hours for the default template).



9.2 Import Isotopic Data from Picarro

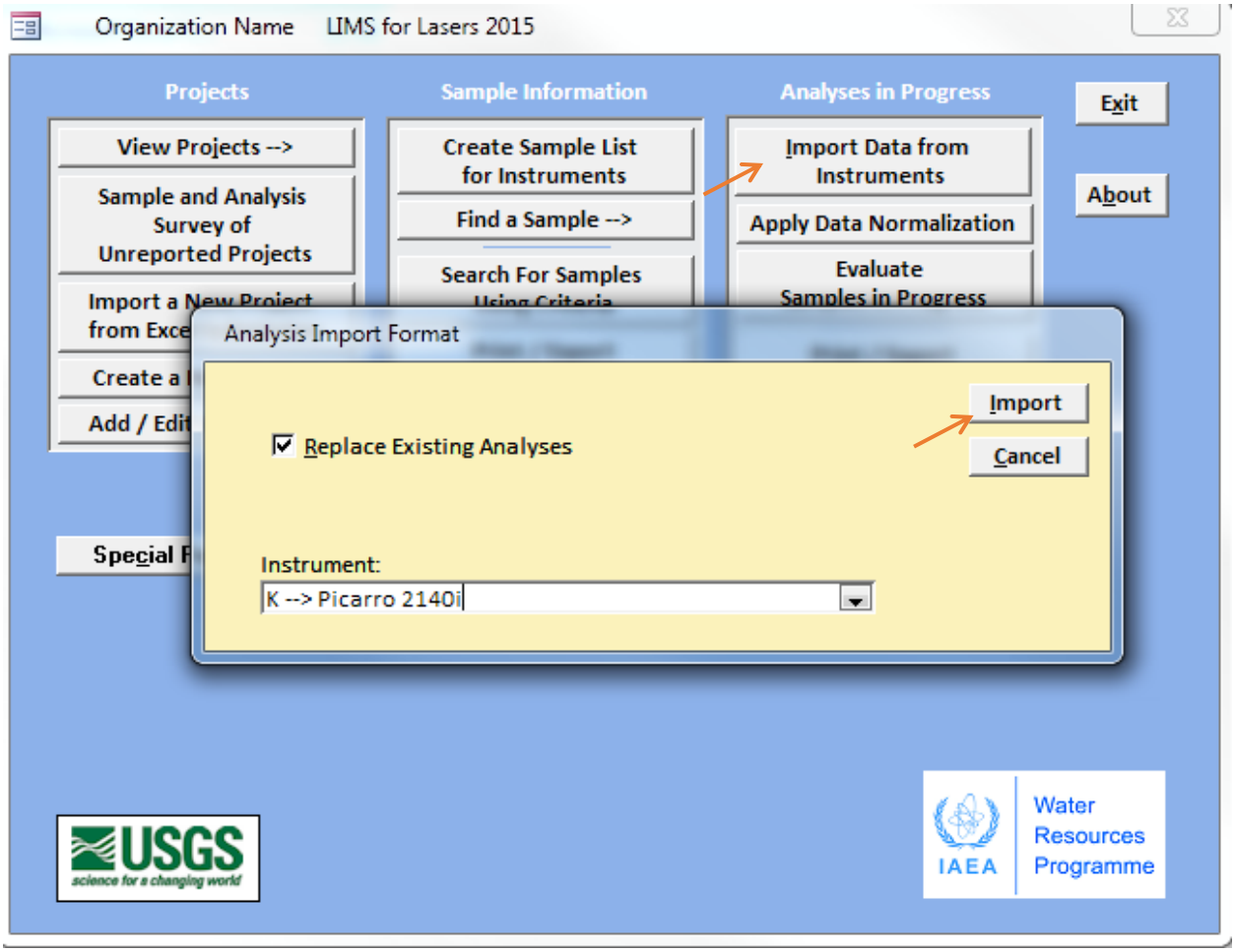
Once a Picarro water isotope analysis run, loaded with the LIMS Identifier fields, has finished, the measured isotopic results can be imported into *LIMS for Lasers 2015* for screening, data normalization, processing and evaluation, and final reporting to the customer.

The completed autorun CSV file is located on the Picarro instrument, usually in the disk location called C:\IsotopeData. The output file name will be the same one assigned in the Coordinator software at the start of the analysis run. Some example Picarro CSV autorun files are shown below.

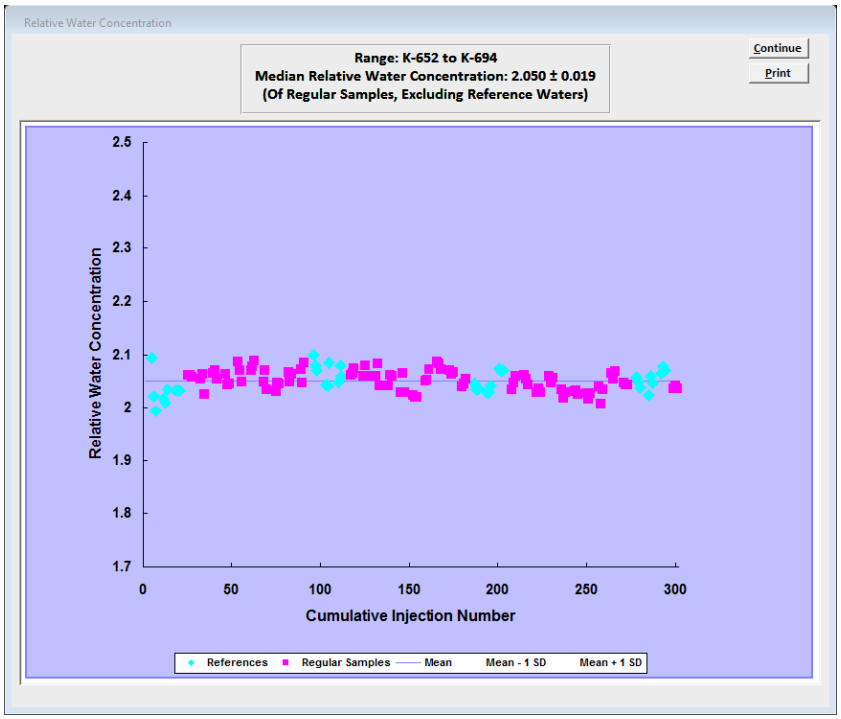


1. Copy the correct Picarro CSV autorun data file to a USB flash drive or to a LIMS accessible network location.
2. On the LIMS main page, click “Import Data from Instruments”, choose the Picarro instrument from the pull down menu, and then click “Import”. Choose the appropriate data output file from the USB flash drive or the network location.

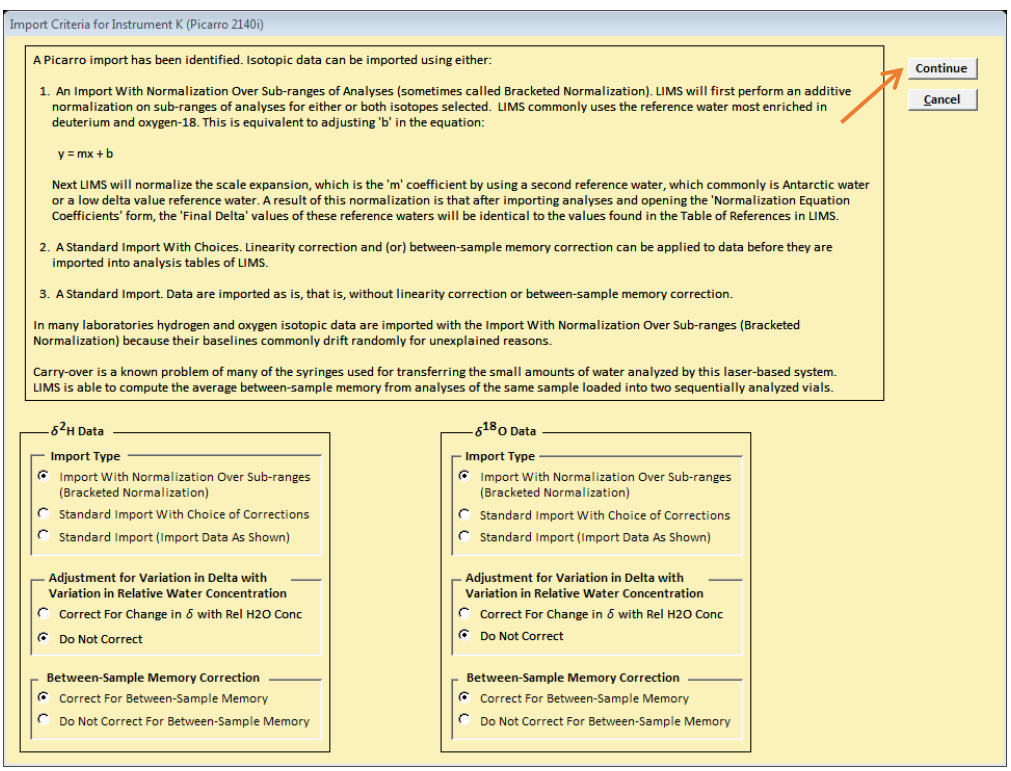
Note: Checking the “Replace Existing Analyses” box will overwrite the previous import of this same data file *provided that data was not normalized or stored*. This is useful if you wish to import the same data several times and examine the effects of different import options described in Chapter 11.1, or to correct a mistake. This setting is checked by default.



3. A screen appears showing the injection amounts over the course of the analysis run. If the injection amounts vary widely, then the syringe or septa is likely faulty. This preview is critical to ensure that water injections are consistent throughout the autorun. *LIMS for Lasers 2015* divides the measured Picarro concentration by 10,000 to determine the relative H_2O concentration.



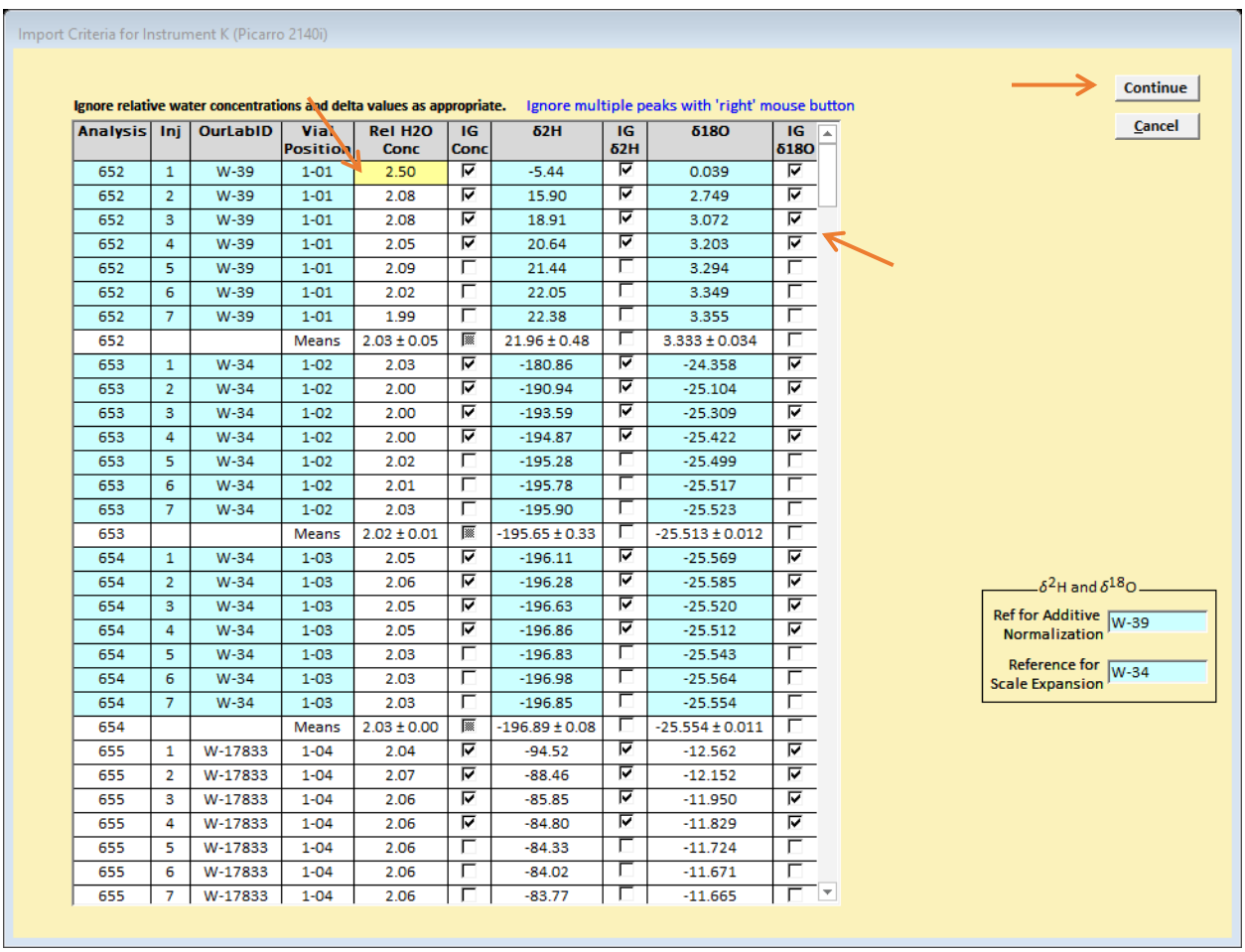
4. If no import warnings occur (Chapter 11), the following screen appears:



5. On this import screen, accept the default options and click, “Continue”. The various import options available are described in Chapter 11.1, and a discussion of correcting for variations in δ values with variations in relative water concentrations appears in Appendix 3. Accept the defaults for now.
6. A color-coded summary of the autorun with all measured δ^2H and δ^{18}O values and relative H_2O concentration appear with column headings of analysis number, injection number, Our Lab ID, vial position, relative H2O concentration, and δ values (with ignore columns). The summary statistics (using non-ignored injections) for each sample are shown. Note that the first 4 injections per sample are ignored, as specified in the Instrument settings for this specific instrument. (Note: Coordinator ignore flags are ignored in *LIMS for Lasers 2015*).

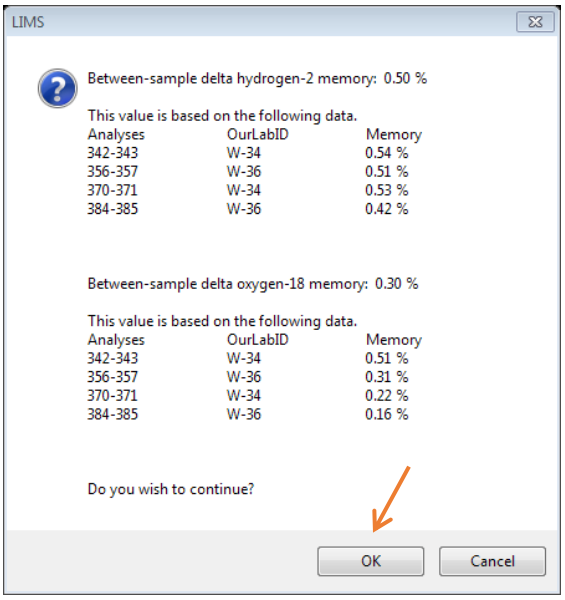
   Before clicking “Continue”, use the scroll bar to scan for outliers in “Rel H_2O Conc” (2.03 is a reduced number to represent a volume fraction of H_2O of 20,300 ppm in the Picarro instrument) and for any δ-value outliers. Colour-flagged outliers may be ignored by clicking the Ignore box next to each item. Checking “IG Conc” automatically checks the ignore boxes of both of the corresponding δ^2H and δ^{18}O data.

   If all of the data appear OK, click “Continue”.

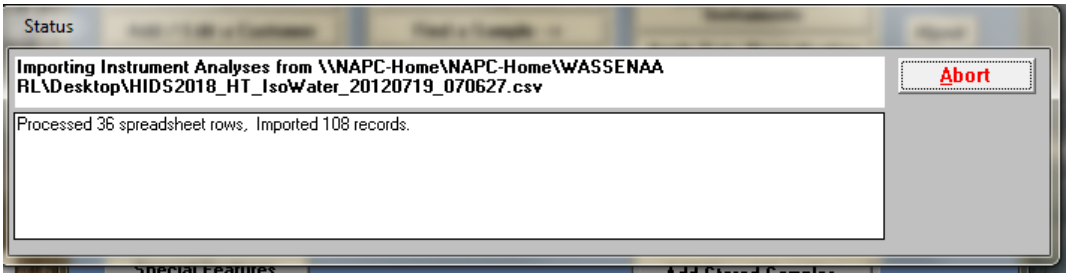


Analysis	Inj	OurLabID	Vial Position	Rel H2O Conc	IG Conc	δ2H	IG δ2H	δ18O	IG δ18O
652	1	W-39	1-01	2.50	☑	-5.44	☑	0.039	☑
652	2	W-39	1-01	2.08	☑	15.90	☑	2.749	☑
652	3	W-39	1-01	2.08	☑	18.91	☑	3.072	☑
652	4	W-39	1-01	2.05	☑	20.64	☑	3.203	☑
652	5	W-39	1-01	2.09	☐	21.44	☐	3.294	☐
652	6	W-39	1-01	2.02	☐	22.05	☐	3.349	☐
652	7	W-39	1-01	1.99	☐	22.38	☐	3.355	☐
652			Means	2.03 ± 0.05	▩	21.96 ± 0.48	☐	3.333 ± 0.034	☐
653	1	W-34	1-02	2.03	☑	-180.86	☑	-24.358	☑
653	2	W-34	1-02	2.00	☑	-190.94	☑	-25.104	☑
653	3	W-34	1-02	2.00	☑	-193.59	☑	-25.309	☑
653	4	W-34	1-02	2.00	☑	-194.87	☑	-25.422	☑
653	5	W-34	1-02	2.02	☐	-195.28	☐	-25.499	☐
653	6	W-34	1-02	2.01	☐	-195.78	☐	-25.517	☐
653	7	W-34	1-02	2.03	☐	-195.90	☐	-25.523	☐
653			Means	2.02 ± 0.01	▩	-195.65 ± 0.33	☐	-25.513 ± 0.012	☐
654	1	W-34	1-03	2.05	☑	-196.11	☑	-25.569	☑
654	2	W-34	1-03	2.06	☑	-196.28	☑	-25.585	☑
654	3	W-34	1-03	2.05	☑	-196.63	☑	-25.520	☑
654	4	W-34	1-03	2.05	☑	-196.86	☑	-25.512	☑
654	5	W-34	1-03	2.03	☐	-196.83	☐	-25.543	☐
654	6	W-34	1-03	2.03	☐	-196.98	☐	-25.564	☐
654	7	W-34	1-03	2.03	☐	-196.85	☐	-25.554	☐
654			Means	2.03 ± 0.00	▩	-196.89 ± 0.08	☐	-25.554 ± 0.011	☐
655	1	W-17833	1-04	2.04	☑	-94.52	☑	-12.562	☑
655	2	W-17833	1-04	2.07	☑	-88.46	☑	-12.152	☑
655	3	W-17833	1-04	2.06	☑	-85.85	☑	-11.950	☑
655	4	W-17833	1-04	2.06	☑	-84.80	☑	-11.829	☑
655	5	W-17833	1-04	2.06	☐	-84.33	☐	-11.724	☐
655	6	W-17833	1-04	2.06	☐	-84.02	☐	-11.671	☐
655	7	W-17833	1-04	2.06	☐	-83.77	☐	-11.665	☐

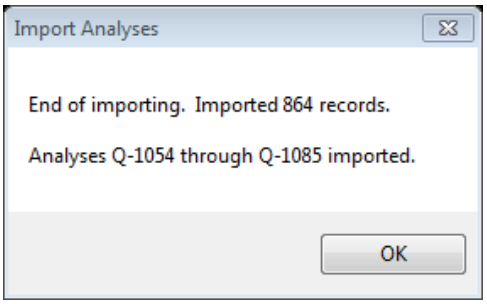
7. The between-sample memory calculations are now quantified and averaged for the entire autorun. These should be less than 1 to 2 per cent. Click “OK” to continue.



8. The sample drift and memory-corrected data is imported into LIMS.



9. At the end of the import *LIMS for Lasers 2015* verifies the data has been imported. Click “OK”.



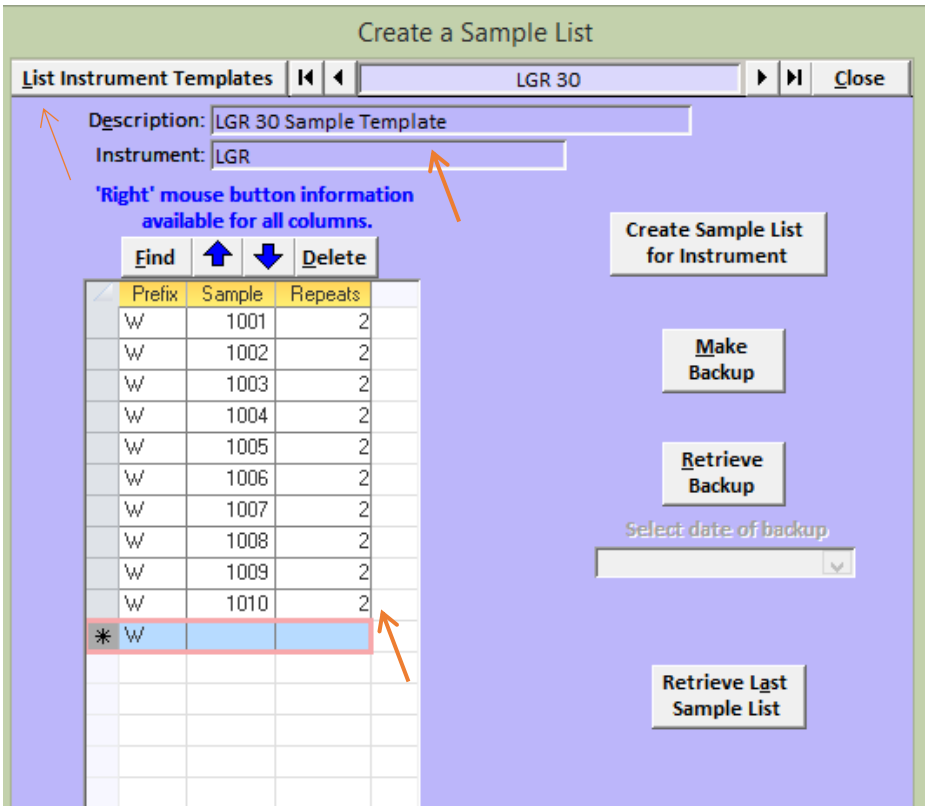
10. Normalization, evaluation and storing of final results are outlined in Chapter 12.

10 Run Samples on a Los Gatos Research Laser

10.1 Create a Sample List for a Los Gatos Research Instrument

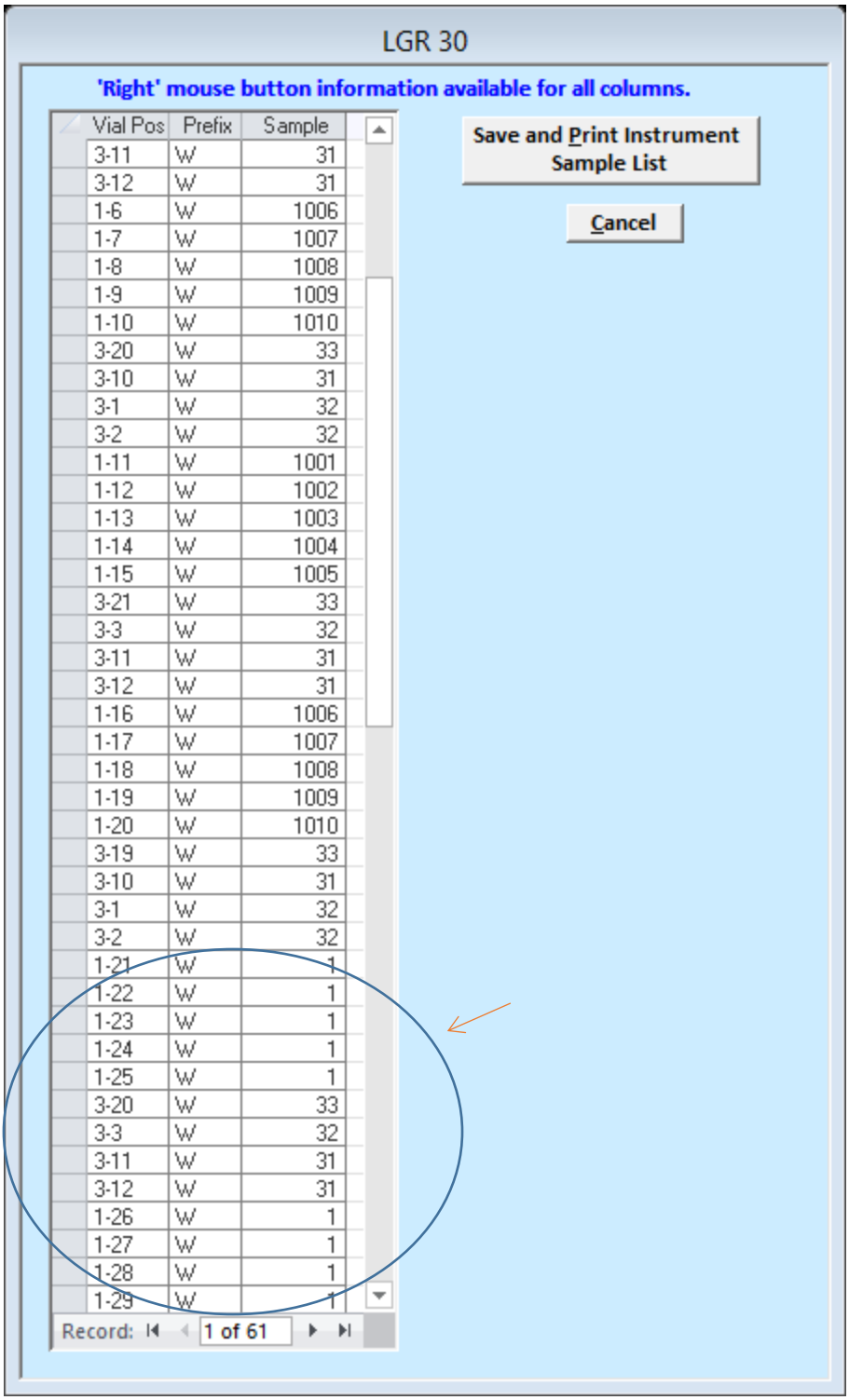
By example, we will create a sample run list for a Los Gatos Research laser instrument.

1. Ensure samples are added to the Los Gatos Research queue (see Chapter 8.9).
2. In the Main LIMS Page, click “Create Sample List for Instruments”.
3. Choose “List” and click on “LGR 30 Samples”, and the sample queue opens:



4. In the Los Gatos Research queue above, Smith’s 10 samples (W-1001 to W-1010) are queued to be analysed twice on a 30-sample template. This leaves 10 extra positions, which will be automatically filled with W-1 (dummy) repeats, which can be deleted (see below).

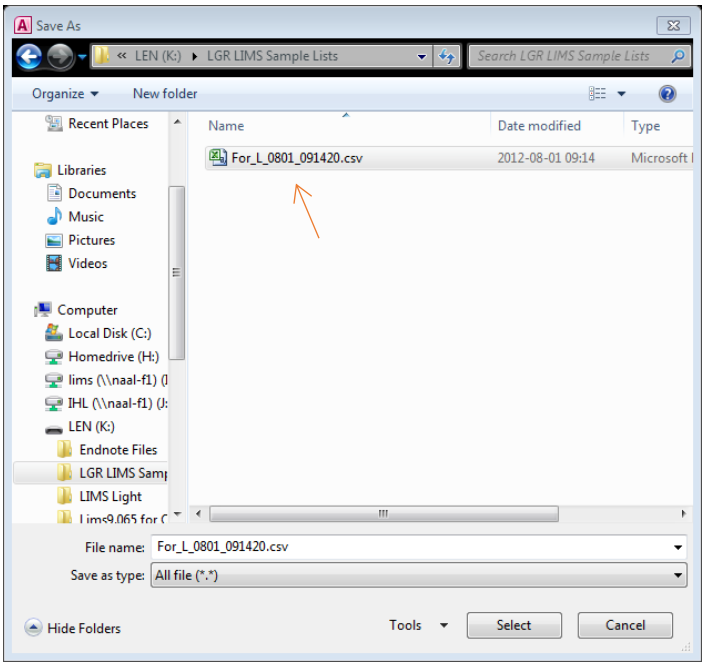
5. Click on “Create Sample List for Instrument”, a dialog box confirms the 10 (times 2 repeats are in the queue. Click “OK”.



Vial Pos	Prefix	Sample
3-11	W	31
3-12	W	31
1-6	W	1006
1-7	W	1007
1-8	W	1008
1-9	W	1009
1-10	W	1010
3-20	W	33
3-10	W	31
3-1	W	32
3-2	W	32
1-11	W	1001
1-12	W	1002
1-13	W	1003
1-14	W	1004
1-15	W	1005
3-21	W	33
3-3	W	32
3-11	W	31
3-12	W	31
1-16	W	1006
1-17	W	1007
1-18	W	1008
1-19	W	1009
1-20	W	1010
3-19	W	33
3-10	W	31
3-1	W	32
3-2	W	32
1-21	W	1
1-22	W	1
1-23	W	1
1-24	W	1
1-25	W	1
3-20	W	33
3-3	W	32
3-11	W	31
3-12	W	31
1-26	W	1
1-27	W	1
1-28	W	1
1-29	W	1

6. The analysis sequence containing the wash samples, local measurement standards, control standards, and Smith's samples opens (right figure). Note that samples on lines 1-21 onward are not needed since they are dummy placeholders. These can be highlighted and deleted (hit delete key).

7. Click on “Save and Print”.
8. A Windows dialog box opens asking where to save the Los Gatos Research sample/sequence file. This sample list file will be transferred to Los Gatos Research instrument, and it should be saved to a USB flash drive. Insert a USB flash drive into the PC.
9. Click “Select” to save the file to the USB flash drive. This CSV filename is a concatenation of instrument prefix “For L” (Los Gatos Research) and the current date. This file naming convention helps the laboratory keep track of Los Gatos Research sample lists as they accumulate.



10. A Printer dialog box may open, asking where to print the sample list (e.g. default printer). A one-page summary of the analysis sequence is printed.
11. After printing, the queue reopens and we note the sample repeats have been decremented from 2 to 0. These samples are now flagged with a “0” since they will have been analysed twice, albeit within the same autorun. They can be deleted from the queue.
12. An example printed list of samples to be analysed (next page) reveals the vial position and the Our Lab ID of the local measurement standards, controls, and the samples.
13. Fill the 68 vials each with ~ 1.5 mL. Use the small “W” labels affixed (or written) to the side of each sample vial. Load the autosampler trays with the sample and standard vials according to the printed list.

3/10/2015 9:00:31 PM

LGR 30 Samples To Be Analyzed

Vial Pos	Our Lab ID	Sample ID	Project	Notes	Vial Pos	Our Lab ID	Sample ID	Project	Notes
3-28	W-3	DIW Wash	Refere 2012092	_____	3-1	W-32	Low Standard	Refere 2012092	_____
3-28	W-3	DIW Wash	Refere 2012092	_____	3-2	W-32	Low Standard	Refere 2012092	_____
3-10	W-31	High Standard	Refere 2012092	_____					
3-1	W-32	Low Standard	Refere 2012092	_____					
3-2	W-32	Low Standard	Refere 2012092	_____					
1-1	W-1001	Sample1	Smith 20150304	_____					
1-2	W-1002	Sample2	Smith 20150304	_____					
1-3	W-1003	Sample3	Smith 20150304	_____					
1-4	W-1004	Sample4	Smith 20150304	_____					
1-5	W-1005	Sample5	Smith 20150304	_____					
3-19	W-33	Control	Refere 2012092	_____					
3-3	W-32	Low Standard	Refere 2012092	_____					
3-11	W-31	High Standard	Refere 2012092	_____					
3-12	W-31	High Standard	Refere 2012092	_____					
1-6	W-1006	Sample6	Smith 20150304	_____					
1-7	W-1007	Sample7	Smith 20150304	_____					
1-8	W-1008	Sample8	Smith 20150304	_____					
1-9	W-1009	Sample9	Smith 20150304	_____					
1-10	W-1010	Sample10	Smith 20150304	_____					
3-20	W-33	Control	Refere 2012092	_____					
3-10	W-31	High Standard	Refere 2012092	_____					
3-1	W-32	Low Standard	Refere 2012092	_____					
3-2	W-32	Low Standard	Refere 2012092	_____					
1-11	W-1001	Sample1	Smith 20150304	_____					
1-12	W-1002	Sample2	Smith 20150304	_____					
1-13	W-1003	Sample3	Smith 20150304	_____					
1-14	W-1004	Sample4	Smith 20150304	_____					
1-15	W-1005	Sample5	Smith 20150304	_____					
3-21	W-33	Control	Refere 2012092	_____					
3-3	W-32	Low Standard	Refere 2012092	_____					
3-11	W-31	High Standard	Refere 2012092	_____					
3-12	W-31	High Standard	Refere 2012092	_____					
1-16	W-1006	Sample6	Smith 20150304	_____					
1-17	W-1007	Sample7	Smith 20150304	_____					
1-18	W-1008	Sample8	Smith 20150304	_____					
1-19	W-1009	Sample9	Smith 20150304	_____					
1-20	W-1010	Sample10	Smith 20150304	_____					
3-19	W-33	Control	Refere 2012092	_____					
3-10	W-31	High Standard	Refere 2012092	_____					

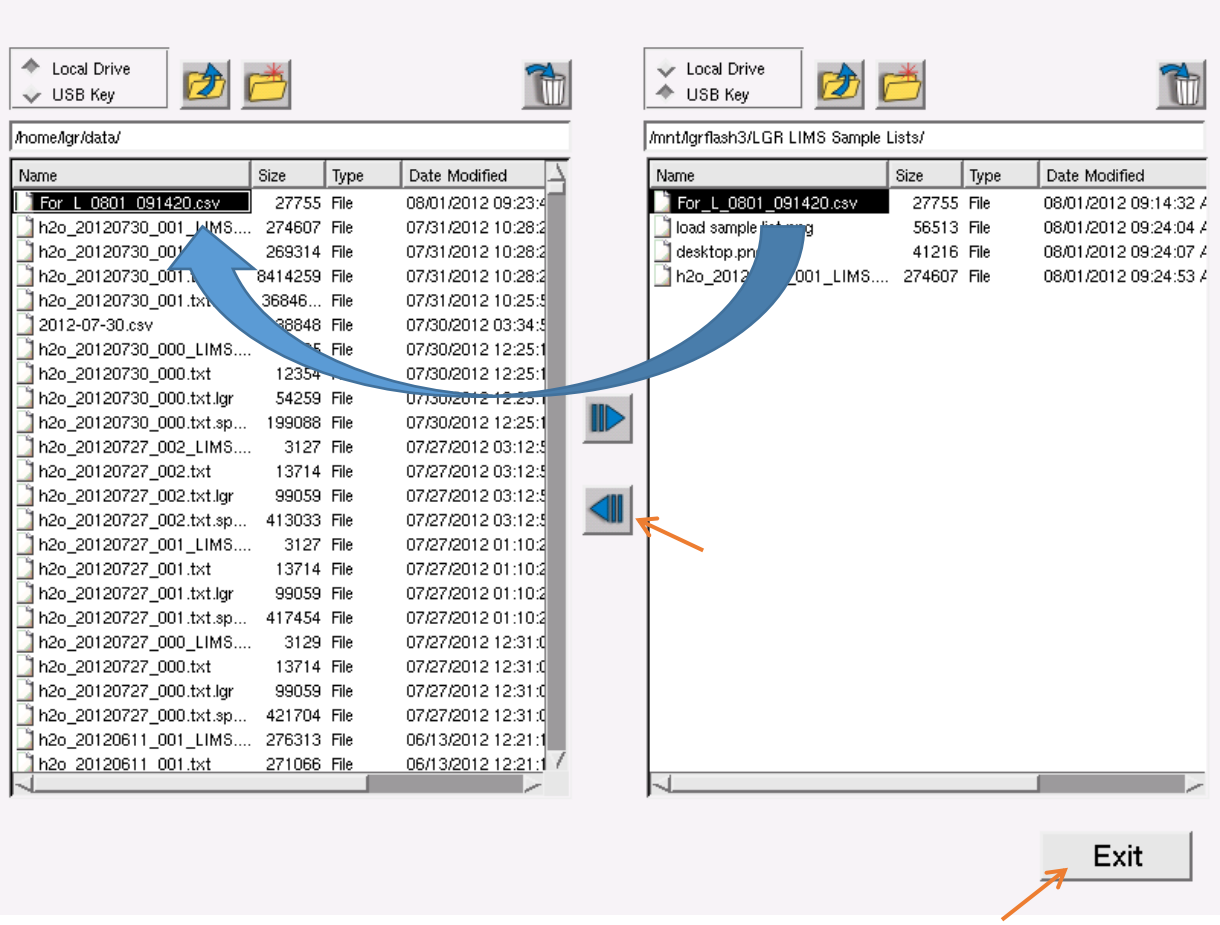
LGR run list for the laser analyser.

14. On the Los Gatos Research autosampler, the laboratory standard and sample vials are set up using the analysis layout(s) shown in Table 1. Compare the printed LIMS run list to ensure that all vials are located in the correct tray position.

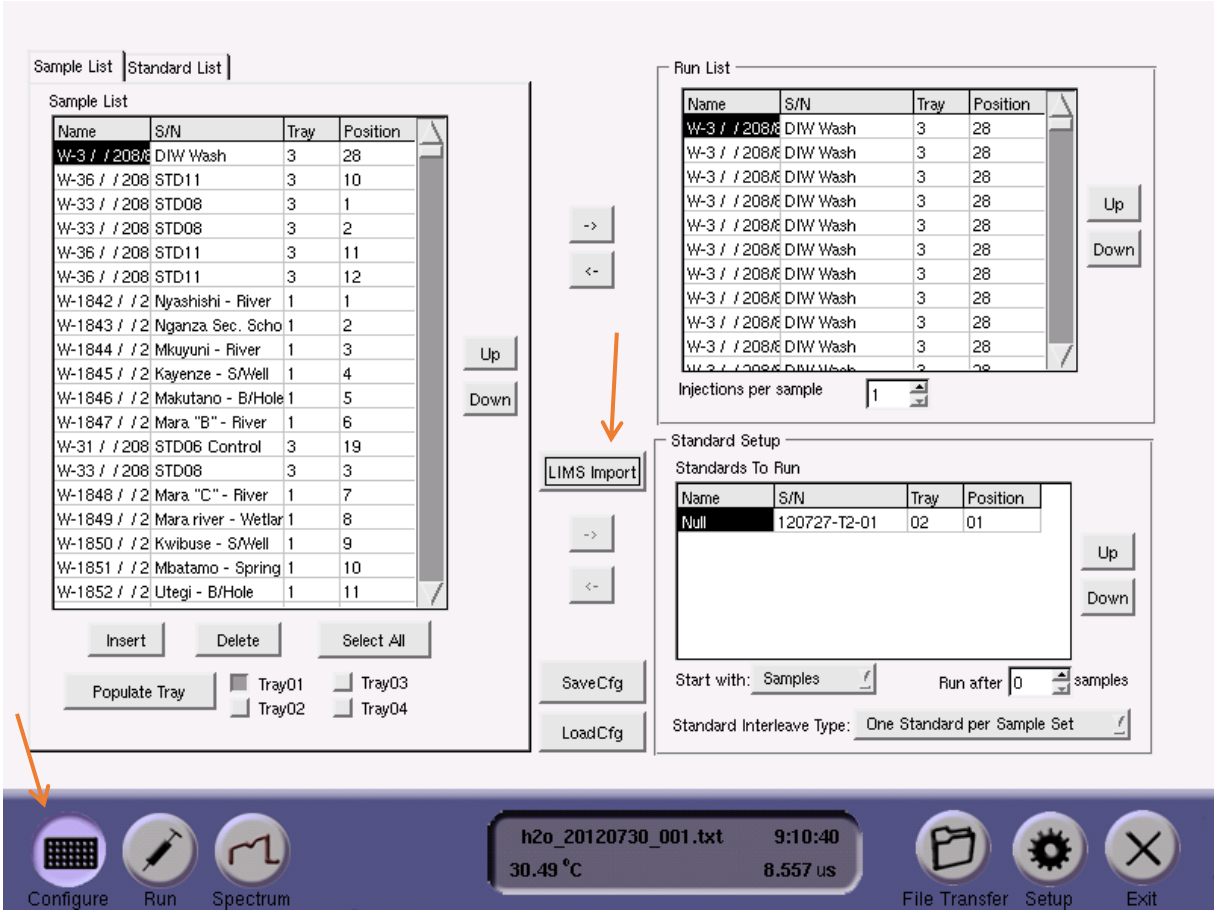
Running the Sample List on the Los Gatos Research DLT-100/24D Series Instrument (2007–2013)

The LIMS-generated sample list saved to the flash drive is loaded directly into the Los Gatos Research DLT-100 instrument (2007–2013), and it links sample data to the corresponding LIMS information. The instrument should be ready to run as per manufacturer user instructions:

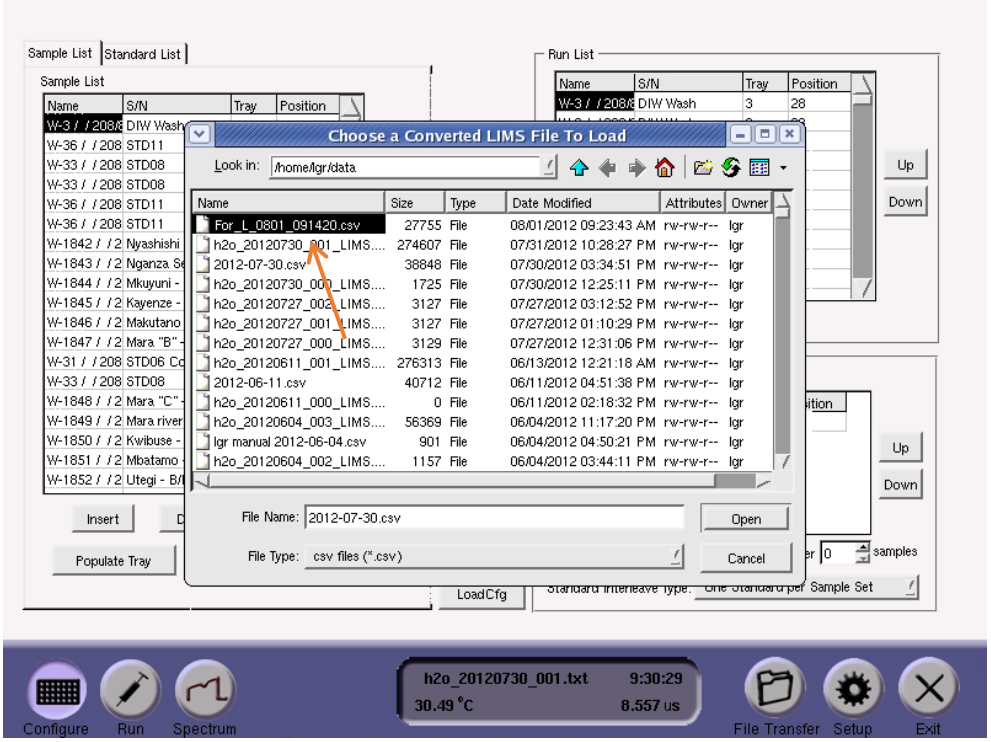
1. Place the flash drive containing the Los Gatos Research sample list file into the USB port of the laser instrument.
2. On the Los Gatos Research instrument, click the “File Transfer” button located at the bottom of the main screen.
3. In the file management pane, highlight the LIMS sample list. “For_L_xxxx.csv” and copy it from the USB flash drive side to the LGR data folder using the file transfer button located between the two panes.
4. When the file transfer is completed, click the “Exit” button.



