A Laboratory Information Management System for Stable Hydrogen and Oxygen Isotopes in Water Samples by Laser Absorption Spectroscopy

User Manual & Tutorial

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Foreword

The routine measurement of the stable isotope ratios of hydrogen and oxygen (δ^2H and δ^{18}O) in liquid water samples by laser absorption spectroscopy (LAS) is an increasingly common and cost-effective analytical tool in hydrologic and environmental studies around the world.

While LAS instrumentation is relatively easy to operate, the adoption of LAS into routine laboratory operations is not so easy, owing to substantive offline data manipulation required by the instrument operator. Other day-to-day LAS challenges include client sample-project management, storage and tracking of instrument measurement data files, derivation and application of algorithms to correct for between-sample memory, and correcting for linear and non-linear instrumental drift over the course of analysis autoruns. Many LAS users, including the International Atomic Energy Agency (IAEA), developed complex Excel data processing spreadsheets that can be difficult for new users to adopt. Further, the use of spreadsheets presents a challenge to maintaining and reporting long-term QA/QC and laboratory audits.

A new Microsoft Access-based *Laboratory Information Management System (LIMS) for Lasers* is presented which simplifies and automates these difficult processes, and eliminates the need for offline data manipulation. *LIMS for Lasers* makes use of prescribed analysis templates that consistently apply the Principles of Identical Treatment to all sample and measurement standard analyses. Analysis templates include multiple occurrences of two measurement standards to quantify between-sample memory, determine instrumental drift, and normalize results to the VSMOW–SLAP scale. A control standard is used to quantify long-term QA/QC and laboratory performance.

LIMS for Lasers manages clients and their project data, and generates instrument-sample-list templates for all LAS instruments, which otherwise requires extensive typographical data input. Autorun output files from LAS instrumentation are directly imported by LIMS for processing. The results are screened in *LIMS for Lasers* for outliers, and between-sample memory and instrumental drift are corrected for, as required. LAS performance is monitored using control standards to assess QA/QC and by δ^2H versus δ^{18}O cross-plots. These automated processing features reduce mistakes and operator errors.

In short, *LIMS for Lasers* greatly eases the adoption of LAS technology into new and current laboratories by introducing productivity efficiencies and improved reliability through consistent approaches based on the Principles of Identical Treatment.

This document describes how to implement *LIMS for Lasers* for Los Gatos Research or Picarro instruments into a new or an existing laboratory. To facilitate use of *LIMS for Lasers* in Member States, this document also contains download links to the latest software repository.

The IAEA Officers involved in producing this work were L.I. Wassenaar, with extensive laboratory testing by L. Pöltenstein and M. van Duren, and in collaboration with T.B. Coplen of the U.S. Geological Survey, Reston, Virginia.

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1

Introduction to LIMS for Lasers

1.0 What is LIMS for Lasers?

LIMS for Lasers is a Laboratory Information Management System (LIMS) for all off-axis (OA-ICOS) and cavity ring-down (CRDS) laser absorption spectrometers (LAS) used for the purposes of δ^2H and δ^{18}O assays of liquid water samples in hydrological and environmental studies. *LIMS for Lasers* provides a convenient Windows environment to manage clients, projects, samples and instrumental data.

Key Features

- Full client, project and sample management and reporting system.
- LAS sample analysis and laboratory standard calibration templates.
- Automated between-sample memory corrections.
- Automated instrumental drift correction and outlier identification.
- Automated normalization of data to the VSMOW-SLAP scales.
- Track My Lab QA/QC for instrument and laboratory assessment.
- Excel client sample submission templates.

User Benefits

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

LIMS for Lasers is built upon the MS Access code of *LIMS for Light Stable Isotopes* [1], and can be used concurrently on an existing *v.9* back-end 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.

The software is a result of a collaborative effort between the IAEA Isotope Hydrology Laboratory (IHL) and the U.S. Geological Survey (USGS). *LIMS for Lasers* is provided at no cost to users.

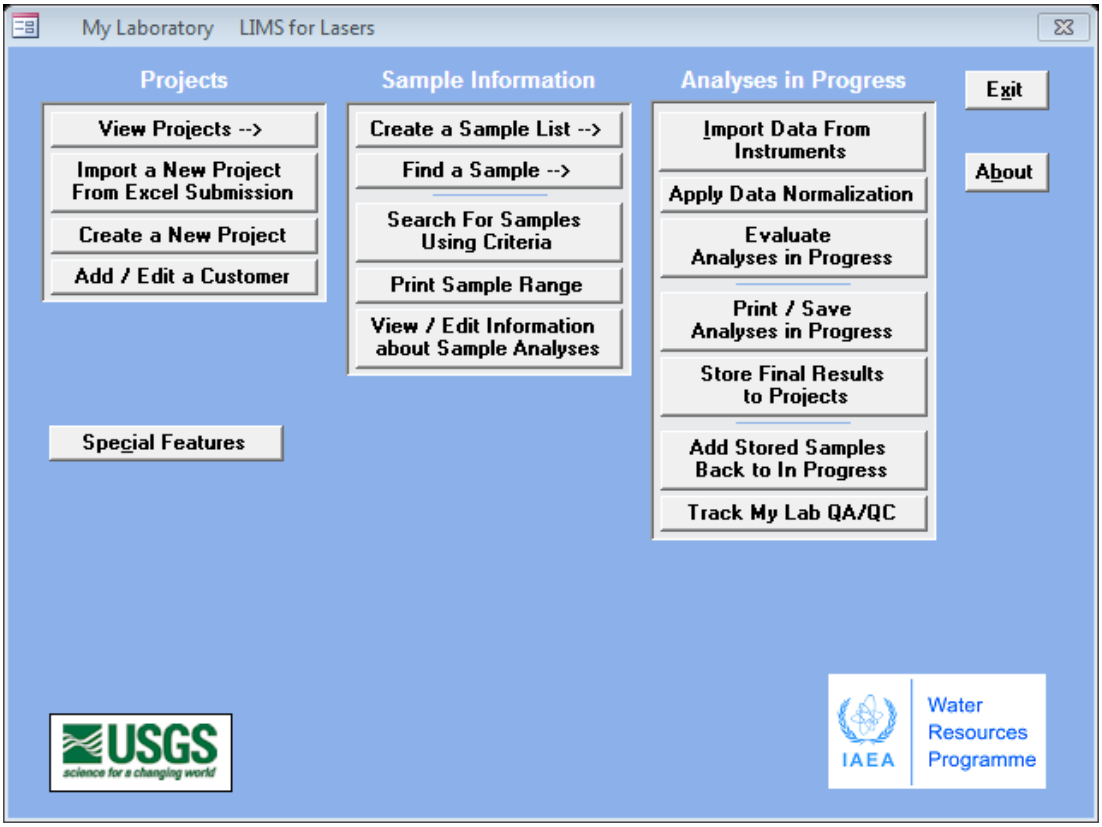
Currently, OA-ICOS laser instrumentation is offered by Los Gatos Research Inc.* (www.lgrinc.com) and CRDS laser instrumentation is offered commercially by Picarro Inc.* (www.picarro.com).

*Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the IAEA.

2

LIMS for Lasers at a Glance

2.0 LIMS for Lasers at a Glance



The user interface of LIMS for Lasers.

Projects

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

Special Features

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

Sample Information

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

Analyses in Progress

- Import sample data 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

2.1 Routine Sample Autorun Checklist

After *LIMS for Lasers* is installed this autorun procedural checklist provides an overview for the routine isotopic analysis of water samples.

A. Projects Column

1. Ensure customer is added to *LIMS for Lasers* (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 Project(s) samples to a laser Analysis Template queue (Chp. 8.8, 8.9).

B. Sample Information Column

4. Create the autorun Sample List for the laser instrument (Chp. 9.1, 10.1).

C. In the Laboratory

5. Pipette project sample waters and laboratory standards into labelled 2mL 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 via USB stick (Chp.9, 10).
8. Run the sample list on Los Gatos Research or Picarro laser instrument.
9. Copy the completed autorun data output file to USB stick.

E. Analysis in Progress Column

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

F. Projects Column

15. View Projects – Reporting Results (Chp. 13.1).
16. Submit final results to Customer.

3

Computer and Software Requirements

3.0 Computer and Software Requirements

Required:

- Windows PC with USB or connection to a laser instrument.
- Microsoft Access 2007/2010 (32-bit only) for Windows, installed.
- *LIMS for Lasers* frontend (*v.10.054* or later).
- A new or an existing LIMS back-end database for current LIMS users.
- A new or an existing LIMS folder location for the back-end database (network or PC).
- An Example Client Sample submission Excel spreadsheet.

Software:

The *LIMS for Lasers* software is composed of 3 components:

- The *LIMS for Lasers v10.054*, or later, frontend interface
- A *LIMS for Lasers* new backend database for Picarro or Los Gatos Research instruments.
- An Excel client sample submission template

The latest software can be downloaded at no cost from the IAEA or USGS websites:

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 LAS instrument(s).
- A backup disk (network or external storage location).

Required Security Settings

LIMS for Lasers requires adding trusted locations in Microsoft Access. You may require Administrator rights to change these settings. If you get macro errors, in the same security location set Access to enable all macros.

Trusted Locations

For example, assume C:\LIMS is the database location. We need to add this location to Trusted Locations in Access:

Access 2010: 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 do not allow the Windows Desktop as a trusted location.

4

Getting Started with LIMS for Lasers

4.1 Setting up LIMS for Lasers in a New Laboratory

1. Create *LIMS for Lasers* folders on your laboratory PC for the user interface, back-end database and daily backups (e.g. C:\LIMS). The LIMS folder should be located on a dedicated computer, or on a reliable (and preferably fast) networked drive.

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

2. Ensure Microsoft Access 2007/2010 (32-bit) is installed with the latest service pack. Ensure 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* front-end interface (e.g. LIMS_for_Lasers _10.054.zip) into C:\LIMS\Frontend.

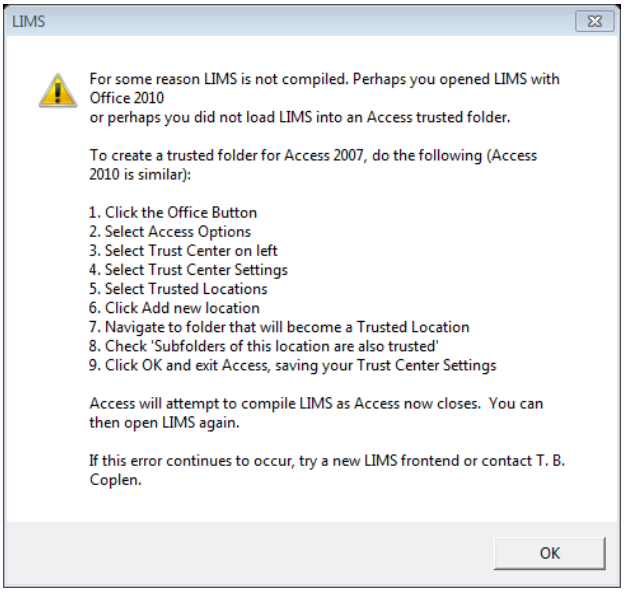
4. Download and extract an unopened instrument-specific back-end for new laboratories (e.g. LIMS Back-end for Picarro.zip) into C:\LIMS\Backend.

5. Consider renaming the LIMS back-end database to one that is descriptive of your laboratory, such as "My Laboratory LIMS Backend.accdb".

6. Keep copies of the original unopened LIMS ZIP files in a backup location for safekeeping.

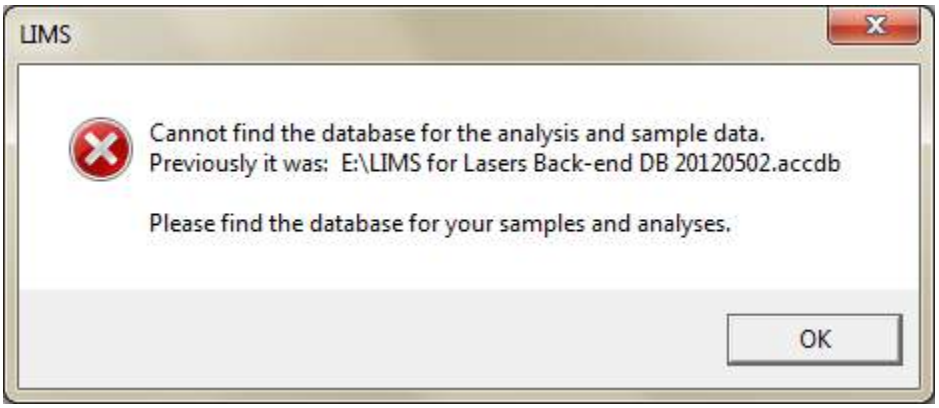
7. In the Frontend folder, open the file "LIMS_for _Lasers_10.054.accdb", or later version.

    a. When opening a newly extracted version of *LIMS for Lasers* it may recompile, and you may see the screen below. If this occurs, click "OK" (*this can take a few minutes).* Access may close without further notice when the compilation is done.