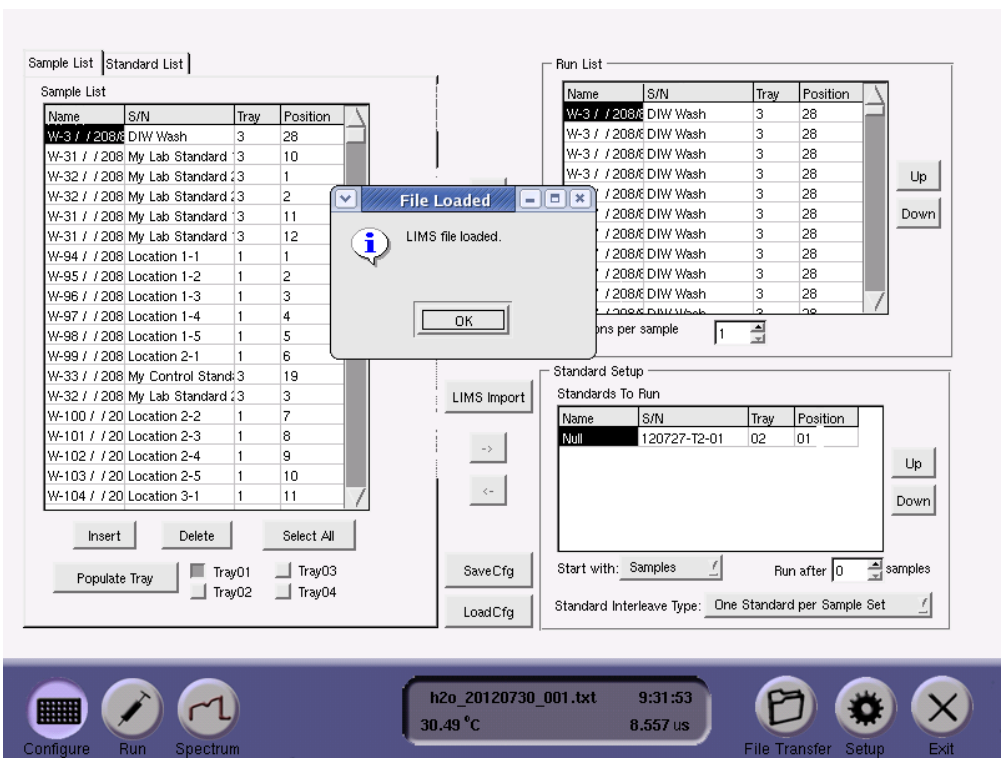
5. The LIMS sample run list can now be loaded into the Los Gatos Research Sample List side in order to start the isotopic analysis.
6. In the middle of the Los Gatos Research “Configure” tab, click the “LIMS Import” button.



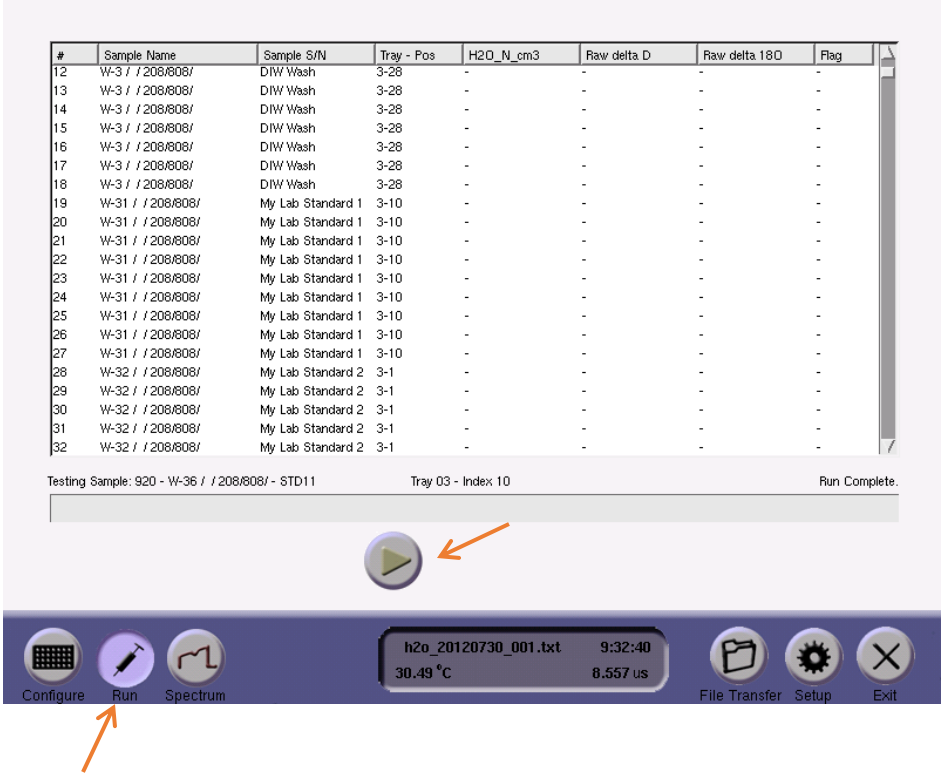
7. Select and double click to open the LIMS sample list CSV file (“For_L_xxxx.csv”) that was copied over to the instrument.



8. The LIMS-generated sample list is then confirmed as “loaded”, and the Sample List on the left hand pane should match your printed LIMS run list.



9. Click on the instrument “Run” tab and then click the “Go” arrow. No further action or editing of the configuration is needed. Allow the Los Gatos Research analyser to successfully complete the sample autorun (20+ hours).

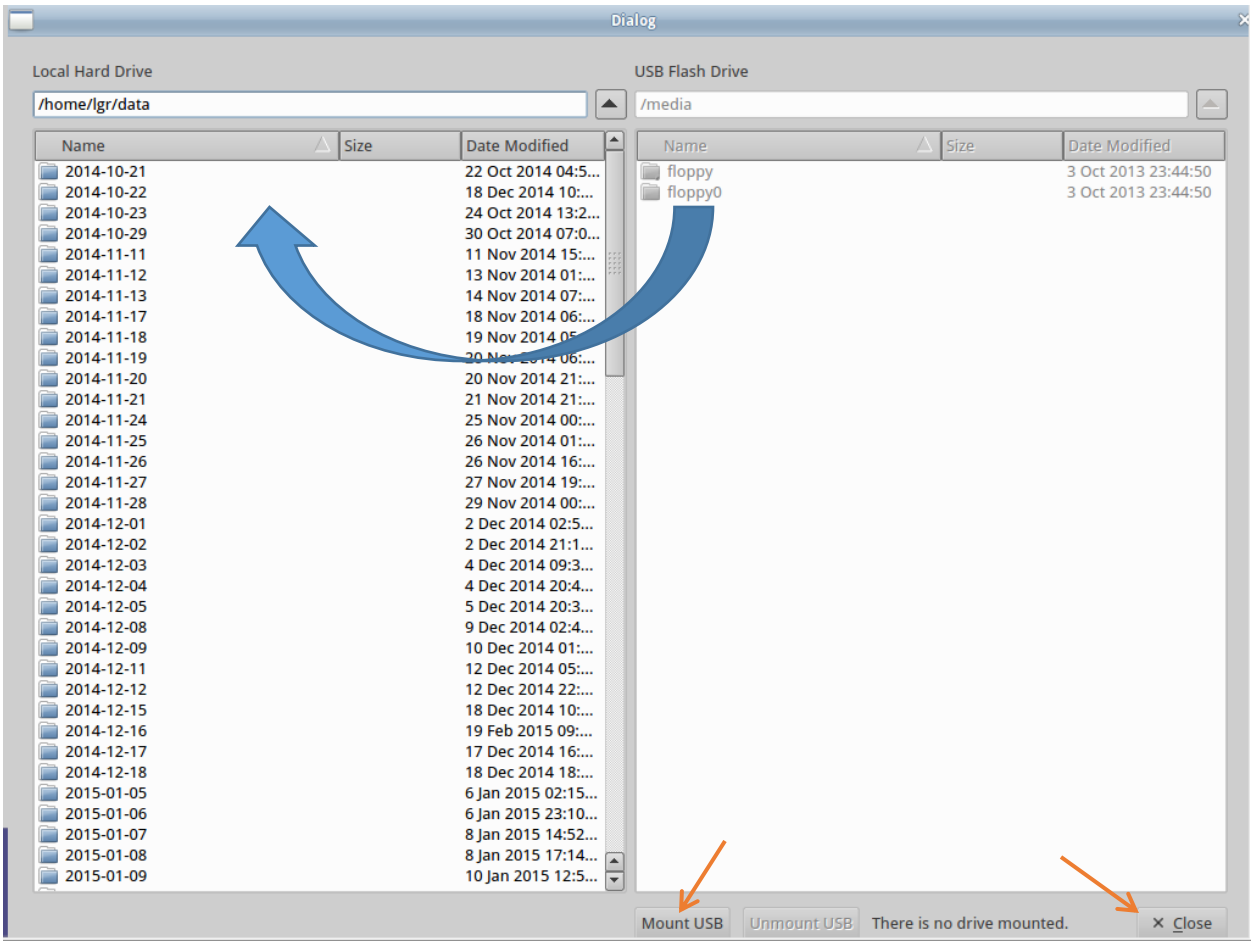


#	Sample Name	Sample S/N	Tray - Pos	H2O_N_cm3	Raw delta D	Raw delta 18O	Flag
12	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
13	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
14	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
15	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
16	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
17	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
18	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
19	W-31 / / 208/808/	My Lab Standard 1	3-10	-	-	-	-
20	W-31 / / 208/808/	My Lab Standard 1	3-10	-	-	-	-
21	W-31 / / 208/808/	My Lab Standard 1	3-10	-	-	-	-
22	W-31 / / 208/808/	My Lab Standard 1	3-10	-	-	-	-
23	W-31 / / 208/808/	My Lab Standard 1	3-10	-	-	-	-
24	W-31 / / 208/808/	My Lab Standard 1	3-10	-	-	-	-
25	W-31 / / 208/808/	My Lab Standard 1	3-10	-	-	-	-
26	W-31 / / 208/808/	My Lab Standard 1	3-10	-	-	-	-
27	W-31 / / 208/808/	My Lab Standard 1	3-10	-	-	-	-
28	W-32 / / 208/808/	My Lab Standard 2	3-1	-	-	-	-
29	W-32 / / 208/808/	My Lab Standard 2	3-1	-	-	-	-
30	W-32 / / 208/808/	My Lab Standard 2	3-1	-	-	-	-
31	W-32 / / 208/808/	My Lab Standard 2	3-1	-	-	-	-
32	W-32 / / 208/808/	My Lab Standard 2	3-1	-	-	-	-

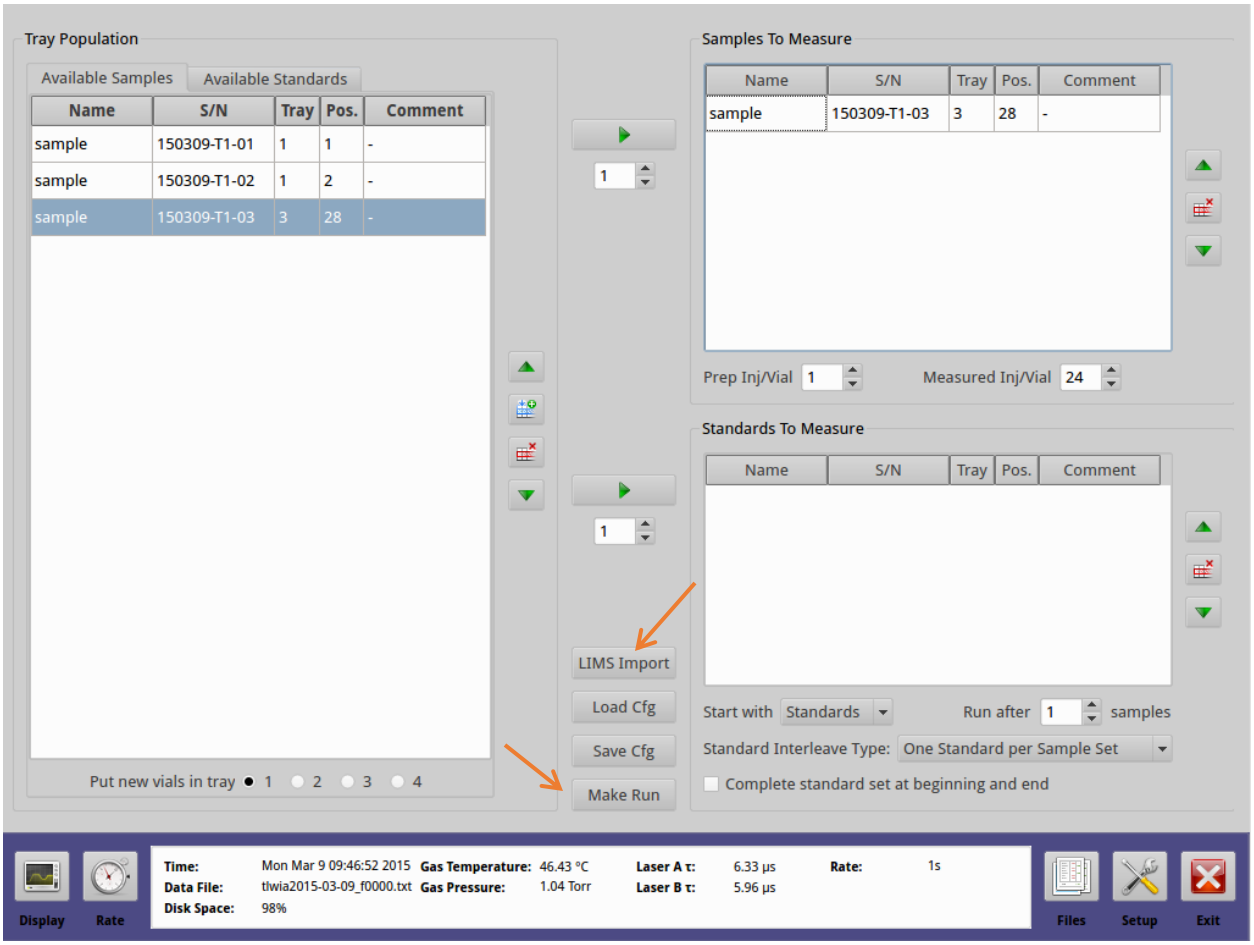
Running a Sample List on a Los Gatos Research IWA-35/TIWA-45EP Instrument (2014-present)

The LIMS-generated sample list saved to the flash drive is loaded directly into the Los Gatos Research IWA-35EP or TIWA-45EP instrument, and it links sample data to the corresponding LIMS information. The instrument should be ready to run as per manufacturer instructions:

1. Place the flash drive containing the Los Gatos Research sample list file into the USB port of the IWA-35EP or TIWA-45EP laser instrument.
2. On the Los Gatos Research instrument, click the “Files” button located at the bottom right of the main screen. Mount the USB flash drive.
3. In the file management pane, drag the LIMS sample list. “For_L_xxxx.csv” and copy it from the USB side to the LGR data folder using the file transfer button located between the two panes.
4. When the file transfer is completed, click the “Done” button.



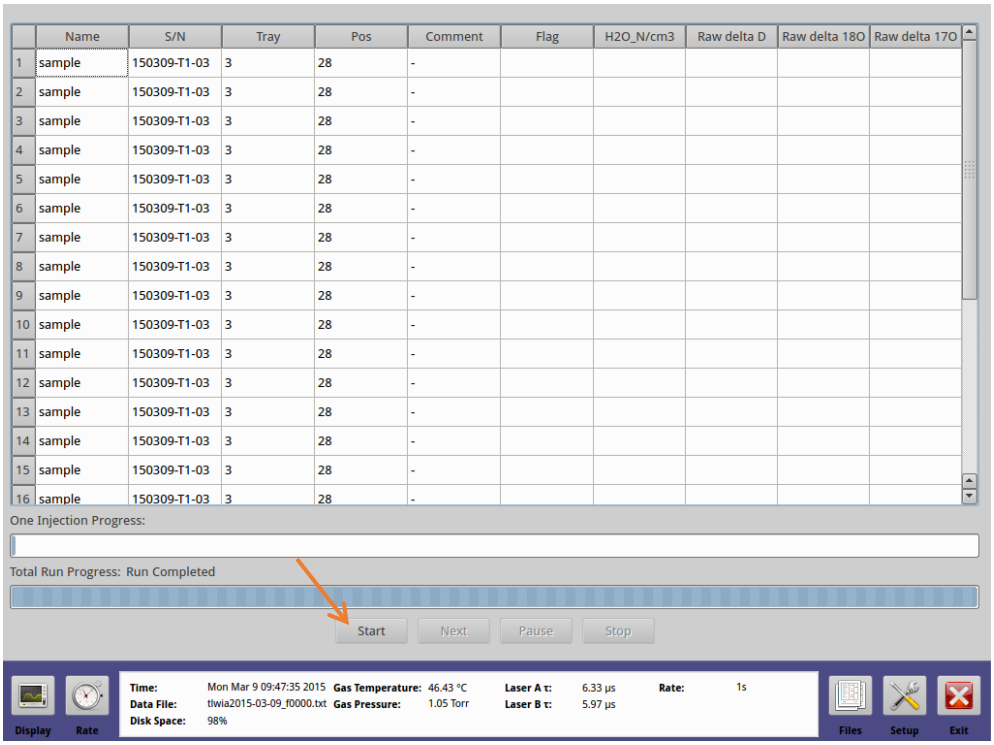
5. The LIMS sample analysis list can now be loaded into the Los Gatos Research Sample List side in order to start the isotopic analysis.
6. In the lower middle of the Los Gatos Research “Display” tab, click the “LIMS Import” button.



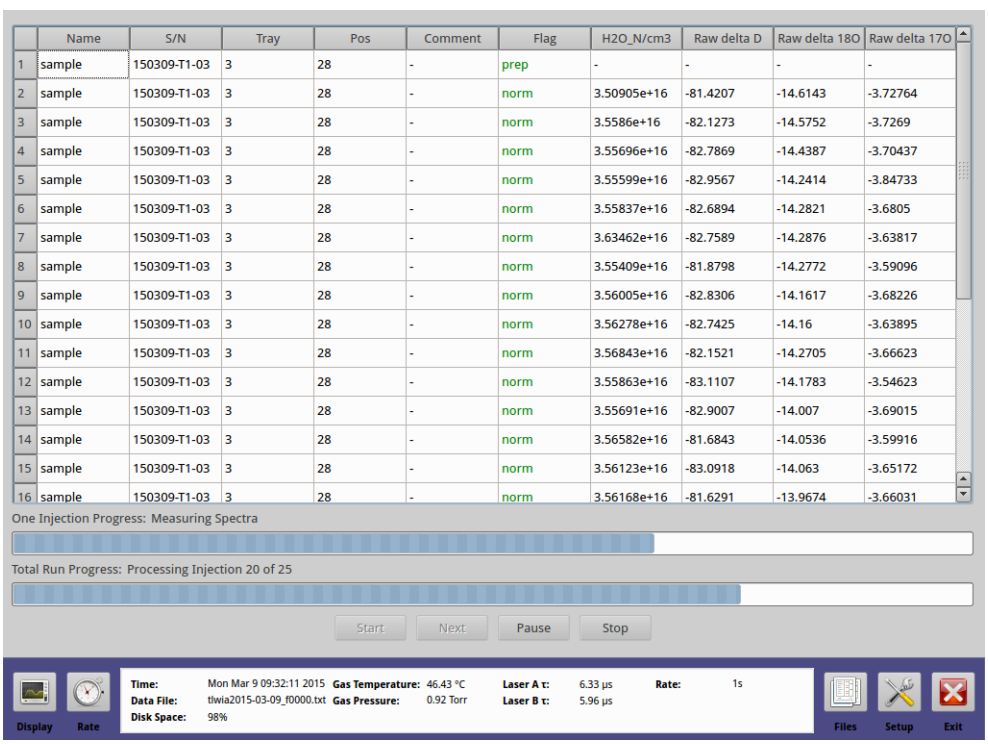
7. Select and double click to open the LIMS sample list CSV file ("For_L_xxxx.csv") that was copied over to the instrument.
8. To analyse the samples, click on the display tab – the loaded sample list should be visible.

Note: Do not click on the "Make Run" after loading a LIMS file (the sample list will disappear). Go immediately to the Display tab.

If the "LIMS Import" button is greyed out on the above screen you will need an instrument firmware update from Los Gatos Research (see details in Chapter 5.2)



9. Click on the “Start” button. No further action or editing of any configuration is needed. Allow the Los Gatos Research analyser to successfully complete the sample autorun (below).



10.2 Import Isotopic Data from Los Gatos Research

Once the Los Gatos Research autorun is finished, the hydrogen and oxygen isotopic data are imported into *LIMS for Lasers 2015* for data normalization, processing, evaluation and reporting.

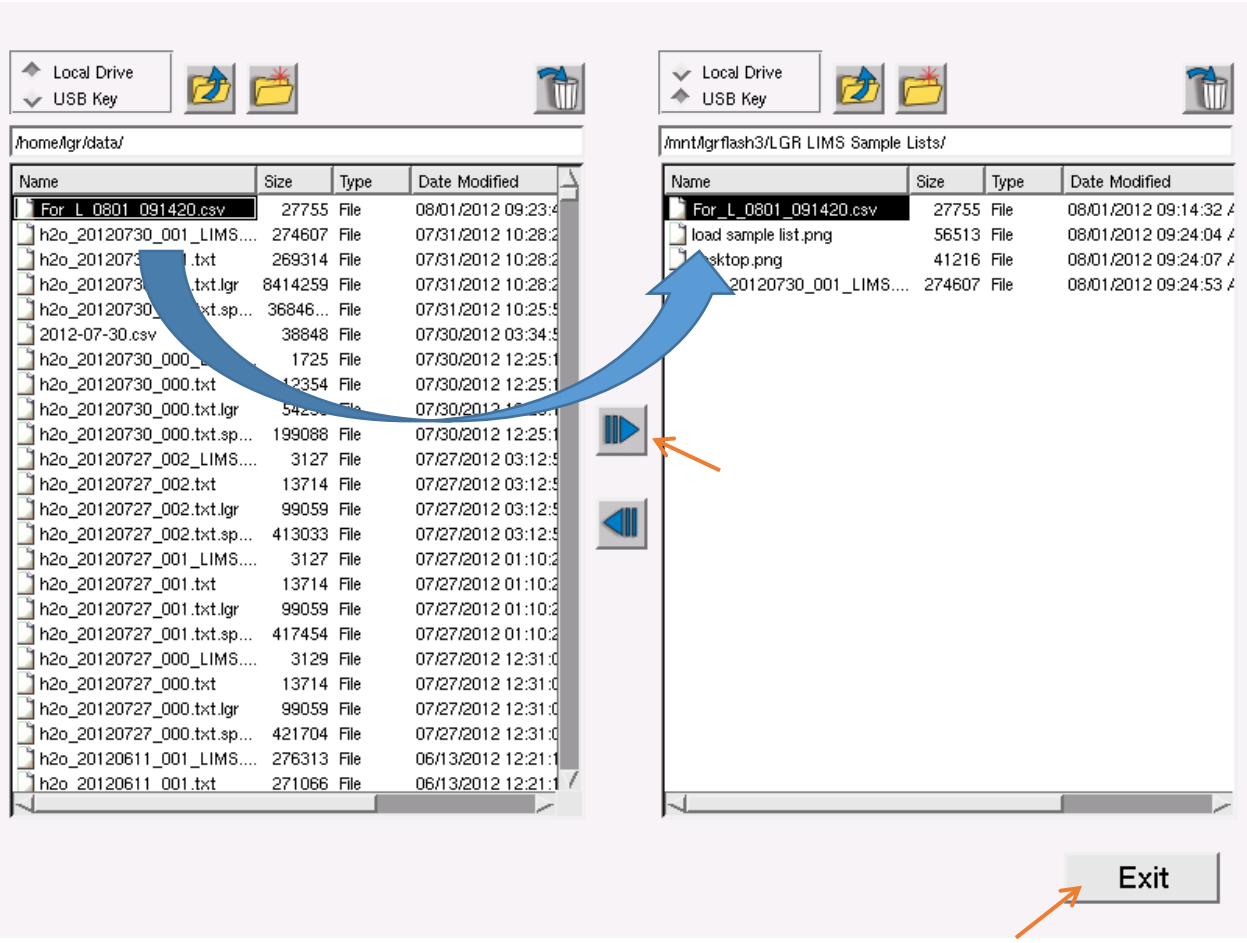
The completed autorun file is located in the Los Gatos Research data directory and must be transferred to the LIMS PC for data importing (via flash drive or over a network connection). The output file naming convention of the Los Gatos Research data file is "h2o_date_000_LIMS.csv". The "date" in this filename is the same as the imported sample list filename.

Los Gatos Research DLT-100 Instruments (2007–2013)

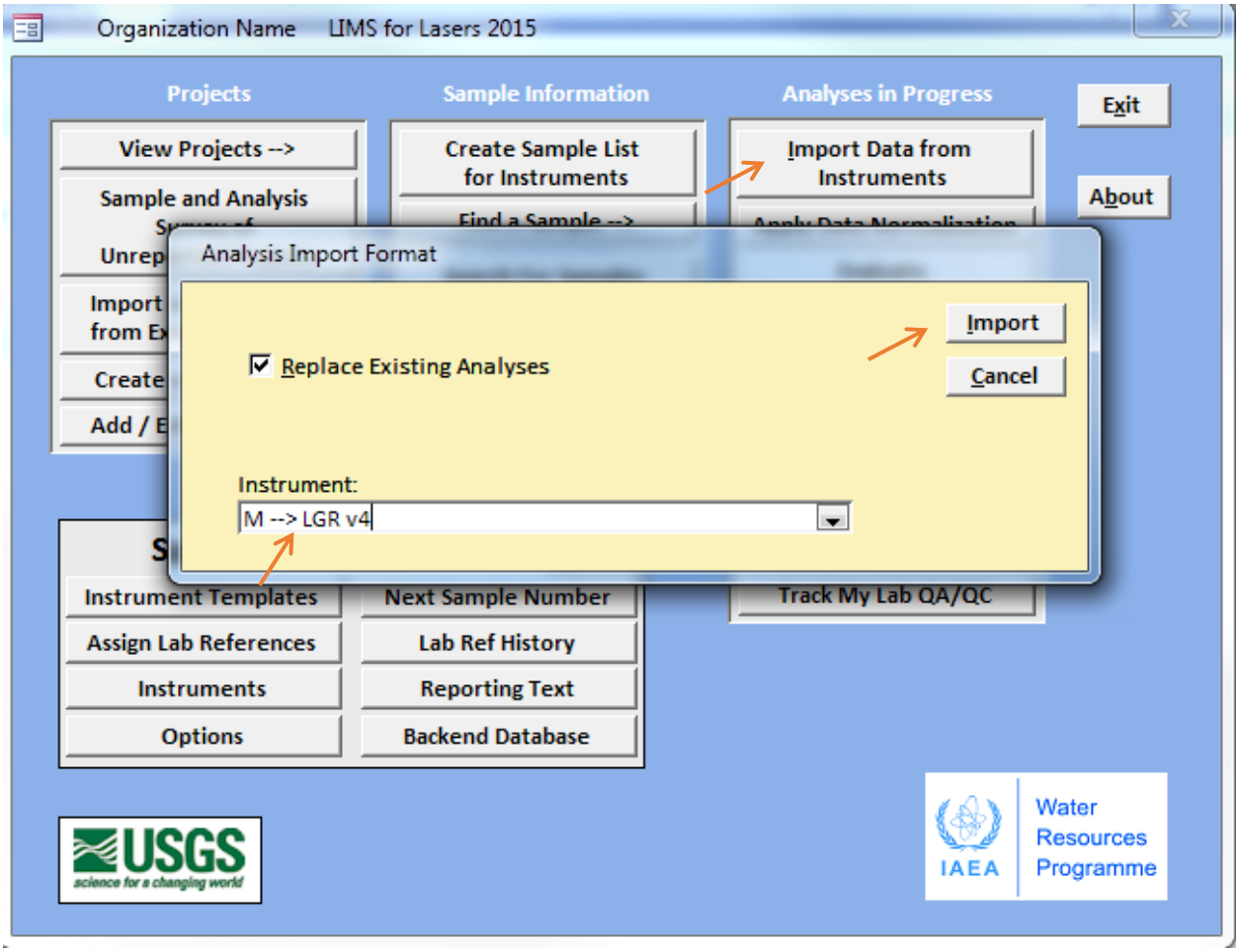
1. Place a flash drive into the USB port of the Los Gatos Research instrument.
2. On the instrument, click on the "File Transfer" button located between the panes.
3. On the left file management pane, highlight the appropriate LIMS output file called "h2o_date_000_LIMS" and copy it to the USB flash drive using the file transfer button between the two panes.
4. When the file copy is complete, click the "Exit" button. Remove the USB flash drive and place it into the LIMS computer USB port.
5. On the LIMS main page, click "Import Data from Instruments". Choose the appropriate Los Gatos Research instrument from the pull down menu and then click "Import". Select the appropriate instrument data output file from the USB flash drive.

Los Gatos Research IWA-35EP or TIWA-45EP Instruments (2014-present)

1. Place a flash drive into the USB port of the Los Gatos Research instrument. Mount the drive.
2. Click on the "Files" button located at the lower right.
3. On the left file management pane, highlight the appropriate LIMS output file called, for example, "(t)lwia2015-03-10_lims0001.csv.zip" and copy it to the USB flash drive using the file transfer button between the two panes.
4. When the file copy is complete, click the "Close" button. Remove the USB flash drive and place it into the LIMS computer USB port. Extract the sample output ZIP file to your computer.
5. On the LIMS main page, click "Import Data from Instruments". Choose the appropriate Los Gatos Research instrument from the pull down menu and then click "Import". Select the appropriate instrument data output file from the USB flash drive.

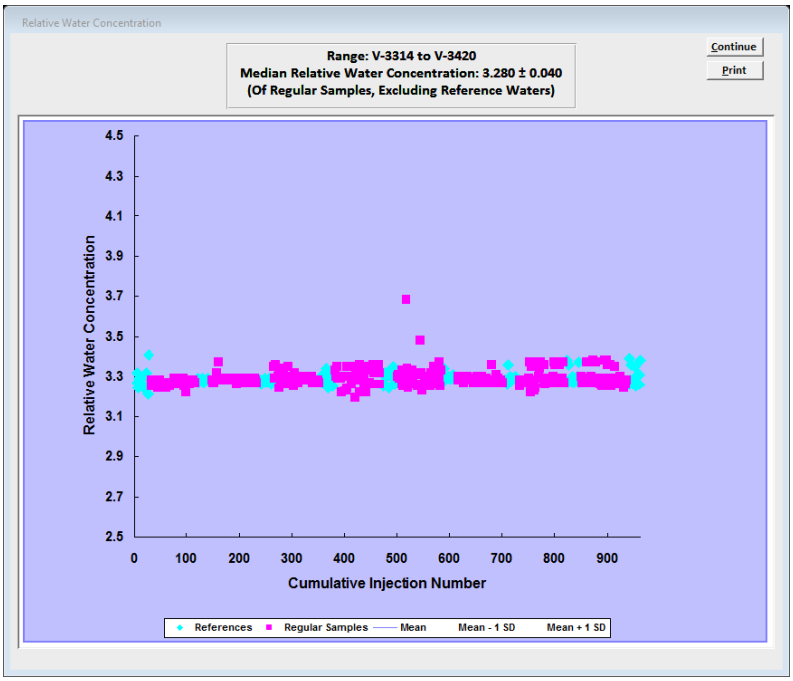


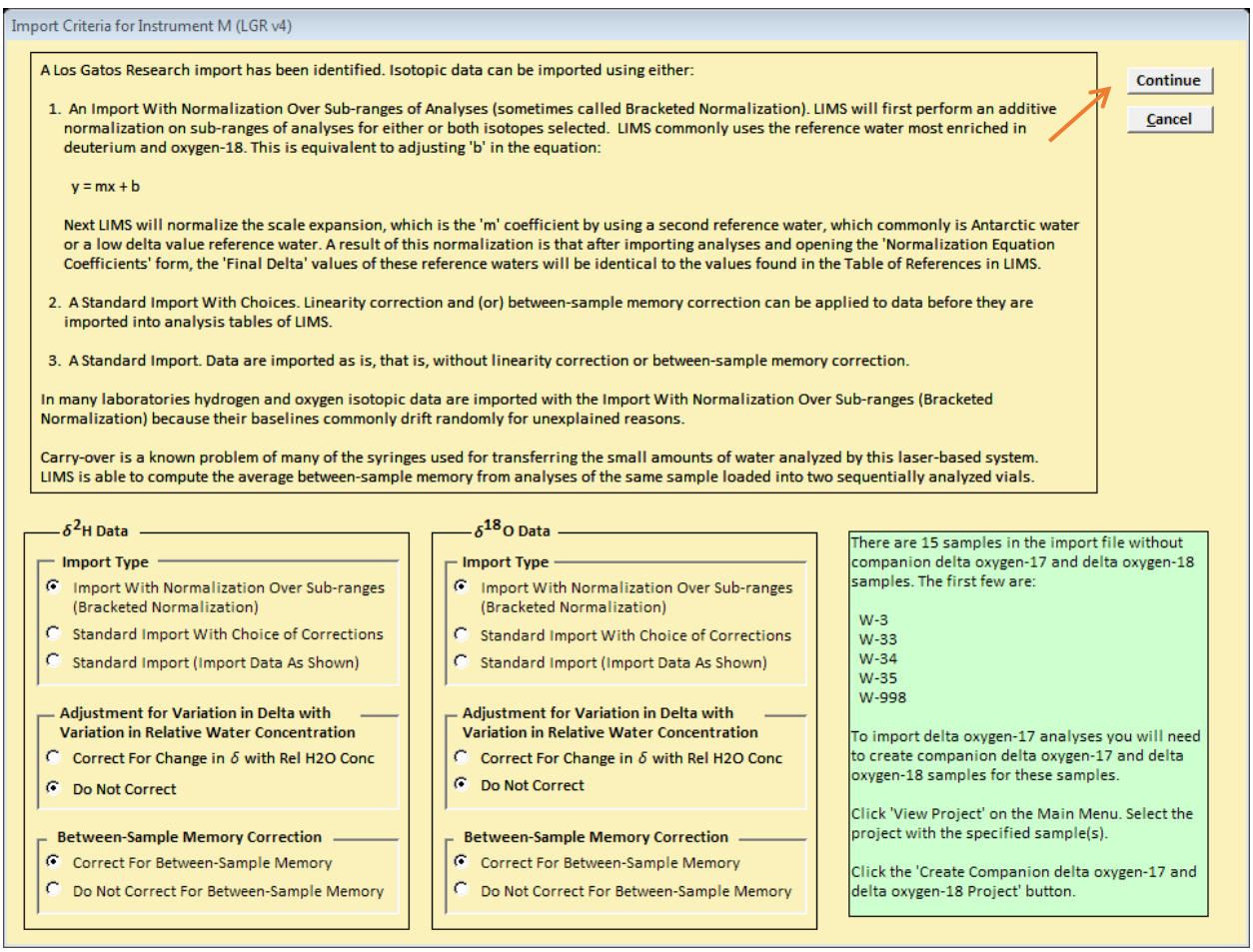
Example output file transfer from Los Gatos instrument DLT-100.



Note: The "Replace Existing Analyses" box overwrites any previous import of the data file *provided that data was not normalized or stored*. This is useful to examine the impact of different import options or wish to correct a mistake. The default setting is checked.

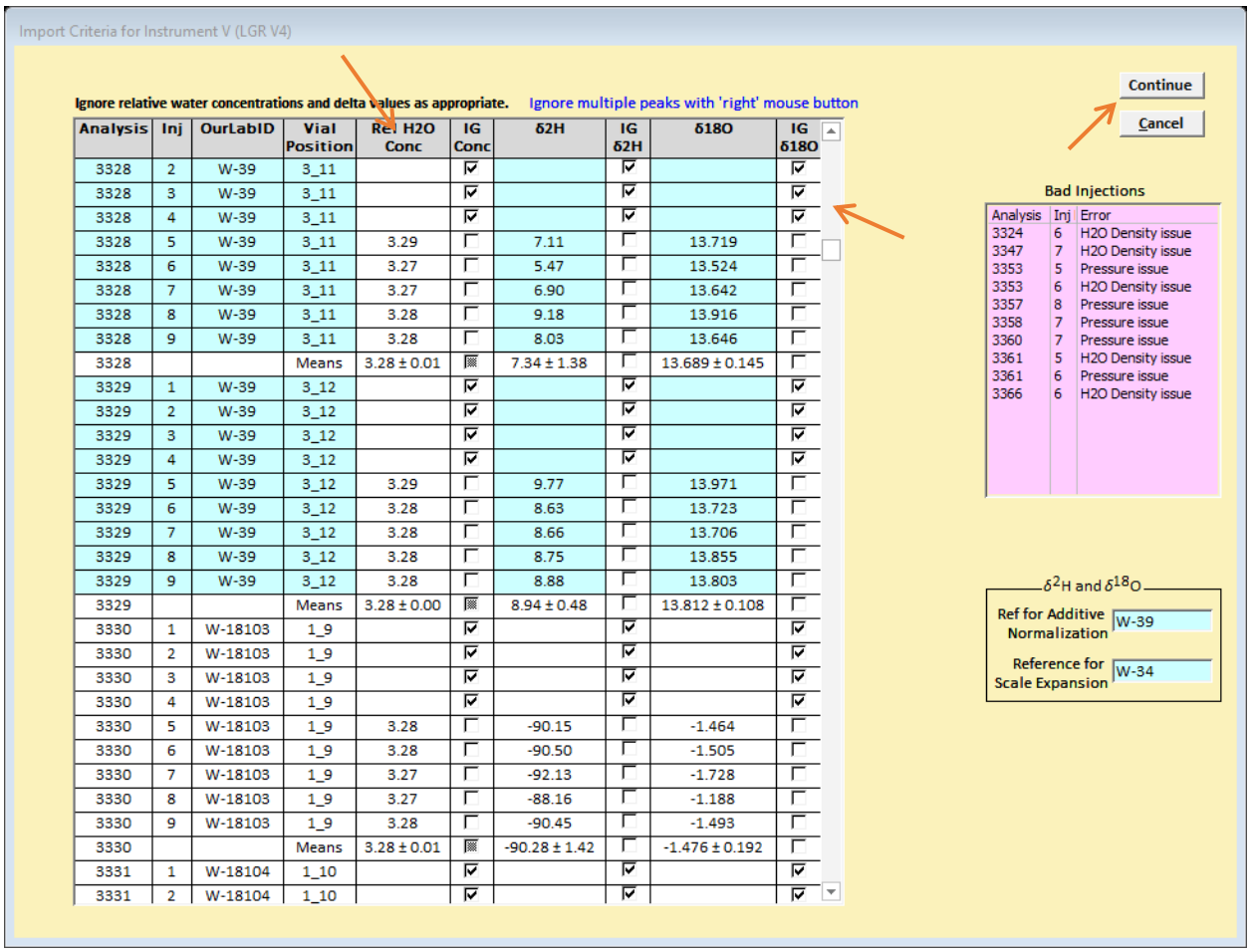
6. If no import warnings appear (see Chapter 11), the following screen appears summarizing the H_2O injections (note graph auto scales). This preview is critical to ensure that water injections are consistent throughout the autorun. *LIMS for Lasers 2015* divides the measured Los Gatos Research concentration by 1×10^{16} to determine the relative H_2O concentration. If the injections H_2O appear to be normal (within tolerance and stable), click "Continue".