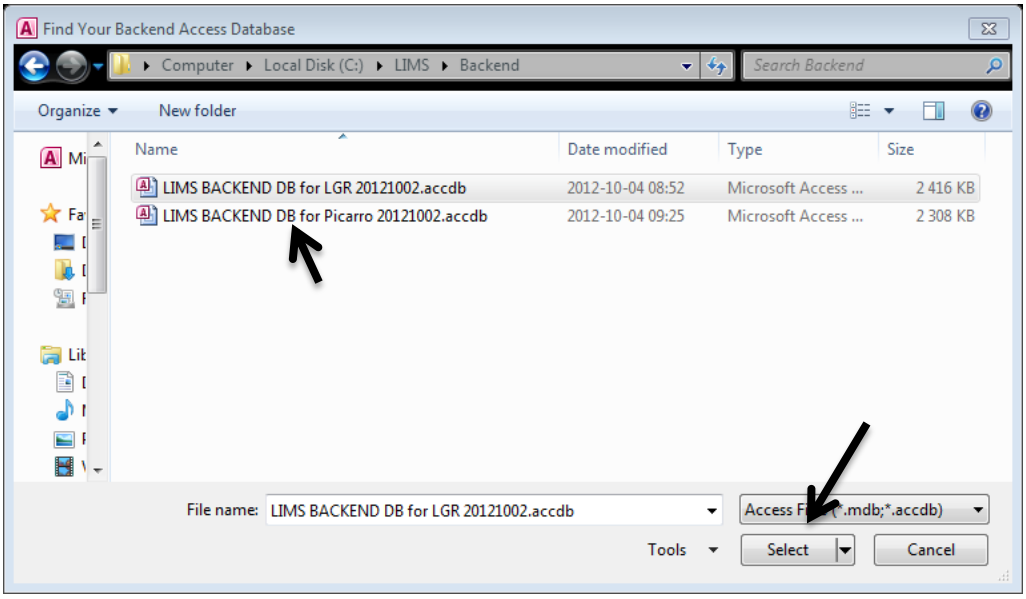


b. Re-open the compiled “LIMS_Light_Lasers_10.050”, or later version. If you see a security warning, then “trusted locations” were not set up properly–see previous section:

8. Click “Open” (this warning will not occur if Trusted Locations are set up).
9. LIMS will ask for the location of your LIMS “Back-end” database.



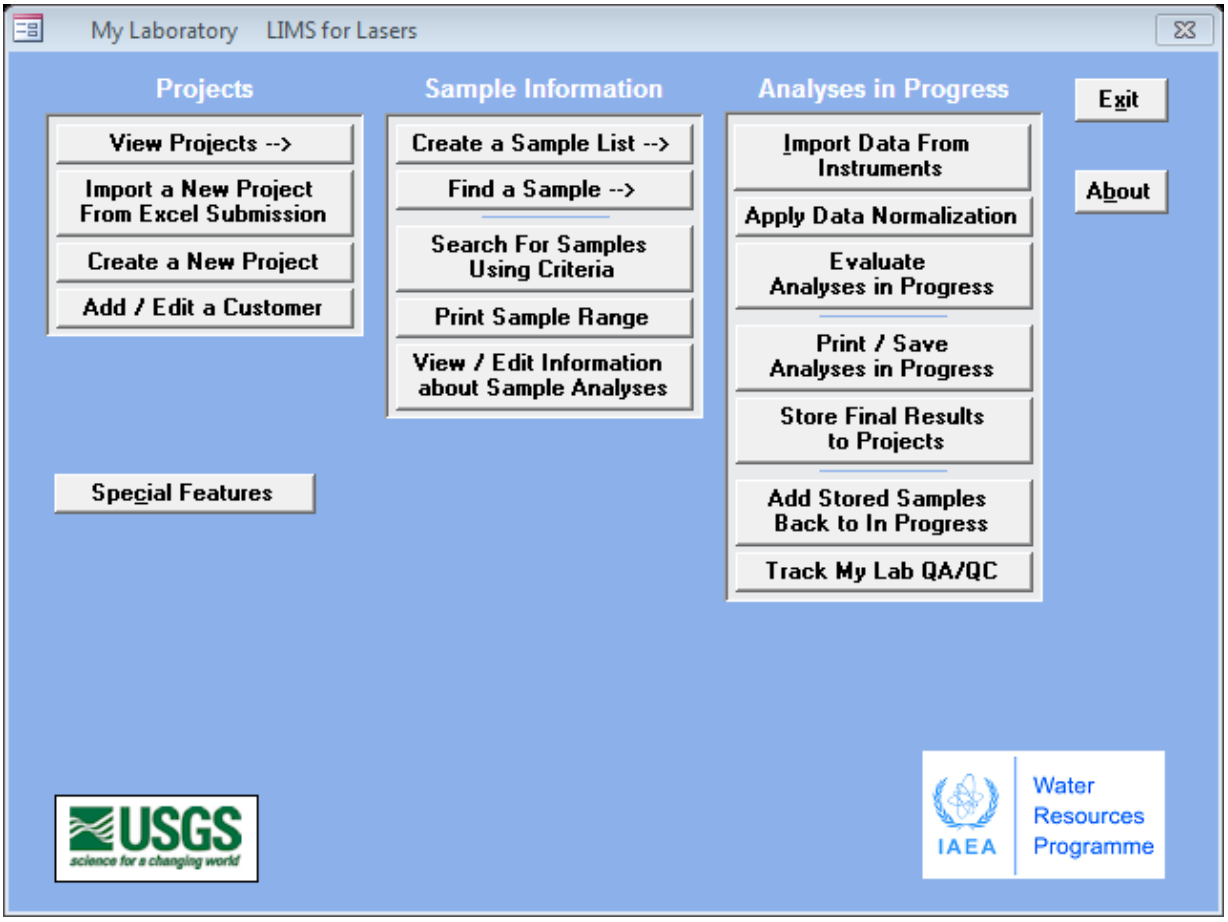
10. Click “OK”, and use the file dialog to navigate to C:\LIMS\Backend and “Select” the new Picarro or Los Gatos Research, or newly renamed back-end file that you copied in Step 4.



11. Next, a Welcome message appears, Click OK (security warning pops up if Trusted Locations are not setup), click "Open":

12. A reminder that new laser instruments may need to be installed into your laboratory database. Click "OK". Another reminder about daily backups, Click "OK" again.

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



LIMS for Lasers Main Page.

Registering for Support

It is a good idea to register *LIMS for Lasers* by emailing tbcoplen@usgs.gov. Registration ensures you will be informed of updates to *LIMS for Lasers*. Similarly, suggestions for improvements to *LIMS for Lasers*, reporting of bugs, and improvements to the user manual would be 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* will function properly with either choice, but the figures in this document were created with a point as the decimal separator.

4.2 Setting up in a LIMS v9 laboratory:

In laboratories currently using *LIMS for Light Stable Isotopes v.9*, follow the procedure for a new laboratory (Steps 1–7 above), but use the existing LIMS back-end directory. Some warnings do not apply. In step 7e, select the LIMS (*v*.9) back-end database. A *LIMS for Lasers* restart will still be required.

Note: When using a *v*.9 back-end database, only medium "W" (water δ^{18}O and δ^{2}H) and the laser instruments are visible. This is intentional - no IRMS instruments or any other isotopic media (e.g. C->carbonates, S->sulphur, etc) are visible, even though they are still present in the database. There is no danger to the back-end database, and all *v*.9 preferences are retained. You may switch back and forth between *LIMS for Light Stable Isotopes* and *LIMS for Lasers*. Staff using the lasers, for example, may prefer to use the simpler *LIMS for Lasers* interface.

4.3 Quick-Start Back-ends

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

However, to get new users running quickly, we have provided separate "ready-made" *LIMS for Lasers* back-end data bases – one for Los Gatos Research and one for a Picarro laser instruments. These are downloadable (Chapter 3.0) backend databases that assume:

- The Picarro instrument software has the identification prefix "P" (default).
- The Los Gatos Research instrument software has the identification prefix "L" (default).
- The default 30- (Los Gatos Research) or 20- sample (Picarro) Analysis Templates, described in this manual will be created by the user.
- 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.

For Los Gatos Research users:

1. Download the Los Gatos Research *LIMS for Lasers* back-end data base from the link above.
2. Review Chapters 4–6 to customize LIMS, and to edit or add your local measurement standards and create analysis templates.
3. Then go to Chapter 8.4 to get started with samples to be measured.

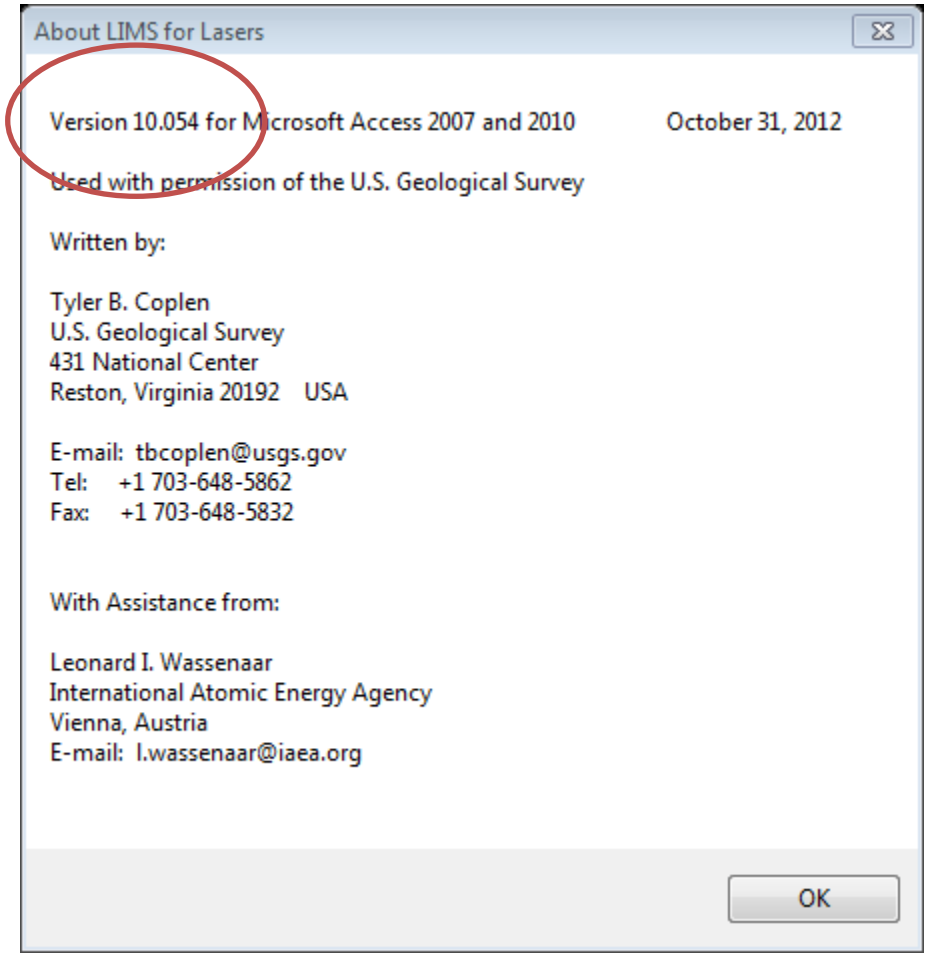
For Picarro users:

1. Download the Picarro *LIMS for Lasers* new back-end data base from the link above.
2. Review Chapters 4–6 to customize LIMS, to edit or add your local measurement standards and create analysis templates.
3. The go to Chapter 8.5 to get started with samples to be measured.

4.4 Checking LIMS for Lasers Versions

LIMS for Lasers software is continually improved. 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 Steps3, then Step 7 in Chapter 4.0, above. If you created a Windows desktop "shortcut" to the frontend interface folder, be sure to update the shortcut to the newer version.



4.5 Customizing Your Laboratory Settings

Prior to adding your own laser instrument to *LIMS for Lasers*, one should create laboratory customizations (your location, laboratory name, paper size, printers, etc.). This customization will create a new file in the LIMS interface subdirectory named "LM9PREFS.ACCDB", which stores your custom laboratory information. Depending upon your computer settings, the file extension ACCDB might not be visible.

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

Important Tip: To protect against mistaken entries and deletions in daily use, most forms in LIMS require the user to purposely click on the **"Edit"** button at the top of the screen before any changes can be made. This may be confusing at first – but remember it is for your data protection! Think "**Click Edit**" and it will become a routine habit.

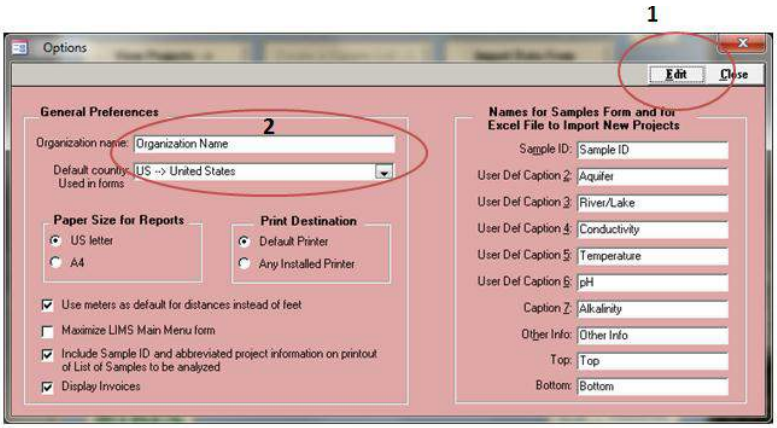
On the Main Page - Click "Special Features" / Options.