Relative Water Concentration
Range: V-3314 to V-3420
Median Relative Water Concentration: 3.280 ± 0.040
(Of Regular Samples, Excluding Reference Waters)
Continue
Print
Relative Water Concentration
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
0
100
200
300
400
500
600
700
800
900
Cumulative Injection Number
References
Regular Samples
Mean
Mean - 1 SD
Mean + 1 SD


Import Criteria for Instrument M (LGR v4)
A Los Gatos Research import has been identified. Isotopic data can be imported using either:
1. An Import With Normalization Over Sub-ranges of Analyses (sometimes called Bracketed Normalization). LIMS will first perform an additive normalization on sub-ranges of analyses for either or both isotopes selected. LIMS commonly uses the reference water most enriched in deuterium and oxygen-18. This is equivalent to adjusting 'b' in the equation:
y = mx + b
Next LIMS will normalize the scale expansion, which is the 'm' coefficient by using a second reference water, which commonly is Antarctic water or a low delta value reference water. A result of this normalization is that after importing analyses and opening the 'Normalization Equation Coefficients' form, the 'Final Delta' values of these reference waters will be identical to the values found in the Table of References in LIMS.
2. A Standard Import With Choices. Linearity correction and (or) between-sample memory correction can be applied to data before they are imported into analysis tables of LIMS.
3. A Standard Import. Data are imported as is, that is, without linearity correction or between-sample memory correction.
In many laboratories hydrogen and oxygen isotopic data are imported with the Import With Normalization Over Sub-ranges (Bracketed Normalization) because their baselines commonly drift randomly for unexplained reasons.
Carry-over is a known problem of many of the syringes used for transferring the small amounts of water analyzed by this laser-based system. LIMS is able to compute the average between-sample memory from analyses of the same sample loaded into two sequentially analyzed vials.
Continue
Cancel
δ2H Data
Import Type
Import With Normalization Over Sub-ranges (Bracketed Normalization)
Standard Import With Choice of Corrections
Standard Import (Import Data As Shown)
Adjustment for Variation in Delta with Variation in Relative Water Concentration
Correct For Change in δ with Rel H2O Conc
Do Not Correct
Between-Sample Memory Correction
Correct For Between-Sample Memory
Do Not Correct For Between-Sample Memory
δ18O Data
Import Type
Import With Normalization Over Sub-ranges (Bracketed Normalization)
Standard Import With Choice of Corrections
Standard Import (Import Data As Shown)
Adjustment for Variation in Delta with Variation in Relative Water Concentration
Correct For Change in δ with Rel H2O Conc
Do Not Correct
Between-Sample Memory Correction
Correct For Between-Sample Memory
Do Not Correct For Between-Sample Memory
There are 15 samples in the import file without companion delta oxygen-17 and delta oxygen-18 samples. The first few are:
W-3
W-33
W-34
W-35
W-998
To import delta oxygen-17 analyses you will need to create companion delta oxygen-17 and delta oxygen-18 samples for these samples.
Click 'View Project' on the Main Menu. Select the project with the specified sample(s).
Click the 'Create Companion delta oxygen-17 and delta oxygen-18 Project' button.

7. On the import criteria screen, accept the default options and then click, “Continue”. The import options available are fully described in Chapter 11, and a discussion of correcting for variations in δ values with variations in relative water concentrations appears in Appendix 3. Accept default settings for now. In the example above, since δ^{17}O companion samples have never been created, they are identified in a pane shown as a separate colour.

8. A summary of all measured δ^{2}H and δ^{18}O data and relative H_2O yields appear with column headings of analysis number, injection number (Pk), Our Lab ID, vial position, and analysis data. Statistics (based on non-ignored injections) for each sample are also shown. *LIMS for Lasers 2015* ignored the first 4 injections per sample, as specified in the LIMS Instrument settings for this instrument.

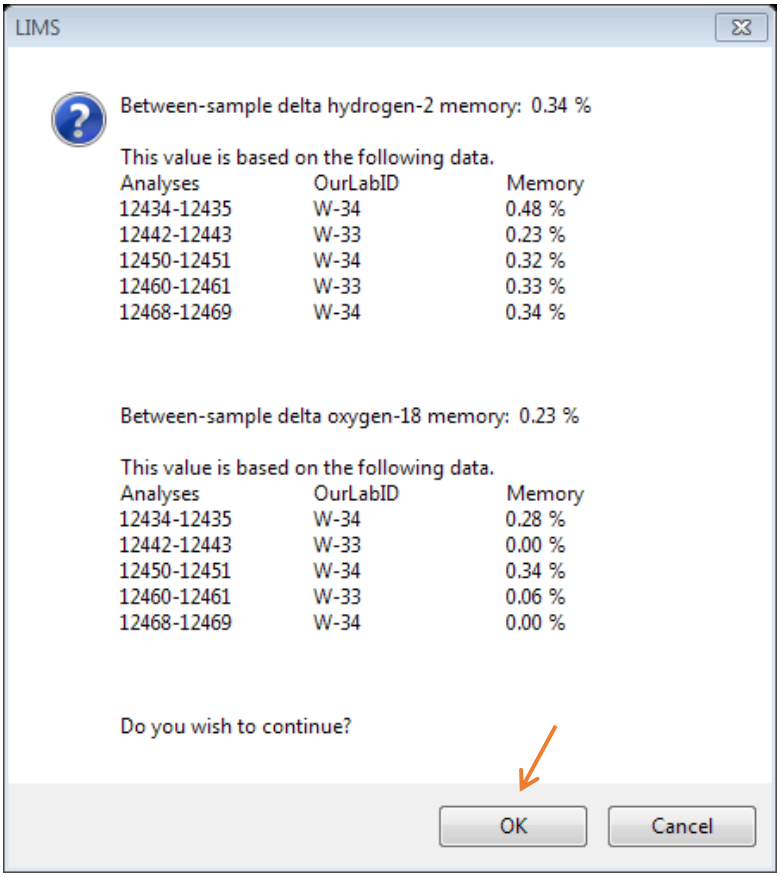


Analysis	Inj	OurLabID	Vial Position	Rel H2O Conc	IG Conc	δ2H	IG δ2H	δ18O	IG δ18O
3328	2	W-39	3_11		☑		☑		☑
3328	3	W-39	3_11		☑		☑		☑
3328	4	W-39	3_11		☑		☑		☑
3328	5	W-39	3_11	3.29	☐	7.11	☐	13.719	☐
3328	6	W-39	3_11	3.27	☐	5.47	☐	13.524	☐
3328	7	W-39	3_11	3.27	☐	6.90	☐	13.642	☐
3328	8	W-39	3_11	3.28	☐	9.18	☐	13.916	☐
3328	9	W-39	3_11	3.28	☐	8.03	☐	13.646	☐
3328			Means	3.28 ± 0.01	▩	7.34 ± 1.38	☐	13.689 ± 0.145	☐
3329	1	W-39	3_12		☑		☑		☑
3329	2	W-39	3_12		☑		☑		☑
3329	3	W-39	3_12		☑		☑		☑
3329	4	W-39	3_12		☑		☑		☑
3329	5	W-39	3_12	3.29	☐	9.77	☐	13.971	☐
3329	6	W-39	3_12	3.28	☐	8.63	☐	13.723	☐
3329	7	W-39	3_12	3.28	☐	8.66	☐	13.706	☐
3329	8	W-39	3_12	3.28	☐	8.75	☐	13.855	☐
3329	9	W-39	3_12	3.28	☐	8.88	☐	13.803	☐
3329			Means	3.28 ± 0.00	▩	8.94 ± 0.48	☐	13.812 ± 0.108	☐
3330	1	W-18103	1_9		☑		☑		☑
3330	2	W-18103	1_9		☑		☑		☑
3330	3	W-18103	1_9		☑		☑		☑
3330	4	W-18103	1_9		☑		☑		☑
3330	5	W-18103	1_9	3.28	☐	-90.15	☐	-1.464	☐
3330	6	W-18103	1_9	3.28	☐	-90.50	☐	-1.505	☐
3330	7	W-18103	1_9	3.27	☐	-92.13	☐	-1.728	☐
3330	8	W-18103	1_9	3.27	☐	-88.16	☐	-1.188	☐
3330	9	W-18103	1_9	3.28	☐	-90.45	☐	-1.493	☐
3330			Means	3.28 ± 0.01	▩	-90.28 ± 1.42	☐	-1.476 ± 0.192	☐
3331	1	W-18104	1_10		☑		☑		☑
3331	2	W-18104	1_10		☑		☑		☑

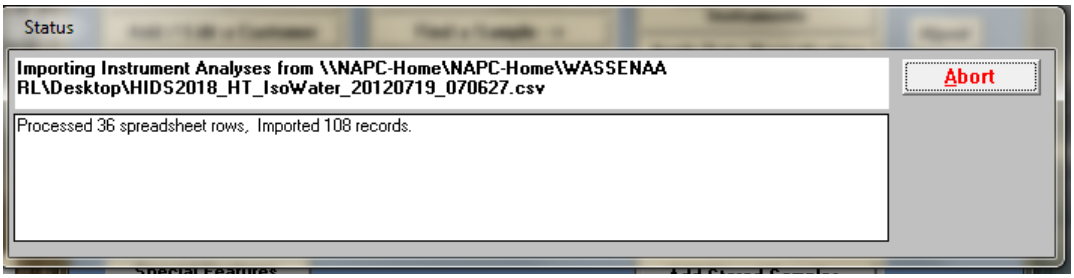
9. Before clicking “Continue”, use the scroll bar to quickly scan for outliers in “Rel H2O Conc” (2.38 is a reduced number to represent 2.38×10^{16} H_2O molecules as reported by the Los Gatos Research instrument) and any δ-value outliers. Outliers may be ignored by clicking the “Ignore” box next to the item. Checking “IG Conc” also checks the ignore boxes of the corresponding δ^{2}H, δ^{18}O and δ^{17}O data. Also note any injections with instrumental errors in the box on the right.

If all of the data appear to be OK, click on “Continue”.

10. The between-sample memory is quantified and averaged. These should be less than 1 to 2 per cent. Click “OK” to continue.



11. The sample drift and memory-corrected Los Gatos Research data is now imported into LIMS for final processing.



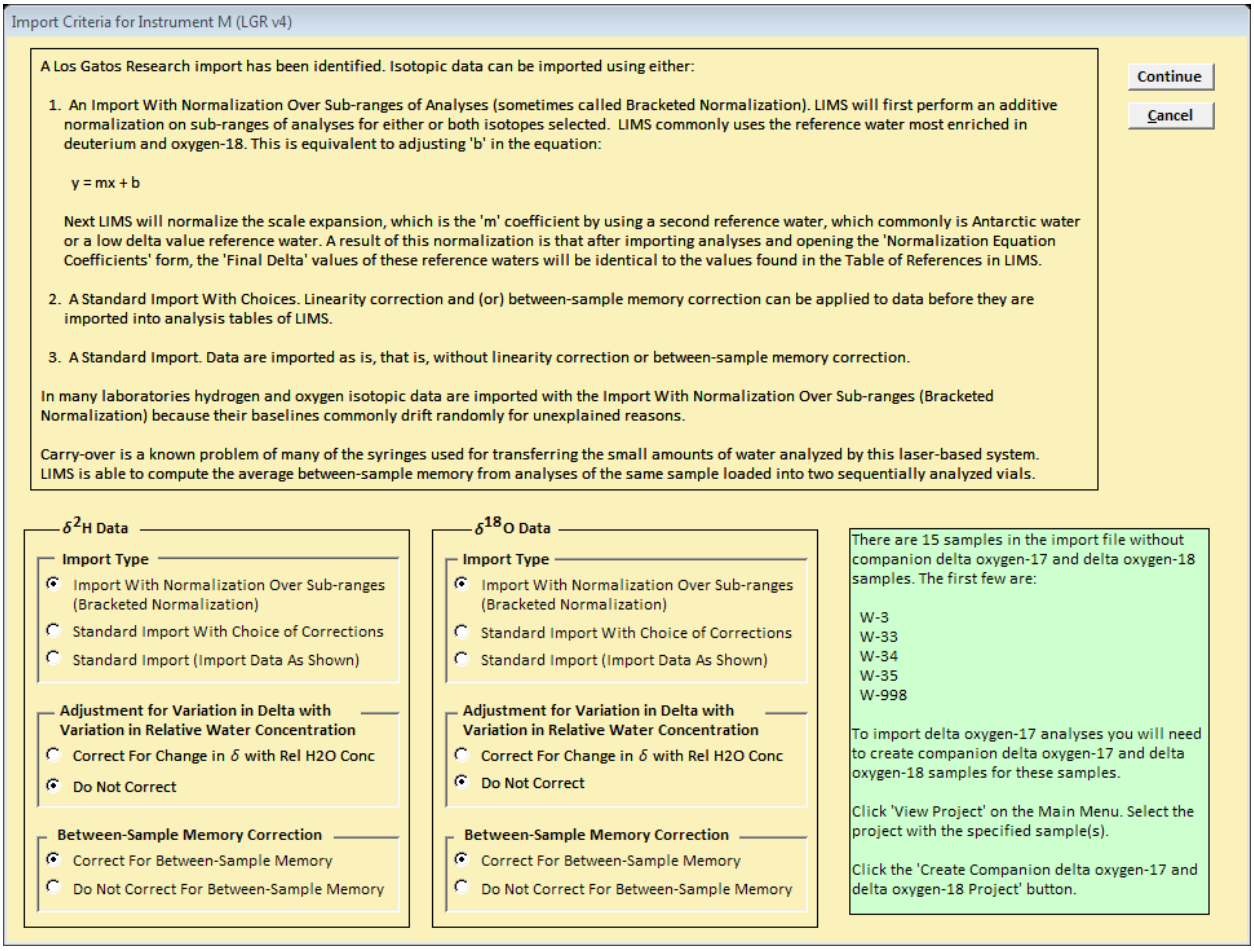
12. At the end of the import *LIMS* verifies the data has been imported. Click “OK”.

13. Normalization, evaluation and storing final data is outlined in Chapter 12.

11 Data Import - Options and Errors

11.1 Data Import Options Explained

There are several import options available in *LIMS for Lasers 2015*. These options are described in detail below. The user may select different data import options for importing δ^2H, δ^{18}O and δ^{17}O (if present) data.



Isotopic Import Type (default = Import with Normalization over Sub-ranges)

Standard Import

The isotopic data from the laser CSV file are simply imported as-is with no corrections applied. No instrumental drift or memory corrections are applied during the data import, and the other options are greyed out. After the import, a linear drift correction may be applied when the measurement data are normalized to the VSMOW-SLAP scale.

Standard Import with Choice of Corrections

This option uses *all* of the data in the autorun that are not ignored, with choice of linear drift and between-sample memory correction applied. This option uses all data for normalization that is not ignored, and all the measurement results are treated as a single batch. There is no bracketed normalization applied, which is often used to correct for non-linear instrumental drift that may have occurred over the autorun.

Import with Normalization Over Sub-ranges (Bracketed Normalization) - Default

This is also known as "bracketed normalization". This is the recommended default import option in *LIMS for Lasers 2015*. This option uses the special layout of the default analysis template and the arrangement of standards to normalize the sample data between groups of the measurement standards. The normalization equations are applied to the bracketed segments of the autorun shown in Table 1 and 2, and therefore this import option also corrects for non-linear instrumental drift.

Adjustments for *δ* with Variation in Relative Water Concentration

Dependency of instrument *δ* values with relative H_2O concentrations are significant for most laser instruments. Typically, H_2O amount variations in the laser cavity arise from syringe underperformance or leaks, or may be purposely manipulated by the user. The *δ* dependency on H_2O amount can be corrected by using linear or non-linear fitting methods. Appendix 3 shows how implementing a concentration correction algorithm can substantially improve the accuracy and precision of *δ* results for all isotopic species.

Between-Sample Memory Correction *(default = correct for memory)*

This option makes use of the *LIMS for Lasers 2015* default template layout to determine the between-sample memory correction over the course of the entire autorun by using groupings of measurement standards distributed across the autorun (low to high, high to low, etc.). As noted above, we recommend initially using 9 sample injections and ignoring the first 4 to minimize the between-sample memory.

Between-sample memory is calculated by comparing the means of the non-ignored *δ* values of the first standard (high delta) to the mean values of two sequential occurrences of a second (low delta) standard, or vice-versa (high to low, low to high). For an autorun containing distributed groups of a high/low standard followed by two identical low/high standards (e.g. HighStd, LowStd1, LowStd2), the between-sample memory is determined using the mean of all non-ignored measurement standards as follows:

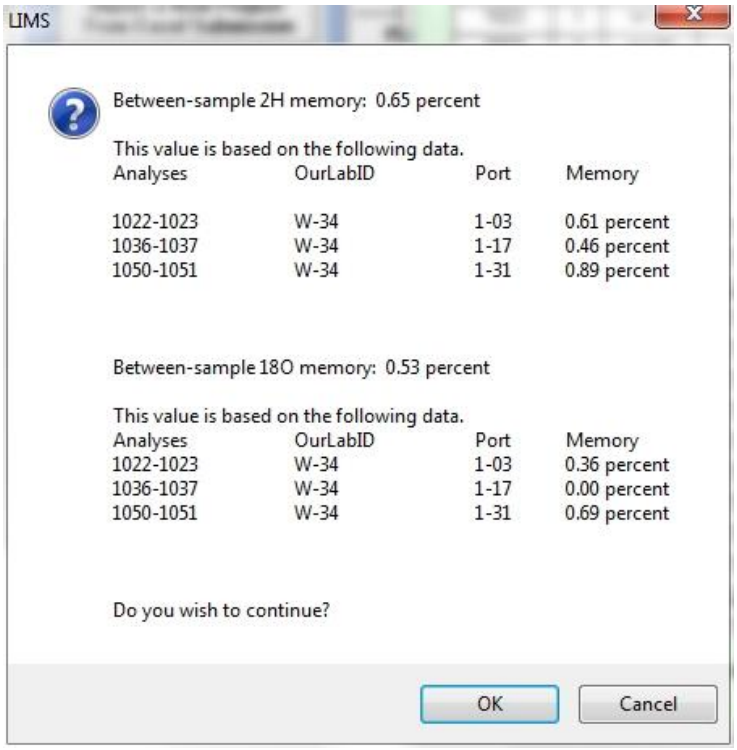
Between-sample memory (%) = (avg LowStd1 – (avg Low Std2)) / avg (HighStd – (avg Low Std2))

δ^2H Memory Example: 0.68 % = (–401.57 ‰ – (–404.03 ‰)) / (–41.89 ‰ – (–404.03 ‰))

The between-sample memory correction is averaged using all appropriate reference groupings in the autorun, and then applied to all samples and measurement standards:

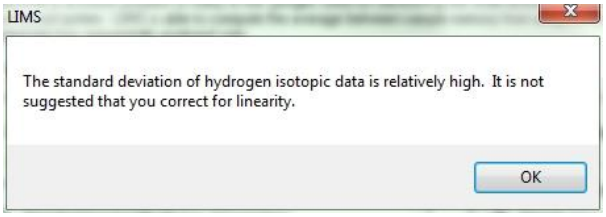
Adjusted Sample δ^2H = 1.0068 * (Sample Mean – Prior Sample Mean) + Prior Sample Mean

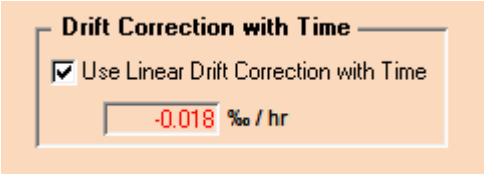
Final Corrected δ Result = Mean Sample Value – (Mean Adjusted Value – Mean Sample Value)



Drift Correction with Time

This option enables a user to correct instrument data from an autorun exhibiting strong linear drift (using laboratory standards) over time. This is rarely the case, as typically shown by a high error on the slope of the regression of the standard δ value versus time. One can evaluate this option, but one usually obtains the following message:



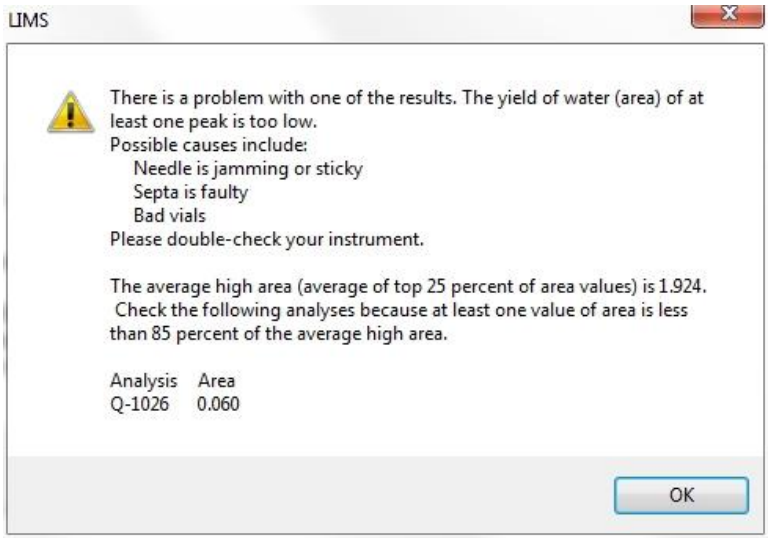


Note: The Linear Drift Correction with Time is only available if Standard Import option is selected. The value of the drift correction with time is also visible on the data normalization page in the column labelled "Hourly Corr" (see Section 12.2).

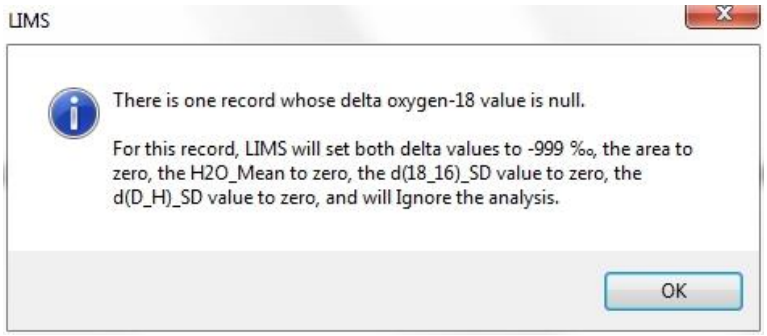
11.2 Laser Data Import Error Messages

The two most common import errors stem from poor analyses, such as those with low or highly variable H_2O yields as a result of syringe or septa failure, or from null data from dropped analyses, or some other instrumental malfunction.

LIMS for Lasers 2015 will warn the user about faulty sample and analysis conditions when data is imported. This pre-screening feature helps to ensure that users do not import bad data. These warnings will not appear if the autorun data passes the preliminary screening tests.



Example: this sample vial was either insufficiently or over-filled, resulting in a low H_2O yield in the laser analyser, with concomitant bad isotopic assay. *LIMS for Lasers 2015* warns the user which sample was problematic.



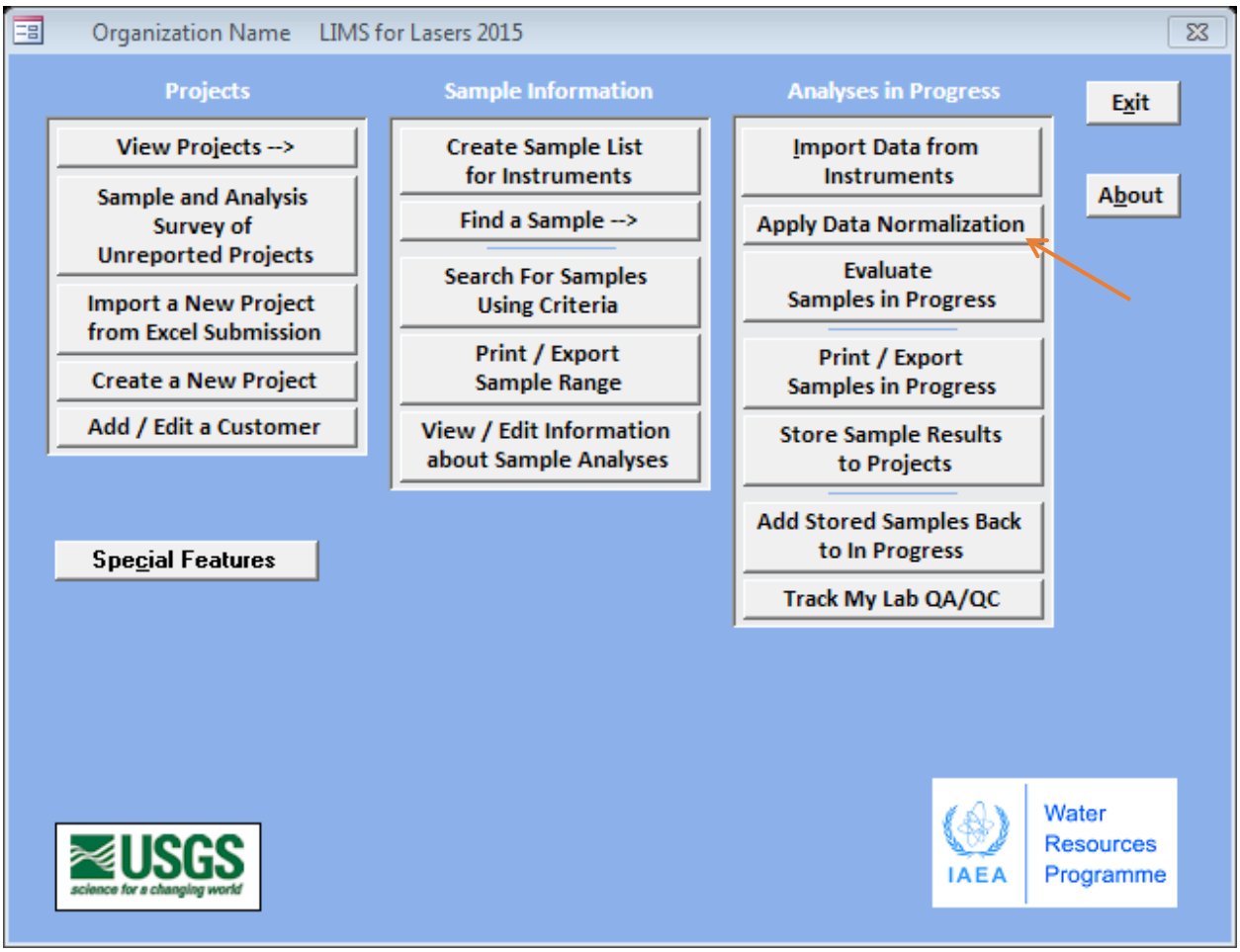
Example: occasionally instrument faults may result in the reporting of null or blank isotopic data for one or more injections. *LIMS for Lasers 2015* screens for null values in order to exclude null values in the sample normalization.

12 Normalize, Evaluate, and Store Results

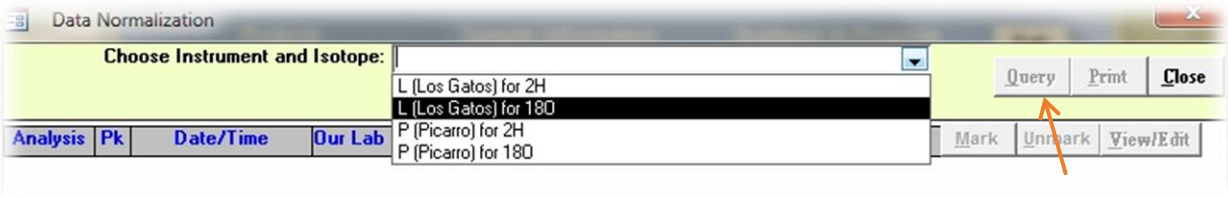
12.1 Normalize Data to VSMOW and SLAP Scales

In this chapter we illustrate data marking, normalization and evaluation. Because the identical procedure applies to Los Gatos Research and Picarro instruments, and it is repeated for $\delta^{18}O$, $\delta^{17}O$ and $\delta^{2}H$ measurements, the process will be shown once using a single isotope example.

1. After data files have been successful imported from a laser instrument (Chapters 9 and 10), on the main page of *LIMS for Lasers 2015*, click on the "Apply Data Normalization" button.



2. From the pull down menu at the top of the window, choose the appropriate instrument and the specific isotope delta to be processed. Remember: this procedure is performed twice - once for ^{2}H and once for ^{18}O (and optionally a third time for ^{17}O). Choose one instrument and isotope delta, and click on "Query".



In the window that opens (below), the last 500 analyses for the selected laser instrument will be shown. The analysis list is sorted by date; the most recent samples are shown by default. Older data can be viewed by lowering the analysis numbers "from and to" fields, and then re-querying the database.

The data fields shown are:

Analysis – The instrument prefix and its counter (L, P, etc.), as provided by the laser instrument.
Inj – This is the sample injection number. Here each single sample is comprised of nine injections. There are two instances of each peak number– one is labelled ^{2}H and the other is labelled ^{18}O.
Date/time – The instrument date and time stamp of the analysis.
Our Lab ID – The LIMS sample name. The plus (+) sign beside Our Lab ID denotes the isotope delta selected in Step 2 to be normalized (here ^{2}H on a Picarro).
Vial Pos – The autosampler tray position of each sample.

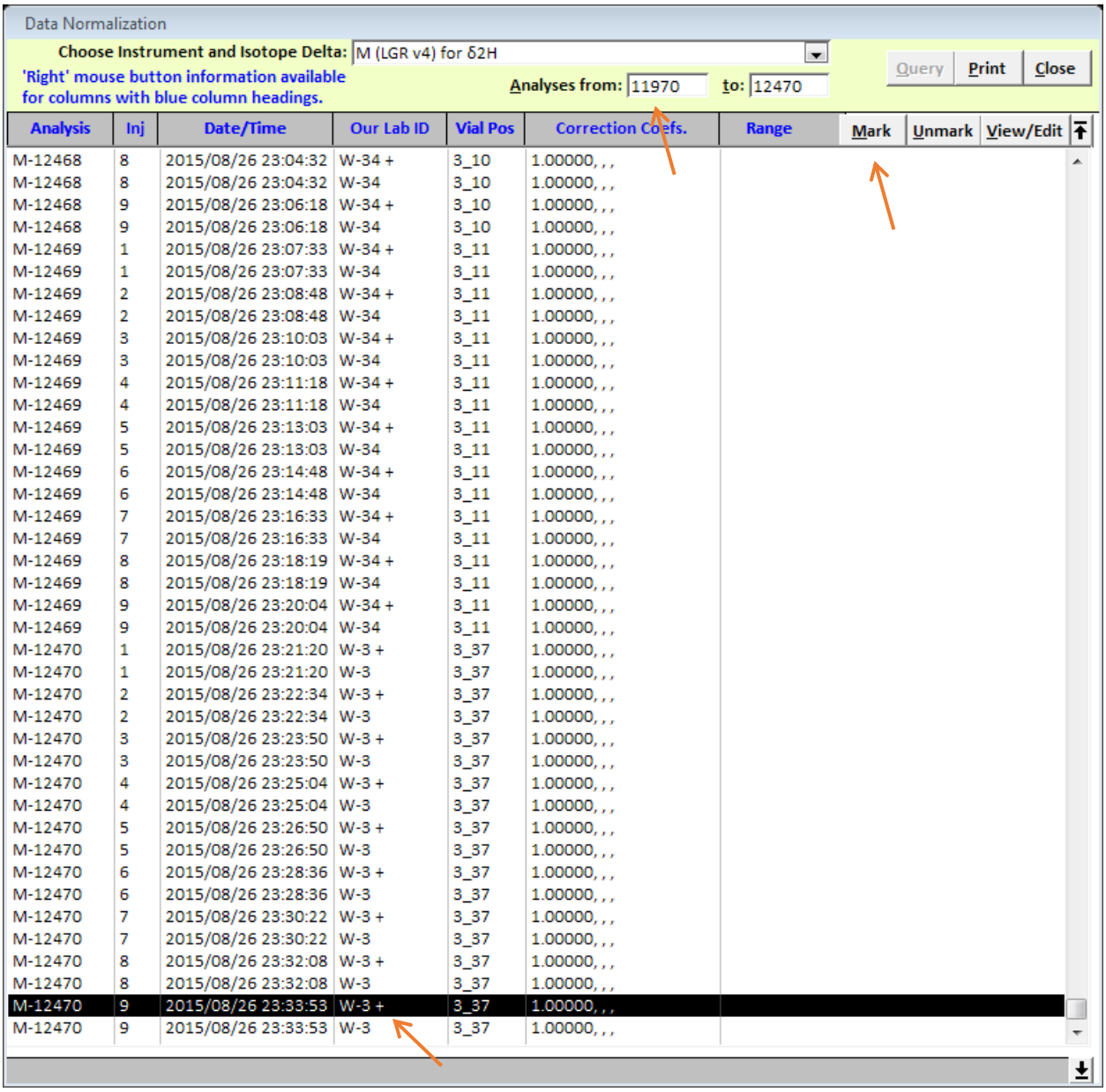
Importance of Marking and Normalizing Imported Data Immediately

Because dual/triple isotope data are imported concurrently in CSV files, *LIMS for Lasers 2015* cannot distinguish one autorun from the next. The analyst must manually instruct *LIMS for Lasers 2015* which data correspond to each autorun, on a per isotope basis. The procedure is known as "Marking", whereby the analyst explicitly defines the beginning and end of each autorun (e.g. Range of Analyses) to be normalized for each isotope, as shown by example below.

Tips:

- It is good practice to import, Mark, and normalize each autorun for all isotopes as soon as it is completed; do not accumulate laser data files or import later in random fashion
- The Marked end of each autorun defines the start of the next autorun of imported data when imported in chronological order (e.g. by consecutive Analysis number).
- If you import data and forget to Mark and normalize it, the next set of data will be appended to it and will appear as a large autorun (appending autoruns is strongly discouraged!)
- If you want to re-import an autorun for alternate processing, you must first UnMark those data that were previously Marked and normalized, and then re-import. *LIMS for*

Lasers 2015 will warn you if you try to re-import data overtop previously Marked and normalized data.



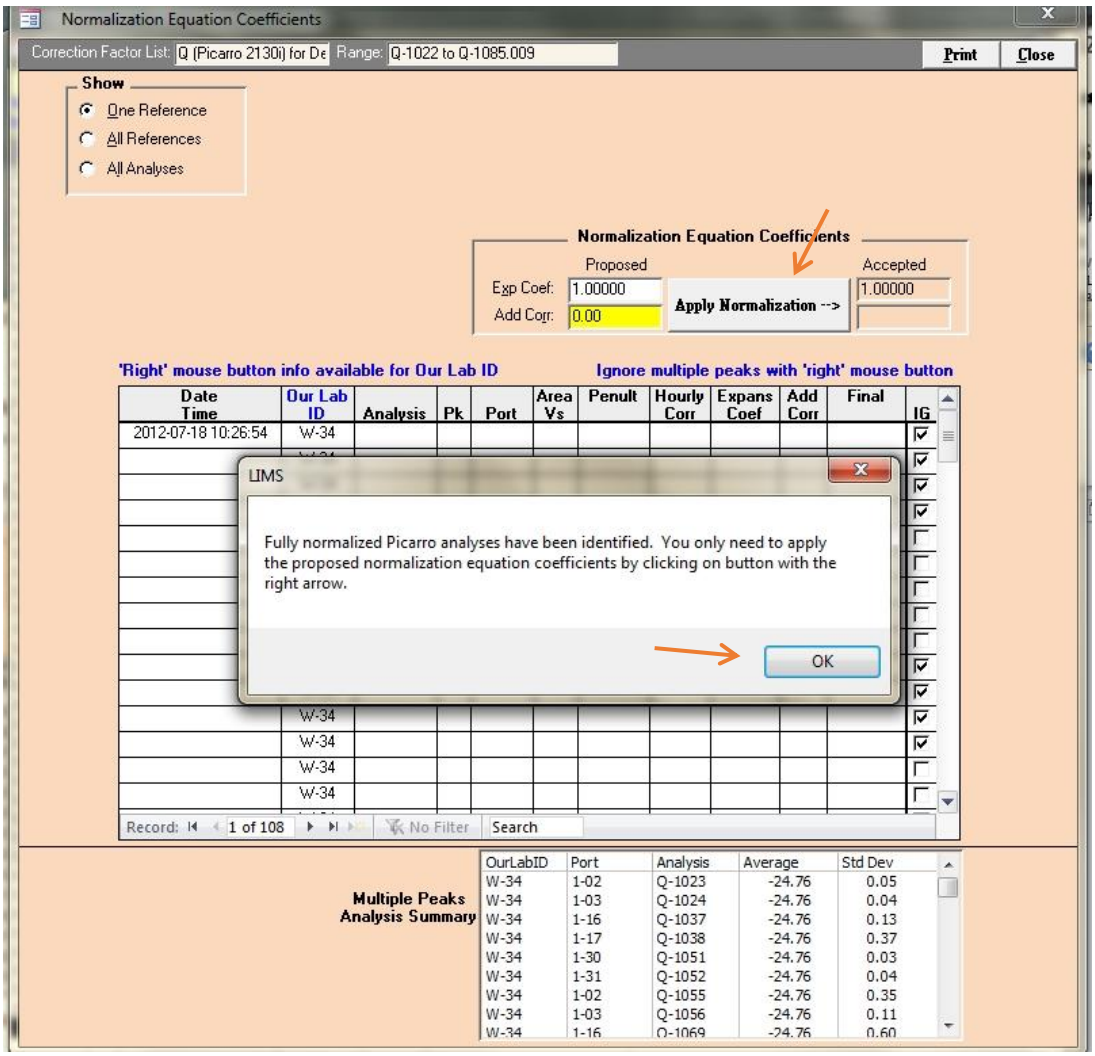
Analysis	Inj	Date/Time	Our Lab ID	Vial Pos	Correction Coefs.	Range
M-12468	8	2015/08/26 23:04:32	W-34 +	3_10	1.00000, , ,	
M-12468	8	2015/08/26 23:04:32	W-34	3_10	1.00000, , ,	
M-12468	9	2015/08/26 23:06:18	W-34 +	3_10	1.00000, , ,	
M-12468	9	2015/08/26 23:06:18	W-34	3_10	1.00000, , ,	
M-12469	1	2015/08/26 23:07:33	W-34 +	3_11	1.00000, , ,	
M-12469	1	2015/08/26 23:07:33	W-34	3_11	1.00000, , ,	
M-12469	2	2015/08/26 23:08:48	W-34 +	3_11	1.00000, , ,	
M-12469	2	2015/08/26 23:08:48	W-34	3_11	1.00000, , ,	
M-12469	3	2015/08/26 23:10:03	W-34 +	3_11	1.00000, , ,	
M-12469	3	2015/08/26 23:10:03	W-34	3_11	1.00000, , ,	
M-12469	4	2015/08/26 23:11:18	W-34 +	3_11	1.00000, , ,	
M-12469	4	2015/08/26 23:11:18	W-34	3_11	1.00000, , ,	
M-12469	5	2015/08/26 23:13:03	W-34 +	3_11	1.00000, , ,	
M-12469	5	2015/08/26 23:13:03	W-34	3_11	1.00000, , ,	
M-12469	6	2015/08/26 23:14:48	W-34 +	3_11	1.00000, , ,	
M-12469	6	2015/08/26 23:14:48	W-34	3_11	1.00000, , ,	
M-12469	7	2015/08/26 23:16:33	W-34 +	3_11	1.00000, , ,	
M-12469	7	2015/08/26 23:16:33	W-34	3_11	1.00000, , ,	
M-12469	8	2015/08/26 23:18:19	W-34 +	3_11	1.00000, , ,	
M-12469	8	2015/08/26 23:18:19	W-34	3_11	1.00000, , ,	
M-12469	9	2015/08/26 23:20:04	W-34 +	3_11	1.00000, , ,	
M-12469	9	2015/08/26 23:20:04	W-34	3_11	1.00000, , ,	
M-12470	1	2015/08/26 23:21:20	W-3 +	3_37	1.00000, , ,	
M-12470	1	2015/08/26 23:21:20	W-3	3_37	1.00000, , ,	
M-12470	2	2015/08/26 23:22:34	W-3 +	3_37	1.00000, , ,	
M-12470	2	2015/08/26 23:22:34	W-3	3_37	1.00000, , ,	
M-12470	3	2015/08/26 23:23:50	W-3 +	3_37	1.00000, , ,	
M-12470	3	2015/08/26 23:23:50	W-3	3_37	1.00000, , ,	
M-12470	4	2015/08/26 23:25:04	W-3 +	3_37	1.00000, , ,	
M-12470	4	2015/08/26 23:25:04	W-3	3_37	1.00000, , ,	
M-12470	5	2015/08/26 23:26:50	W-3 +	3_37	1.00000, , ,	
M-12470	5	2015/08/26 23:26:50	W-3	3_37	1.00000, , ,	
M-12470	6	2015/08/26 23:28:36	W-3 +	3_37	1.00000, , ,	
M-12470	6	2015/08/26 23:28:36	W-3	3_37	1.00000, , ,	
M-12470	7	2015/08/26 23:30:22	W-3 +	3_37	1.00000, , ,	
M-12470	7	2015/08/26 23:30:22	W-3	3_37	1.00000, , ,	
M-12470	8	2015/08/26 23:32:08	W-3 +	3_37	1.00000, , ,	
M-12470	8	2015/08/26 23:32:08	W-3	3_37	1.00000, , ,	
M-12470	9	2015/08/26 23:33:53	W-3 +	3_37	1.00000, , ,	
M-12470	9	2015/08/26 23:33:53	W-3	3_37	1.00000, , ,	

Select the last + line to Mark a range of samples.

3. To normalize imported laser data, **double click on the last occurrence** of an analysis number having a "+" sign beside it. This will "Mark" for normalization all the H (or O) data accumulated since the last import and data normalization. Because the default normalization method used in *LIMS for Lasers 2015* is "bracketed normalization", LIMS has already pre-processed and normalized all of the isotopic data, and the message "Fully normalized Instrument (Picarro or Los Gatos Research) analyses have been identified"

appears. Click “OK”. Then, click on “Apply Normalization” button to accept the LIMS normalization.

4. You are finished! Repeat this process from Step 2 for the second or third isotope delta (e.g. δ^{18}O, δ^{17}O). LIMS has used bracketed (memory and drift corrected) measurement standards to normalize sample H and O isotopic data to the VSMOW and SLAP scales. Next, we can evaluate the results as outlined in Chapter 12.3.



To avoid confusion, always Mark and normalize δ^{18}O and δ^{2}H results from each autorun *before* importing data from the next run. This avoids combining datasets from different autoruns.

LIMS for Lasers 2015 assigns a new injection number during importing to all δ^{17}O analyses. The new injection number is equal to the sum of the δ^{2}H injection number and 70. When

normalizing δ^{17}O results, user will observe something similar to the following in which injection numbers from 71 and up are seen for δ^{17}O results.

Data Normalization

Choose Instrument and Isotope Delta: M (LGR v4) for δ17O

'Right' mouse button information available for columns with blue column headings.

Analyses from: 11970 to: 12470

Query Print Close

Analysis	Inj	Date/Time	Our Lab ID	Vial Pos	Correction Coefs.	Range	Mark	Unmark	View/Edit
M-12469	8	2015/08/26 23:18:19	W-34	3_11	1.00000, , ,				
M-12469	8	2015/08/26 23:18:19	W-34	3_11	1.00000, , ,				
M-12469	9	2015/08/26 23:20:04	W-34	3_11	1.00000, , ,				
M-12469	9	2015/08/26 23:20:04	W-34	3_11	1.00000, , ,				
M-12469	71	2015/08/26 23:07:33	W-100 +	3_11	1.00000, 0.00, ,				
M-12469	72	2015/08/26 23:08:48	W-100 +	3_11	1.00000, 0.00, ,				
M-12469	73	2015/08/26 23:10:03	W-100 +	3_11	1.00000, 0.00, ,				
M-12469	74	2015/08/26 23:11:18	W-100 +	3_11	1.00000, 0.00, ,				
M-12469	75	2015/08/26 23:13:03	W-100 +	3_11	1.00000, 0.00, ,				
M-12469	76	2015/08/26 23:14:48	W-100 +	3_11	1.00000, 0.00, ,				
M-12469	77	2015/08/26 23:16:33	W-100 +	3_11	1.00000, 0.00, ,				
M-12469	78	2015/08/26 23:18:19	W-100 +	3_11	1.00000, 0.00, ,				
M-12469	79	2015/08/26 23:20:04	W-100 +	3_11	1.00000, 0.00, ,				
M-12470	1	2015/08/26 23:21:20	W-3	3_37	1.00000, , ,				
M-12470	1	2015/08/26 23:21:20	W-3	3_37	1.00000, , ,				
M-12470	2	2015/08/26 23:22:34	W-3	3_37	1.00000, , ,				
M-12470	2	2015/08/26 23:22:34	W-3	3_37	1.00000, , ,				
M-12470	3	2015/08/26 23:23:50	W-3	3_37	1.00000, , ,				
M-12470	3	2015/08/26 23:23:50	W-3	3_37	1.00000, , ,				
M-12470	4	2015/08/26 23:25:04	W-3	3_37	1.00000, , ,				
M-12470	4	2015/08/26 23:25:04	W-3	3_37	1.00000, , ,				
M-12470	5	2015/08/26 23:26:50	W-3	3_37	1.00000, , ,				
M-12470	5	2015/08/26 23:26:50	W-3	3_37	1.00000, , ,				
M-12470	6	2015/08/26 23:28:36	W-3	3_37	1.00000, , ,				
M-12470	6	2015/08/26 23:28:36	W-3	3_37	1.00000, , ,				
M-12470	7	2015/08/26 23:30:22	W-3	3_37	1.00000, , ,				
M-12470	7	2015/08/26 23:30:22	W-3	3_37	1.00000, , ,				
M-12470	8	2015/08/26 23:32:08	W-3	3_37	1.00000, , ,				
M-12470	8	2015/08/26 23:32:08	W-3	3_37	1.00000, , ,				
M-12470	9	2015/08/26 23:33:53	W-3	3_37	1.00000, , ,				
M-12470	9	2015/08/26 23:33:53	W-3	3_37	1.00000, , ,				
M-12470	71	2015/08/26 23:21:20	W-96 +	3_37	1.00000, 0.00, ,				
M-12470	72	2015/08/26 23:22:34	W-96 +	3_37	1.00000, 0.00, ,				
M-12470	73	2015/08/26 23:23:50	W-96 +	3_37	1.00000, 0.00, ,				
M-12470	74	2015/08/26 23:25:04	W-96 +	3_37	1.00000, 0.00, ,				
M-12470	75	2015/08/26 23:26:50	W-96 +	3_37	1.00000, 0.00, ,				
M-12470	76	2015/08/26 23:28:36	W-96 +	3_37	1.00000, 0.00, ,				
M-12470	77	2015/08/26 23:30:22	W-96 +	3_37	1.00000, 0.00, ,				
M-12470	78	2015/08/26 23:32:08	W-96 +	3_37	1.00000, 0.00, ,				
M-12470	79	2015/08/26 23:33:53	W-96 +	3_37	1.00000, 0.00, ,	1.000 - 12470.079; 1.00000*pd+0.0			

Marked sample range with normalization applied.

12.2 Normalize Data (Without Bracketed Normalization)

If you imported isotopic data using the optional “Standard Import” or “Standard Import with Choice of Corrections”, the autorun is treated as a single batch, and other normalization options, like linear drift correction, may be applied after following Steps 1–3 in Chapter 12.1.

1. Click “Normalize with All References”. The calculated *R*-Squared value should be >0.9. If significantly less than <0.9, it suggests unexpected isotopic variability in the standards. Check for outliers.
2. Click on “Apply Normalization”. The proposed expansion coefficient and additive correction factors derived from the measurement standards in the autorun are applied to the data. Optionally, check for instrumental drift by checking “Use Linear Drift Correction”.
3. You are finished! Repeat the process for the second isotope delta (e.g. δ^{18}O). Then, evaluate your results (Chapter 12.3).

Note: *LIMS for Lasers 2015* reveals 4 ignored injections as set in instrument options. Check for outliers here, and ignore as needed. The bottom panel reveals a summary of the measurement standard results used in the normalization – note that bad measurement standards can also be ignored.

Normalization Equation Coefficients

Correction Factor List: K (Picarro 2140i) for δ2H Range: K-1.000 to K-470.007 Ignore Some Deltas Ignore All Deltas Print Close

Show
- One Reference
- All References
- All Analyses

Drift Correction with Time
- [x] Use Linear Drift Correction with Time
- -0.018 ‰ / hr

Normalization
- Normalize with This Reference:
- Normalize with All References
- R-Squared: 0.999989
- [ ] Force Exp Coef to 1.00000

'True' Value:

Multiple Injections/Analysis
Mean Intermediate Delta:
Std Dev:

Normalization Equation Coefficients

	Proposed		Accepted
Exp Coef:	0.98207	Apply Normalization -->	1.000000
Add Corr:	3.47		

'Right' mouse button info available for Our Lab ID

Ignore multiple peaks with 'right' mouse button

Date Time	Our Lab ID	Analysis	Inj	Vial Pos	Rel H2O Conc	Instr Error	Penult δ2H	Hourly Corr	Expans Coef	Add Corr	Final δ2H	IG
2015/08/27 14:31:12	W-998	K-456	3	1-03	1.747		-84.28	-0.03	0.98207	3.47	-79.33	☑
2015/08/27 14:39:59	W-998	K-456	4	1-03	1.776		-84.18	-0.03	0.98207	3.47	-79.24	☑
2015/08/27 14:48:47	W-998	K-456	5	1-03	1.734		-84.37	-0.04	0.98207	3.47	-79.43	☐
2015/08/27 14:57:34	W-998	K-456	6	1-03	1.717		-84.52	-0.04	0.98207	3.47	-79.58	☐
2015/08/27 15:06:22	W-998	K-456	7	1-03	1.235		-85.06	-0.04	0.98207	3.47	-80.11	☐
2015/08/27 15:15:09	W-33	K-457	1	1-04	1.973		-152.43	-0.05	0.98207	3.47	-146.27	☑
2015/08/27 15:23:57	W-33	K-457	2	1-04	1.987		-155.22	-0.05	0.98207	3.47	-149.02	☑
2015/08/27 15:32:45	W-33	K-457	3	1-04	1.99		-156.01	-0.05	0.98207	3.47	-149.80	☑
2015/08/27 15:41:33	W-33	K-457	4	1-04	1.984		-156.21	-0.05	0.98207	3.47	-149.99	☑
2015/08/27 15:50:21	W-33	K-457	5	1-04	2.009		-156.42	-0.06	0.98207	3.47	-150.21	☐
2015/08/27 15:59:09	W-33	K-457	6	1-04	2.007		-156.51	-0.06	0.98207	3.47	-150.29	☐
2015/08/27 16:07:58	W-33	K-457	7	1-04	1.955		-156.69	-0.06	0.98207	3.47	-150.48	☐
2015/08/27 16:16:45	W-34	K-458	1	1-05	2.046		-14.12	-0.06	0.98207	3.47	-10.46	☑
2015/08/27 16:25:33	W-34	K-458	2	1-05	2.034		-8.35	-0.07	0.98207	3.47	-4.80	☑
2015/08/27 16:34:22	W-34	K-458	3	1-05	2.034		-7.26	-0.07	0.98207	3.47	-3.74	☑

Record: 1 of 119 No Filter Search

Multiple Injections Analysis Summary

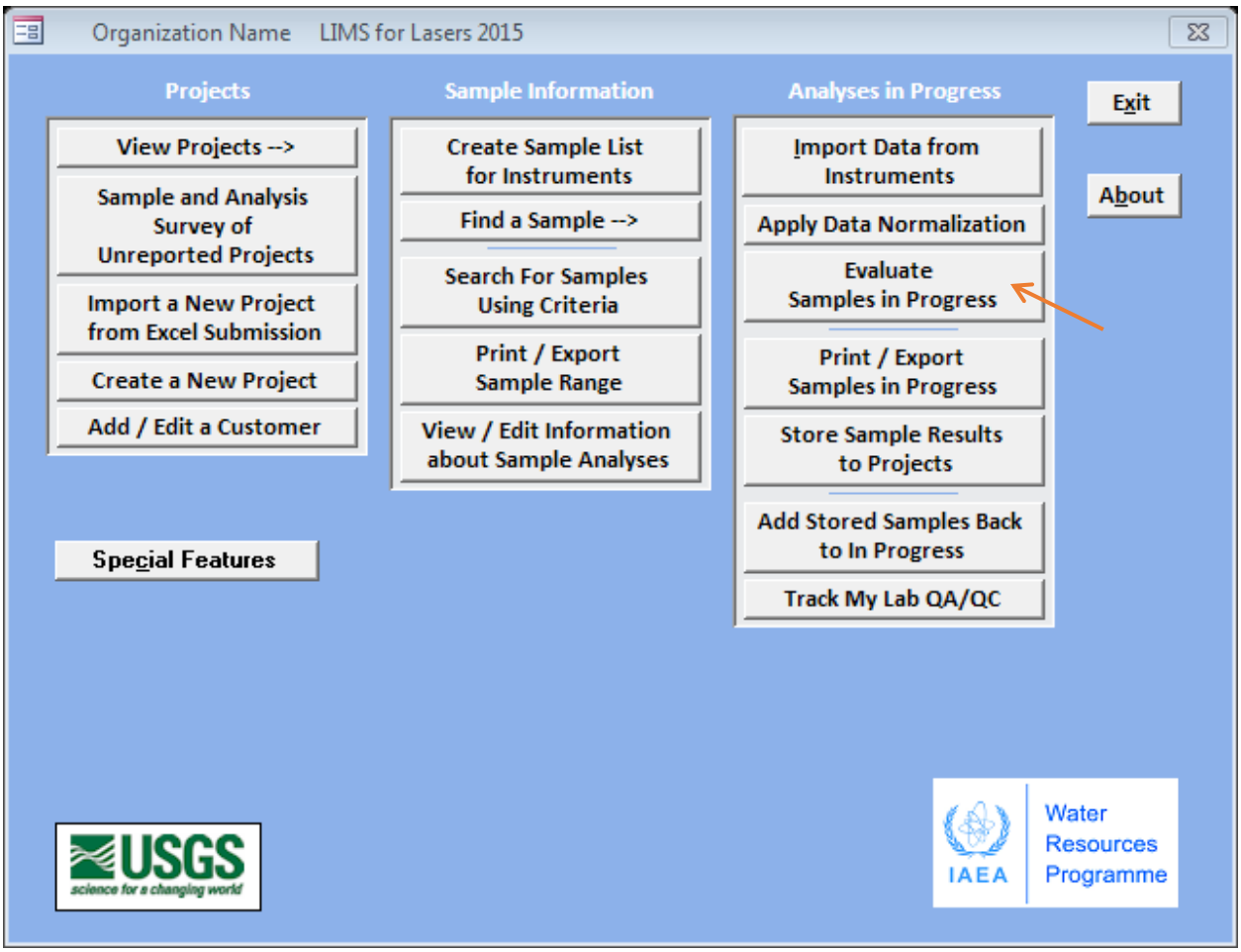
OurLabID	Vial Pos	Analysis	Average	Std Dev
W-33	1-04	K-457	-150.32	0.14
W-33	1-16	K-469	-149.96	0.27
W-33	1-17	K-470	-150.32	0.07
W-34	1-05	K-458	-2.34	0.19
W-34	1-06	K-459	-1.62	0.04
W-34	1-15	K-468	-2.04	0.11

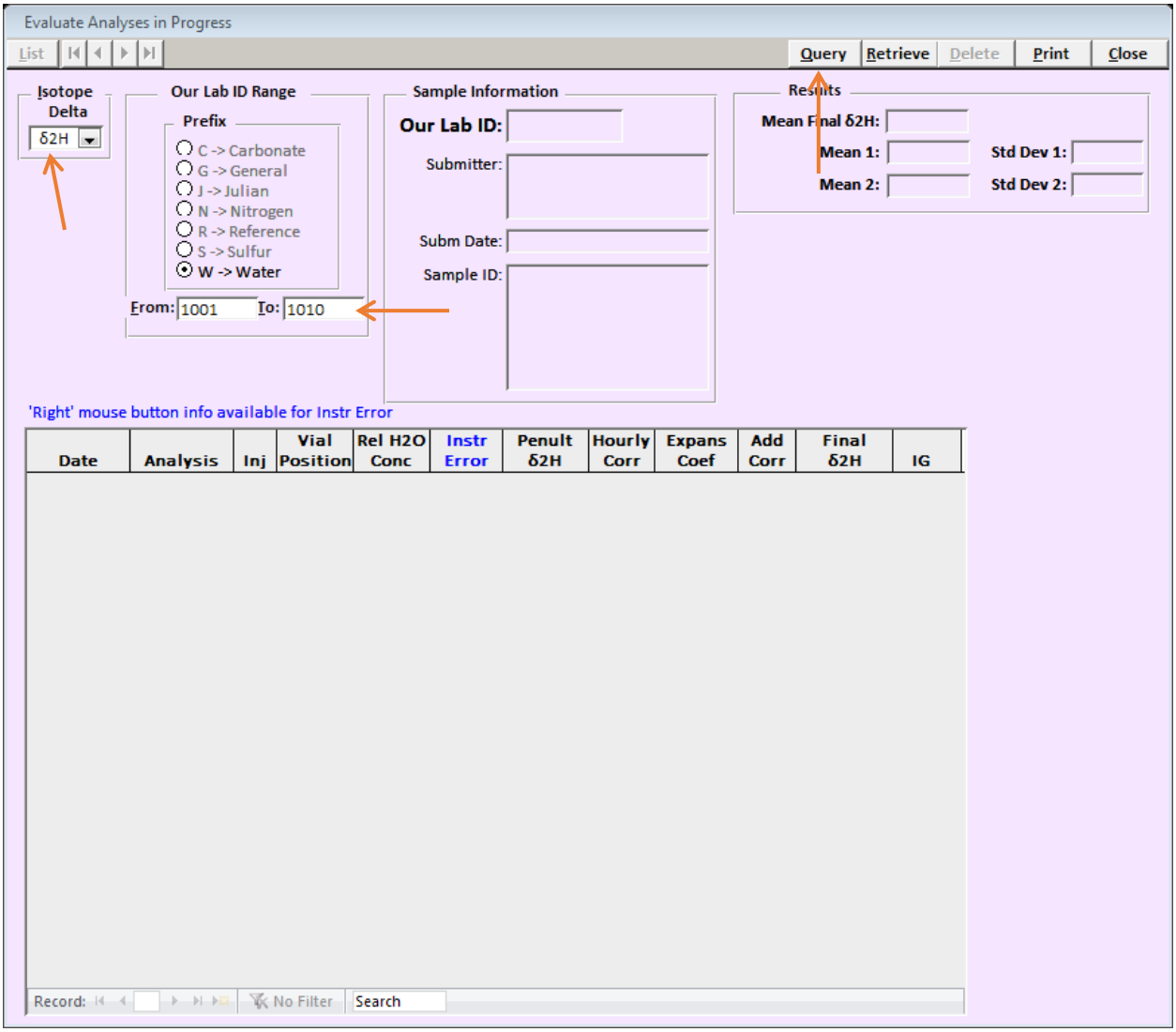
12.3 Evaluate Analyses in Progress

Once samples have been measured and normalized to the VSMOW-SLAP scales, they remain "in progress" until they are evaluated by the analyst and stored. The analyst should evaluate all results before storing them and passing them on to the customer.

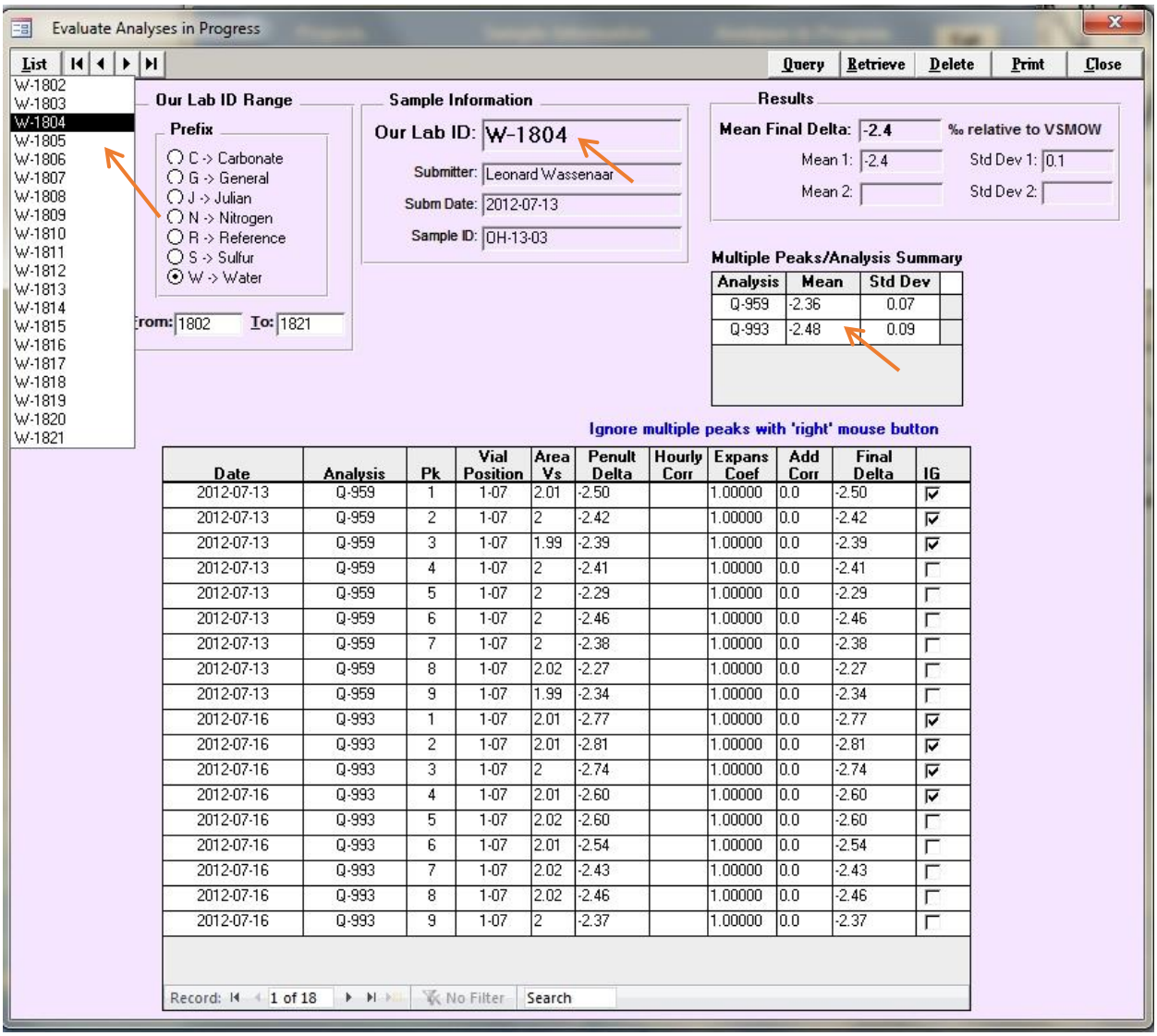
The *LIMS for Lasers 2015* data evaluation consists of two parts: (1) checking the repeatability of all normalized samples that were measured twice or more, and (2) checking the performance of control standards included in each autorun, and over time (see Chapter 12.7).

1. On the main page of *LIMS for Lasers 2015*, click on "Evaluate Samples in Progress".





2. Choose one Isotope Delta – such as δ^2H - that you want to evaluate from the pull down menu located in the upper left (remember to repeat the procedure for δ^{18}O).
3. The available Prefix in *LIMS for Lasers 2015* is "W" for water (the other prefixes are not enabled).
4. Enter the "W" range of the normalized samples or control standards you want to evaluate. In the example below, W-1802 to W-1821 corresponded to the last data run.
5. Then, click on "Query".
6. A new window opens showing a summary of all of the results for each sample in the "W" range queried.



7. By clicking the "List" button (top left) or by using the navigation buttons (arrow keys), one views individual samples to examine the measurement result(s). In the above example, the sample with Our Lab ID W-1804 was selected for δ^2H. One can also navigate through samples by using the scroll wheel on the mouse.

This window displays the Sample Information (ID, customer, analysis date) and a summary of the normalized results (Mean and Std Dev). Here, we note sample W-1804 was analysed twice as Analysis numbers Q-959 and Q-993 in the Multiple Peak Summary window. The mean normalized (VSMOW) values for each set of injections are summarized, and both mean measurements for this sample (δ^2H of –2.36 ‰ and –2.48 ‰) agree well, which indicated we can accept the final result.

The bottom table shows W-1804 was measured on July 13 and on July 16, 2012. We see the normalized data and the ignored injections. Also shown are the vial positions used and the scale expansion and additive correction factors (if applicable).

Using the navigation arrows or the scroll wheel on the mouse, check all of the samples that need to be evaluated. Ensure that you check all samples within each autorun, for example, if samples from several projects (difference groupings of W numbers) were included.

If there is a significant disagreement between the δ^2H or δ^{18}O values of replicates of the same sample, that sample should be measured a third time. If two of the three results agreed well, one can conclude the third “outlier” might have been a bad analysis (or a mixed-up vial).

Judging what is a significant discrepancy is a matter of professional judgement. That judgement takes into consideration accuracy and the precision that the instrument used can reasonably achieve.

As a first suggestion (and this is instrument-specific), δ^2H repeats that repeat within 1.5 ‰ of each other are generally considered acceptable for hydrological studies. For δ^{18}O, repeats that lie within 0.2 ‰ of each other are generally considered acceptable. This assessment, however, remains for each laboratory to decide, and is a bar upon which the laboratory sets its own performance standards (see also Track My Laboratory QA/QC in Chapter 12.7 for obtaining long-term performance metrics).

Important! If a sample has been 2–3 times and there is a clear outlier, in Evaluate Analyses in Progress that outlier must be manually “Ignored”. In the bottom window, check the IG (ignore) boxes for the outlier sample (e.g. all instances having the same analysis number). Or right click to ignore all injections of an analysis with a single click. The analysis will disappear from the Multiple Peak Summary window, and these bad results will not be used in calculating the mean reported final result for that sample.

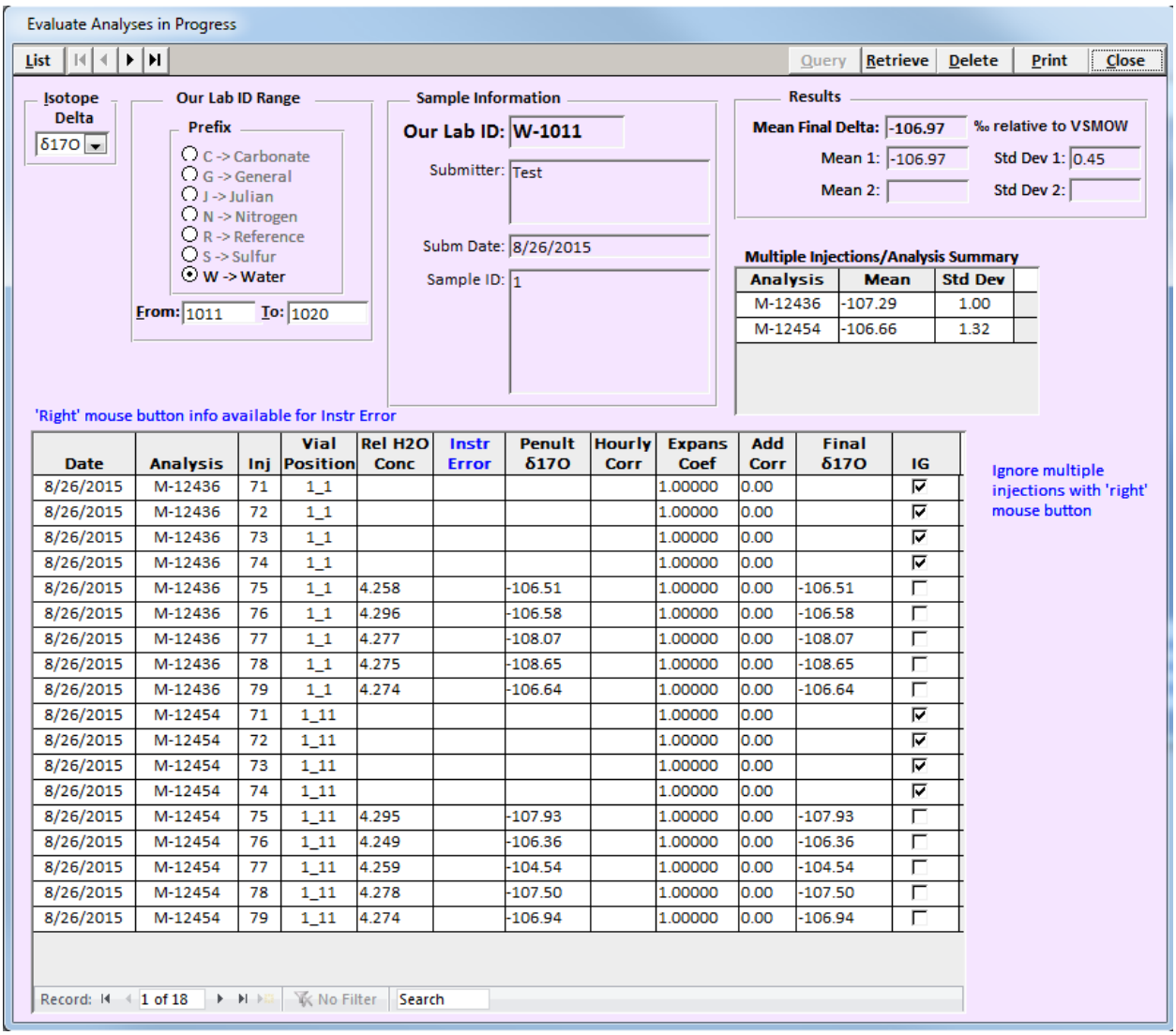
Caution: If you do not ignore bad results, they are included in the final reported mean value!

By clicking the "Retrieve" button, the user can add a sample to the Samples in Progress queue for the selected isotope. For adding more than one sample at a time, consult section 12.6.

By clicking the "Delete" button, the user can remove a sample from the Samples in Progress queue for the selected isotope. This is useful for deleting dummy or test samples from the queue whose results are no longer needed. Note that the analyses are not deleted from the LIMS for Lasers 2015 database. They may be added back to the Samples in Progress queue using the "Retrieve" button or the "Add Stored Results Back to In Progress form discussed in section 12.6.

The Print button will print the analytical results of the selected samples. An expanded print capability is discussed in the next section (section 12.4).

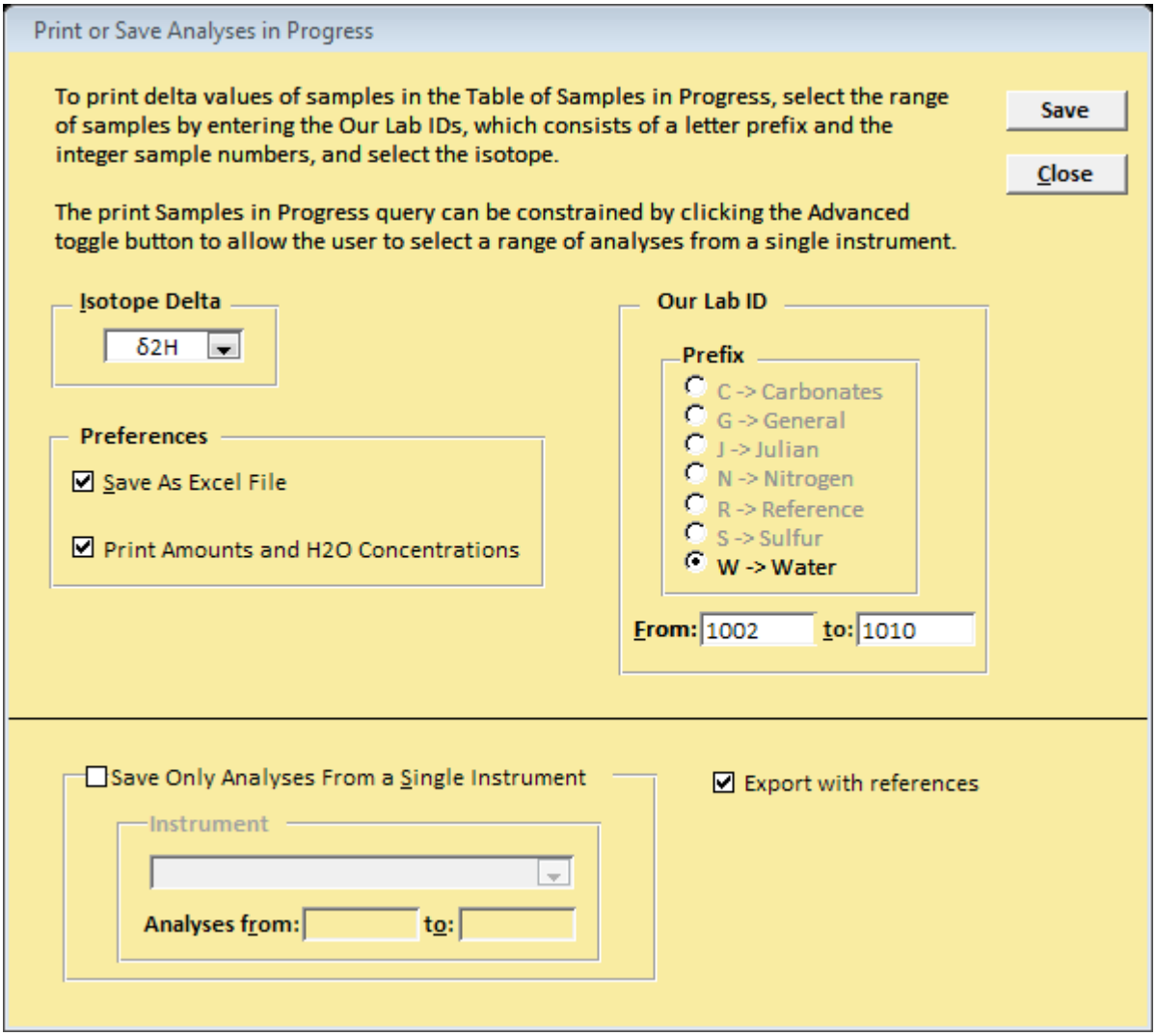
Because *LIMS for Lasers 2015* assigns a new injection number during importing to all δ^{17}O analyses that are 70 plus the injection number of each equivalent δ^{2}H analysis, when evaluating δ^{17}O results, users will observe something similar to the following in which injection numbers from 71 and up are seen for δ^{17}O results.



Date	Analysis	Inj	Vial Position	Rel H2O Conc	Instr Error	Penult δ17O	Hourly Corr	Expans Coef	Add Corr	Final δ17O	IG
8/26/2015	M-12436	71	1_1					1.00000	0.00		☑
8/26/2015	M-12436	72	1_1					1.00000	0.00		☑
8/26/2015	M-12436	73	1_1					1.00000	0.00		☑
8/26/2015	M-12436	74	1_1					1.00000	0.00		☑
8/26/2015	M-12436	75	1_1	4.258		-106.51		1.00000	0.00	-106.51	☐
8/26/2015	M-12436	76	1_1	4.296		-106.58		1.00000	0.00	-106.58	☐
8/26/2015	M-12436	77	1_1	4.277		-108.07		1.00000	0.00	-108.07	☐
8/26/2015	M-12436	78	1_1	4.275		-108.65		1.00000	0.00	-108.65	☐
8/26/2015	M-12436	79	1_1	4.274		-106.64		1.00000	0.00	-106.64	☐
8/26/2015	M-12454	71	1_11					1.00000	0.00		☑
8/26/2015	M-12454	72	1_11					1.00000	0.00		☑
8/26/2015	M-12454	73	1_11					1.00000	0.00		☑
8/26/2015	M-12454	74	1_11					1.00000	0.00		☑
8/26/2015	M-12454	75	1_11	4.295		-107.93		1.00000	0.00	-107.93	☐
8/26/2015	M-12454	76	1_11	4.249		-106.36		1.00000	0.00	-106.36	☐
8/26/2015	M-12454	77	1_11	4.259		-104.54		1.00000	0.00	-104.54	☐
8/26/2015	M-12454	78	1_11	4.278		-107.50		1.00000	0.00	-107.50	☐
8/26/2015	M-12454	79	1_11	4.274		-106.94		1.00000	0.00	-106.94	☐

12.4 Print or Export Samples in Progress

Some analysts prefer to further evaluate results offline using Excel, or print-out detailed summaries for individual samples before they are stored. This is facilitated with the "Print/Export Samples in Progress" button on the main LIMS page, which opens the form below.

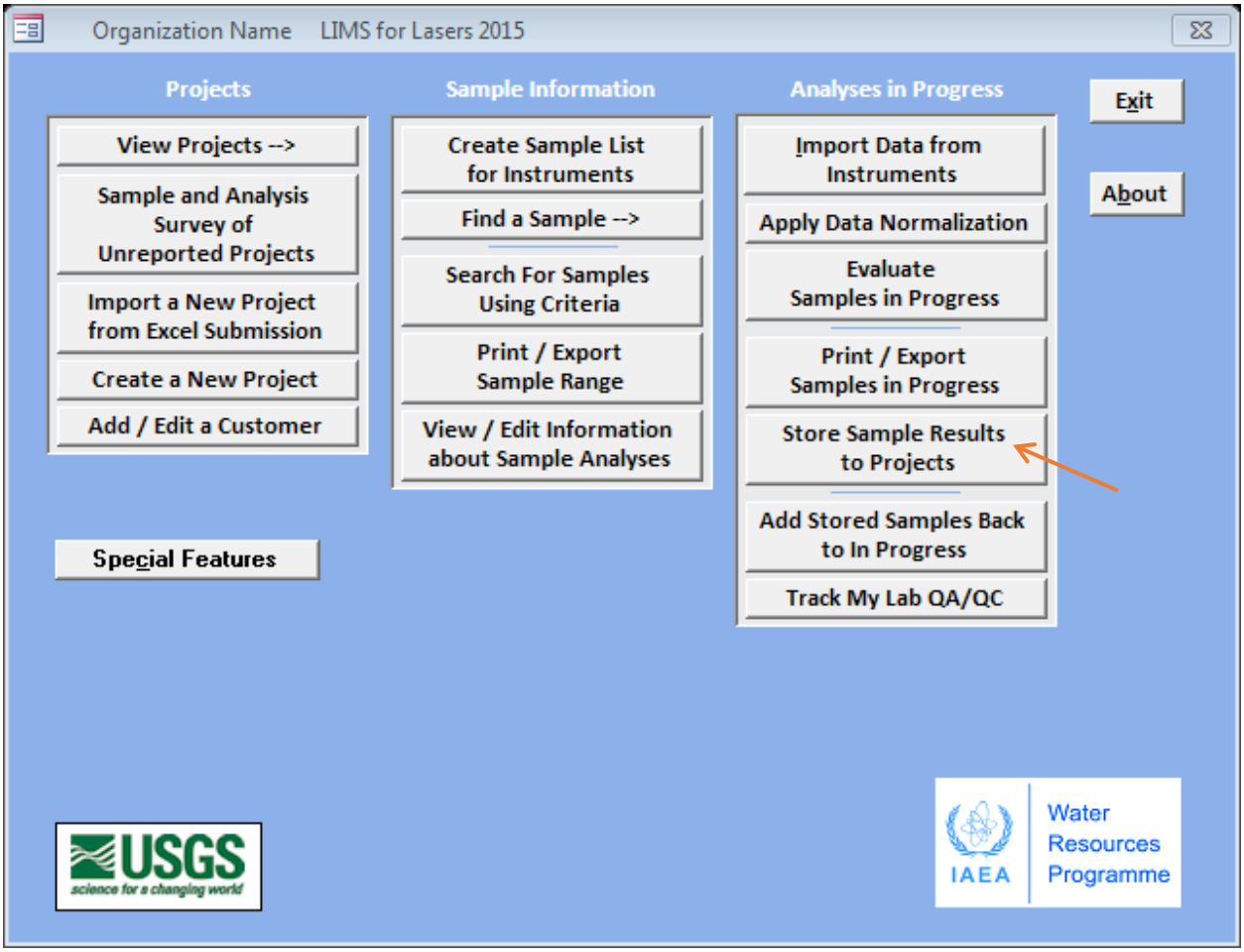


In the above example, all δ^2H analyses of W-1804 to W-1821 can be printed or "Saved" to a spreadsheet for analysis. Optionally, one may select analyses from only one instrument, or include the reference data that accompanied the samples, or (and) include the relative water concentrations recorded in the laser cavity. Some clients want to receive the isotope-delta values of isotopic reference waters analysed with their samples in an Excel file. Checking the "Export with references" box provides this option.

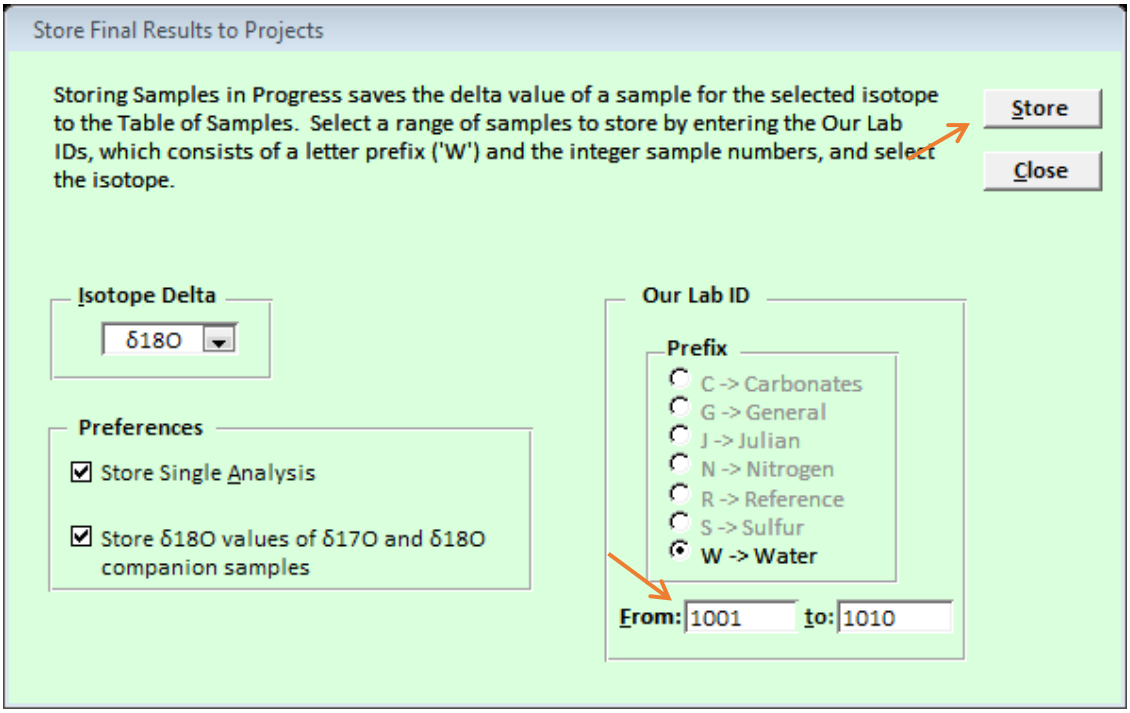
12.5 Store Final Results to Projects

The action of "storing" final results to a Project means that the analyst has normalized all of the samples and controls that were measured, and is satisfied that their results are acceptable within their evaluation criteria.