Click "Edit" (the control now changes to "Save").

Type in your Organization Name; choose your Country, and printer paper size. Choosing "Any Installed Printer" will bring up the Windows Print 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 disabled as desired. Include 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.

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

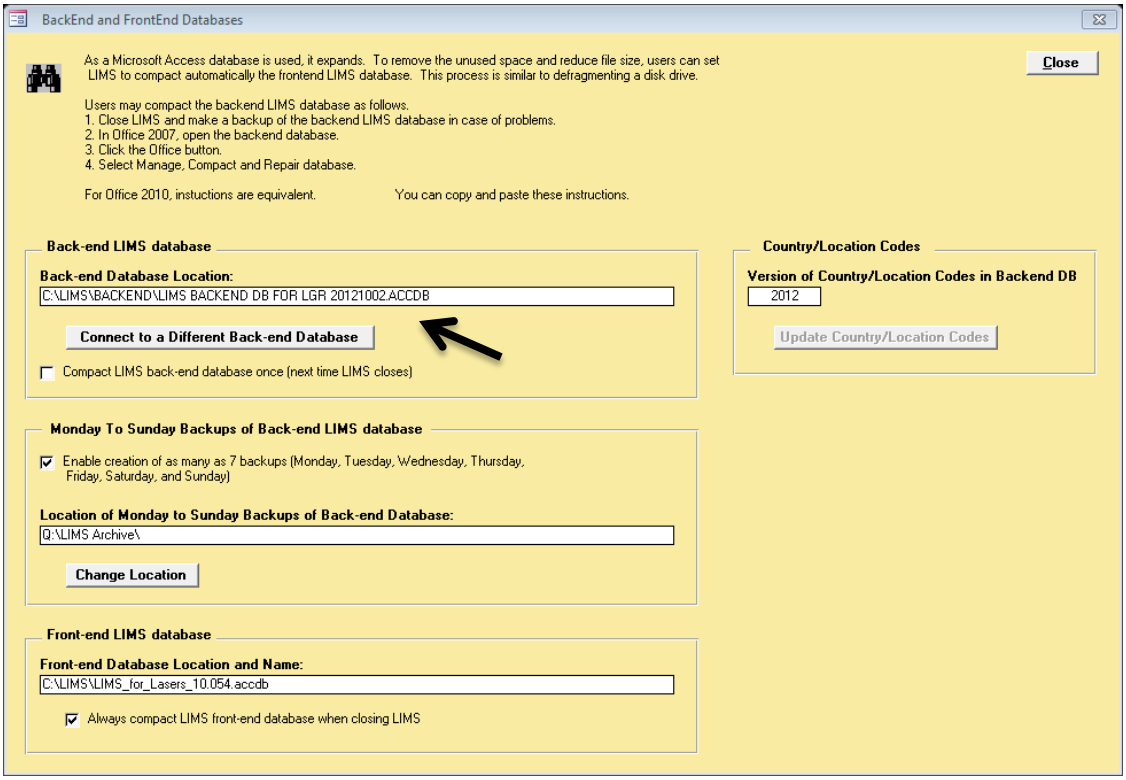


4.6 LIMS for Lasers Database Locations

It is a good idea to ensure your LIMS back-end database location and the file backup locations are set up permanently, and reliably.

Open *LIMS for Lasers*

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



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

NOTE: Backups are only made when *LIMS for Lasers* closes. *These are NOT unattended or automatic backups.* Users are strongly encouraged to use other forms of automated backup (network, DVD, flash disks, etc.).

5

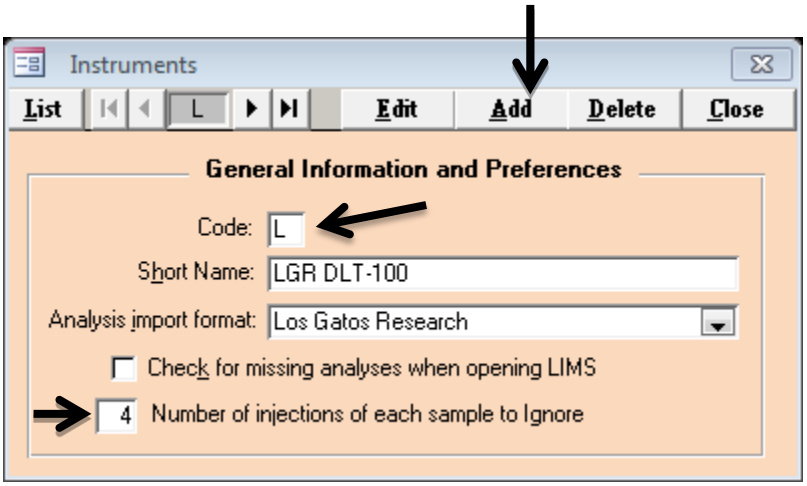
Adding Laser Instruments

5.1 Adding or Removing a Los Gatos Research Laser Instrument

To install or remove a Los Gatos Research laser instrument in *LIMS for Lasers*:

1. Start *LIMS for Lasers.*
2. Click "Special Features".
3. Click "Instruments".

In the screen below, click "Add".



4. Enter "L" in the Code box.
5. Enter a short descriptive name for the Los Gatos Research instrument.
6. From "Analysis import format", pick Los Gatos Research.
7. Click "Save", then Click on "List" - the new Los Gatos Research instrument should appear here.

For best results, we recommend a total of 9 injections per sample and by default ignore the first 4 injections (shown above). See discussion on templates for rationale for ignoring injections and other options (Chapter 8.2).

To remove a Los Gatos Research instrument, click on "Delete". If analyses for the Los Gatos Research instrument have been imported into *LIMS for Lasers*, the instrument cannot be deleted.

***Note*:** 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".

***Note*:** The instrument ID Prefix "L" is hard coded into Los Gatos Research instruments. For laboratories having two or more Los Gatos Research instruments, this code must be unique for each instrument (L, Q, but not P). Changing the prefix will require access to the LINUX shell on the Los Gatos Research instrument and a minor edit to an instrument file. Contact Los Gatos Research for instructions on how to change the default instrument Prefix ID.

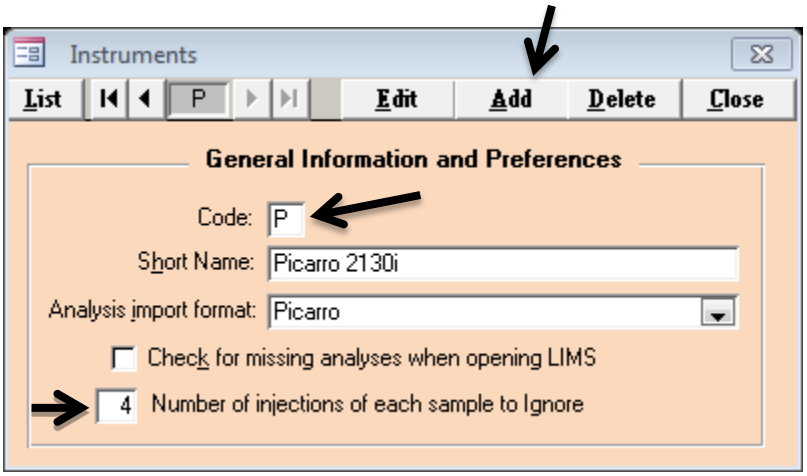
Caution: If you return your instrument for repair and Los Gatos Research replaces the hard drive, please ensure that Los Gatos Research resets the prefix letter and analysis number to the values on the instrument at the time you returned it for repair.

5.2 Adding or Removing a Picarro Laser Instrument

To install or remove a Picarro laser instrument in *LIMS for Lasers*:

1. Start *LIMS for Lasers.*
2. Click “Special Features”.
3. Click “Instruments”.

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, pick Picarro.
7. Click “Save”, then Click on “List” - the new Picarro instrument should appear here.

For best results, we recommend a total of 9 injections per sample and ignore 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 the Picarro instrument have been imported into *LIMS for Lasers*, the instrument cannot be deleted.

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

***Note*:** The ID prefix “P” is coded into the Picarro instrument software. For laboratories having two or more Picarro instruments this code must be unique for each instrument (e.g. P, Q, but not L). This requires editing the Coordinator.ini file and the “Instrument prefix” header. Contact Picarro for detailed instructions on changing the default instrument 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

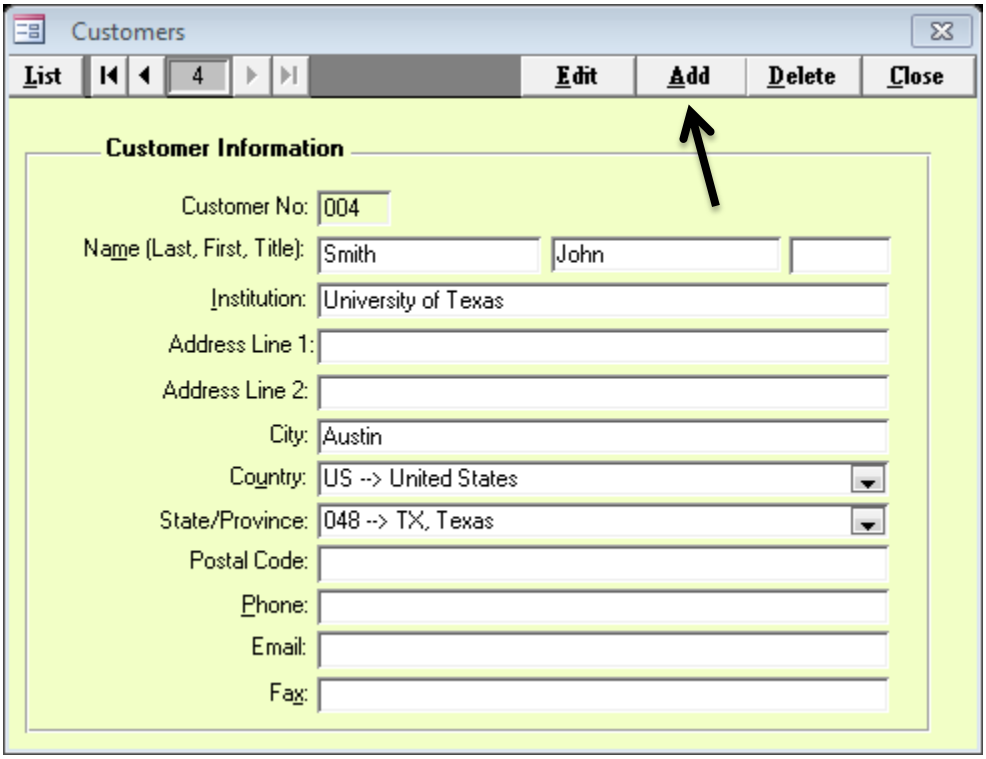
6.1 Adding or Removing Customers

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

A customer list can be populated with a list of regular clients, or customers may be added over time. Ensure that a customer exists in *LIMS for Lasers* before attempting to create new projects. Pay close attention to name spelling to avoid duplicating the same customer (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 Lastname, Firstname, 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".



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

6.2 Adding Projects and Samples

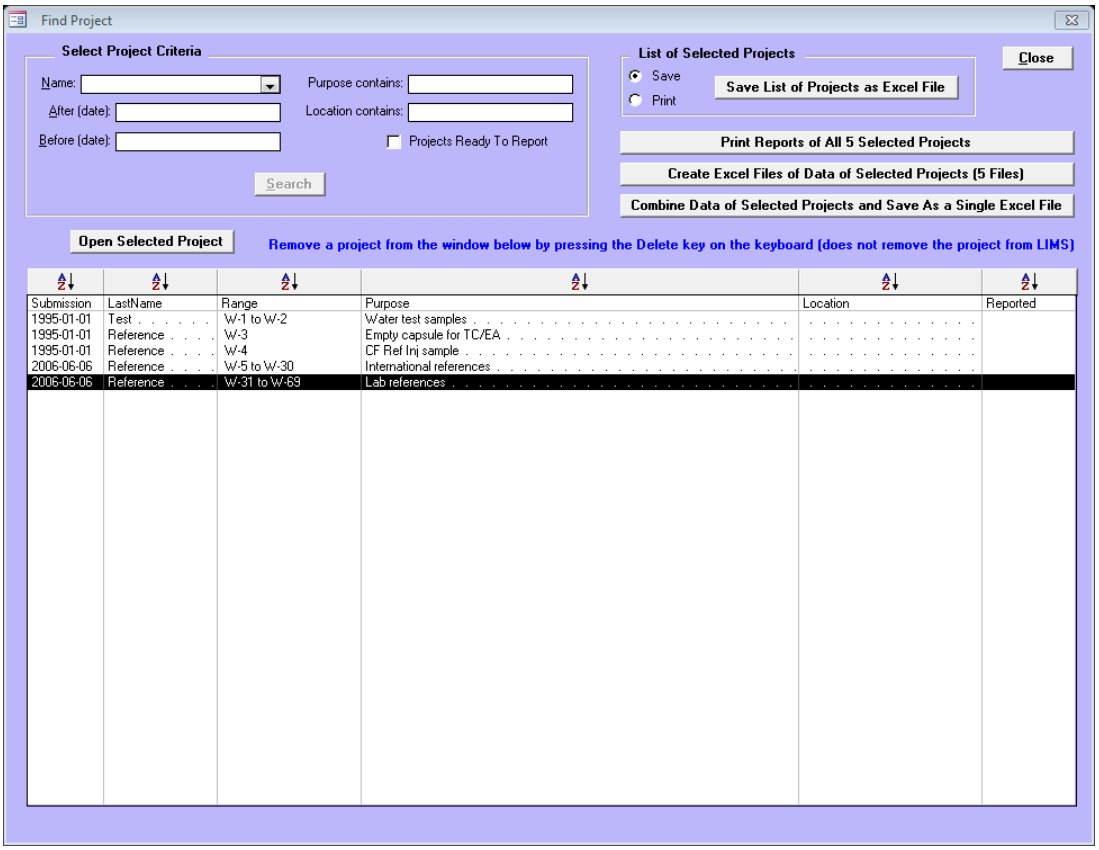
Projects are defined as a group of water samples submitted by a customer for the analysis of δ^2H and/or δ^{18}O for a particular purpose and/or from a specific location (e.g. Project Name, Location).

LIMS for Lasers comes with a project for international measurement standards (e.g. VSMOW2, SLAP2), and a project for local measurement standards (e.g. your own laboratory standards). A test project is also included - typically used for dummy or conditioning samples. These predefined projects should not be deleted. Your laboratory measurement standards and tests waters can be added to and edited in these projects.

New customer projects are created in one of two ways:

- Manually entering customers and their sample information.
- Automatically importing customer sample information from an Excel template.

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



The Projects Summary Page

Searching for Projects

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

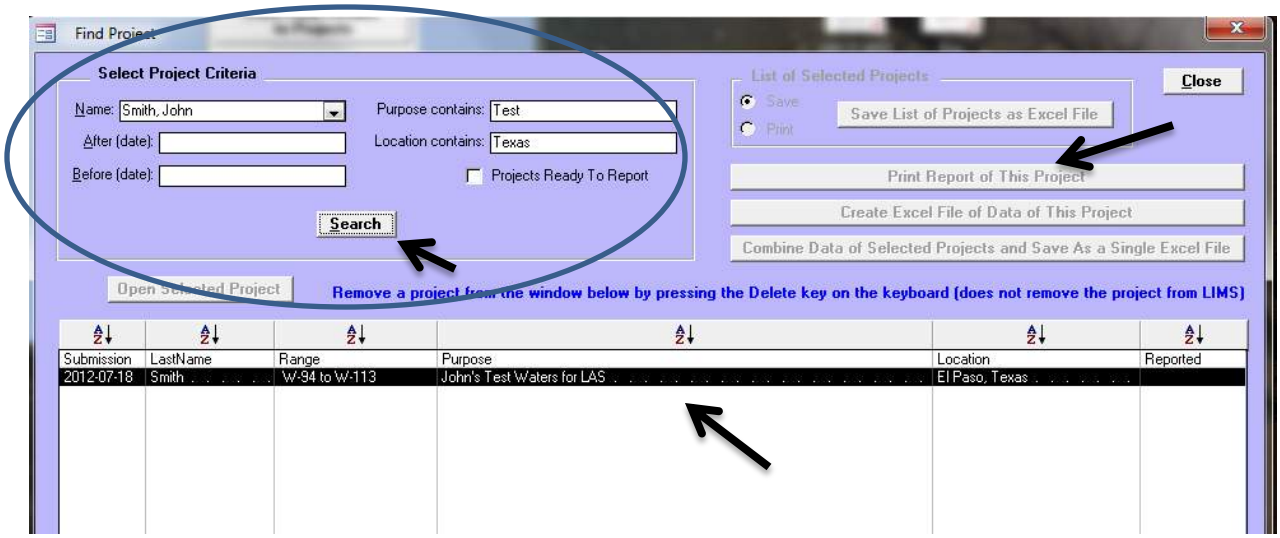
- Customer Name.
- Purpose.
- Before and/or after dates.
- Completed projects.
- Project Location.

Sorting Projects

Simple sorting of Project information can be accomplished by clicking on project column headers, like Project, Location, Submission Date, Sample ID, Customer, or date Reported.

Reporting and Exporting

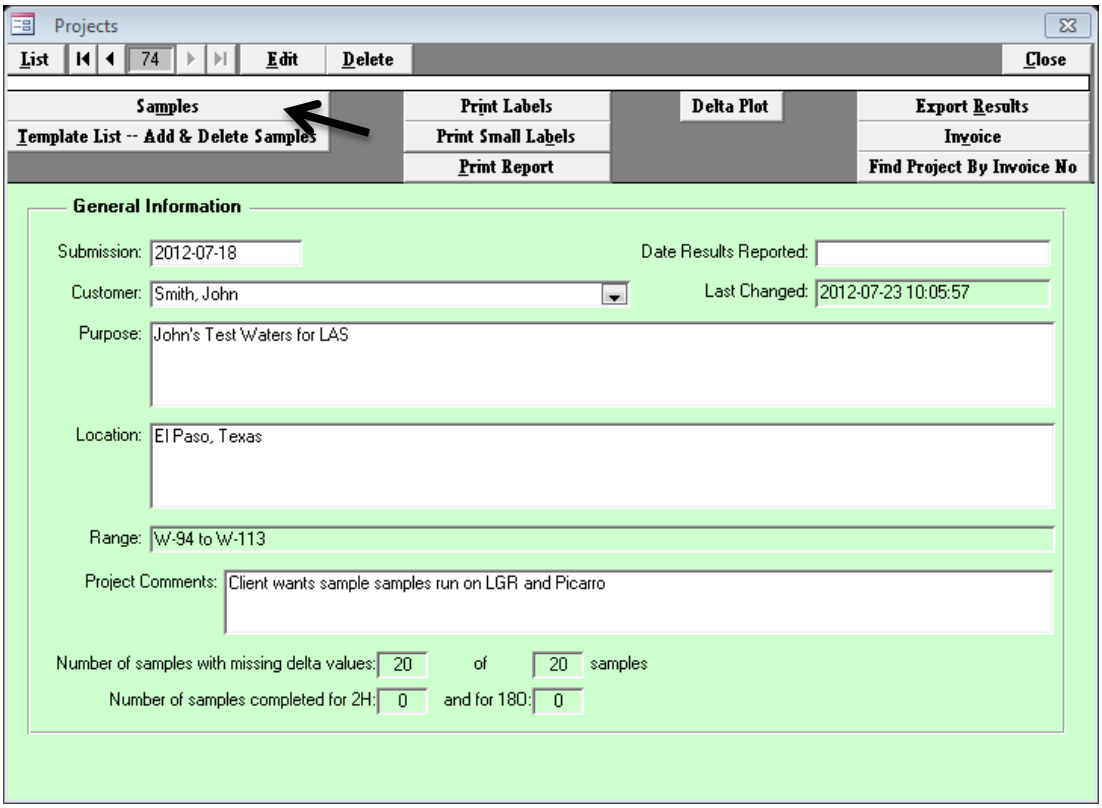
Searching, exporting, and combining projects into a single report or a single or combined Excel files are done on the Project overview page. Summary lists of all current or searched or sorted laboratory projects may be printed or saved to Excel files. This feature provides a quick way to search, acquire, and summarize laboratory productivity information for annual reports.



Project Information

A customer project is opened up by double clicking on the highlighted project. The lower part of the project window displays a summary of mandatory and optional information about that project, including:

- The submission date when the samples arrived or were logged (required).
- The Customer name (required).
- Purpose - a descriptive, searchable field (optional).
- Project Location - a descriptive, searchable field (optional).
- Sample Our Lab ID Range (these numbers are 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 window (grey buttons) display several action items that apply to the opened Project. These include:

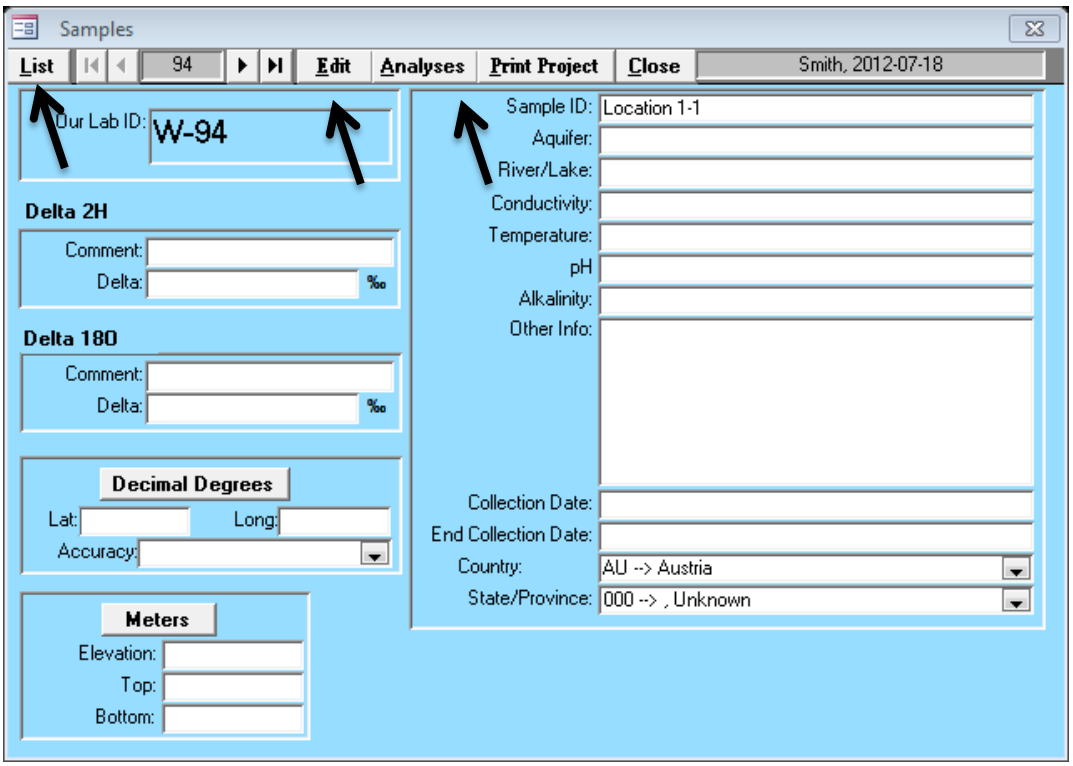
- Editing and viewing individual sample details.
- Adding or deleting the project or individual samples to/from an analysis template.
- Printing of sample bottle and LAS vial labels.

- Printing a hard copy of the final project report for the customer.
- Graphing a δ^2H vs. δ^{18}O cross-plot of the results.
- Exporting Project results to an Excel spreadsheet.
- Invoicing.
- Deleting a Project – click the "Delete" button –this action can only be done if no analyses have been imported into *LIMS for Lasers*.

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

Samples and Analyses

Within the project summary window, clicking on the "Samples" button opens up information pertaining to individual samples in the project. Navigation through the list of samples is performed by using the arrow buttons or the List button, both at the top left of the Window.



On each page information about each sample is summarized. This information includes:

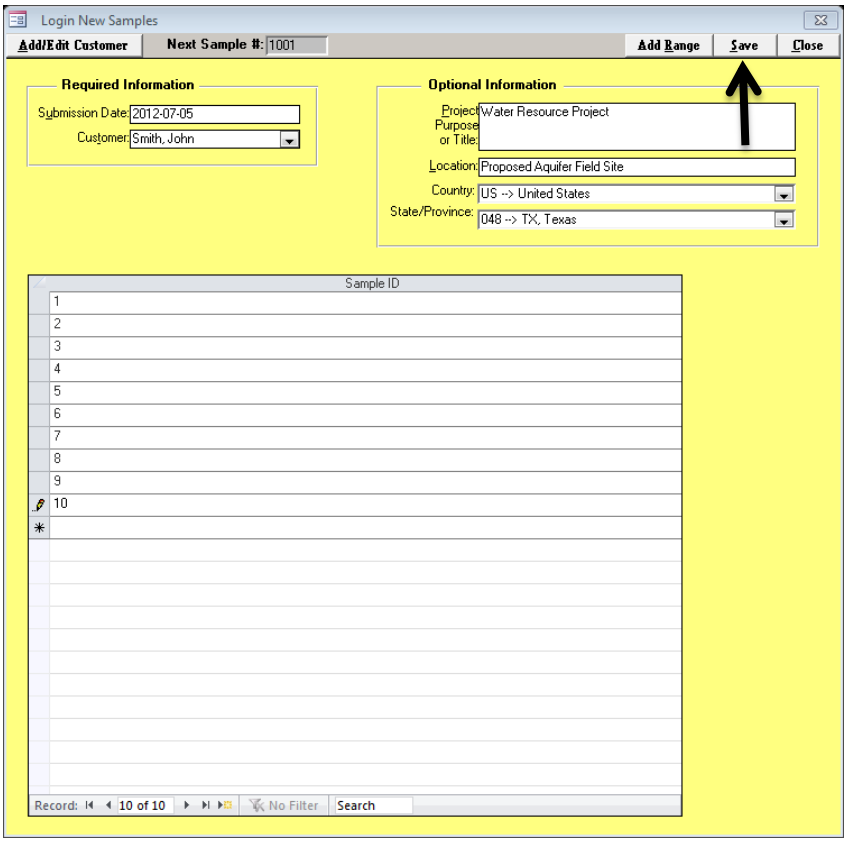
- The sample Our Lab ID (assigned by LIMS).
- The sample δ^2H and δ^{18}O results, if evaluated and stored.
- Various optional customer supplied information about the specific sample.