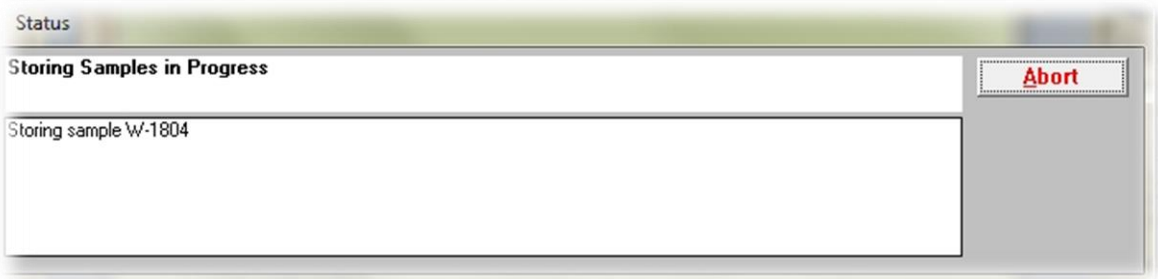
The last step is to "Store" the final results of the samples into the customer Project for final reporting purposes.



1. Click on the "Store Sample Results to Projects" button.
2. In the window that opens, choose the isotope delta (δ^2H or δ^{18}O), and then enter the Our Lab ID range (W-numbers) of the samples to be stored.



3. In the above example, the final δ^{18}O results for samples W-1802 to W-1821 are selected to be "Stored" for reporting. To store a single sample, type its W number in the From box, but leave the To box empty.
4. Click on "Store" and *LIMS for Lasers 2015* shows the samples being stored, and a message indicates its completion.



5. Repeat the process for δ^{2}H using the pull down menu. Then, close the Store Samples page.
6. All samples for hydrogen and oxygen isotopic analysis for the selected range are now stored in Projects for final reporting (Chapter 13).

Important: By default, *LIMS for Lasers 2015* does not store final data unless samples have been analysed twice or more. To override this feature, check the "Store Single Analysis" box – only then will samples analysed only once be stored. Overriding this feature is generally not recommended, but may be used for testing purposes, or in case there was insufficient sample water for a duplicate analysis.

12.6 Add Stored Results Back to In Progress

There may be occasions when stored sample results need to be placed back "In Progress" again. This could be for several reasons:

- Mistaken storage of singly analyzed samples
- Incorrect vials were used and one needs to ignore some of the data
- One has re-evaluated the correction factors and the stored delta values need to reflect these re-evaluations

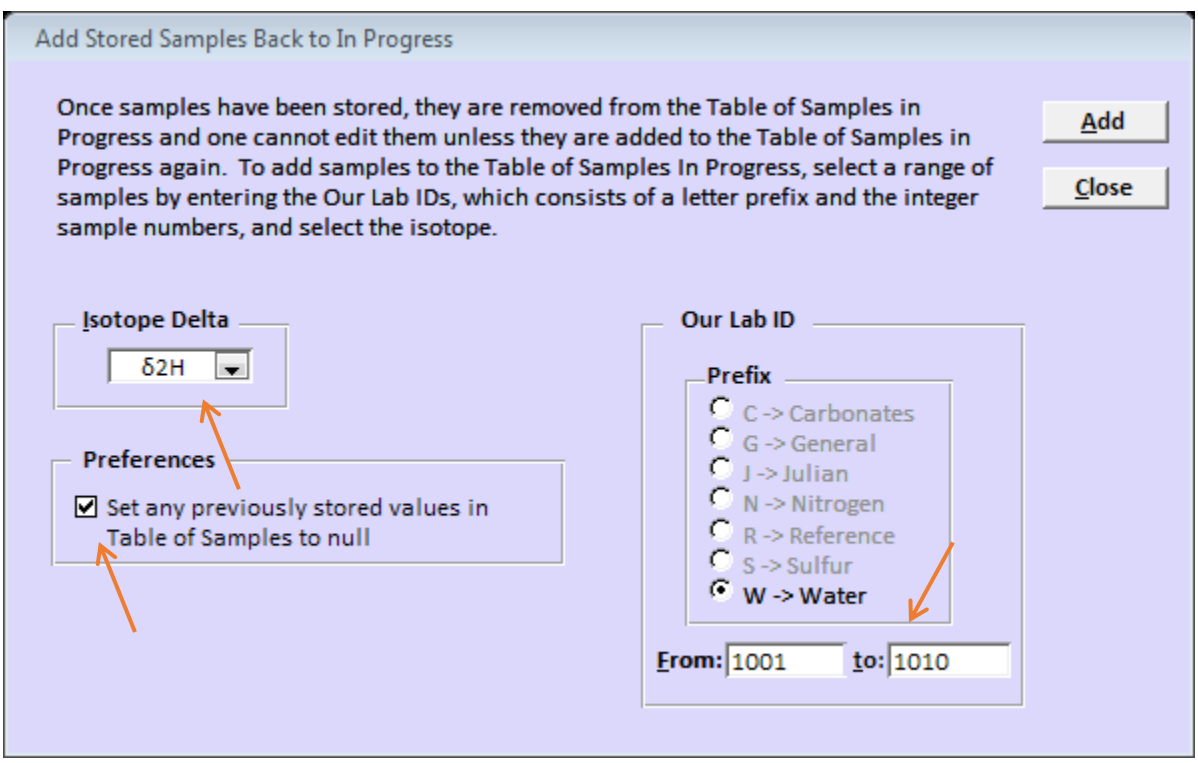
Adding samples back to "In Progress" allows the analyst to re-process the data, correct or ignore errors, or remove faulty data from the client's project. Note: If a sample was already stored and is re-analyzed, *LIMS for Lasers 2015* automatically loads that sample back to "In Progress".

To manually add stored results back to In Progress:

1. On the main page, click "Add Stored Samples Back to In Progress".

2. Choose the isotope delta (δ^2H or δ^{18}O) and then enter the Our Lab ID numbers in the From and To boxes; repeat for the second isotope delta, as needed.

3. Click "Add" – the samples are now In Progress until they are re-stored.



Note: If you mistakenly "Store" data, the Project will retain the incorrect data that was stored. If you want remove incorrect data completely, check the box "Set previously stored values in the Table of Samples to null", then click "Add". This will remove any stored results for the selected "W" numbers.

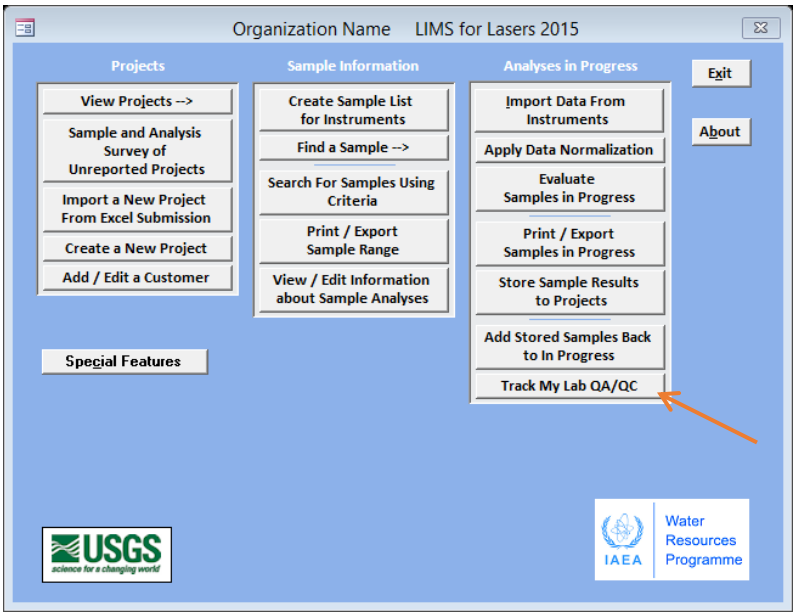
12.7 Track My Lab QA/QC

A key part of data evaluation is to examine results of Controls in each autorun and confirm they agree with known values or results of those control standards over time (usually before storing final results). This QA/QC evaluation is made through the systematic use and monitoring of laboratory control standards, as depicted in the default *LIMS for Lasers 2015* analysis templates.

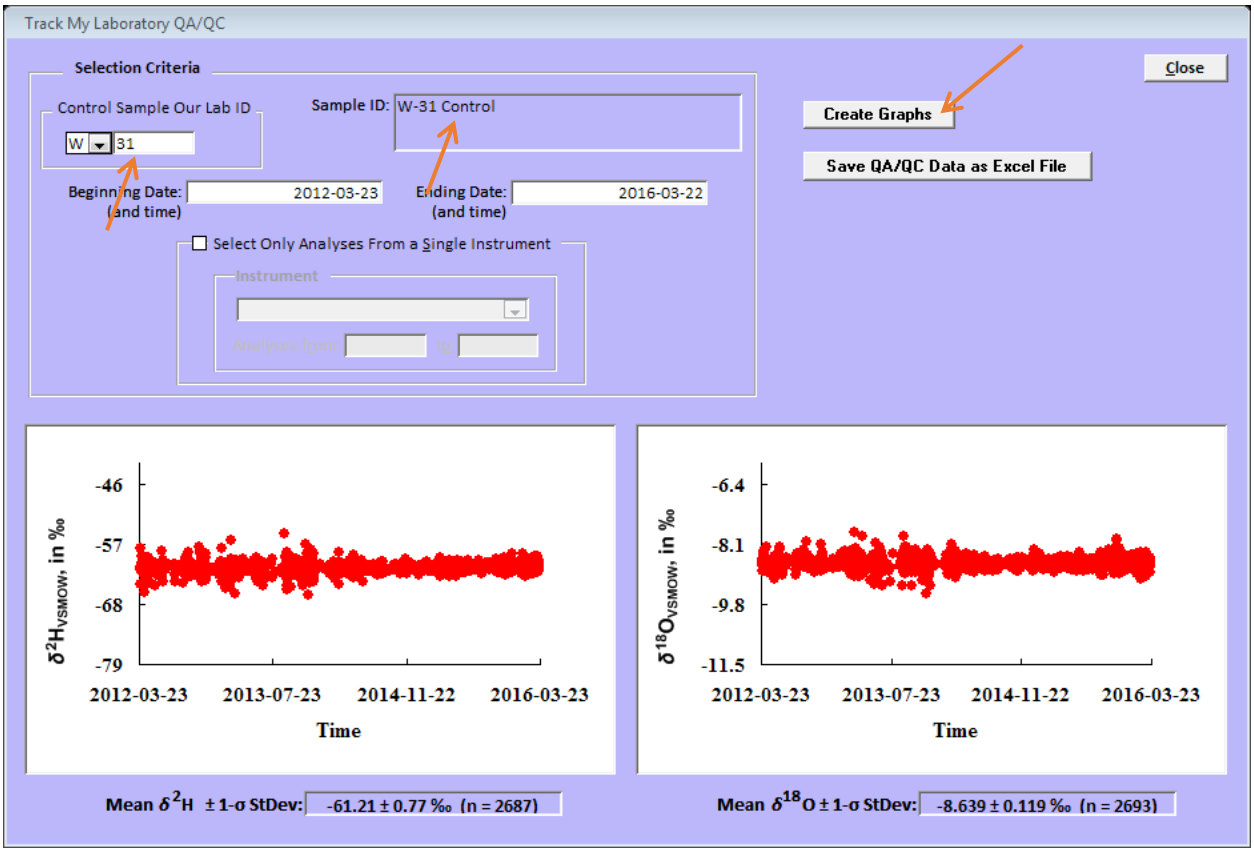
Following each autorun, *LIMS for Lasers 2015* allows evaluation of the control standard. Over time, this assessment provides the analyst with realistic metrics of long-term instrumental precision, and allows one to quickly spot unexpected changes in the control outcomes.

Gradual or abrupt changes in the δ values of a control standard can stem from improper storage of the control water sample or laboratory standards (e.g. inadvertent evaporation), or human error in the laboratory (e.g. mixed-up vials).

1. On the LIMS main page, click on "Track My Lab QA/QC".



2. Enter the Our Lab ID number of the control standard (W-31 in example below).
3. Click any field to accept all of the analyses or to define a range of analysis dates.
4. Optionally, select a specific instrument if the control standard is measured on several instruments (e.g. multiple lasers).
5. Click "Create Graph". *LIMS for Lasers 2015* displays a graphical summary and statistics for the laboratory control standard for the selected search criteria.
6. Examine the graph, or export these data to isolate outliers and to determine a cause (e.g. mixed-up vials).
7. Optionally, the control standard data may be exported to Excel for offline analysis or used for annual reporting of laboratory performance and audits.



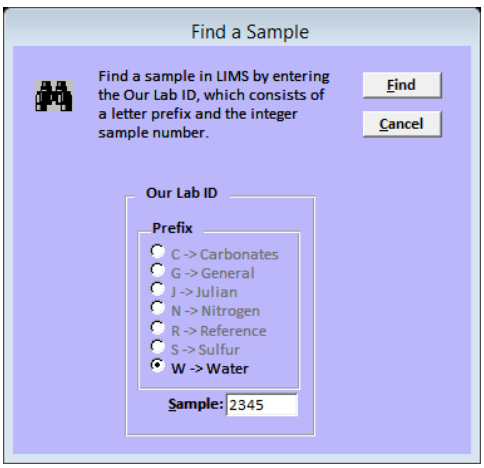
LIMS for Lasers 2015 monitors laboratory performance through the use of control standards.

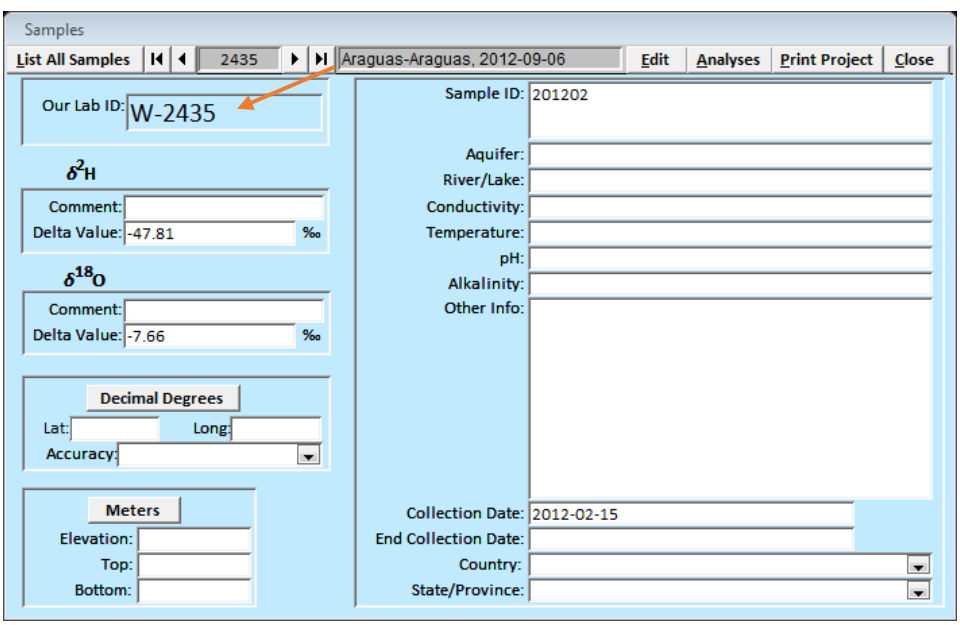
12.8 Query and Edit Sample Results and Information

On the “Sample Information” column of the Main Page of *LIMS for Lasers 2015* are additional querying features that allow the analyst to quickly find information about individual or groups of samples and analyses.

Find a Sample

Click on “Find a Sample” and enter the Our Lab ID “W” number; click “Find”. LIMS returns the page containing that specific sample information, whether it was completed or not.



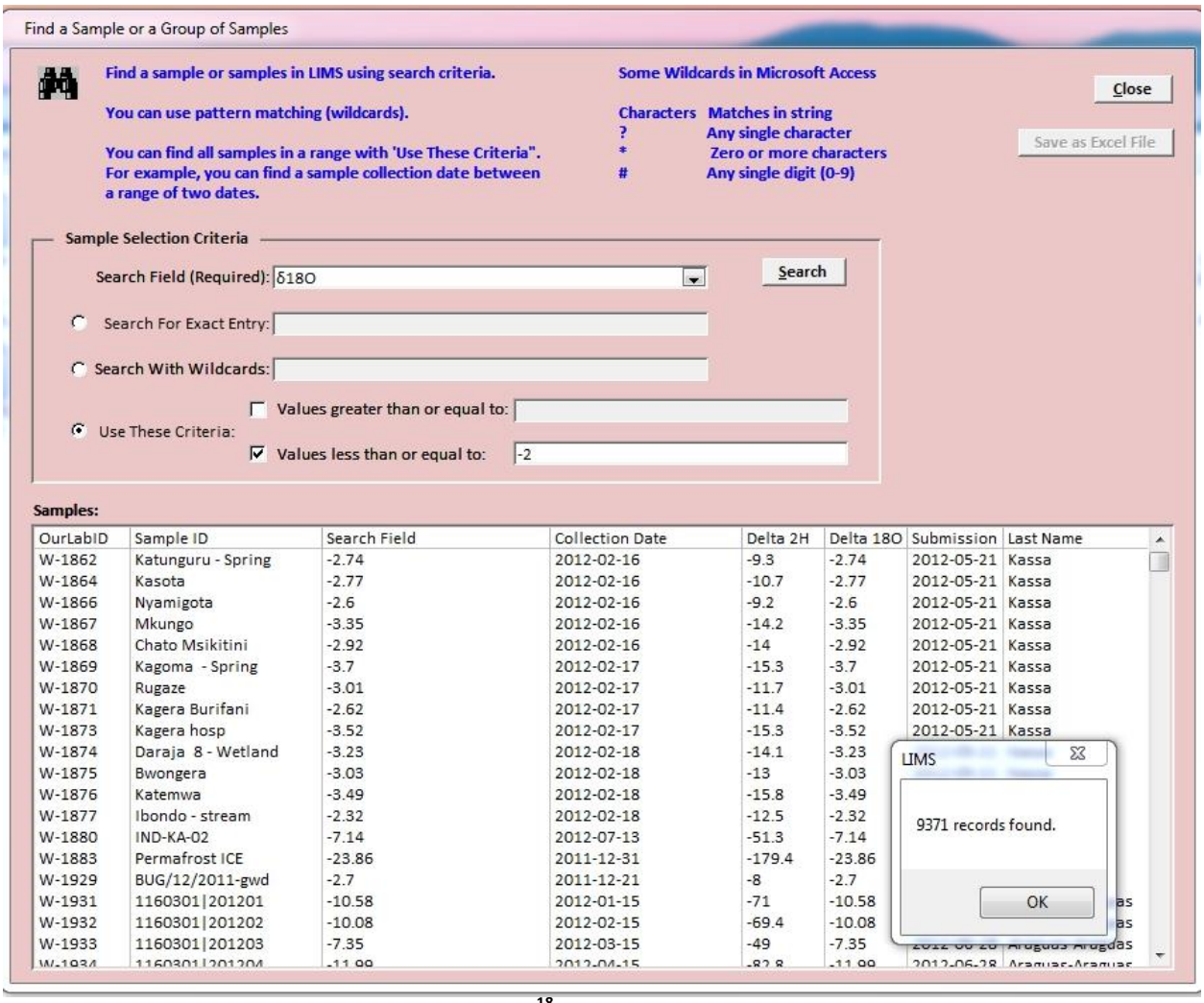


Results of Find a Sample

Find a Sample or Group of Samples Using Criteria

Click on “Find a Sample using Criteria”. Here are a number or options to search for one or all samples in all Projects that meet certain search criteria using text field wildcards or Boolean criteria based on δ values or dates.

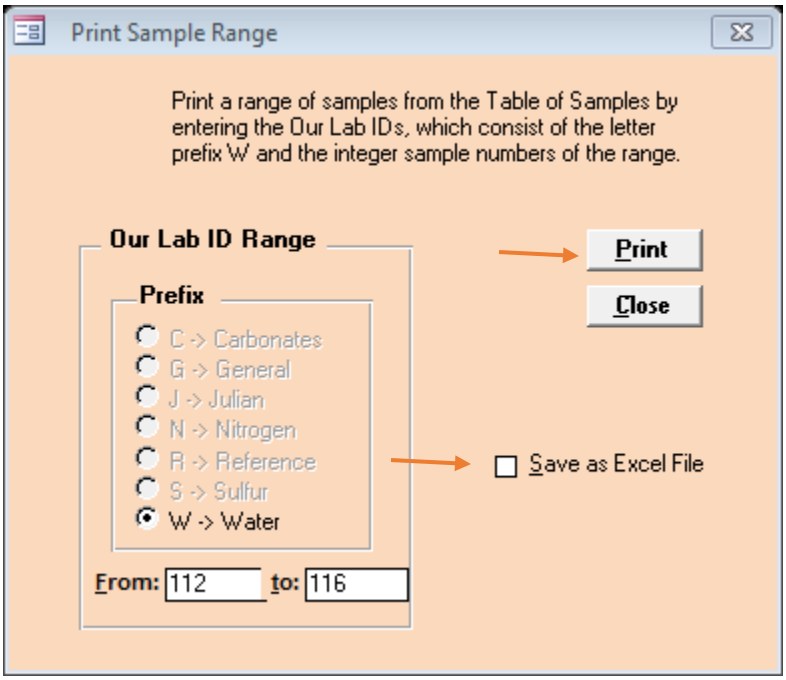
For example, one can quickly locate all data or samples from a specific region, aquifer, or formation regardless of the client, provided the sought information was supplied with the project. These search findings can be saved to Excel.

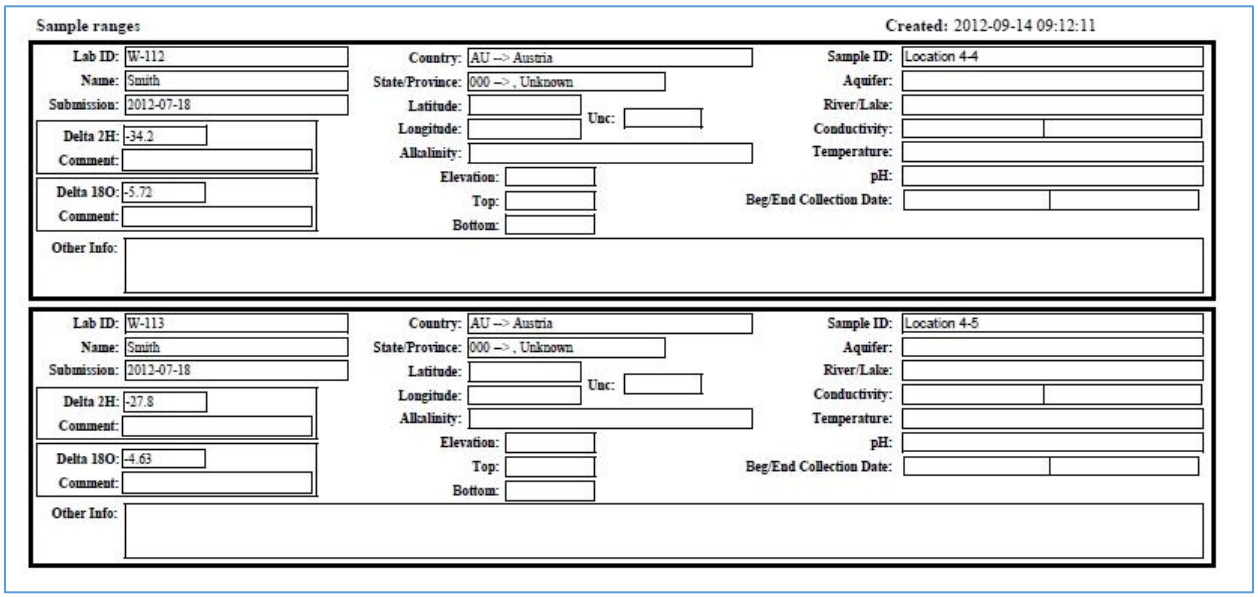


Example search for all samples in all Projects with ^{18}O values less than or equal to -2 ‰.

Print a Sample Range

To print the information and data from a range of samples, Click on “Print Sample Range” and enter the range of “W” numbers, click “Print”. Alternately, the information can also be saved into an Excel file.





Sample ranges — Created: 2012-09-14 09:12:11

Lab ID:	W-112	Country:	AU --> Austria	Sample ID:	Location 4-4
Name:	Smith	State/Province:	000 --> , Unknown	Aquifer:	
Submission:	2012-07-18	Latitude:		River/Lake:	
Delta 2H:	-34.2	Longitude:	Unc:	Conductivity:	
Comment:		Alkalinity:		Temperature:	
Delta 18O:	-5.72	Elevation:		pH:	
Comment:		Top:		Beg/End Collection Date:	
		Bottom:			
Other Info:					

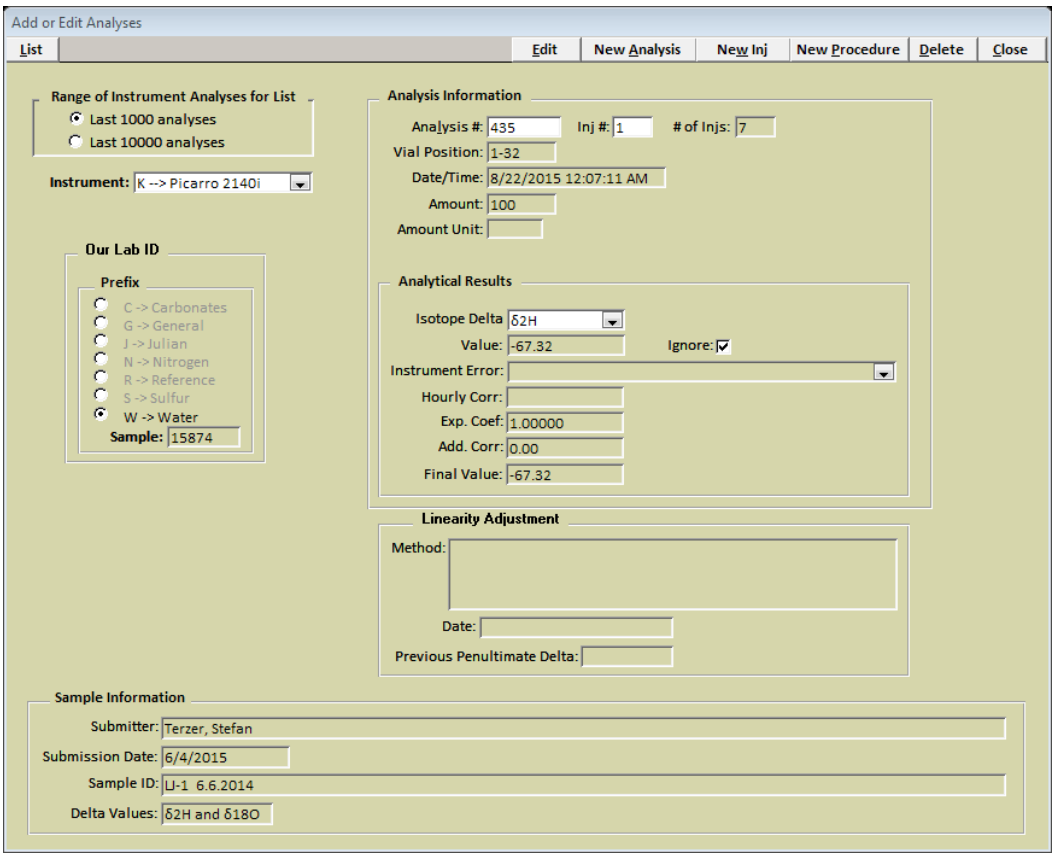
Lab ID:	W-113	Country:	AU --> Austria	Sample ID:	Location 4-5
Name:	Smith	State/Province:	000 --> , Unknown	Aquifer:	
Submission:	2012-07-18	Latitude:		River/Lake:	
Delta 2H:	-27.8	Longitude:	Unc:	Conductivity:	
Comment:		Alkalinity:		Temperature:	
Delta 18O:	-4.63	Elevation:		pH:	
Comment:		Top:		Beg/End Collection Date:	
		Bottom:			
Other Info:					

Example of a one-page printout of a Sample Range.

View / Edit Information about Sample Analyses

Detailed information and an advanced option to directly edit analyses (including single laser injections) can be found by querying a specific sample on the "View / Edit Information about Sample Analyses". All sample details and its isotopic results can be manually edited and saved.

In the example, we can see the 1st injection of Analysis #435 for δ^2H on a Picarro instrument with Prefix ID "K", and it corresponds to analysis of sample W-15874. We also see it was ignored, being 1st of 7 injections.



All of the fields shown above can be manually edited by clicking the "Edit" button, changing the data, and saving the updated information. As noted, these editing options here can be used to edit and change single analyses. One can add a new analysis, new peak (injection), or a new procedure.

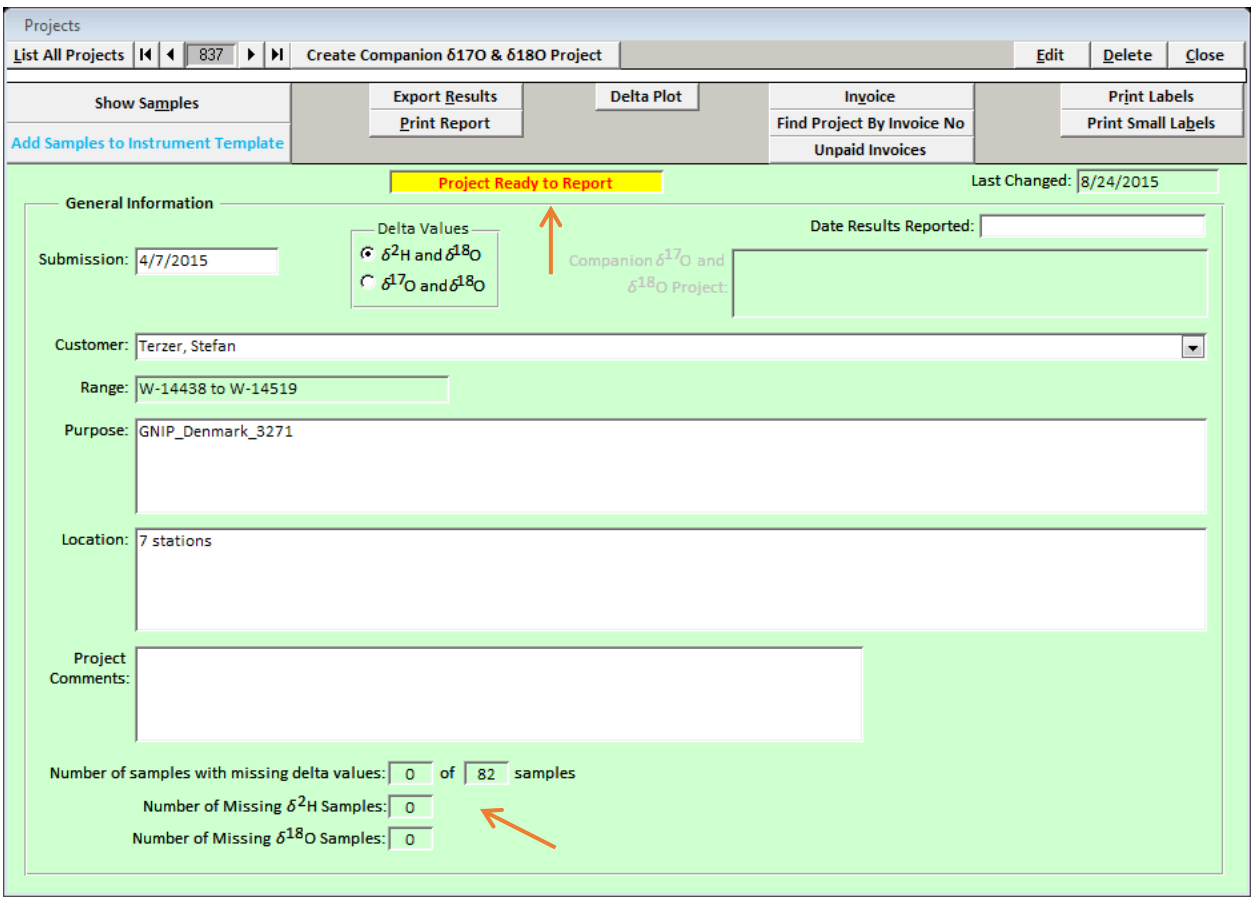
Important: Advanced editing features are intended to facilitate repair of faulty analyses, where the analyst has corrected the data offline. However, an autorun of bad results is better to be repeated, than to be manually edited. *In short, manual editing of sample results is discouraged under normal operation.*

13 Report Isotopic Results

13.1 Report δ^{18}O, δ^{2}H and δ^{17}O Results to the Customer

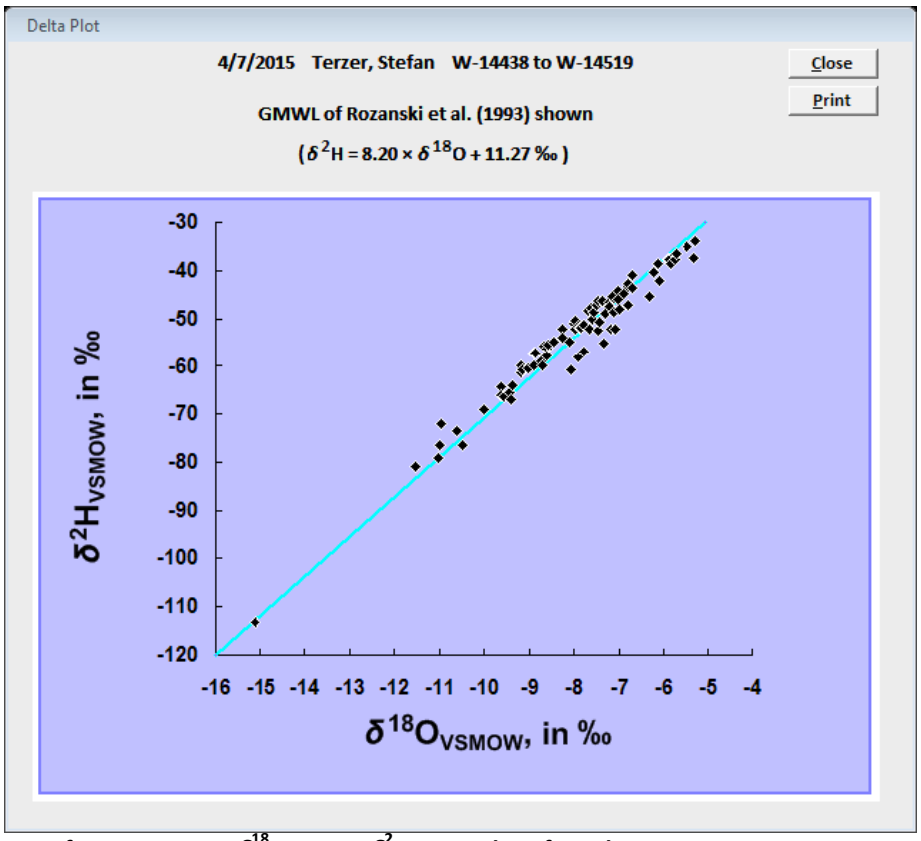
The reporting of final stored δ^{18}O, δ^{17}O and δ^{2}H results to the customer is done from the Projects Page. *LIMS for Lasers 2015* reports the mean value of all sample repeats that have been evaluated, accepted and stored by the analyst. There are a number of options for final reporting. Clients may receive a printed copy or, more typically, results in an Excel spreadsheet.

1. On the main LIMS page, click on "View Projects", then double click on the completed project to be reported. In this example, double clicking on a completed project gave the following screen:



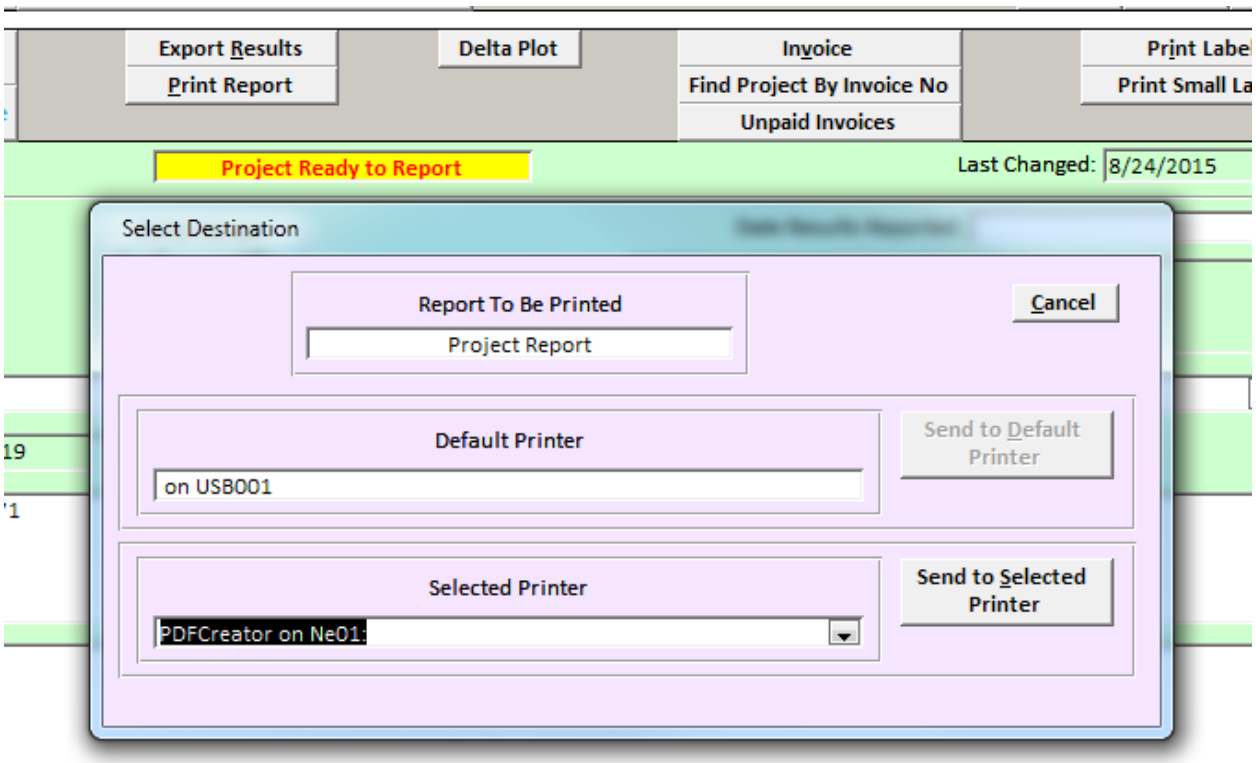
2. Because all samples were measured twice, evaluated, accepted, and stored by the analyst, the project status is shown highlighted in yellow as "Project Ready to Report". The bottom panel of the window shows that 0 of the 23 samples are left outstanding for δ^{18}O or δ^{2}H measurements.

3. Before reporting the final results, one last step is to examine the results using the "Delta Plot" feature. Clicking on the "Delta Plot" button produces a δ^2H versus δ^{18}O cross plot for the Project samples. Be aware the data axes will scale according to the project data. This plot provides a quick means of visualizing the correlation between the two isotope deltas arising from the "global meteoric water line" (GMWL) relationship. Outliers that fall away from the GMWL may be suspect or they may be OK. Non-linear relationships on this plot may result from added isotopic tracers distorting the correlation, natural evaporation, from analysis of landfill samples (δ^2H values can plot substantially above the GMWL), from spectral interferences for which the laser instrument has failed to account (giving a substantially incorrect delta value compared to that measured by IRMS),[2] or when there is little to no isotopic variation in the project samples (axis scaling artifacts).



LIMS for Lasers 2015 δ^{18}O versus δ^2H cross plot of results.

To print the hard copy of a Customer Project report click on "Print Report". The report will print on the default printer, to an optionally selected printer, or to a PDF if a PDF creator is installed.