Clicking on the "Analyses" button opens another window that gives detailed information about the specific isotopic analyses of each sample, including the date analysed, the instrument name, method, etc. This window opens only if one or more sample analyses have been completed.

6.3 Manually Create a New Project

Manual project creation and entry of samples is illustrated using an example. John Smith (a previously added Customer) submitted 10 water samples from a proposed aquifer test site in Texas for the Purpose of a water resources evaluation project. The sample bottles arriving in the laboratory are 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 pull down menu.
4. Type “Water Resource Project” in Project Purpose or Title field.
5. For Location – type “Proposed Aquifer Field Site”.
6. Choose “US” from country pull down menu.
7. In the Sample ID box, type the sample names (1 to 10), one sample per line.
8. When done, click “Save” (top right).
9. A dialog box confirms that you want to create this new project containing 10 new water samples with LIMS assigned ID ranging from W-1001 to W1010. Click Yes.
10. The new Project is completed and is now visible in the “View Projects” tab.

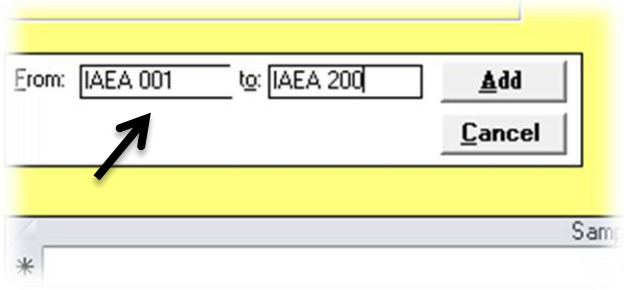


The minimum information required is Submission Date, Customer, and Sample ID. Optional Information can be updated later (see Advanced Features Chapter). Note that sample names must be unique, any duplicates should be renamed (Sample1, Sample1a, Sample1b, etc).

The "Add Range" Option

Manual project entry can be aided by 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 incremental numbering.

Clicking on "Add Range" button opens an additional "From:" and "To:" field in the white box below Required Information:



The format of the From and To fields requires that both entries have the same nonnumeric prefix if there is a nonnumeric prefix:

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 a Range Error)

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

Submission: 2012-07-18 Smith, John **W-94 to W-113** 2012-07-19

Purpose: John's Test Waters for LAS

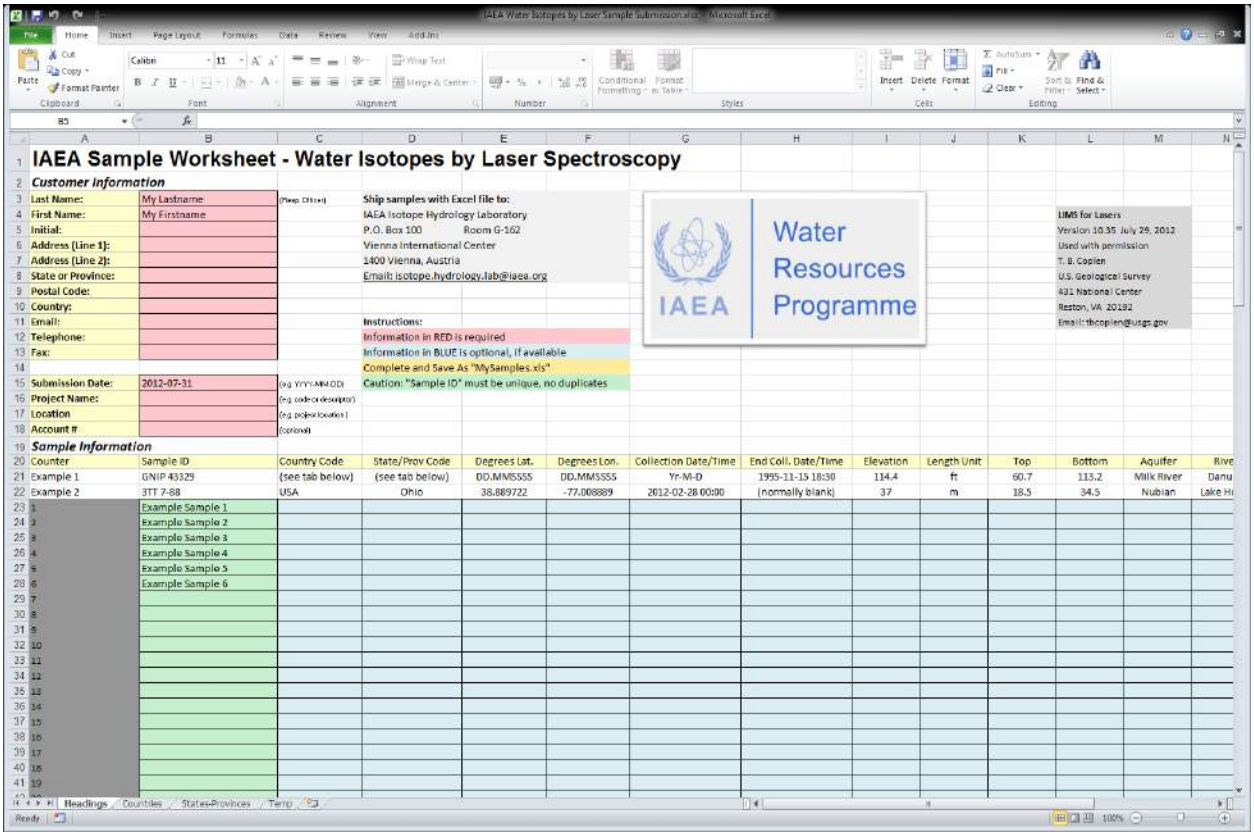
Location: Texas

Sample ID:	Collection Date	Our Lab ID	$1000\,\delta^{2}H_{VSMOW}$ Value	Comment	$1000\,\delta^{18}O_{VSMOW}$ Value	Comment
Location 1-1		W-94				
Location 1-2		W-95				
Location 1-3		W-96				
Location 1-4		W-97				
Location 1-5		W-98				
Location 2-1		W-99				
Location 2-2		W-100				
Location 2-3		W-101				
Location 2-4		W-102				
Location 2-5		W-103				
Location 3-1		W-104				
Location 3-2		W-105				
Location 3-3		W-106				
Location 3-4		W-107				
Location 3-5		W-108				
Location 4-1		W-109				
Location 4-2		W-110				
Location 4-3		W-111				
Location 4-4		W-112				
Location 4-5		W-113				

An example of test project printed from the LIMS Project Page having no completed and stored samples .

6.4 Importing a Project using Excel Submission Forms

An easy way to create a new project is to import Excel sample submission templates containing sample and project information provided by your Customers. Having customers complete and provide the sample names and details and submitting an Excel file (by email or diskette) along with the samples saves staff time and eliminates laboratory transcription errors. A user editable sample submission template is available from the IAEA website (Chapter 3).



To Import and Create a New Project using an Excel Template

1. On the LIMS Main Page, click on "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. The New Project will appear under "View Projects".

***Reminder**:* Before importing an Excel file, ensure the Customer is added and their first and last name are spelled the same as in the Excel file (see Chapter 6.1).

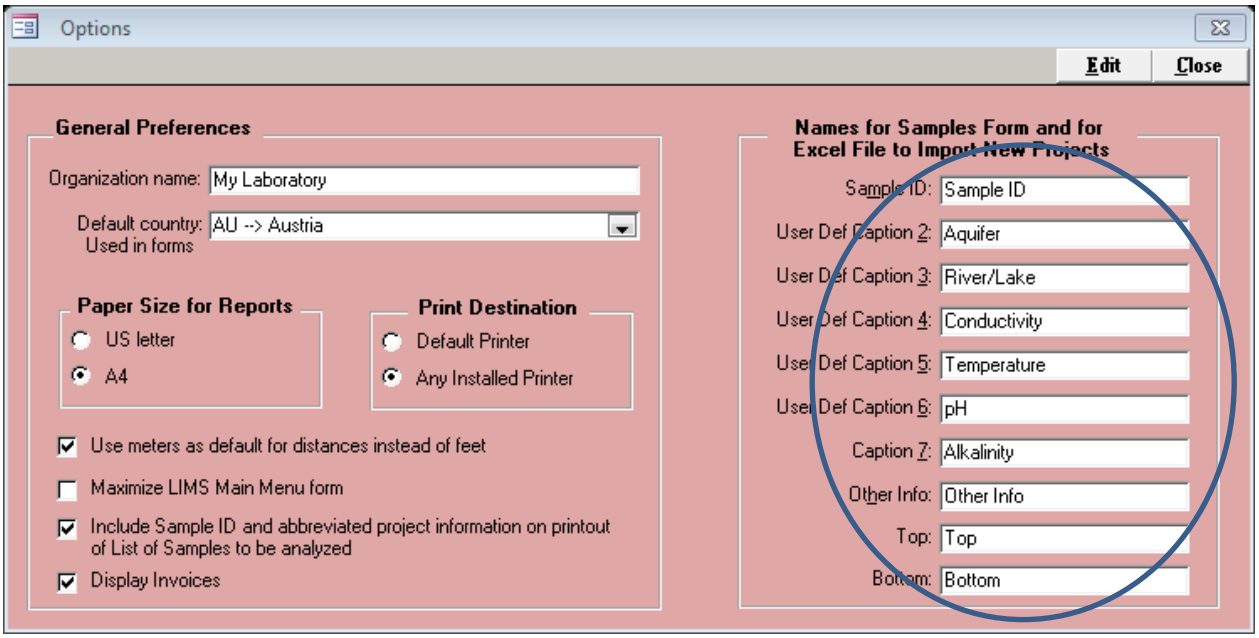
6.5 Customizing Client Excel Submission Templates

A convenient way to create New Projects is to deploy customized Excel sample submission templates to your laboratory customers.

An editable "unprotected" *LIMS for Lasers* Excel Sample Submission template is available from the links in Chapter 3.0. This Excel file may be edited and changed to construct your own laboratory information needs and graphics.

Any data field customizations to the Excel template will require editing *LIMS for Lasers* 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*.

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 be used in the Excel file.



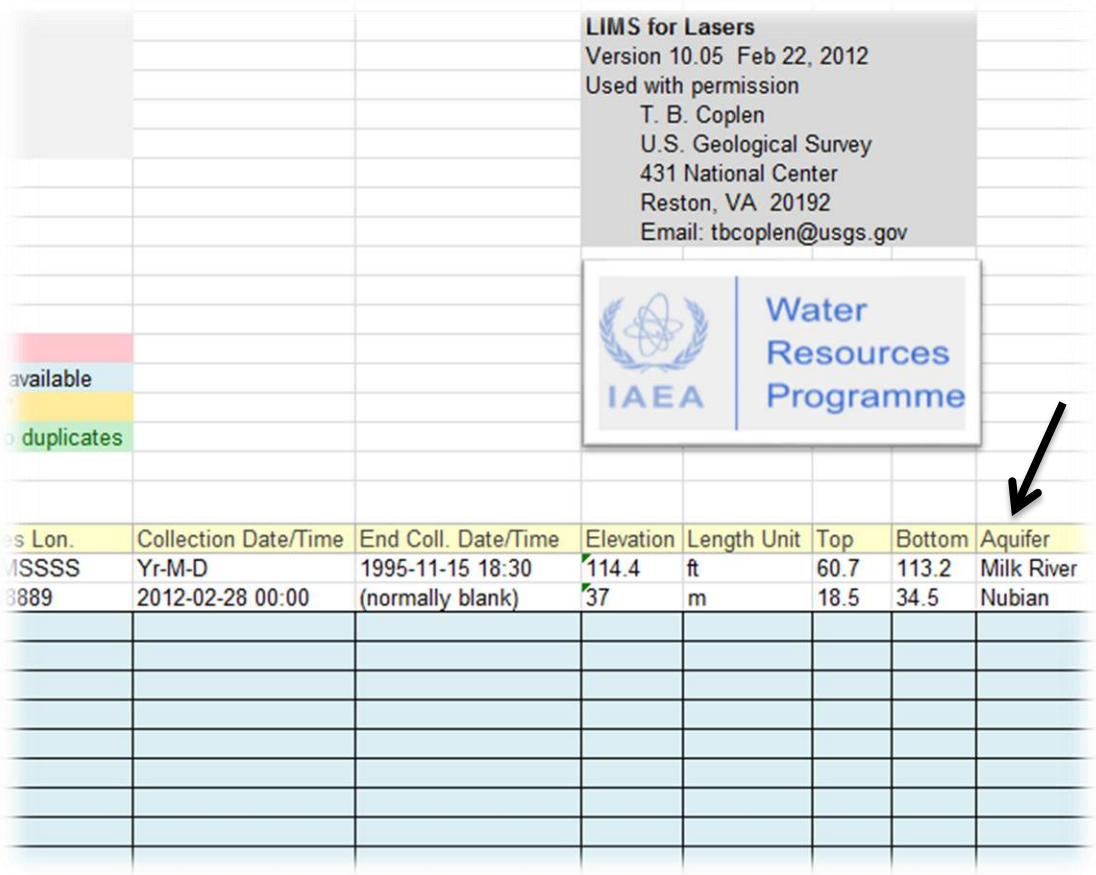
To change any of the field names (e.g. Aquifer, Conductivity, pH, etc.) to your own preferences, click "Edit" and change the fields. For example, "Aquifer" might be changed to "Site Name".

Not all of the field names are required. *LIMS for Lasers* requires only the Sample ID in this custom list. Thus, if you do not need Caption 7 (e.g. Alkalinity), delete the text from the Caption 7 textbox, and delete the "Alkalinity" column from the default Excel template. Once all required edits are made, click "Save" and then "Close".

LIMS will now expect matching headers in the customized Excel import file.

Changing the Headers in the Excel Submission Template

Open the default "unprotected" Excel Sample 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 options fields, or the import will fail. For optional fields left blank in *LIMS for Lasers*, delete that same column from the submission spreadsheet.

***Caution*:** Repeatedly changing LIMS field header names over time is strongly discouraged. Give clear thought to what information is required for your laboratory, and stick with it.

***Note*:** The *LIMS for Lasers* 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.

Sample Submission Template Protection

Long experience has shown that distributed Excel sample templates are invariably tampered with by customers (e.g. customers may delete or add columns, paste incorrect cell formats, paste to a new spreadsheet, etc.), all of which cause an import failure in *LIMS for Lasers*.

For this reason, the submission worksheet may be "protected" to allow customers to fill out only those fields required by the laboratory. While the Excel cell protection is not foolproof, your laboratory should also provide explicit instruction on its 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.

6.6 Tips for Successful Excel Submission Templates

Based on our LIMS experience with hundreds of clients, here are some tips for the successful use of client supplied Excel sample submission forms:

In the Laboratory

- Download the provided unprotected Excel template to add/edit your required data (contact information, address, add laboratory logos, etc.).
- Ensure any changed optional fields in Excel *exactly* match those in 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.
- **Do not** combine different customer samples into a single project – this will be confusing.

To the Customers

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

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

6.7 Printing Sample and Vial Labels

Printing Large Sample Labels

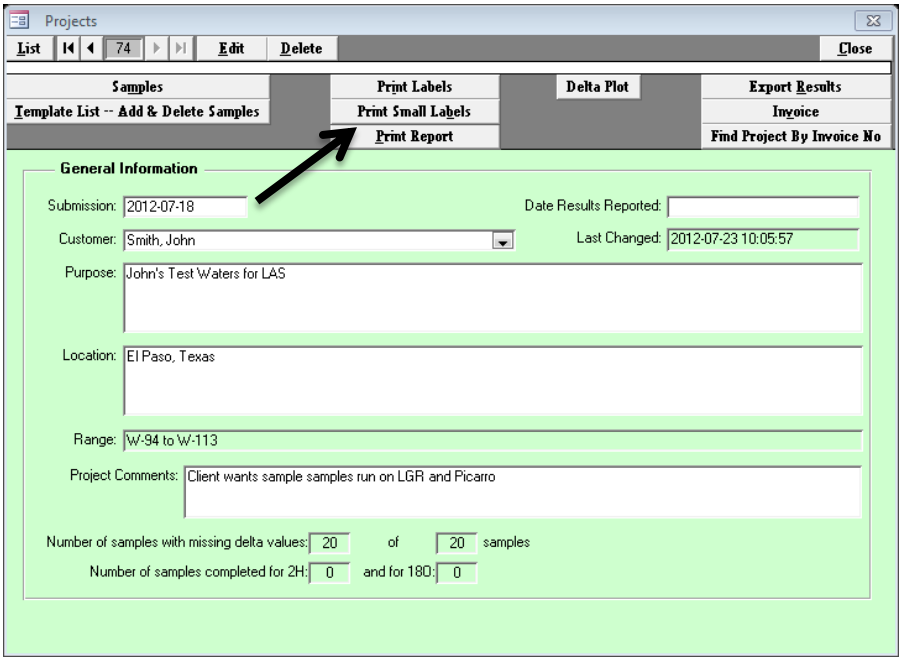
LIMS for Lasers can print large adhesive labels (Avery or equivalent) that can be affixed to the sample bottles. This will allow laboratory staff to organize and better locate client sample bottles.

1. In the Customer Project, click Print Labels, and 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 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 or A4). Click Print.
4. Affix the printed LIMS large sample labels to the correct customer sample bottles.

Print Small Labels for LAS Sample Vials

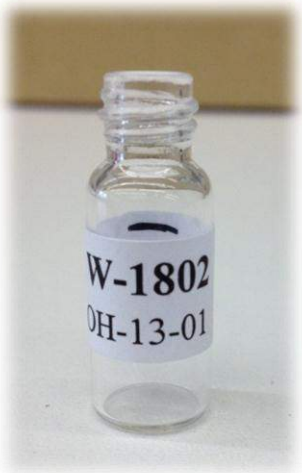
LIMS for Lasers can print small labels to be affixed to 2 mL sample vials that are used on the laser instrument autosampler.

1. In the Project window, click on Print Small Labels, and click Yes.
2. The default number of labels per sample printed is 1 (pick 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).



W-94 Location 1-1	**W-95** Location 1-2	**W-96** Location 1-3	**W-97** Location 1-4
W-98 Location 1-5	**W-99** Location 2-1	**W-100** Location 2-2	**W-101** Location 2-3
W-102 Location 2-4	**W-103** Location 2-5	**W-104** Location 3-1	**W-105** Location 3-2
W-106 Location 3-3	**W-107** Location 3-4	**W-108** Location 3-5	**W-109** Location 4-1
W-110 Location 4-2	**W-111** Location 4-3	**W-112** Location 4-4	**W-113** Location 4-5

Example printout of small labels.



LAS instrument 2 ml vial with small label attached.

7

Isotopic Measurement Standards

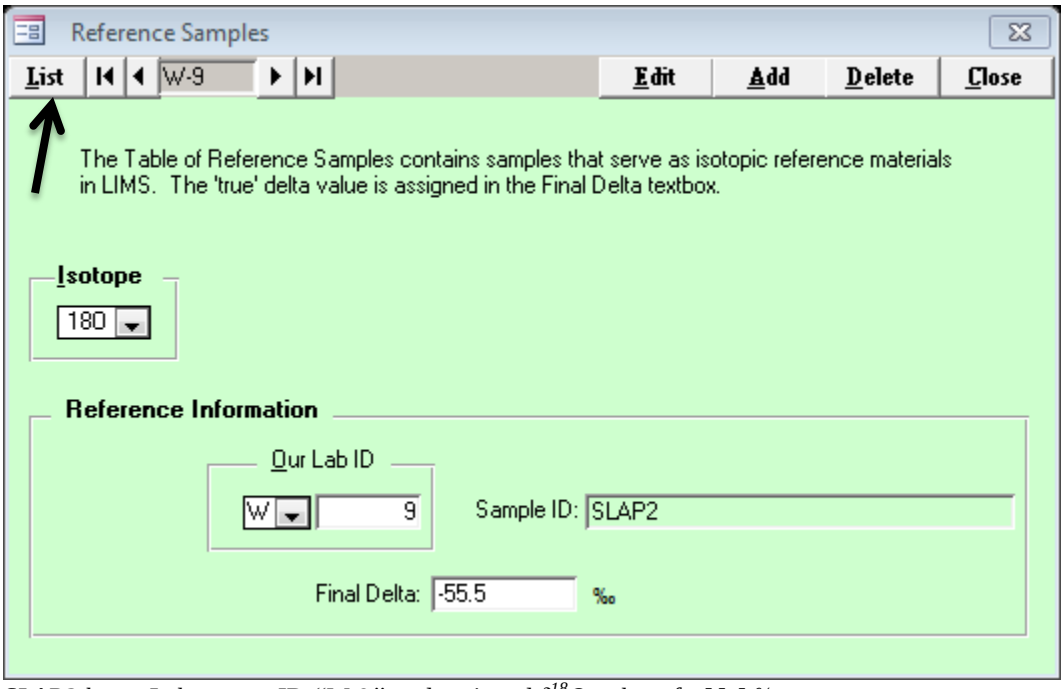
7.1 Reference and Laboratory Isotopic Measurement Standards

LIMS for Lasers comes with projects for international measurement standards, and for daily use measurement standards used in normalizing the analytical results of water samples.

International Measurement Standards (VSMOW2, SLAP2)

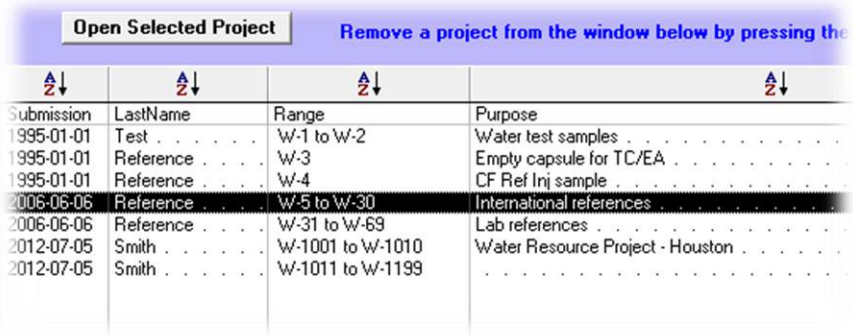
To view the table of assigned values for international measurement standards:

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



SLAP2 has a Laboratory ID "W-9" and assigned $\delta^{18}O$ value of –55.5 ‰

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



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 Adding Daily Use Measurement Standards and Controls

Daily-use measurement standards (or in-house standards) are used to normalize the measured isotopic results of samples to the VSMOW-SLAP scales for final reporting[2]. The onus is on the laboratory to obtain and use appropriate local measurement standards, and ensure they are carefully calibrated against the VSMOW-SLAP international measurement scales (see Appendices for Sources and recommended Calibration Templates for Daily-use standards).

LIMS for Lasers comes with over 35 placeholders for user-supplied local measurement standards in a Project called "Laboratory references" whose Customer is named "Reference". These local measurement standards have pre-assigned LIMS Laboratory ID numbers from W-31 to W-69 (see previous Figure). This project is where your laboratory can add its own standards.

Be aware that a newly installed version of the *LIMS for Lasers* does not have any isotopic values assigned to the local measurement standard placeholders in the Table of References. To assign their known values, one must edit the local measurement standards, and add their assigned isotopic compositions to the *LIMS* table of references.

By example, here we will edit and add two new local measurement standards and a control standard into our Table of References. These have the following known isotopic composition:

My Laboratory Standard 1	δ^{18}O = –0.07 ‰	δ^{2}H = –4.1 ‰ (relative to VSMOW)
My Laboratory Standard 2	δ^{18}O = –24.76 ‰	δ^{2}H = –189.2 ‰ (relative to VSMOW)
My Control Standard	δ^{18}O = –999 ‰	δ^{2}H = not assigned

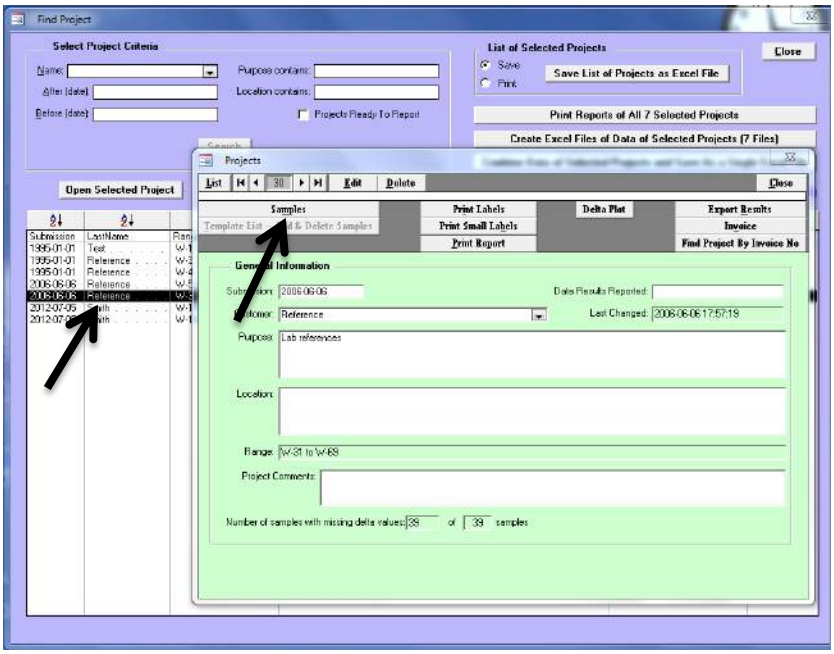
Note: The Control Standard must be assigned an δ^{18}O value of –999 ‰ which acts as a LIMS flag to denote the δ^{18}O of this standard is always null. It should not be assigned any δ^{2}H value. Because the control is null, LIMS will not use it in any normalization when it is included in analysis runs, although you will be able to monitor its results. The isotopic composition of the control does not matter, although a control standard with δ^{2}H and δ^{18}O values lying in between the local measurement standards is preferable. The sole purpose of the control standard will be to track our laboratory QA/QC over time.