Export Results
Print Report
Delta Plot
Invoice
Find Project By Invoice No
Unpaid Invoices
Print Labe
Print Small La
Project Ready to Report
Last Changed: 8/24/2015
Select Destination
Report To Be Printed
Project Report
Cancel
Default Printer
on USB001
Send to Default Printer
Selected Printer
PDFCreator on Ne01:
Send to Selected Printer

LIMS for Lasers 2015 Example Report to the Customer

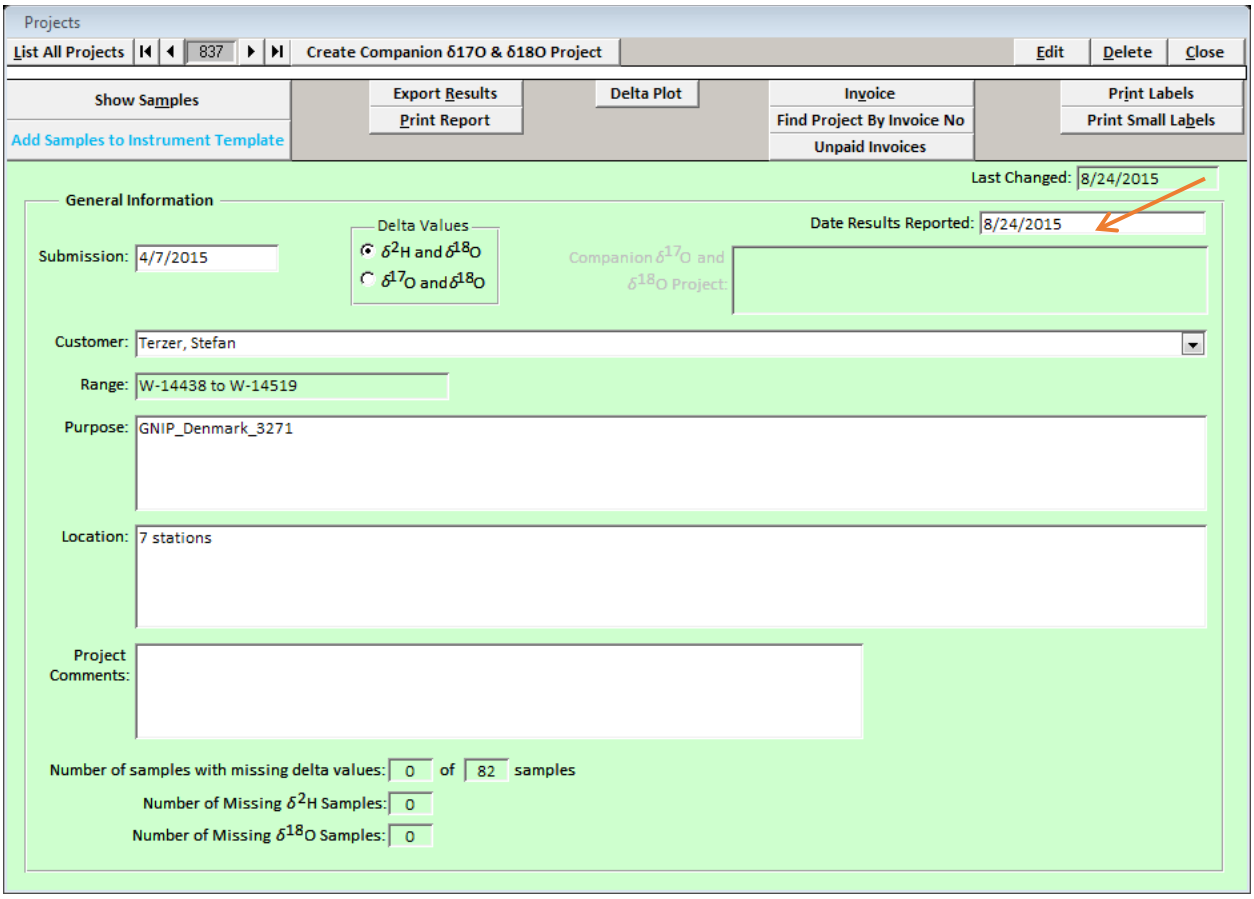
Submission: 2/2/2015 Terzer, Stefan **W-12720 to W-12742** 3/8/2015

Purpose: GNIP_Benin_3231

Location: Bohicon, Kandi, Natitingou

Sample ID:	Collection Date	Our Lab ID	δ^2H_{VSMOW}, in ‰ Value	Comment	$\delta^{18}O_{VSMOW}$, in ‰ Value	Comment
Kandi 201404	4/15/2014	W-12720	1.6		-1.19	
Kandi 201405	5/15/2014	W-12721	-20.0		-4.36	
Kandi 201406	6/15/2014	W-12722	-3.7		-2.05	
Kandi 201407	7/15/2014	W-12723	-8.1		-2.58	
Kandi 201408	8/15/2014	W-12724	-24.9		-4.58	
Kandi 201409	9/15/2014	W-12725	-37.0		-6.43	
Kandi 201410	10/15/2014	W-12726	-23.6		-4.35	
Bohicon 201403	3/15/2014	W-12727	-2.3		-1.41	
Bohicon 201404	4/15/2014	W-12728	-8.6		-2.96	
Bohicon 201405	5/15/2014	W-12729	-44.5		-7.43	
Bohicon 201406	6/15/2014	W-12730	-32.3		-5.88	
Bohicon 201407	7/15/2014	W-12731	-23.1		-4.37	
Bohicon 201408	8/15/2014	W-12732	-20.6		-4.36	
Bohicon 201409	9/15/2014	W-12733	-31.0		-5.01	
Bohicon 201410	10/15/2014	W-12734	-34.1		-5.81	
Bohicon 201411	11/15/2014	W-12735	-13.0		-3.08	
Natitingou 201403	3/15/2014	W-12736	9.6		0.28	
Natitingou 201404	4/15/2014	W-12737	-6.2		-2.43	
Natitingou 201405	5/15/2014	W-12738	-17.9		-3.56	
Natitingou 201406	6/15/2014	W-12739	-17.0		-3.58	
Natitingou 201407	7/15/2014	W-12740	-6.8		-2.43	
Natitingou 201408	8/15/2014	W-12741	-6.7		-2.47	
Natitingou 201409	9/15/2014	W-12742	-27.5		-4.73	

4. To export the Project results to an Excel file, click on “Export Results”. LIMS asks where you want to save the Excel file and gives it the default name of the first occurrence of the Our Lab ID in the project (e.g. W-12720.XLS for example above). This file can be emailed to the customer.
5. LIMS will automatically fill in the “Date Reported” field of the Customer Project.


Projects
List All Projects
837
Create Companion δ17O & δ18O Project
Edit
Delete
Close
Show Samples
Add Samples to Instrument Template
Export Results
Print Report
Delta Plot
Invoice
Find Project By Invoice No
Unpaid Invoices
Print Labels
Print Small Labels
Last Changed: 8/24/2015
General Information
Date Results Reported: 8/24/2015
Submission: 4/7/2015
Delta Values
δ2H and δ18O
δ17O and δ18O
Companion δ17O and δ18O Project:
Customer: Terzer, Stefan
Range: W-14438 to W-14519
Purpose: GNIP_Denmark_3271
Location: 7 stations
Project Comments:
Number of samples with missing delta values: 0 of 82 samples
Number of Missing δ2H Samples: 0
Number of Missing δ18O Samples: 0

13.2 Combine Results from Multiple Projects

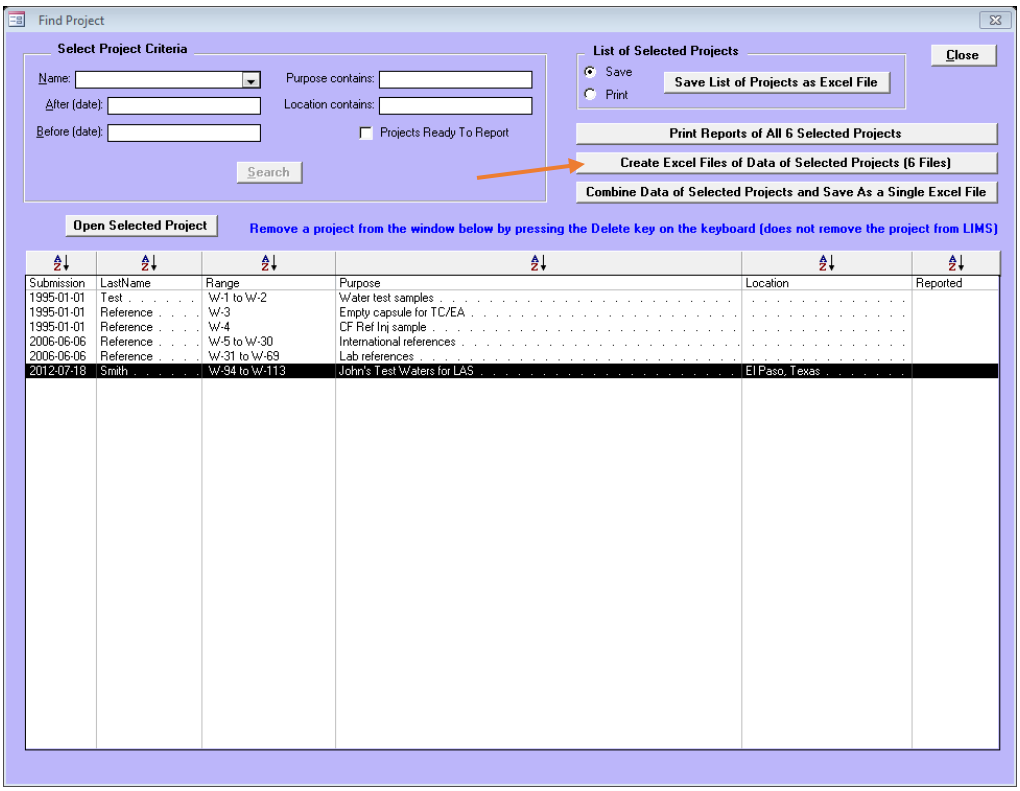
Occasionally, a Customer may have several projects, or may request results in a single Excel file, rather than in multiple spreadsheets or printed reports.

After *LIMS for Lasers 2015* accumulates client projects, use the search function described in Chapter 6.2 to search for the client project(s). After the search results are displayed, click on any of the following options:

Print Reports of All # Selected Projects – this prints hard copies of all of the projects appearing in the search result window.

Create Excel Files of Data of Selected Projects (# Files) – this creates individual Excel files for all of the projects resulting in the search window.

Combine Data of Selected Projects and Save as a Single Excel File – this combines the sequential data of the projects in the search result window into a single Excel file, the Excel default name is the lowest W number (e.g. W-1001.xls).

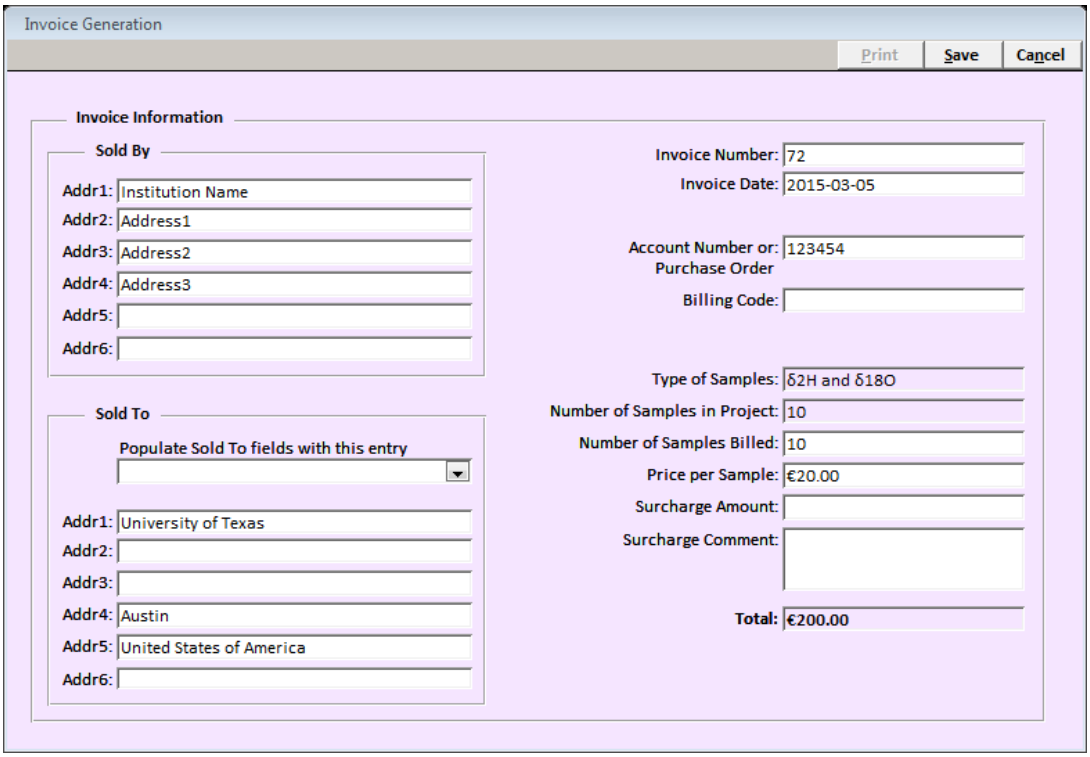


Note: To delete a Project from a search result, highlight it and enter the delete key. Only the search is deleted, not the Project itself.

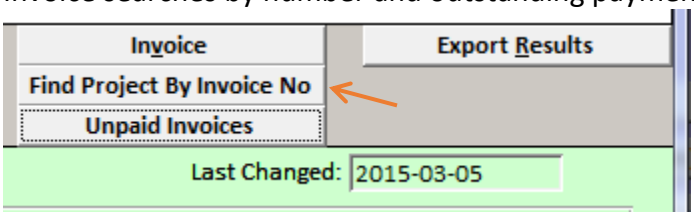
13.3 Project Invoicing

Some laboratories may want *LIMS for Lasers 2015* to generate a Customer invoice. Assuming the user has checked the "Display Invoices" box on the Options form (see Chapter 4.6), one can perform the following steps.

1. In the "View Project" pane, open the customer project to be invoiced.
2. In the Project page, click on the "Invoice" button.
3. Click "Edit". This automatically fills in previously supplied Customer information in *LIMS for Lasers 2015.*
4. Complete the Sold By and Sold To fields. Enter the price per sample.
5. Print the invoice.



Invoice searches by number and outstanding payment are found on the main Project page:



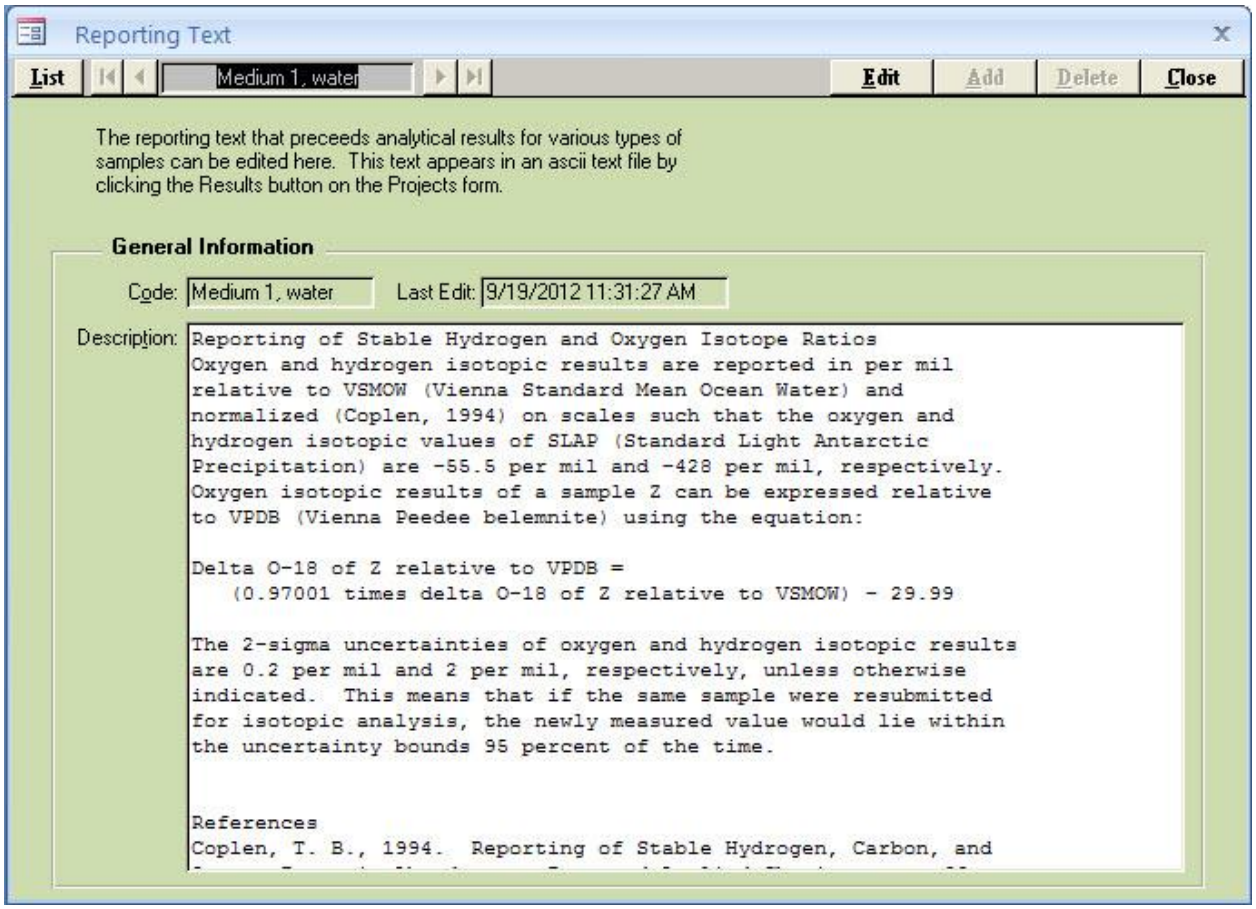
***Note*:** The currency format on this form is obtained from the Windows Control Panel -> Regional Settings on your PC.

13.4 Export to ASCII file with Reporting Text

On the Project page, clicking on “Export Results” shows the option to export to ASCII text. While few Clients prefer ASCII over an Excel file, it allows for an additional option – the inclusion of frequently requested additional textual analysis and laboratory information.

This additional information may be about methods used or the statistics of the laboratory.

1. In LIMS main page, click on “Special Features”
2. Open “Reporting Text”.
3. Click on “Add”.
4. Enter descriptive information – this information will appear as a header on the ASCII exported project data.



An example of Reporting Text for the ASCII data export.

14 Sources and Calibration of Local Laboratory Standards

14.1 Sources of Primary Water Isotopic Reference Materials

VSMOW2 and SLAP2 are the currently available primary measurement reference standards for water isotopes. They are available from the IAEA at the following Web link: http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable_Isotopes/2H18O-water-samples/index.htm

Information Sheet

on the

new International Measurement Standards

VSMOW2 and SLAP2

VSMOW2 Vienna Standard Mean Ocean Water 2
SLAP2 Standard Light Antarctic Precipitation 2

The two reference materials VSMOW2 and SLAP2 were produced to replace the exhausted reference materials VSMOW and SLAP. Their isotopic compositions for both δ^2H and δ^{18}O were adjusted to be as close as possible to the predecessor materials. The reference values were assessed from data measured by three laboratories in a calibration exercise measuring the δ^2H and δ^{18}O data of VSMOW2 and SLAP2 in direct reference to those of VSMOW and SLAP (Table 1). The stated combined standard uncertainties are evaluated from the measurement uncertainties in the laboratories for the involved materials and the assessment of isotopic homogeneity of the prepared ampoules of VSMOW2 and SLAP2.

Table 1: δ^2H and δ^{18}O reference values for the two international measurement standards VSMOW2 and SLAP2 and their associated combined standard uncertainties.

IAEA name	Material	Reference value $10^3\ \delta^2H_{VSMOW/SLAP}$	Combined standard uncertainty $10^3\ \delta^2H_{VSMOW/SLAP}$	Reference value $10^3\ \delta^{18}O_{VSMOW/SLAP}$	Combined standard uncertainty $10^3\ \delta^{18}O_{VSMOW/SLAP}$
VSMOW2	Water	**0.0**	**0.3**	**0.00**	**0.02**
SLAP2	Water	**– 427.5**	**0.3**	**– 55.50**	**0.02**

In order to calibrate and normalize any measurement to the VSMOW – SLAP scale (especially for the calibration of internal laboratory water standards), one uses the formula below (Gonfiantini, 1978). In that formula the measured values for the new international measurement standards VSMOW2 and SLAP2 have to be entered instead of those of VSMOW and SLAP, as well as the corresponding new calibrated δ_{SLAP2} value for SLAP2 from Table 1:

$$\delta = ((R_{sample} / R_{VSMOW2}) - 1) \cdot \delta_{SLAP2} / ((R_{SLAP2} - R_{VSMOW2}) / R_{VSMOW2})$$

By using this procedure all data are still reported on the VSMOW/SLAP scale, despite the use of VSMOW2 and SLAP2 for their calibration. Of course the standard uncertainties of VSMOW2 and SLAP2 isotopic values should be included as uncertainty component in any combined uncertainty statement of measurements performed.

It is recommended to clearly state in any publication, that the calibration was performed using VSMOW2 and SLAP2.

IAEA Isotope Hydrology Laboratory, 20 June 2007

InfoSheet-VSMOW2-SLAP2.doc

14.2 Source of Daily-Use Measurement Standards

U.S. Geological Survey

Users may purchase cases of 144 glass ampoules each containing 5 mL of calibrated secondary daily-use measurement standards. The recommendation is that ampoules with two substantially different δ values be opened daily and used for data normalization and a third intermediate delta value water can be used as a control standard. Unused water from the ampoule should be discarded. Use of these working reference waters aids a laboratory in achieving high level QA/QC levels.

- Cases of 144 glass ampoules each containing 5 mL of calibrated water in a variety of isotopic compositions.
- VSMOW is a primary measurement reference standard for water isotopes. VSMOW (25 mL, provided in five 5-mL autoclaved glass ampoules; see http://isotopes.usgs.gov/lab/referencematerials/VSMOW.pdf)
- All are available from the USGS at the following Web link: (see http://isotopes.usgs.gov/lab/referencematerials.html):

USGS45	Case of 144 ampoules having 4 mL of Biscayne Aquifer Drinking Water per ampoule	576 mL	$835	$\delta^2H = -10.3$ ‰ $\delta^{18}O = -2.238$ ‰	USGS45
USGS45	Case of 144 ampoules having 5 mL of Biscayne Aquifer Drinking Water per ampoule	720 mL	$874	$\delta^2H = -10.3$ ‰ $\delta^{18}O = -2.238$ ‰	USGS45
USGS46	Case of 144 ampoules having 4 mL of Ice Core Water per ampoule	576 mL	$835	$\delta^2H = -235.8$ ‰ $\delta^{18}O = -29.80$ ‰	USGS46
USGS46	Case of 144 ampoules having 5 mL of Ice Core Water per ampoule	720 mL	$874	$\delta^2H = -235.8$ ‰ $\delta^{18}O = -29.80$ ‰	USGS46
USGS47	Case of 144 ampoules having 5 mL of Lake Louise Drinking Water per ampoule	720 mL	$874	$\delta^2H = -150.2$ ‰ $\delta^{18}O = -19.80$ ‰	USGS47
USGS48	Case of 144 ampoules having 5 mL of Puerto Rico Precipitation per ampoule	720 mL	$874	$\delta^2H = -2.0$ ‰ $\delta^{18}O = -2.224$ ‰	USGS48

International Atomic Energy Agency – Water Resources Section

The IAEA provides daily use laboratory standards to member states through its Technical Cooperation (TC) programs. Please consult the IAEA Web site or TC officer.

14.3 Analysis Templates for Calibrating Local Measurement Standards

LIMS for Lasers 2015 is provided with 20-sample Analysis Templates for the δ^{18}O and δ^{2}H calibration of daily-use (or in-house) laboratory measurement standards. These analysis templates use the primary reference standards VSMOW and SLAP (or VSMOW2 and SLAP2), measured along with sufficient replicates of the proposed local laboratory standards. New templates using primary reference standards can also be constructed using the *LIMS for Lasers 2015* analysis template wizards (Chapter 8.4 and 8.5).

Each proposed daily-use δ^{18}O and δ^{2}H laboratory measurement standard should be measured 10-times, or more, against these isotopic reference standards in order to provide sufficient data to determine measurement uncertainty. It is good practice to have other laboratories measure your proposed laboratory standards for external verification before assigning their assigned delta values in the *LIMS for Lasers 2015* table of references.

Table 3. Template for Calibration of Laboratory Standards using Los Gatos Research Instrument

In this template, 20 laboratory standards are arranged sequentially in Tray 1. As shown, 10 each of two proposed laboratory measurement standards are arranged sequentially. The primary reference standards VSMOW & SLAP (or VSMOW2 & SLAP2) and wash samples are arranged in Tray 3 (rear tray) each in their own row. The recommended procedure is 9 injections per sample, ignoring the first 4 injections. List # is the order which samples are analysed.

Sample	Vial Pos	List #	LIMS for Lasers 2015 Function
Deionized Water	3-19	1	Instrument Conditioning
Deionized Water	3-19	2	Instrument Conditioning
VSMOW / VSMOW2	3-10	3	Between-Sample Memory
SLAP / SLAP2	3-1	4	Between-Sample Memory
SLAP / SLAP2	3-2	5	VSMOW-SLAP Normalization
Lab Std High δ	1-1	6	Sample
Lab Std High δ	1-2	7	Sample
Lab Std High δ	1-3	8	Sample
Lab Std High δ	1-4	9	Sample
Lab Std High δ	1-5	10	Sample
SLAP / SLAP2	3-1	11	Between-Sample Memory
VSMOW / VSMOW2	3-11	12	Between-Sample Memory
VSMOW / VSMOW2	3-10	13	VSMOW-SLAP Normalization
Lab Std High δ	1-6	14	Sample
Lab Std High δ	1-7	15	Sample

Lab Std High δ	1-8	16	Sample
Lab Std High δ	1-9	17	Sample
Lab Std High δ	1-10	18	Sample
VSMOW / VSMOW2	3-11	19	Between-Sample Memory
SLAP / SLAP2	3-2	20	Between-Sample Memory
SLAP / SLAP2	3-1	21	VSMOW-SLAP Normalization
Lab Std Low δ	1-11	22	Sample
Lab Std Low δ	1-12	23	Sample
Lab Std Low δ	1-13	24	Sample
Lab Std Low δ	1-14	25	Sample
Lab Std Low δ	1-15	26	Sample
SLAP / SLAP2	3-2	27	Between-Sample Memory
VSMOW / VSMOW2	3-10	28	Between-Sample Memory
VSMOW / VSMOW2	3-11	29	VSMOW-SLAP Normalization
Lab Std Low δ	1-16	30	Sample
Lab Std Low δ	1-17	31	Sample
Lab Std Low δ	1-18	32	Sample
Lab Std Low δ	1-19	33	Sample
Lab Std Low δ	1-20	34	Sample
VSMOW / VSMOW2	3-10	35	Between-Sample Memory
SLAP / SLAP2	3-1	36	Between-Sample Memory
SLAP / SLAP2	3-2	37	VSMOW-SLAP Normalization
Deionized Water	3-19	38	End Wash

Table 4. Template for Calibration of Laboratory Standards using Picarro Instruments.
In this template, 20 laboratory standards are arranged sequentially with VSMOW-SLAP (or VSMOW2-SLAP2) in the autosampler. Ten each of the two proposed laboratory standards are arranged between reference groupings. The recommended analysis procedure is 9 injections per sample, ignoring the first 4 injections. List # is the order which samples are analysed.

Sample	Vial Pos	List #	LIMS for Lasers 2015 Function
VSMOW / VSMOW2	1-01	1	Between-Sample Memory
SLAP / SLAP2	1-02	2	Between-Sample Memory
SLAP / SLAP2	1-03	3	VSMOW-SLAP Normalization
Lab Std High δ	1-04	4	Sample
Lab Std High δ	1-05	5	Sample
Lab Std High δ	1-06	6	Sample
Lab Std High δ	1-07	7	Sample
Lab Std High δ	1-08	8	Sample
SLAP / SLAP2	1-09	9	Between-Sample Memory
VSMOW / VSMOW2	1-10	10	Between-Sample Memory
VSMOW / VSMOW2	1-11	11	VSMOW-SLAP Normalization
Lab Std High δ	1-12	12	Sample
Lab Std High δ	1-13	13	Sample
Lab Std High δ	1-14	14	Sample
Lab Std High δ	1-15	15	Sample
Lab Std High δ	1-16	16	Sample
VSMOW / VSMOW2	1-17	17	Between-Sample Memory
SLAP / SLAP2	1-18	18	Between-Sample Memory
SLAP / SLAP2	1-19	19	VSMOW-SLAP Normalization
Lab Std Low δ	1-20	20	Sample
Lab Std Low δ	1-21	21	Sample
Lab Std Low δ	1-22	22	Sample
Lab Std Low δ	1-23	23	Sample
Lab Std Low δ	1-24	24	Sample
SLAP / SLAP2	1-25	25	Between-Sample Memory
VSMOW / VSMOW2	1-26	26	Between-Sample Memory
VSMOW / VSMOW2	1-27	27	VSMOW-SLAP Normalization
Lab Std Low δ	1-28	28	Sample
Lab Std Low δ	1-29	29	Sample
Lab Std Low δ	1-30	30	Sample
Lab Std Low δ	1-31	31	Sample
Lab Std Low δ	1-32	32	Sample
VSMOW / VSMOW2	1-33	33	Between-Sample Memory
SLAP / SLAP2	1-34	34	Between-Sample Memory
SLAP / SLAP2	1-35	35	VSMOW-SLAP Normalization

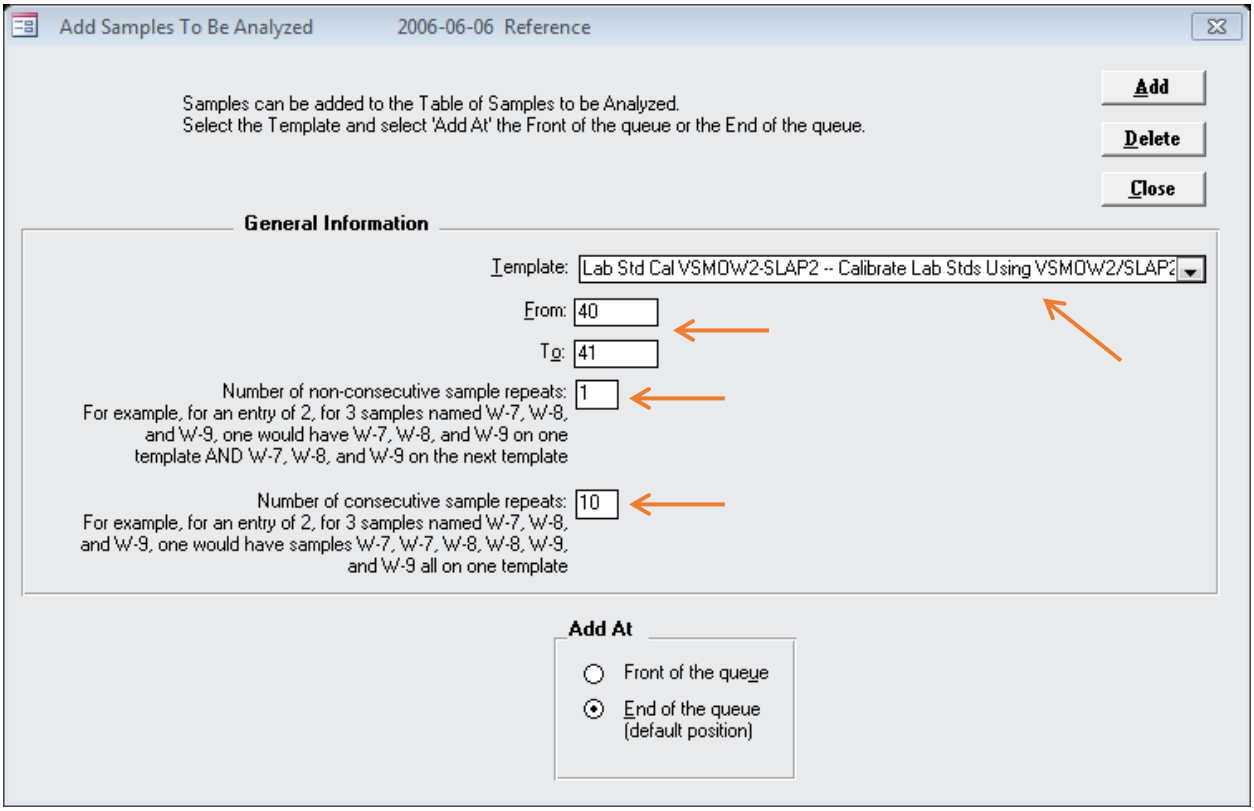
14.4 Calibration Template Procedures

Recall from Chapter 7.1 that *LIMS for Lasers 2015* is provided with a Project called "Lab references", containing placeholders for new local laboratory measurement standards that range from Our Lab ID W-31 to W-69.

In this example, the two new local laboratory standards to be calibrated against VSMOW2-SLAP2 were assigned Our Lab ID values of W-40 and W-41 (see Chapter 7.2 for editing and renaming existing placeholders for laboratory standards).

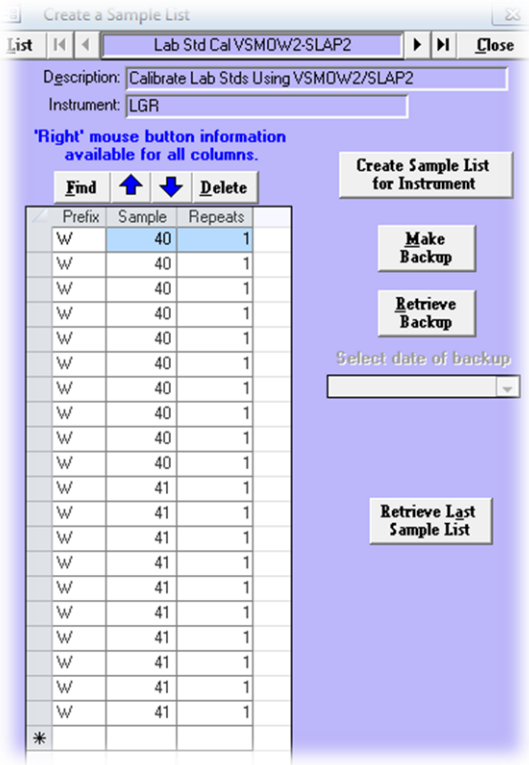
For Los Gatos Research Instruments:

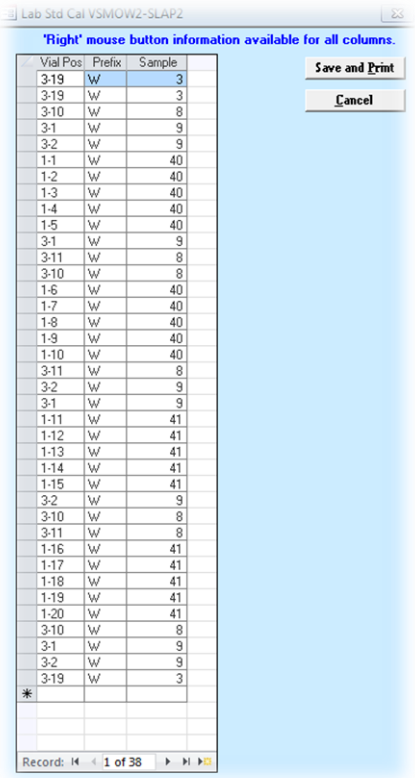
1. On LIMS Main Page click "View Projects"
2. Open the Project called "Lab References"
3. Click on "Template List – Add or Remove Samples"



4. We will calibrate local laboratory standards W-40 and W-41 using the VSMOW2 and SLAP2 primary reference waters. From the template pull down menu (see above), choose the VSMOW2-SLAP2 Analysis Template (or VSMOW-SLAP if using those primary reference materials).

5. In the From and To boxes, enter 40 and 41, respectively.
6. Set the number of non-consecutive repeats to 1 (each will be analysed once).
7. Set the number of consecutive repeats to 10 (each sample will be analysed 10 times in a row as shown in Table 3).
8. Click “Add”, then “Close”.
9. On the *LIMS for Lasers 2015* Main Page, Click “Create Sample List for Instruments”.
10. From the pull down menu, choose the VSMOW2/SLAP2 Analysis Template.
11. In the window that opens (below), we see W-40 and W-41 are now queued to be analysed 10 times each in sequence.
12. Click “Create the Sample List” and save it to the Los Gatos Research instrument (see Chapter 10).
13. Measure the proposed laboratory standards as unknowns on the Los Gatos Research instrument (Chapter 10). Their δ values should be set to –999 ‰ if they exist in the Table of References (Chapter 7.3). Normalize, evaluate, and store the results, as fully described in Chapter 12.
14. Once completed, and you are satisfied that your local measurement standards have been sufficiently characterized, you may assign their δ values in the Table of References (Chapter 7.3).
15. Create new analysis templates for samples based on your new local laboratory measurement standards (Chapter 8).

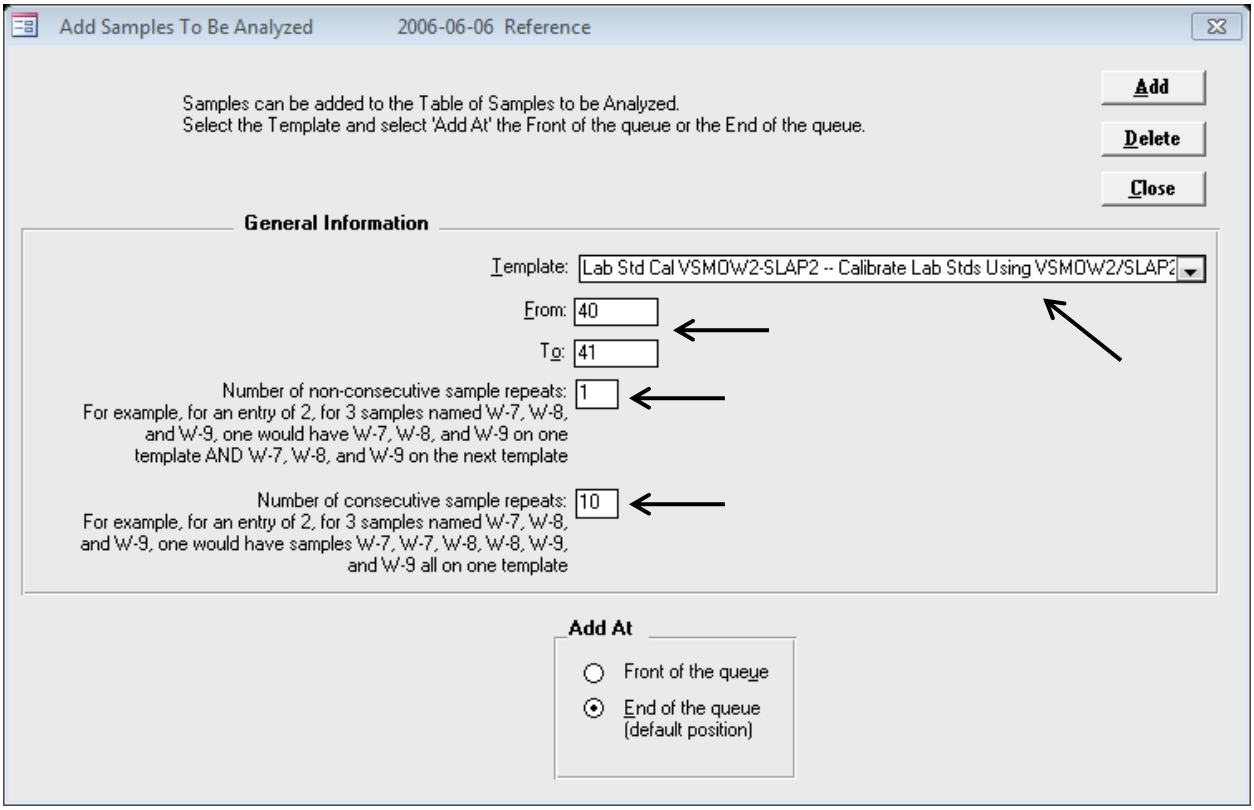




Proposed laboratory measurement standards to be analysed against VSMOW2 (W-8) and SLAP2 (W-9) using a Los Gatos Research instrument. The measurement sequence on the right matches the Analysis Template in Table 3. W-3 is a wash or conditioning sample.