First, we need to edit and rename three "pre-assigned placeholders" for local measurement standards and the control to their actual names or Sample IDs, as listed above.

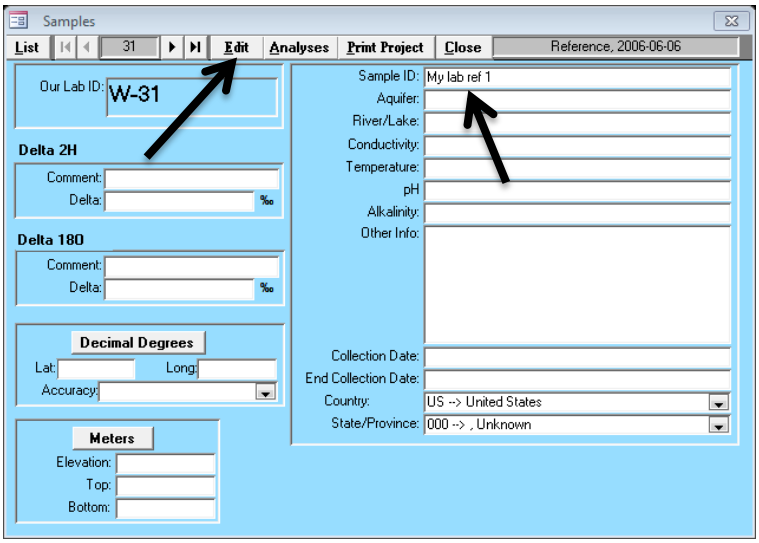
We will assign "My Laboratory Standard 1" to W-31, "My Laboratory Standard 2" to W-32, and our "Control standard" will be assigned to W-33.

1. On the LIMS Main Page, Click "View Projects".
2. Double on click the Project called "Lab References".
3. Click on "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 “My Laboratory Standard 1”, but leave all other entries alone (do not enter δ values!).
7. Click “Save”.
8. Click again on the “List” button and choose W-32 from the pull down menu.
9. Click “Edit”, delete and replace “My laboratory ref 2” with “My Laboratory Standard 2”.
10. Click “Save”.
11. Click again on the “List” button and choose W-33 from the pull down menu.
12. Click “Edit”, delete and replace “My laboratory ref 3” with “My Laboratory Control”.
13. Click “Save”. The renaming of these three samples is completed.
14. Click “Close” to return to the LIMS Main Page.



Project “Laboratory references” with Laboratory IDs W-31 through W-69.



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

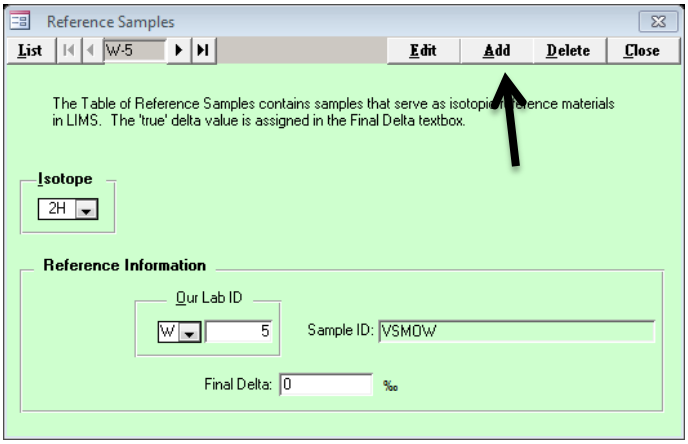
7.3 Assigning Isotopic Values to Daily Measurement Standards

Now we need to assign the known isotopic values to our daily use laboratory measurement standards, and add a special LIMS flag to our control standard.

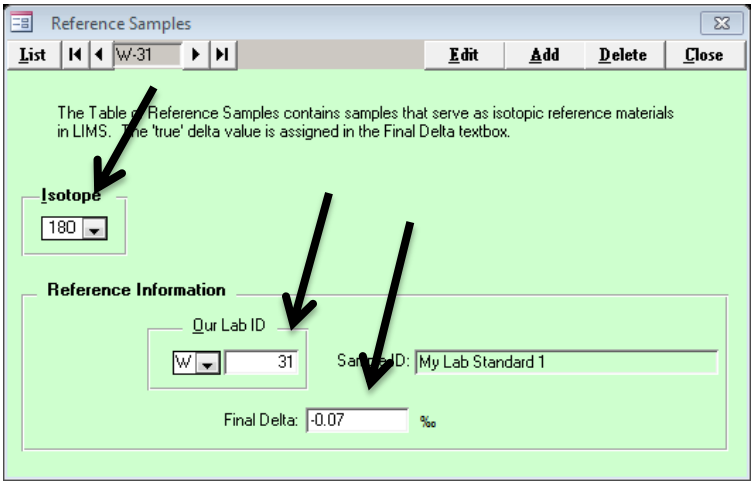
1. On the LIMS Main Page, open “Special Features”.
2. Click “Assign Lab References”.

To Add the First Measurement Standard $\delta\,^{18}O$ and $\delta\,^{2}H$ Isotopic Values

3. To add the known or assigned ^{18}O value, click on “Add”.



4. Click the pull down menu under “Isotope”, choose “18O”.
5. In “Our Lab ID” field, enter “31”. “My Laboratory Standard 1” should appear in the “Sample ID” field.
6. In the “Final Delta” field, enter its assigned value, here –0.07 ‰ for $\delta^{18}O$ as listed on page 42.
7. Click “Save”.



8. Next, to add the known or assigned ^{2}H value, click on “Add”.
9. Click the pull down menu under “Isotope” and choose “2H”.
10. In the “Our LabID field, enter “31”. “My Laboratory Standard 1” will appear in the “SampleID” field.
11. In the “Final Delta” field, enter its assigned value, here –4.1 ‰ for $\delta^{2}H$ that is listed on page 42.
12. Click “Save”.

To Add a Second Measurement Standard $\delta^{18}O$ and $\delta^{2}H$ Isotopic Values

13. To add the second measurement standard, repeat steps 3 to 12 above, instead using W-32 “My Laboratory Standard 2” with the example values for $\delta^{18}O$ and $\delta^{2}H$ ($\delta^{18}O$ = –24.76 ‰, $\delta^{2}H$ = –189.2 ‰ shown on page 42).

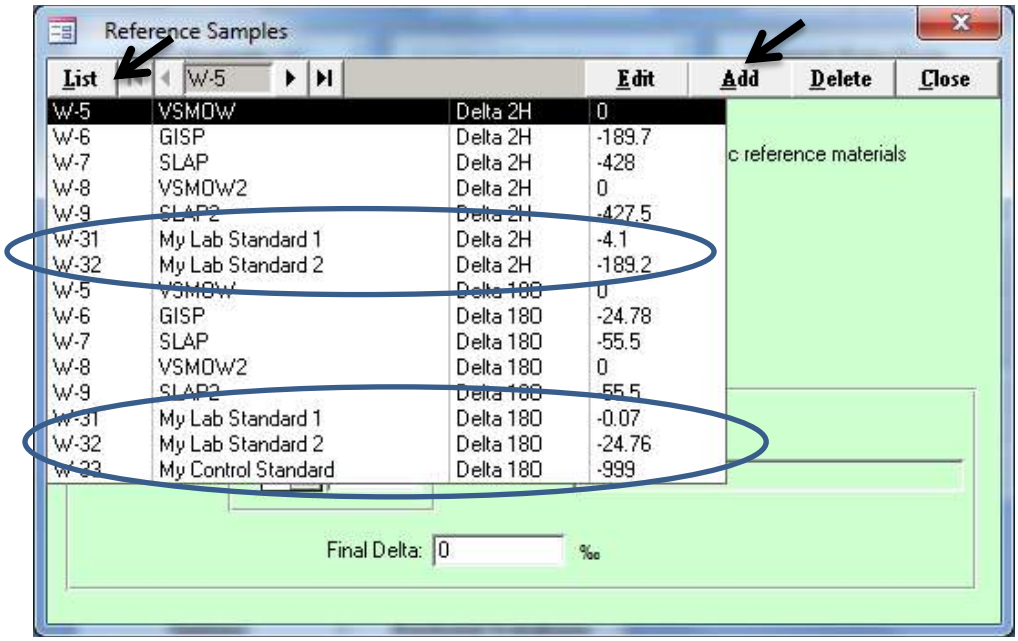
To Add a Control Standard

14. Repeat steps 3 to 7, instead using sample W-33 “My Laboratory Control”.
15. Enter the 18O value of –999 ‰. (remember: do <u>not</u> add ^{2}H)
16. Click “Save”
17. Click “Close”

To review your current list of international and local measurement standards and their assigned isotopic compositions in *LIMS for Lasers*, in the Special Features page click on “Assign Lab References”, and then click the “List” button.

The figure below lists a summary of international measurement standards, the newly added local measurement standards, and the control standard, sorted by element and their corresponding “W” Our Lab ID numbers.

If you need to change the assigned isotopic value of either international or local measurement standards, highlight that standard and isotope to be changed in the list and click “Edit”. Then enter the new value in the Final Delta field and click “Save”.



Example of our newly added daily use measurement standards and a control standard

VERY IMPORTANT NOTE ABOUT MEASUREMENT STANDARD VALUES

Edited laboratory measurement standard values affect only *future results and samples that have not yet been normalized and stored*.

Previously normalized and stored results are not changed retroactively, and they retain all of the normalization parameters and the assigned isotopic standard values that were used at the time of their normalization processing. Prior data normalizations are therefore protected.

8

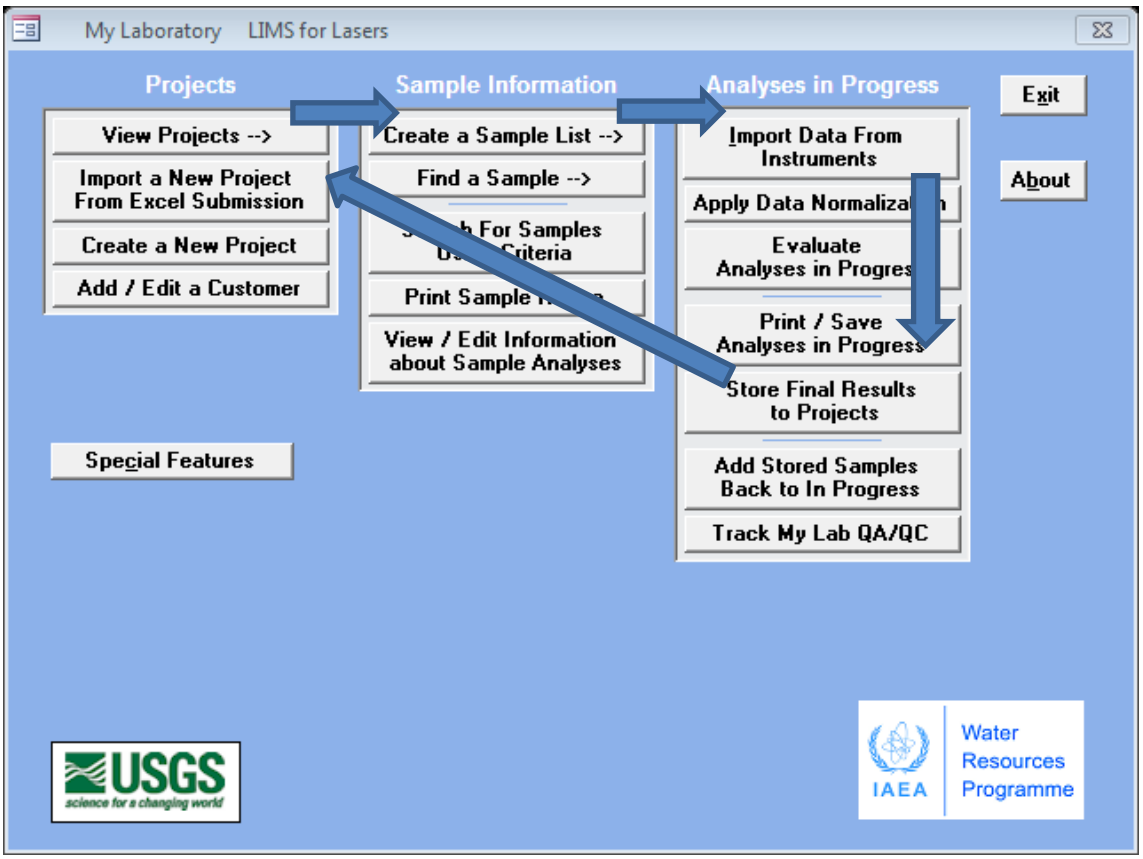
Sample Analysis Templates

8.1 Sample Analysis in LIMS for Lasers

Now that we have learned to add Customers and Project samples into *LIMS for Lasers*, we can begin to prepare and analyse water samples on an LAS instrument, through the use of instrument Analysis Templates (also known as sample lists, queues, or sequence run files).