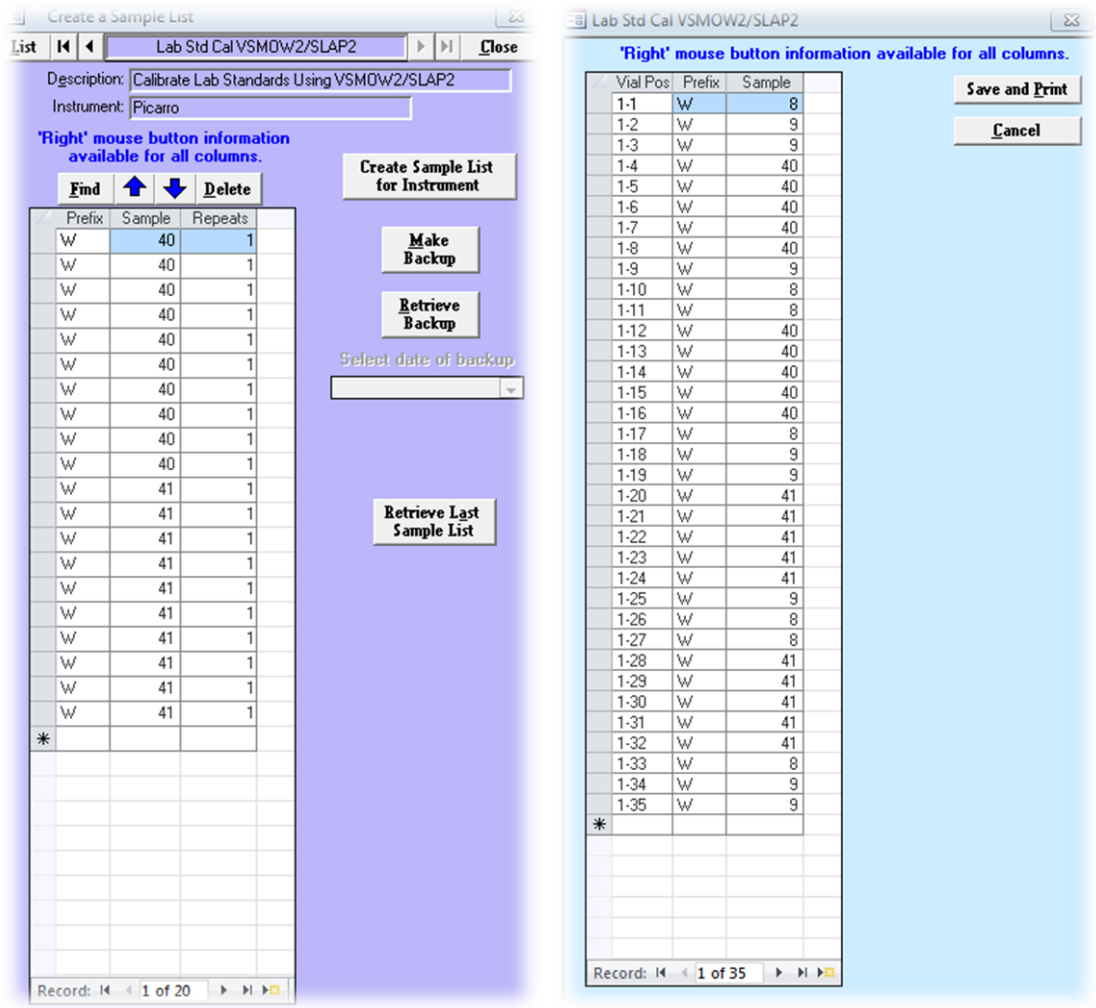
For Picarro Instruments:

1. On the LIMS Main Page, click “View Projects”
2. Open the Project called “Lab References”
3. Click on “Template List – Add or Remove Samples”



4. We will calibrate laboratory standards W-40 and W-41 using VSMOW2 and SLAP2 reference waters. From the template pull down menu, select the Lab Std Cal VSMOW2-SLAP2 analysis template.
5. In the From and To boxes, enter 40 and 41, respectively.
6. Set the number of non-consecutive repeats to 1 (each will be analysed once).
7. Set the number of consecutive repeats to 10 (each is measured 10 times as in Table 4).
8. Click “Add”, then “Close”.
9. On the *LIMS for Lasers 2015* Main Page, Click “Create Sample List for Instruments”.
10. From the pull down menu, choose the VSMOW2-SLAP2 Analysis Template.
11. On the window that opens, we see W-40 and W-41 are queued to be analysed 10 times each.
12. Create the Sample List, and save it to the Picarro (see Chapter 9)
13. Measure the samples and primary standards on the Picarro instrument (Chapter 9). Their δ values should be set to –999 ‰ if they exist in the Table of References (Chapter 7.3). Normalize, evaluate and store the final results, as described in Chapter 12.

14. Once completed and you are satisfied that your new local measurement standards have been sufficiently characterized, you may assign their δ values in the Table of References (Chapter 7.3).
15. Create new measurement templates using your new laboratory standards (Chapter 8).



Proposed laboratory measurement standards to be analysed against VSMOW2 (W-8) and SLAP2 (W-9) on a Picarro. The measurement sequence on the right matches the Analysis Template in Table 4.

15 Spectral Contamination, FAQs, Log Files

15.1 Salt Build-up & Spectral Contamination

Liquid water samples from the natural environment (e.g. surface water, groundwater, lakes) usually contain dissolved ionic species (e.g. TDS, Ca, Mg, Cl^-, HCO_3, etc.), or may have dissolved organic matter or volatile organic compounds (e.g. DOM, VOC, hydrocarbons) present. The concentrations of such dissolved constituents varies widely in nature, ranging from nearly pure water in glaciers or rainfall (µg/L levels), to hyper-saline ponds (g/L levels), or petroleum contaminated groundwater containing a complex mixture of semi- and volatile-organic compounds. Other water test samples may be from extracts of water from plants (high DOM/VOC), or from soil pore water (high DOM or TDS), and may contain unknown VOCs.

There are two main areas of water sample introduction where the dissolved constituents of water samples can cause problems for laser spectrometry:

- *Build-up of inorganic and organic salt in the injector unit*. Aside from the usual jamming of the syringe, salt build-up is a known issue discussed in all of the user manuals. The remedy is periodic washing and cleaning of the heated water injector module interface, or on an as-needed basis. The build-up of salts can cause H_2O transfer line blockage (manifested in lowered or variable H_2O yields), or since some dehydrated salts have a strong affinity for water, isotopic fractionation may occur through dynamic sorption of injected sample water with increasing salt buildup in less heated portions of the injector unit or sample transfer line.

- *Spectral contamination though the incorporation of volatile organic compounds in the laser cavity*. The compromise of sample H_2O isotopic molecular spectra can occur through the introduction of interfering gaseous molecules in samples which absorb or distort the H_2O isotopologue spectra. Some volatile organics (VOCs) that cause spectral problems are alcohols and hydrocarbons like methane or ethane [12,139]. Others have observed spectral contamination from mixed VOCs from plant and leaf water extracts, or landfill leachates [14,15]. Importantly, it may not be possible to predict *a priori* the magnitude of the negative impact that DOC or VOC may have on H_2O laser isotopic analysis without explicit research and knowledge of the molecular absorption properties of the contaminant.[2]

Currently, Los Gatos Research and Picarro provide users with offline software to assess, and in some cases attempt to correct for, spectral contamination through the development of spectral libraries in their *Spectral Contamination Identifier Software™* or *ChemCorrect* ™ software, respectively (see the respective manufacturer Web site for details). The screening output of this software is mainly in the form of a QA/QC "flag" or table, to assess and inform users if samples are OK or not, and to possibly identify what the interfering contaminant(s) might be. Neither of these spectral assessment programs are currently built-in to the laser instrument operational

software used to generate *LIMS for Lasers 2015* output files, thus, additional offline screening effort is required on the part of the laser analyst.

In short, users of laser instruments must be vigilant to inorganic and organic characteristics of unknown water samples they are analysing in order to obtain correct results. Generally, low TDS/DOC waters pose little concern for laser assays. However, when doubtful samples are being considered (high DOC, VOC, salty), it may be prudent to check and clean the injector more frequently, or pre-screen the autorun results through offline spectral software *before* importing data analysis output files into *LIMS for Lasers 2015*. Samples identified by spectral-screening software as being "compromised" may be safely ignored after they are first imported into *LIMS for Lasers 2015*. Other courses of action are to measure or repeat suspect samples by conventional IRMS techniques, if available. In situations where results must be correct, such as forensic science applications, water samples should be verified by isotope-ratio mass spectrometry (IRMS). [2]

15.2 Frequently Asked Questions

Q. Why is *LIMS for Lasers 2015* responding slowly on our networked PCs?

A. When the *LIMS for Lasers 2015* backend database resides on a network drive, slow network bandwidth can cause delayed performance response. One solution is to locate the backend database on a fast network drive, preferably Gigabit speed or better hardware.

Another reason is concurrent users of *LIMS for Lasers 2015*. Relational databases like MS Access lock fields opened by a concurrent user and cannot be accessed until the user has completed the edits. Another common slowdown occurs when another user has inadvertently left open a search or edit screen (e.g. locked tables). To avoid this, be sure to always close *LIMS for Lasers 2015* when you are finished using it.

Q. Why do you recommend measuring every sample twice? This seems unnecessary.

A. Our default approach of running each sample twice is a conservative approach allows one to assess the reproducibility of every sample, not just the control standard and measurement standards. Alternately, users may choose to repeat none, 1 in 10 or 1 in 5 samples, or add more controls. This is a performance and evaluation assessment decision and is easily over-ridden as described in the Analysis Templates section.

Q. Why are 9 injections recommended? Our laser manual recommends 6 injections, ignore 3.

A. As noted in Chapter 8, 8–9 injections per sample is a conservative recommendation to ensure the best results are obtained from *all* generations of laser instruments. The newest laser instruments may indeed require fewer injections and/or ignored results. Whether outcomes differ significantly can be tested by comparing default *LIMS for Lasers 2015* recommendations with those of the same run but using fewer injections and fewer ignored injections. Using fewer injections, you may find precisions worsen and between-sample memory percentage higher. Ultimately, each lab has to establish what will be their acceptable performance criteria.

Q. I decided to conserve laboratory standard consumption by using only 1 vial instead of the recommended 3 vials per standard on the default LGR instrument template. Now *LIMS for Lasers 2015* does not calculate the between-sample memory. What happened?

A. This is normal. LGR and Picarro instruments assume "consecutive samples" with the same vial position are same analysis number. You must therefore alternate vial positions for two or more consecutively identical lab standards in order for them to be treated as different samples. Otherwise between-sample memory cannot be determined in *LIMS for Lasers 2015*.

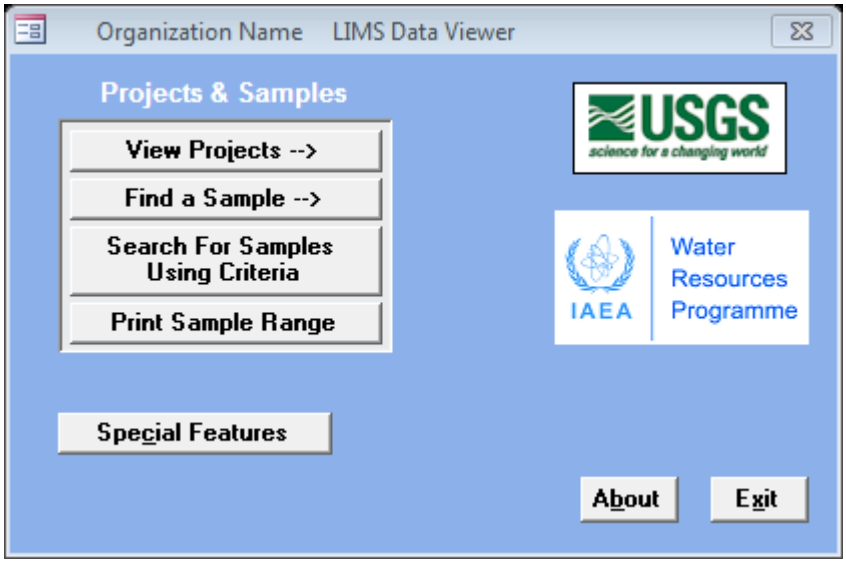
Q. I am stuck. Who can I contact for help with *LIMS for Lasers 2015*?

A. If you have carefully followed the procedures outlined in this manual and are still having trouble, please contact the authors (TBC or LIW) by email (tbcoplen@usgs.gov or l.wassenaar@iaea.org). We may request that you ZIP and email your backend database (in confidence) so that we can help troubleshoot your issue.

16 LIMS Data Viewer Utility

16.1 LIMS Data Viewer

The *LIMS Data Viewer* (*v.*11.02 or later) is an optional utility that can be used in trusted teams, departmental settings, or laboratory group settings. This utility allows network-connected laboratory clients (e.g. co-workers, PIs, colleagues, managers) to access the laboratory backend database (*LIMS for Lasers* v.10 or *LIMS for Light Stable Isotopes* v.9) from their own desktops, but without any capacity to edit or alter information in the database.



This simplified, *read-only,* viewing utility is for convenience, and it may be used by trusted laboratory clients to:

- View and extract current laboratory workload and client projects.
- View their projects and analysis status.
- Download or export project data to Excel or print a report.
- Reduce their need for emailing or phoning the laboratory concerning sample or project status.

Note: The utility is for use in trusted settings because the Viewer gives client access to all of the Projects in the LIMS database. Full viewing access may not be appropriate in all settings or where projects are deemed confidential.

16.2 Computer and Software Requirements

Required:

- Computer running Windows XP or later
- Microsoft Office 2007, 2010, 2013 or 2016 Pro (with Access) for Windows, installed
- Network access to the isotope laboratory LIMS backend database

Software:

- The *LIMS Data Viewer v11.02,* or later

The *LIMS Data Viewer* can be downloaded at no cost from the IAEA or USGS Web sites:

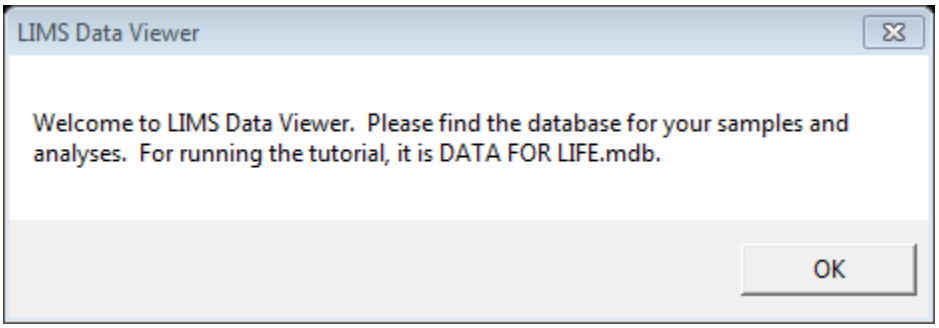
http://www-naweb.iaea.org/napc/ih/IHS_resources_sampling.html#lims
http://isotopes.usgs.gov/research/topics/lims.html

16.3 Installation

1. Download and extract the *LIMS Data Viewer* to your desktop (or a folder). Ensure Microsoft Office 2007 or Office 2010–16 (32-bit) with Microsoft Access is installed. Ensure Access has the Viewer file location added as a Trusted Location (see Chapter 3.1).

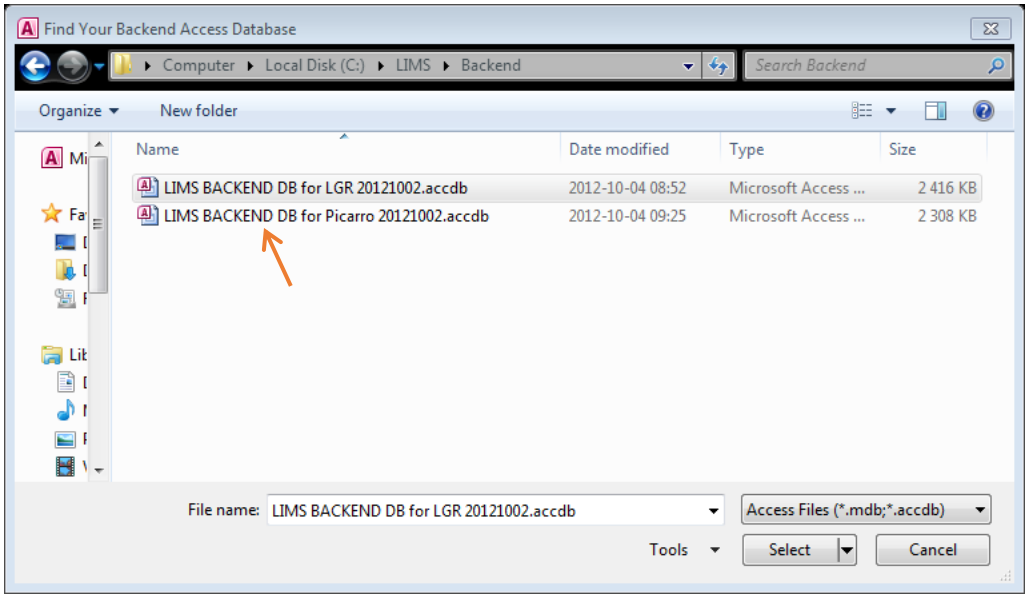
2. Double click to open the file "LIMS Data Viewer.accdb".

3. The following message will appear, requesting the location of the laboratory LIMS backend database:

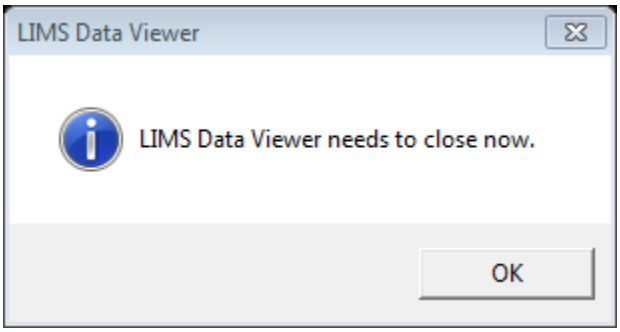


4. Click "OK", and use the file dialog to navigate to the backend database location, *as provided by your isotope laboratory manager or administrator*. This may be a network location or a mapped network drive. As an example below, C:\LIMS\Backend, the "Select" the backend database.

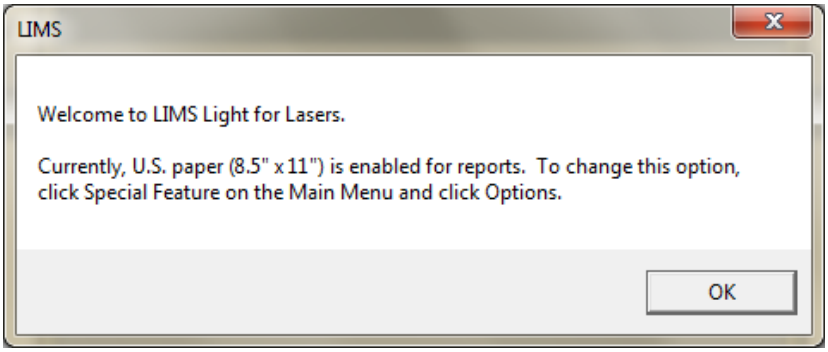
Note to Laboratory Managers: It may be prudent to provide client access to a synchronized copy of the laboratory LIMS database on a different network drive, rather than use the original database file.

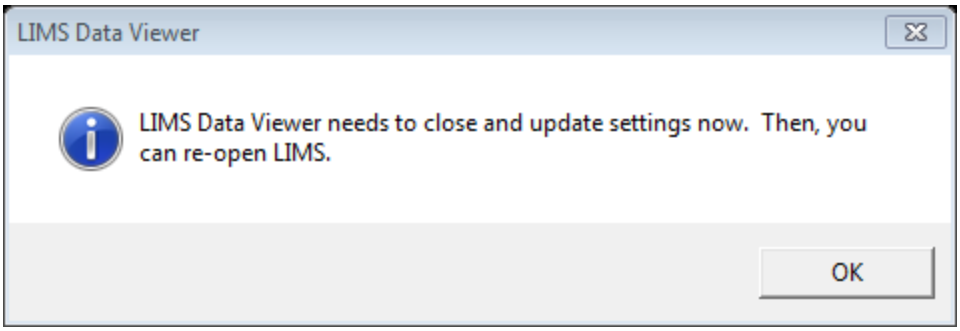


5. Next, the *LIMS Data Viewer* needs to close. Click "OK" (a security warning may pop up if Trusted Locations were not setup):

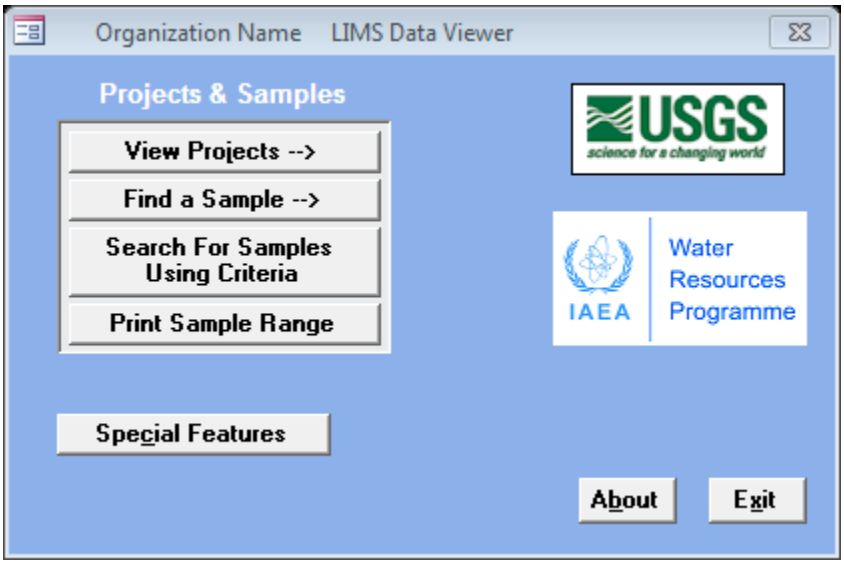


6. Double click to re-open the file "LIMS Data Viewer.accdb". Click "OK" to the next 2 dialog boxes, and re-open "LIMS Data Viewer.accdb" a final time.





7. The *LIMS Data Viewer* is now successfully installed. This should be your screen upon start up:



LIMS Data Viewer - Main Page.

In order to use the utility, the Projects, Find a Sample, Search, Printing, and Special Features are fully described in Chapters of the *LIMS for Lasers* user manual, with the restriction that no fields may be edited or modified. Not all menus will be visible, and some are inaccessible in the *LIMS Data Viewer*.

View Projects – To view, print or export data. Review appropriate sections of Chapter 13.
Find a Sample – Review appropriate sections of Chapter 12.8
Search for Samples Using Criteria – Review Chapter 12.8
Print Sample Range – Review Chapter 12.8
Special Features – Set printer defaults and change the location of the backend database – Review Chapter 4

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User Manual Change Notes

Nov 12, 2012 to v 1.1

- Added new section 15.3 on spectral contamination pre-cautions and corresponding literature citations.
- Added the minimum O/H per mil difference required for adjacent standard vials in order to correctly obtain between memory corrections in LIMS for Lasers (in Chp. 8.2).
- Added LGR question on between-sample memory to FAQ when using one reference vial per laboratory standard.
- Reorganized Chapter 15.

Dec 13, 2012 to v 1.2

- Added Chapter 16 on LIMS Data Viewer.

Jan 3, 2013 to v 1.3

- Minor edits and precautions added to page 63 & 68 on the duplicating and editing of templates.

June 28, 2013 to v 1.4

- Minor typos, figure updates, and addition of Appendix 1 guide to optimize templates for G2000 series liquid autosampler for Picarro 20xx series laser spectrographs.

September 23, 2013 to v 1.5

- Minor typo updates.
- Added reset stored data to null values update to Section 12.6.
- Added Appendix 2.

September 10, 2015 to v 2.0

- Completely revised for LIMS for Lasers 2015 user manual.

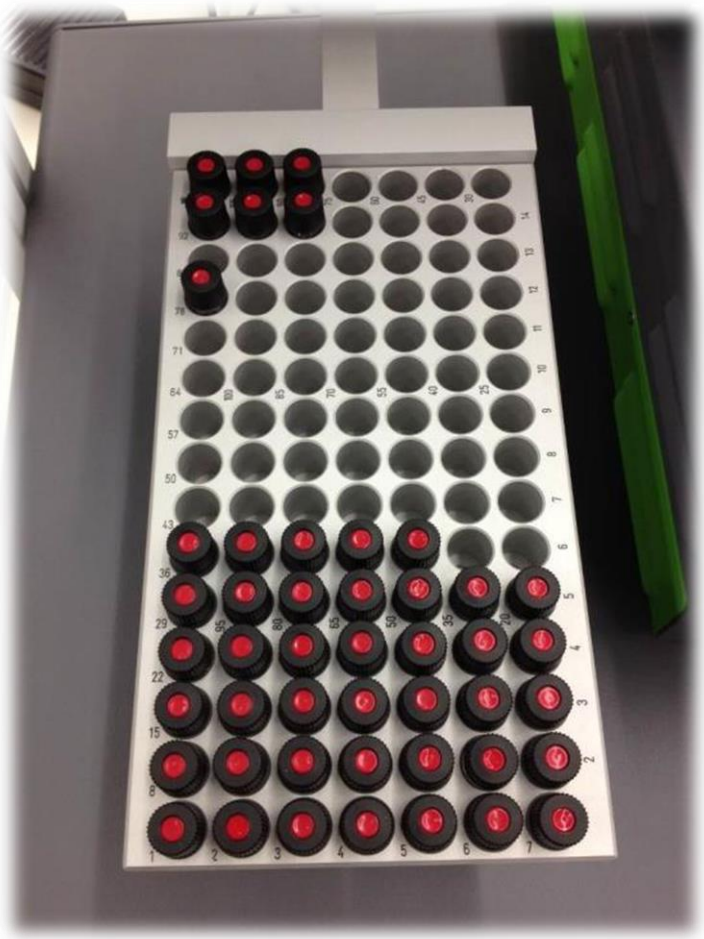
March 21, 2016 to v 2.1

- Revised introduction, minor updates to some text and figures.
- Addition of new import screening tools.
- Added explanation of bracketed normalization.

Appendix 1 Picarro G2000 Autosampler Templates

The introduction of the G2000 liquid autosampler on Picarro instruments in 2012 added software control and more flexibility than the CTC PAL unit. The figures below demonstrate a sample tray layout where unknowns are sequentially placed at the front of the tray, and the measurement standards and control standard (or wash) are located at the back of the tray. This layout is more convenient than having to intersperse laboratory standard vials amongst samples, and it facilitates the between-sample memory and drift corrections in *LIMS for Lasers 2015*.

40 Sample Layout (Tray Position)



Hi, Lo, Lo Standards (99,100, 101)
Lo, Hi, Hi Standards (92, 93, 94)

Control Standard (optional, or end of run wash vial) (78)

|
|
|
|
|
Samples in positions (1 to …40)
|
|
|
|

The G-2000 autosampler software configuration corresponding to the 40-sample layout shown in the above figure is given below, here showing 7 injections per sample.

The primary software constraint is the 10 line Sequence limitation, and each of these lines must contain sequentially sampled vials. Thus the Hi/Low laboratory standard triplets must be defined in single rows (see Table A1).

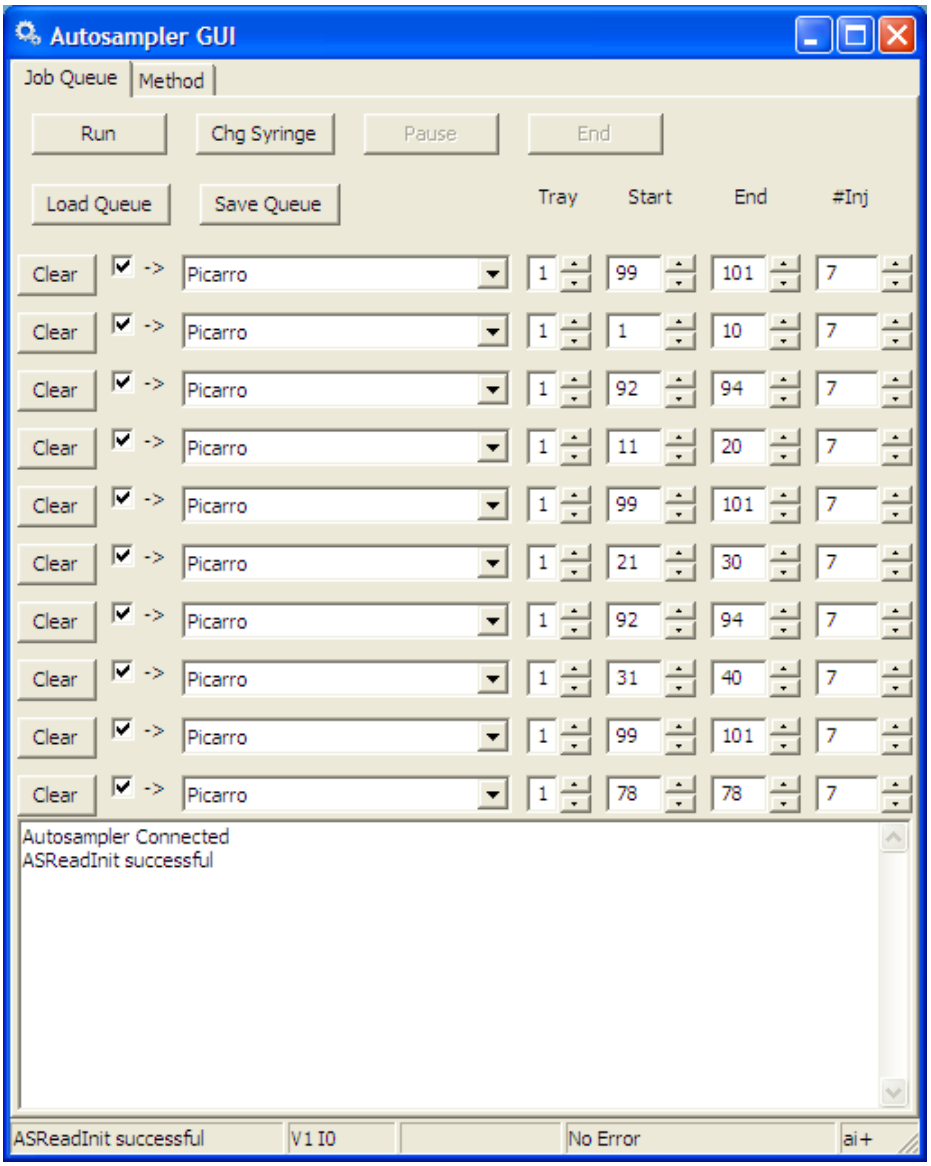


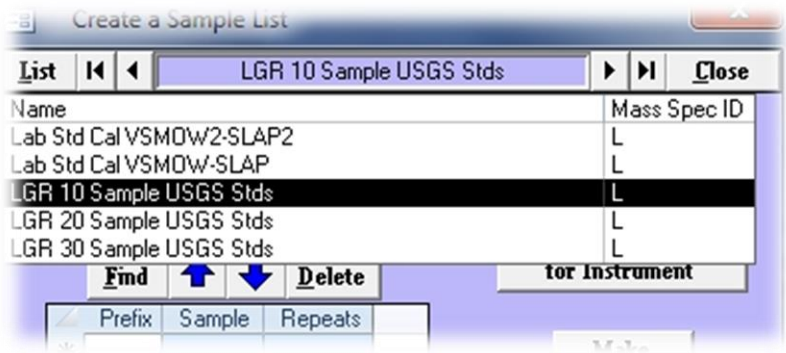
Table A1. Recommended *LIMS for Lasers 2015* template layout for a 40-sample Picarro G-2000 autosampler list shown below (see previous chapters on template construction). Total runtime for this template is approximately 38 hours.

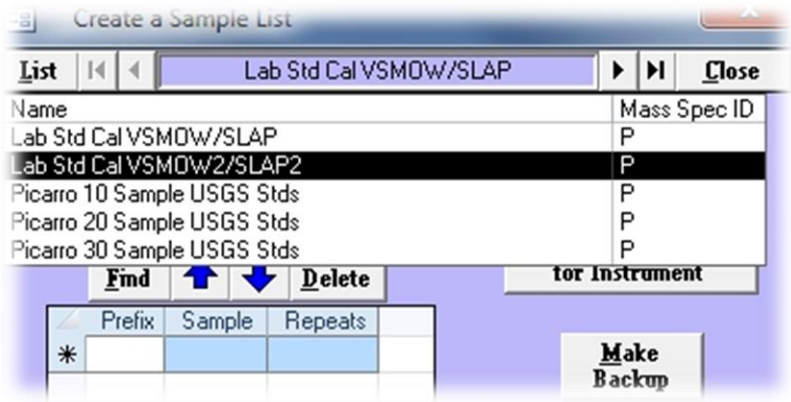
Sample	Vial Pos	List #	LIMS for Lasers 2015 Function
Hi Std	1-99	1	Between-Sample Memory
Lo Std	1-100	2	Between-Sample Memory
Lo Std	1-101	3	VSMOW-SLAP Normalization
Sample 1	1-01	4	Sample
Sample 2	1-02	5	Sample
Sample 3	1-03	6	Sample
Sample 4	1-04	7	Sample
Sample 5	1-05	8	Sample
Sample 6	1-06	9	Sample
Sample 7	1-07	10	Sample
Sample 8	1-08	11	Sample
Sample 9	1-09	12	Sample
Sample 10	1-10	13	Sample
Lo Std	1-92	14	Between-Sample Memory
Lo Std	1-93	15	Between-Sample Memory
Hi Std	1-94	16	VSMOW-SLAP Normalization
Sample 11	1-11	17	Sample
Sample 12	1-12	18	Sample
Sample 13	1-13	19	Sample
Sample 14	1-14	20	Sample
Sample 15	1-15	21	Sample
Sample 16	1-16	22	Sample
Sample 17	1-17	23	Sample
Sample 18	1-18	24	Sample
Sample 19	1-19	25	Sample
Sample 20	1-20	26	Sample
Control Standard	1-78	27	Control Standard
Hi Std	1-99	28	Between-Sample Memory
Lo Std	1-100	29	Between-Sample Memory
Lo Std	1-101	30	VSMOW-SLAP Normalization
Sample 21	1-21	31	Sample
Sample 22	1-22	32	Sample
Sample 23	1-23	33	Sample
Sample 24	1-24	34	Sample
Sample 25	1-25	35	Sample
Sample 26	1-26	36	Sample
Sample 27	1-27	37	Sample

Sample 28	1-28	38	Sample
Sample 29	1-29	39	Sample
Sample 30	1-30	40	Sample
Lo Std	1-92	41	Between-Sample Memory
Lo Std	1-93	42	Between-Sample Memory
Hi Std	1-94	43	VSMOW-SLAP Normalization
Sample 31	1-31	44	Sample
Sample 32	1-32	45	Sample
Sample 33	1-33	46	Sample
Sample 34	1-34	47	Sample
Sample 35	1-35	48	Sample
Sample 36	1-36	49	Sample
Sample 37	1-37	50	Sample
Sample 38	1-38	51	Sample
Sample 39	1-39	52	Sample
Sample 40	1-40	53	Sample
Hi Std	1-99	54	Between-Sample Memory
Lo Std	1-100	55	Between-Sample Memory
Lo Std	1-101	56	VSMOW-SLAP Normalization

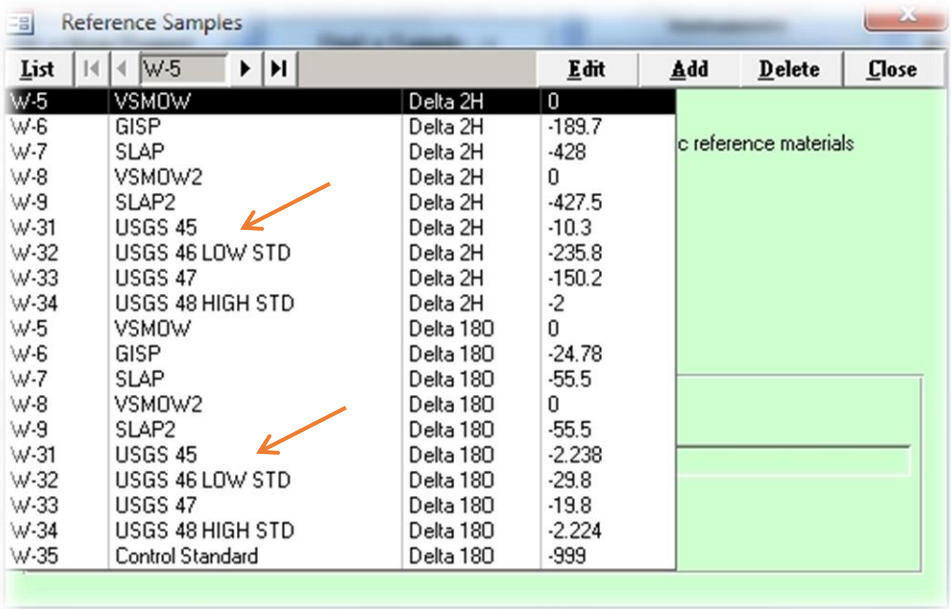
Appendix 2 Backend Databases and Template Design Worksheets

The quick-start backend databases provide convenient, ready-made 10-, 20- and 30-sample templates for Picarro and Los Gatos Research water isotope laser instruments. These new backend files are downloadable from the IAEA and USGS Web sites, as described in Chapter 3.1.





These templates were pre-populated to use USGS 46 and USGS 48 as the daily-use High & Low calibration standards (USGS standards are assigned to Reference Samples W-31 through W-34, plus W-35 is the control standard). These pre-made templates are easily “Duplicated” (see Chapter 8.4 and 8.5) and the USGS standards thereafter edited to be replaced by in-house daily-use high and low calibration standards.



Reference Samples

List | W-5 | Edit | Add | Delete | Close

W-5	VSMOW	Delta 2H	0
W-6	GISP	Delta 2H	-189.7
W-7	SLAP	Delta 2H	-428
W-8	VSMOW2	Delta 2H	0
W-9	SLAP2	Delta 2H	-427.5
W-31	USGS 45	Delta 2H	-10.3
W-32	USGS 46 LOW STD	Delta 2H	-235.8
W-33	USGS 47	Delta 2H	-150.2
W-34	USGS 48 HIGH STD	Delta 2H	-2
W-5	VSMOW	Delta 18O	0
W-6	GISP	Delta 18O	-24.78
W-7	SLAP	Delta 18O	-55.5
W-8	VSMOW2	Delta 18O	0
W-9	SLAP2	Delta 18O	-55.5
W-31	USGS 45	Delta 18O	-2.238
W-32	USGS 46 LOW STD	Delta 18O	-29.8
W-33	USGS 47	Delta 18O	-19.8
W-34	USGS 48 HIGH STD	Delta 18O	-2.224
W-35	Control Standard	Delta 18O	-999

c reference materials

In order facilitate new template design, Excel Template worksheets for Los Gatos and Picarro are provided to help visually guide the implementation. These spreadsheets are used for convenience in editing Vials and Tray Position numbers in manual template design operation (e.g. Figure shown on page 62). A 10-Sample Los Gatos worksheet template is shown below.

	A	B	C	D	E
1		LIMS for Lasers Template Name			
2		LGR 10 Sample			
3		Sample	LIMS List #	Tray Position / Port	LIMS Function
4		Dummy (W-3)	1	3-28	DI Wash
5		High Std	2	3-10	Normalization + Drift + Memory
6		Low Std	3	3-1	Normalization + Drift + Memory
7		Low Std	4	3-2	Normalization + Drift + Memory
8		Sample 1	5	1-1	
9		Sample 2	6	1-2	
10		Sample 3	7	1-3	
11		Sample 4	8	1-4	
12		Sample 5	9	1-5	
13		Low Std	10	3-3	Normalization + Drift + Memory
14		High Std	11	3-11	Normalization + Drift + Memory
15		High Std	12	3-12	Normalization + Drift + Memory
16		Sample 6	13	1-6	
17		Sample 7	14	1-7	
18		Sample 8	15	1-8	
19		Sample 9	16	1-9	
20		Sample 10	17	1-10	
21		Control	18	3-19	Control Standard
22		High Std	19	3-10	Normalization + Drift + Memory
23		Low Std	20	3-1	Normalization + Drift + Memory
24		Low Std	21	3-2	Normalization + Drift + Memory
25		Dummy (W-3)	22	3-28	DI Wash
26					
27		Front Tray 1			
28		Samples	Postitions 1-1 to 1-10		
29					
30		Rear Tray 3			
31		Low Std	Positions 3-1 to 3-3		
32		High Std	Positions 3-10 to 3-12		
33		Control	Position 3-19		
34		DI Wash	Position 3-28		
35					

Appendix 3 Correcting for Variations in *δ* Values with Relative Water Concentrations

It is well-known that the *δ*-values of one or more H_2O isotopologue species may respond positively or negatively (and linearly or non-linearly) to very small changes in the relative amount of water vaporized into the laser cavity. Variations in H_2O amount injected (and corresponding variance in *δ* results) over the course of an autorun can be large or small, depending on the quality and condition of the syringe. Significant H_2O and random concentration variations typically arise from poorly performing syringes or from leaky septa.

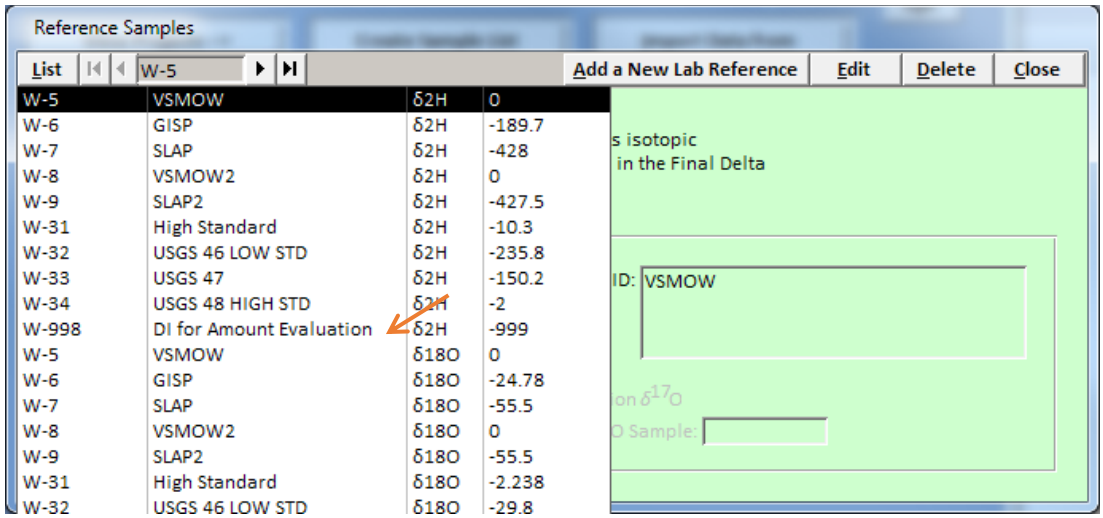
When purposely manipulated, a relative H_2O concentration *δ* dependence correction algorithm allows opportunity to improve the results by normalizing to H_2O injection amount using amount-control standards (e.g. using a 800, 1000 and 1200 µL triplets) placed at the start of or within an autorun. This implementation allows *LIMS for Lasers 2015* to automatically determine and apply an H_2O concentration correction algorithm for each isotope delta.

The purpose of the LIMS for Lasers 2015 concentration dependence correction is to help rectify effects of variable syringe injection performance for all isotope deltas. It is not meant as a replacement for a good performing syringe. Bad syringes should always be replaced!

The relative H_2O – *δ* value adjustment in *LIMS for Lasers 2015* is determined by correlating the measured raw *δ* values of an amount varied control standard (or any other standard) to its measured H_2O concentrations, and then applying a best fit regression model (e.g. linear, quadratic, log, exponential). If the regression model is robust (e.g. R^2 >0.6), the equation may be applied to all samples to normalize their measured *δ* values to a constant water vapour amount. Concentration dependency corrections often result in marked improvement in *δ* results for one or more isotopologues, particularly if syringe performance is variable or if the instrument is highly sensitive to H_2O amount.

When using the provided default Picarro or Los Gatos research backend databases, the pre-assigned amount-control standard for H_2O concentration corrections is W-998. If a $\delta^{17}O$ amount-control standard is required, a companion $\delta^{17}O$ project must be created (typically W-999). In the case where no H_2O amount-control standard has been created, it can be added as described in Chapter 6.

The appropriate amount-control standard must also be added to the Table of References, as described in Chapter 7.2. Note: The assigned value for this amount-control standard is set to –999 ‰ for *all* of the isotope deltas.

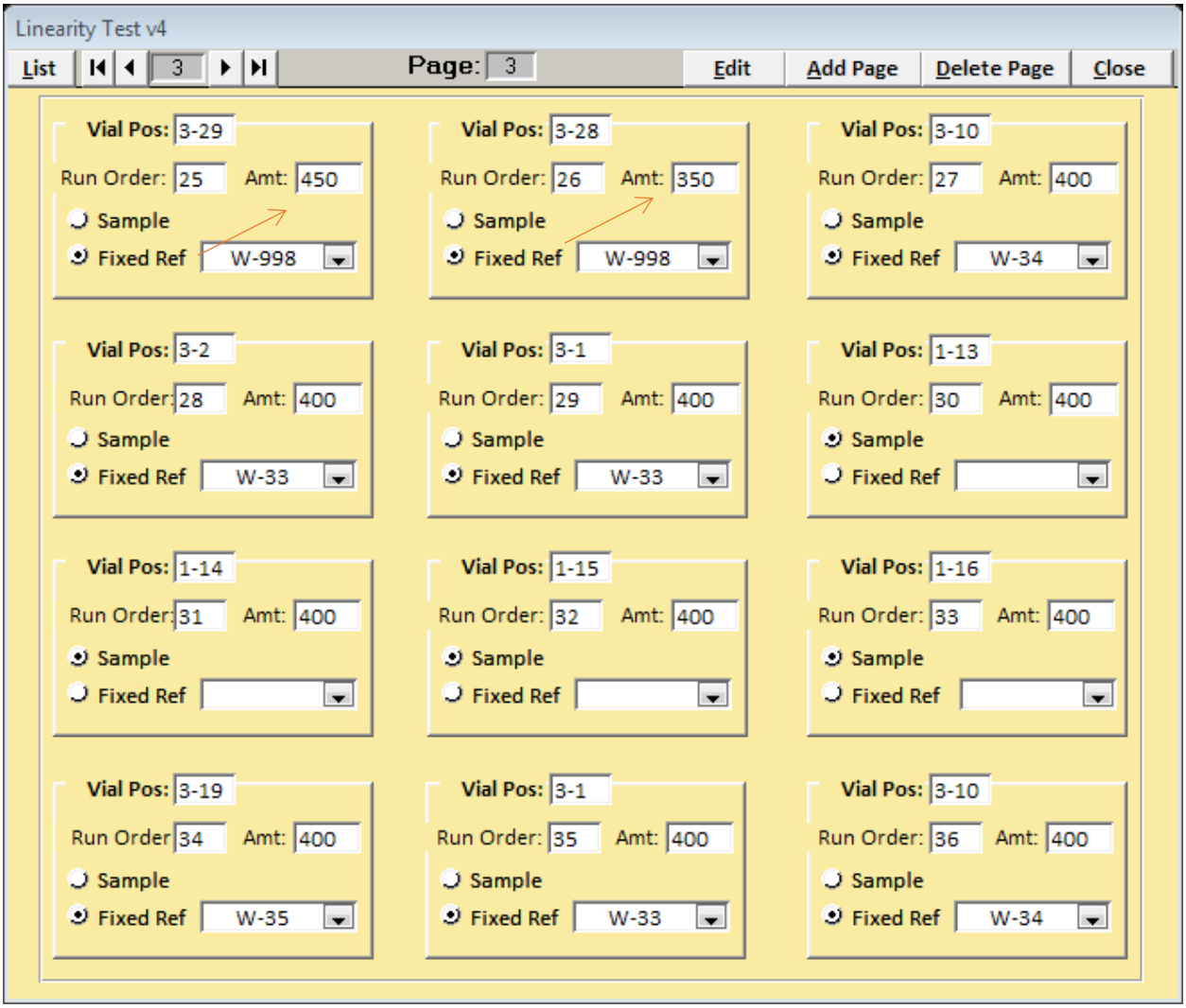


Setting up Amount Controls on Los Gatos Research Laser Instrument

(Note: Only for IWA-35EP or TIWA 45-EP instruments)

1. Create or edit an Analysis template in Excel or in Template Pages.
2. At the beginning or middle of the template add 3 or more Amount control water sample vials each having different water amounts. In the example below, the routine target injection amount using an SGE 5-µL syringe was 400 nL (it will be 900–1200 nL for Hamilton syringes). The amount-control standard W-998 was purposely stepped at 350-, 400- and 450-nL increments, either in Page mode or by using an Excel template. In the example below, the amount-control standard was placed mid-run on Tray 3 in positions 3-28 and 3-29 (sequence order 24 (not shown), 25, 26).
3. The minimum number of amount-control standard required for the concentration correction option is two (for linear fit), and the maximum number is unlimited (for Linear, Quadratic, Logarithmic, etc.), but generally 3 or 4 vials covering the anticipated H_2O range is sufficient.
4. Generally, poor syringe performance results in *lower* than the targeted H_2O yield in the laser cavity, thus volumes of the amount-control standards should span just above the normal target H_2O amount and span several lower H_2O concentrations.

Note: Ensure variable injection volumes are within the operational range of the instrument!



Example templates (above and below) for a new Los Gatos instruments, showing two amount-control standards.

Clipboard Font Alignment

A2 f_x 1

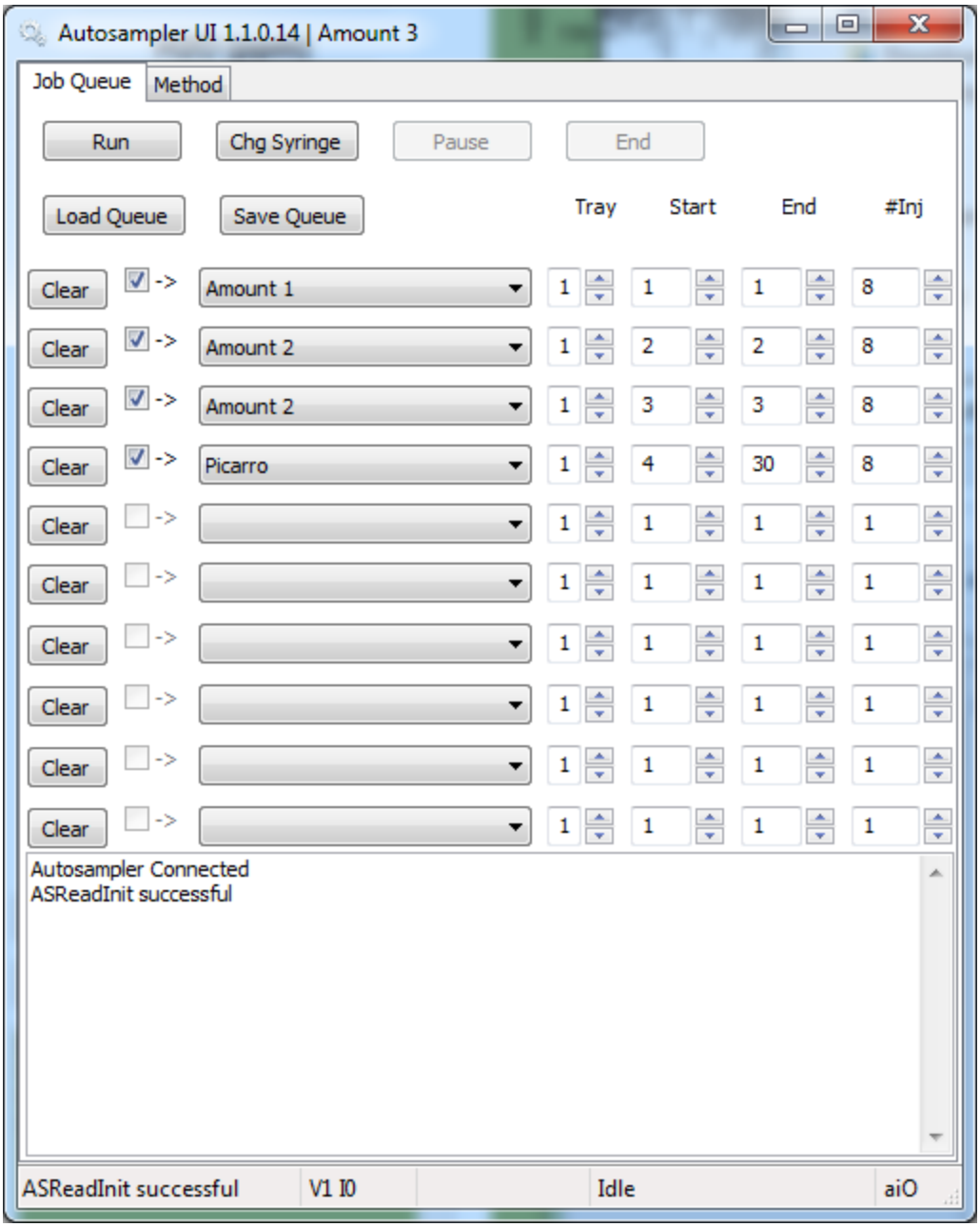
	A	B	C	D	E	F
	LIMS_List_No	Tray_Position	Ref_OurLabID	Page	Page_Position	Amount
3	22	1-11		2	10	400
4	23	1-12		2	11	400
5	24	3-28	W-998	2	12	400
6	25	3-29	W-998	3	1	450
7	26	3-28	W-998	3	2	350
8	27	3-10	W-34	3	3	400
9	28	3-2	W-33	3	4	400
0	29	3-1	W-33	3	5	400
1	30	1-13		3	6	400
2	31	1-14		3	7	400
3	32	1-15		3	8	400

Setting up Amount Controls on Picarro Instruments

For all Picarro instruments, the control of H_2O injection amount is achieved by creating separate Methods on the PAL-CTC or G2000 Autosampler panel. Each method for a targeted volume must be added to the autosampler Job Queue.

For example, a Job Queue might comprise the following 4 methods in a run single sequence, where 1.6 µL here is the target H_2O amount for all samples (e.g. Picarro Method):

1. 1.2 µL Amount Std. (Amount 1 Method)	Job 1 (Sample 1 to 1)
2. 1.6 µL Amount Std. (Amount 2 Method)	Job 2 (Sample 2 to 2)
3. 1.8 µL Amount Std. (Amount 3 Method)	Job 3 (Sample 3 to 3)
4. 1.6 µL Low Std (Picarro Method)	Job 4 (Samples 4 to 20)
5. 1.6 µL High Std (Picarro Method)	…..
6. 1.6 µL High Std (Picarro Method)	
7. 1.6 µL Sample (Picarro Method)	
8. 1.6 µL Sample (Picarro Method)	
9. … and so on…	



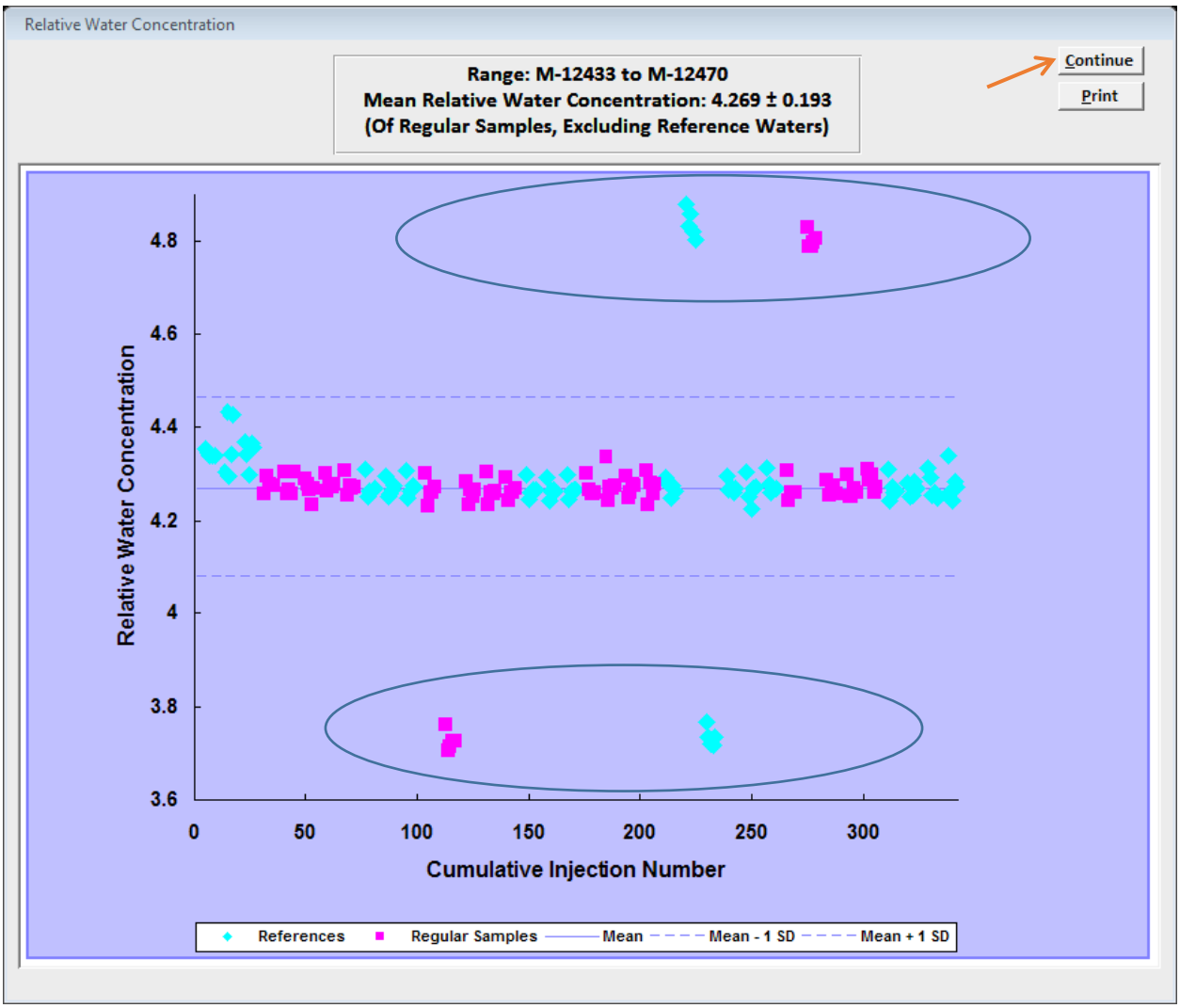
Example Picarro G2000 Job Queue adding three amount linearity samples (e.g. W-998) to the start of the autorun. Each method changes only the injection amount.

When importing data from a Picarro with amount-control-standard vials added, follow the same procedure as for Los Gatos Research as shown in in Steps 3–5 above.

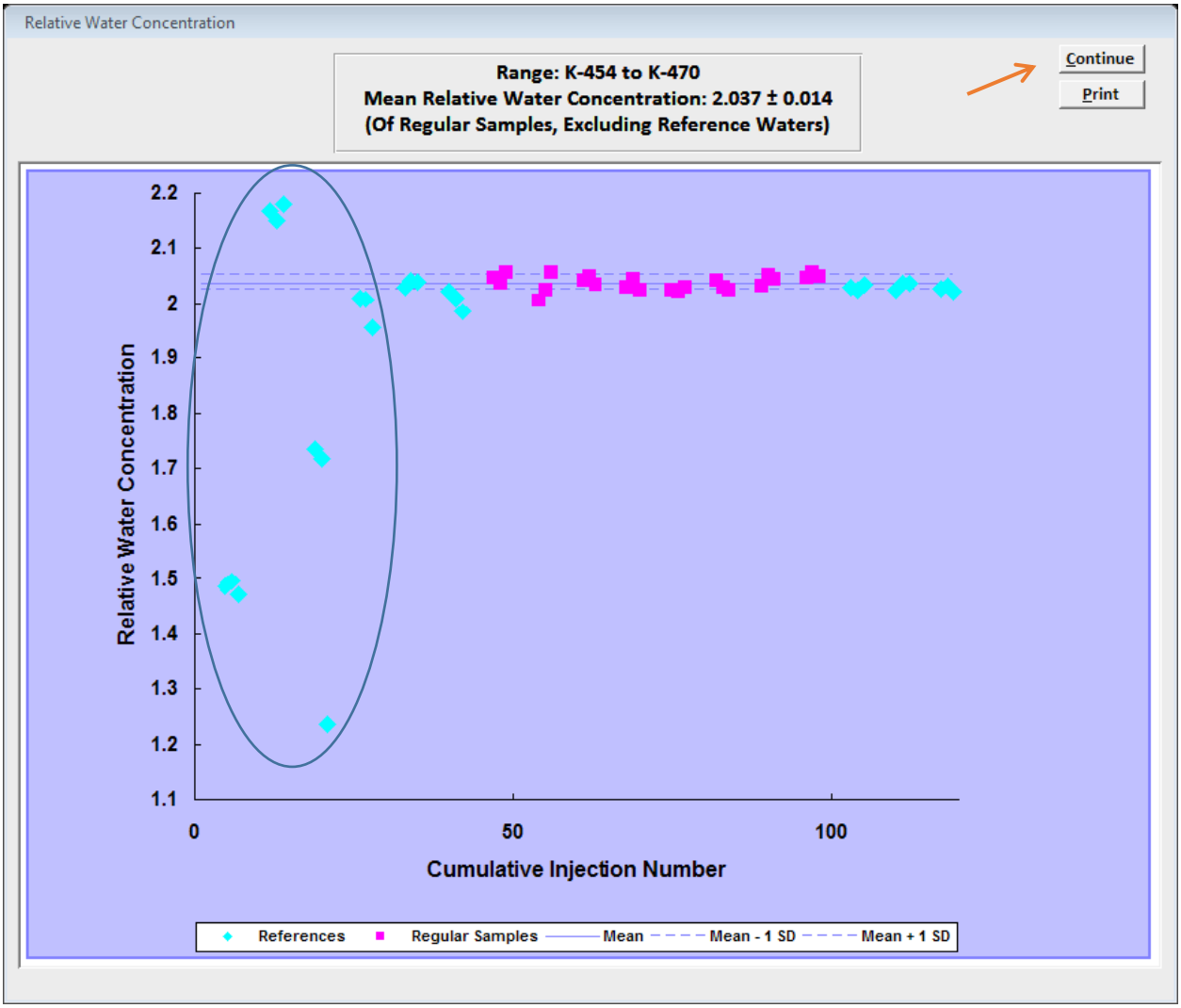
Adjustments for Variations in Delta Values with H_2O Concentration

The import data screen below graphically reveals the injection performance overview, with notable differences from the normal situation. Here the amount-control standard was manipulated in its H_2O concentrations in blue, and unknown samples are in magenta according to the injection sequence number. The injection H_2O response (for a Los Gatos Research instrument) was manipulated from approximately 3.7 to 4.8 × 10^{16} H_2O molecules, with a routine target concentration of 4.3 × 10^{16} H_2O molecules, as above. The relative water amounts in the laser cavity shown on the Y-axis will be different for a Picarro instrument.

Normally, only the amount-control standard (e.g. W-998, in blue) is used for H_2O relative concentration corrections. In the example, two unknown samples (magenta) were also manipulated for a higher and lower injection amount as a test of how well the correction performed.



Example of amount-control standards and variable volume samples on a Los Gatos Research Analyser.

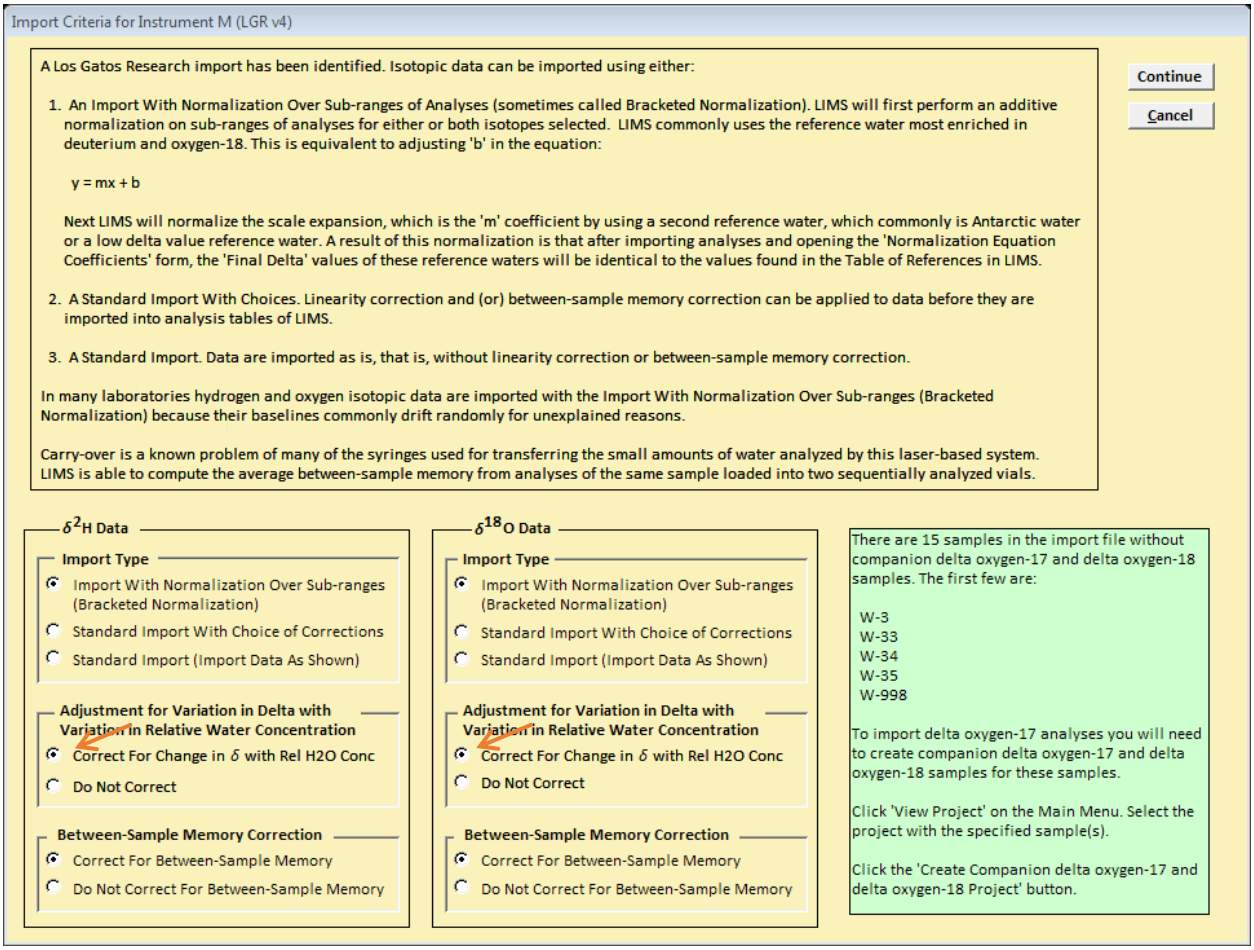


Example showing amount controls placed at the beginning of a Picarro autorun, ranging from a volume fraction of H_2O between approximately 12,000 to 22,000 ppm.

Click Continue...

In the next import screen, options are displayed for import types for all measured isotope deltas (δ^2H, δ^{18}O, δ^{17}O). If δ^{17}O was measured, it will be displayed on the right hand panel. The routine import options are previously described in Chapter 11.

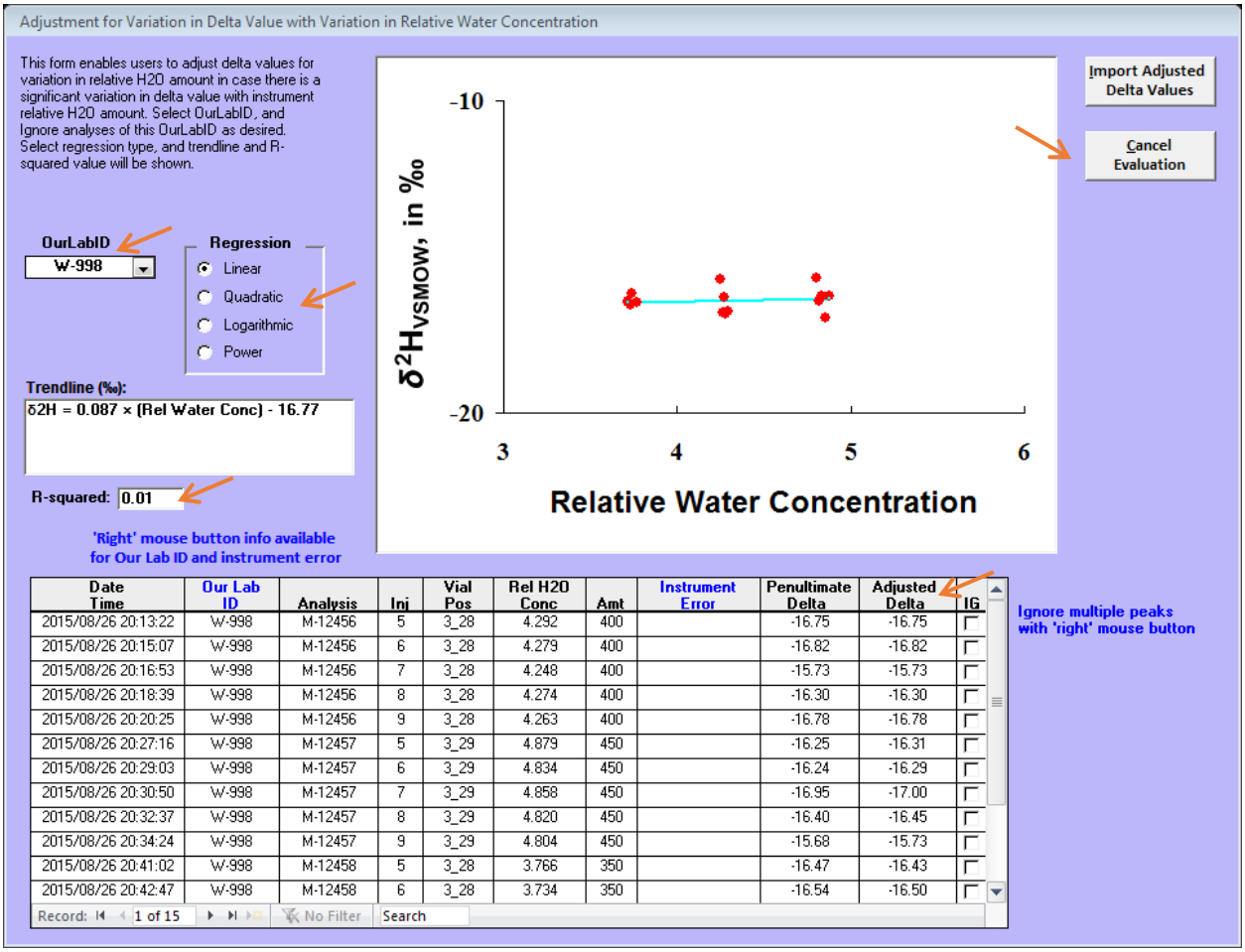
To enable adjustments for H_2O concentration (OFF by default), check the option "Correct for Change in δ with Rel H2O Conc" for each isotope delta:



Click Continue…

Next, user selectable model options for the delta value dependency on H_2O amounts are displayed, sequentially for each isotope delta in turn.

In the panel below, be sure to select the targeted amount-control standard from the Our Lab ID box. In this case, our amount-control standard was W-998.



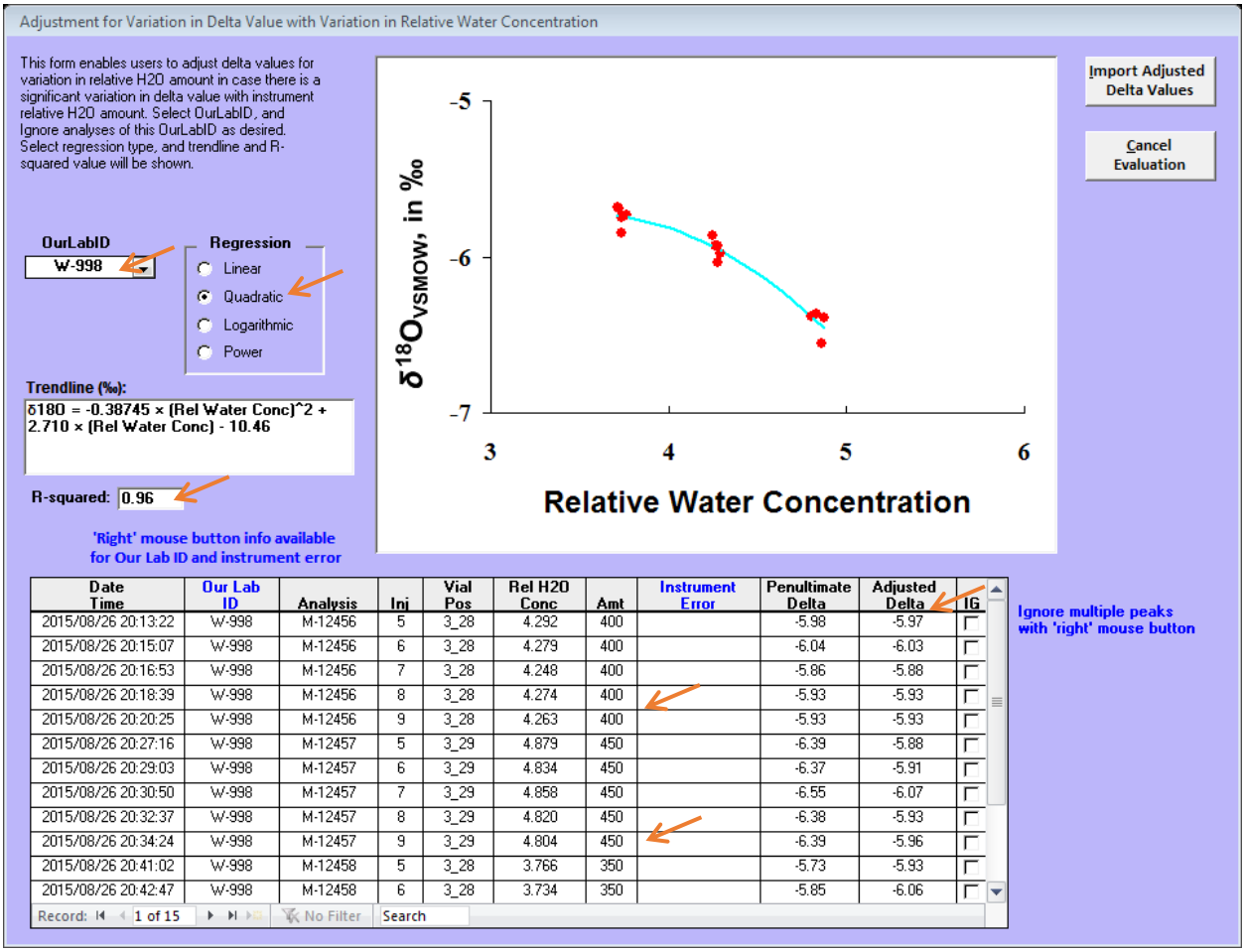
Date Time	Our Lab ID	Analysis	Inj	Vial Pos	Rel H2O Conc	Amt	Instrument Error	Penultimate Delta	Adjusted Delta	IG
2015/08/26 20:13:22	W-998	M-12456	5	3_28	4.292	400		-16.75	-16.75	☐
2015/08/26 20:15:07	W-998	M-12456	6	3_28	4.279	400		-16.82	-16.82	☐
2015/08/26 20:16:53	W-998	M-12456	7	3_28	4.248	400		-15.73	-15.73	☐
2015/08/26 20:18:39	W-998	M-12456	8	3_28	4.274	400		-16.30	-16.30	☐
2015/08/26 20:20:25	W-998	M-12456	9	3_28	4.263	400		-16.78	-16.78	☐
2015/08/26 20:27:16	W-998	M-12457	5	3_29	4.879	450		-16.25	-16.31	☐
2015/08/26 20:29:03	W-998	M-12457	6	3_29	4.834	450		-16.24	-16.29	☐
2015/08/26 20:30:50	W-998	M-12457	7	3_29	4.858	450		-16.95	-17.00	☐
2015/08/26 20:32:37	W-998	M-12457	8	3_29	4.820	450		-16.40	-16.45	☐
2015/08/26 20:34:24	W-998	M-12457	9	3_29	4.804	450		-15.68	-15.73	☐
2015/08/26 20:41:02	W-998	M-12458	5	3_28	3.766	350		-16.47	-16.43	☐
2015/08/26 20:42:47	W-998	M-12458	6	3_28	3.734	350		-16.54	-16.50	☐

Above, we see no significant H_2O amount dependency effects for δ^2H. There are poor *R*-squared values for all fit options, such as quadratic, logarithmic or power.

As a rule of thumb, if the fit R-squared value is < ~0.6, do not apply a correction. This decision must be made by the analyst. Note that outliers (e.g. 1 injection badly affecting an otherwise excellent fit) can be ignored here by checking the appropriate IG boxes in the lower panel.

In the case of δ^2H above, because all fits were poor, we do not want any amount correction applied. To reject all fits, click "Cancel Evaluation" for δ^2H.

Next, *LIMS for Lasers 2015* will proceed to display the $\delta^{18}O$ amount correction fit results (and afterwards $\delta^{17}O$, if applicable).



Date Time	Our Lab ID	Analysis	Inj	Vial Pos	Rel H2O Conc	Amt	Instrument Error	Penultimate Delta	Adjusted Delta	IG
2015/08/26 20:13:22	W-998	M-12456	5	3_28	4.292	400		-5.98	-5.97	
2015/08/26 20:15:07	W-998	M-12456	6	3_28	4.279	400		-6.04	-6.03	
2015/08/26 20:16:53	W-998	M-12456	7	3_28	4.248	400		-5.86	-5.88	
2015/08/26 20:18:39	W-998	M-12456	8	3_28	4.274	400		-5.93	-5.93	
2015/08/26 20:20:25	W-998	M-12456	9	3_28	4.263	400		-5.93	-5.93	
2015/08/26 20:27:16	W-998	M-12457	5	3_29	4.879	450		-6.39	-5.88	
2015/08/26 20:29:03	W-998	M-12457	6	3_29	4.834	450		-6.37	-5.91	
2015/08/26 20:30:50	W-998	M-12457	7	3_29	4.858	450		-6.55	-6.07	
2015/08/26 20:32:37	W-998	M-12457	8	3_29	4.820	450		-6.38	-5.93	
2015/08/26 20:34:24	W-998	M-12457	9	3_29	4.804	450		-6.39	-5.96	
2015/08/26 20:41:02	W-998	M-12458	5	3_28	3.766	350		-5.73	-5.93	
2015/08/26 20:42:47	W-998	M-12458	6	3_28	3.734	350		-5.85	-6.06	

For δ^{18}O, on the above example, we see a very strong δ value dependency on water amount in the laser cavity. Again, by selecting the appropriate amount-control standard W-998, we can examine the options to obtain our best fit H_2O concentration correction model.

- Linear regression: R^2 = 0.92
- **Quadratic regression: R^2 = 0.96** (best fit, shown above)
- Logarithmic regression: R^2 = 0.91
- Power regression: R^2 = 0.91

Selecting the best fit, a Quadratic regression, the proposed equation is displayed in the Trendline box, along with the fit *R*-squared value (0.96). Also shown in the lower panel are the comparative uncorrected penultimate δ^{18}O values of the 350 nL (–5.7 ‰) versus 450 nL (–6.4 ‰) vials, versus the same samples, but now adjusted to normalized H_2O amount (–5.9 ‰) based on the user selected fit.

To accept the proposed Quadratic correction model for δ^{18}O, click "Import Adjusted Delta Values". This action will now import adjusted measured delta values for further processing.

The following screen displays a run summary of data for both δ^2H and δ^{18}O. Be aware these results show measured delta values normalized to a constant H_2O amount (but only for δ^{18}O in this case); no other corrections, such as between-sample memory or linear instrumental drift, have yet been determined or applied.

Nevertheless, to illustrate the efficacy of the amount correction, consider the following results:

Import Criteria for Instrument M (LGR v4)

Ignore relative water concentrations and delta values as appropriate. Ignore multiple peaks with 'right' mouse button

Continue

Cancel

Analysis	Inj	OurLabID	Vial Position	Rel H2O Conc	IG Conc	δ2H	IG δ2H	δ18O	IG δ18O
12456	1	W-998	3_28		☑		☑		☑
12456	2	W-998	3_28		☑		☑		☑
12456	3	W-998	3_28		☑		☑		☑
12456	4	W-998	3_28		☑		☑		☑
12456	5	W-998	3_28	4.29	☐	-16.75	☐	-5.97	☐
12456	6	W-998	3_28	4.28	☐	-16.82	☐	-6.03	☐
12456	7	W-998	3_28	4.25	☐	-15.73	☐	-5.88	☐
12456	8	W-998	3_28	4.27	☐	-16.30	☐	-5.93	☐
12456	9	W-998	3_28	4.26	☐	-16.78	☐	-5.93	☐
12456			Means	4.27 ± 0.02	▩	-16.48 ± 0.47	☐	-5.95 ± 0.06	☐
12457	1	W-998	3_29		☑		☑		☑
12457	2	W-998	3_29		☑		☑		☑
12457	3	W-998	3_29		☑		☑		☑
12457	4	W-998	3_29		☑		☑		☑
12457	5	W-998	3_29	4.88	☐	-16.25	☐	-5.88	☐
12457	6	W-998	3_29	4.83	☐	-16.24	☐	-5.91	☐
12457	7	W-998	3_29	4.86	☐	-16.95	☐	-6.07	☐
12457	8	W-998	3_29	4.82	☐	-16.40	☐	-5.93	☐
12457	9	W-998	3_29	4.80	☐	-15.68	☐	-5.96	☐
12457			Means	4.84 ± 0.03	▩	-16.30 ± 0.45	☐	-5.95 ± 0.07	☐
12458	1	W-998	3_28		☑		☑		☑
12458	2	W-998	3_28		☑		☑		☑
12458	3	W-998	3_28		☑		☑		☑
12458	4	W-998	3_28		☑		☑		☑
12458	5	W-998	3_28	3.77	☐	-16.47	☐	-5.93	☐
12458	6	W-998	3_28	3.73	☐	-16.54	☐	-6.06	☐
12458	7	W-998	3_28	3.72	☐	-16.41	☐	-5.91	☐
12458	8	W-998	3_28	3.72	☐	-16.48	☐	-5.89	☐
12458	9	W-998	3_28	3.74	☐	-16.19	☐	-5.96	☐
12458			Means	3.74 ± 0.02	▩	-16.42 ± 0.14	☐	-5.95 ± 0.07	☐
12459	1	W-34	3_10		☑		☑		☑

δ^2H and δ^{18}O

Ref for Additive Normalization: W-34

Reference for Scale Expansion: W-33

Despite the wide range of injection volumes used, resulting in a range of 3.7–4.8 in relative water concentrations, the newly H_2O normalized measured results for W-998 returned the same δ value of –5.95 ‰, whereas values left uncorrected for H_2O amount differed unacceptably by more than 0.5 ‰.

Click Continue…

From here on, all of the standard *LIMS for Lasers 2015* between-sample memory corrections and data normalization procedures may be applied. See Chapter 11.

Caution: Varying H_2O injection amounts will generate import warnings about inconsistent water yield (e.g. LIMS cannot distinguish a bad syringe from purposely varied injections), and show high variance flags on the import summary table. These warnings may be ignored.