Analysing LAS samples using *LIMS for Lasers* follows a general 8-Step procedure:

1. Adding the customer samples to an instrument Analysis Template (or queue).
2. Creating and printing a list for sample preparation (e.g. filling vials) and transferring the sequence to the Los Gatos Research or Picarro data acquisition and control software.
3. Measuring unknown samples at least twice (on a Los Gatos Research or Picarro, and importing the measured isotopic data into *LIMS for Lasers.*
4. Correcting imported results for between-sample memory and/or instrumental drift.
5. Normalizing the samples to the VSMOW-SLAP scales using calibrated daily-use measurement standards.
6. Evaluating the results for errors, for consistency among runs, tracking the Control standard performance.
7. Checking and storing the accepted results of two or more sample repeats.
8. Reporting final results to the Customer, in hard copy or Excel.



Work flow path in LIMS for Lasers

8.2 The Importance of Analysis Templates

LIMS for Lasers comes with default analysis templates for Los Gatos Research and Picarro instruments. These templates were designed and tested to obtain high quality results, check for problematic analyses based on the sample water yield, correct for between-sample memory, check and correct for instrumental drift, and to normalize the results of the unknown samples to the VSMOW/SLAP scale using calibrated laboratory standards. A control standard is used to monitor results and to report long-term LAS performance for QA/QC purposes.

Systematic analysis templates founded upon the Principles of Identical Treatment[3] are well-known to give the best results. Further, such systematic templates make it easier for operators to identify problems when changes in sample analysis patterns are observed.

In *LIMS for Lasers*, we highly recommend using the 9-injection-ignore-4 analysis template as a starting point for all LAS instruments from Los Gatos Research and Picarro. As LAS instruments improve, users can experiment with templates to tweak performance for their own needs and instruments, or to improve sample throughput by experimenting with fewer injections and ignored injections (e.g. 6 injections-ignore 3). Analysis templates remain fully customizable to the user preferences. **The settings recommended in this manual are intentionally conservative in order to obtain the best possible results from all generations of laser instruments.**

At the IAEA, as an example, various *LIMS for Lasers* templates were created for low latitude waters and contain bracketed laboratory standards with relatively high δ values, or for snow and ice samples that use a set of bracketed laboratory standards with low δ values, or for templates of differing numbers of samples, like a long (60 sample) or short (10 sample) autoruns, or for conducting local measurement standards calibration.

Why We Need Systematic Analysis Templates

There are two hardware factors that constrain the length of an LAS analysis template:

- Sample injection port septum failure. Septa may leak or fail after 300 to 800 injections, depending on the brand and the quality.
- Syringe failure. Microliter syringes can fail after as few as a dozen injections to over 2000 injections. Generally, the higher the dissolved solids (TDS) content of the samples, the sooner the syringe will fail from salt precipitation jamming of the syringe barrel.

As a result, it is recommended that LAS autoruns total no more than 500 to 800 injections, after which the septum must be changed. The syringe should always be monitored for signs of failure. Syringe degradation is manifested by decreased sample H_2O yields on most LAS instruments, in comparison to new syringe performance.

There are two instrumental constraints that impact the quality of LAS sample analysis templates:

- Between-sample "carryover" or memory– this is residual contamination from prior sample water molecules in the laser cavity and/or transfer lines between adjacent samples. This requires multiple injections of the same sample to overcome the memory of the previous sample. In most LAS instruments between-sample memory is less than 1 to 2 per cent after 3 or 4 sequential sample injections[4, 5]. Memory corrections require discarding the results of the first 3 or 4 (or more) injections, calculating and correcting for memory[6], or by averaging the last 3- 4 of 9 or more injections[7]. Between-sample memory corrections, whatever the approach taken, are very time consuming to perform offline in Excel.

- Instrumental drift. The earliest LAS instruments were prone to temperature dependent or random instrumental drift over the course of an autorun[4]. Because LAS instruments do not use a comparative reference gas like an IRMS to counteract this, drift (in either direction) in the final delta results may be observed. To overcome this, most LAS users placed small groups of unknown samples (3 to 5 samples) between groups of local laboratory standards, and they use "bracketed normalization", assuming linear (or no) drift has occurred between these small groups of samples and standards over short time periods (hours). Alternately, unidirectional linear drift may be observed in some LAS instruments, allowing users to apply a linear drift correction to the entire autorun with no need for sample and reference "bracketing". Either way, instrumental drift correction is time consuming to process offline in Excel.

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

Poor Injections - LIMS for Lasers

The failure of syringes and septa often result in low or poorly reproducible H_2O yields in the LAS cavity, as reported by the instrument software. Older laser instruments exhibit a significant change in isotopic composition that is partly dependent on water vapour content; therefore precise and consistent sample water injections remain crucial. While mechanical hardware failure like a jammed syringe may be obvious, less obvious are those bad injections or variable sample yields that occur when vials are insufficiently or over-filled, or if the syringe is performing poorly. A few poor sample injections among many hundreds of injections can be difficult to identify by scanning hundreds of rows of comma-separated (CSV) data in Excel.

To screen for poor injections, all imported LAS data files are checked by *LIMS for Lasers* to ensure H_2O yields are consistent across the autorun. This is done by checking that individual injections are within 85 per cent of the mean H_2O yield. Results falling outside this limit are flagged and their sample IDs displayed, along with a warning that the autorun may be compromised by septum or syringe failure. This gives the LAS operator a chance to double check their instrument hardware and possibly reanalyse the samples before erroneous results are reported to the customer.

This H_2O-based screening method is not fool-proof. Even if there are no errors reported, users should quickly scan H_2O yield summaries in the LIMS import for obvious isotopic outliers.

Between-Sample Memory - LIMS for Lasers

Between-sample memory in *LIMS for Lasers* is quantified using two local measurement standard pairs that differ greatly in their δ values, 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 are applied to all samples in the autorun. LIMS calculates between-sample memory using only "non-ignored" injections of sample and standards.

The advantage to this approach are that memory corrections are accurately calculated using repeating groupings of two references with widely separated delta values throughout the entire autorun, not inconsistently amongst pairs of differing samples having large or small isotopic composition differences. Further, it does not matter how many injections ignored, because the between-sample memory correction is well quantified and follows Principles of Identical Treatment. The determined mean between-sample memory correction is applied to *all* samples analysed regardless of their measured isotopic composition. Regardless, as a matter of good practice, we recommend ignoring the first 4 injections, which results in the lowest between-sample memory (usually < 1 per cent). See Chapter 11 for details on these calculations.

Instrumental Drift in LIMS for Lasers

Temporal instrumental drift in *LIMS for Lasers* 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 the samples. However, LAS 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* gives users the option to check for linear instrumental drift using one or more laboratory standards. One measure of confidence of whether to apply 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 of the measurement standards. Only then can a linear drift correction be applied with any confidence. While linear drift correction is optional, the use of "bracketed data normalization" (default setting) is generally been observed at the IAEA to give better results.

8.3 Using Default Analysis Templates

The following sections describe in detail the default analysis templates for Los Gatos Research and Picarro instruments as used in *LIMS for Lasers*. These default templates were designed to be robust and were tested to produce the best possible results for all generations of LAS 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.

The default *LIMS for Lasers* 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.

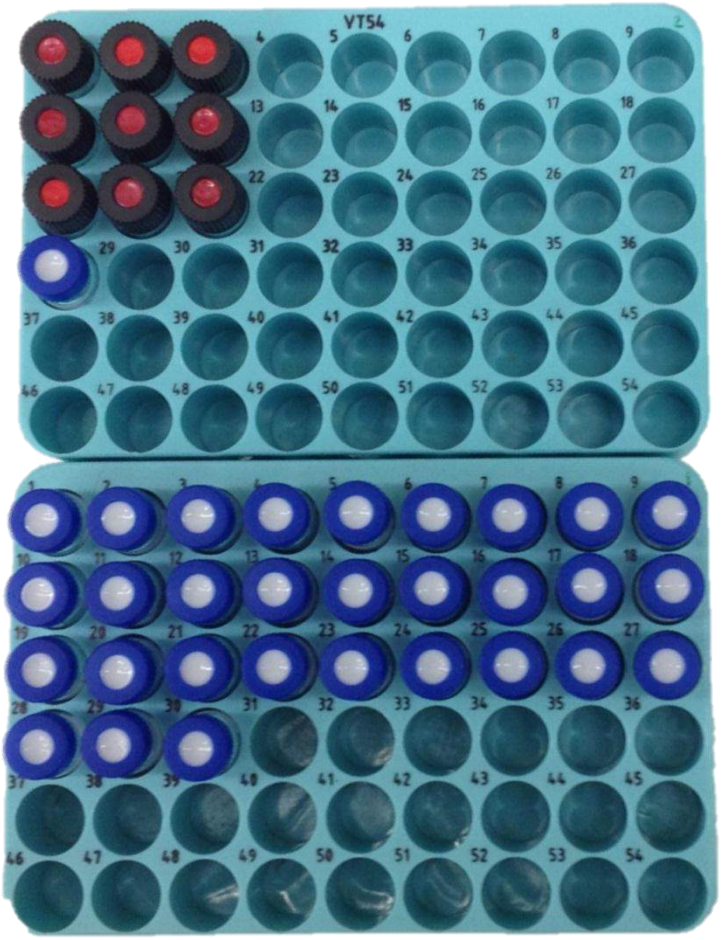
Whereas users are free to design their own analyses templates, the provided default templates are a good place to get started.

Table 1. Default 30-sample Analysis Template for Los Gatos Research Intruments. Samples are arranged sequentially in positions 1–30 of Tray 1 (front tray) in the CombiPAL autosampler. 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 68 rows of 9 injections each = 612 individual injections. Analysis time with a v1/v2 Los Gatos Research instrument is ~20 to 30 hours. See Figure for vial layout. List # is the order in which samples are analysed.

Sample	Vial Pos	List #	LIMS for Lasers 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
High δ Standard	3-11	6	Bracketed Normalization
High δ Standard	3-12	7	Bracketed Normalization
Sample 1	1-1	8	Unknown Sample
Sample 2	1-2	9	Unknown Sample
Sample 3	1-3	10	Unknown Sample
Sample 4	1-4	11	Unknown Sample
Sample 5	1-5	12	Unknown Sample
Sample 6	1-6	13	Unknown Sample
Control Standard	3-19	14	QA/QC
High δ Standard	3-10	15	Between-Sample Memory
Low δ Standard	3-3	16	Between-Sample Memory
Low δ Standard	3-1	17	Bracketed Normalization
High δ Standard	3-11	18	Bracketed Normalization
High δ Standard	3-12	19	Bracketed Normalization
Sample 7	1-7	20	Unknown Sample
Sample 8	1-8	21	Unknown Sample
Sample 9	1-9	22	Unknown Sample
Sample 10	1-10	23	Unknown Sample
Sample 11	1-11	24	Unknown Sample
Sample 12	1-12	25	Unknown Sample
Control Standard	3-20	26	QA/QC
High δ Standard	3-10	27	Between-Sample Memory
Low δ Standard	3-2	28	Between-Sample Memory
Low δ Standard	3-3	29	Bracketed Normalization
High δ Standard	3-11	30	Bracketed Normalization
High δ Standard	3-12	31	Bracketed Normalization
Sample 13	1-13	32	Unknown Sample
Sample 14	1-14	33	Unknown Sample
Sample 15	1-15	34	Unknown Sample

Sample 16	1-16	35	Unknown Sample
Sample 17	1-17	36	Unknown Sample
Sample 18	1-18	37	Unknown Sample
Control Standard	3-21	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
High δ Standard	3-11	42	Bracketed Normalization
High δ Standard	3-12	43	Bracketed Normalization
Sample 19	1-19	44	Unknown Sample
Sample 20	1-20	45	Unknown Sample
Sample 21	1-21	46	Unknown Sample
Sample 22	1-22	47	Unknown Sample
Sample 23	1-23	48	Unknown Sample
Sample 24	1-24	49	Unknown Sample
Control Standard	3-19	50	QA/QC
High δ Standard	3-10	51	Between-Sample Memory
Low δ Standard	3-3	52	Between-Sample Memory
Low δ Standard	3-1	53	Bracketed Normalization
High δ Standard	3-11	54	Bracketed Normalization
High δ Standard	3-12	55	Bracketed Normalization
Sample 25	1-25	56	Unknown Sample
Sample 26	1-26	57	Unknown Sample
Sample 27	1-27	58	Unknown Sample
Sample 28	1-28	59	Unknown Sample
Sample 29	1-29	60	Unknown Sample
Sample 30	1-30	61	Unknown Sample
Control Standard	3-20	62	QA/QC
High δ Standard	3-10	63	Between-Sample Memory
Low δ Standard	3-2	64	Between-Sample Memory
Low δ Standard	3-3	65	Bracketed Normalization
High δ Standard	3-11	66	Bracketed Normalization
High δ Standard	3-12	67	Bracketed Normalization
Deionized Water	3-28	68	End 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 CombiPAL Front and Rear Tray

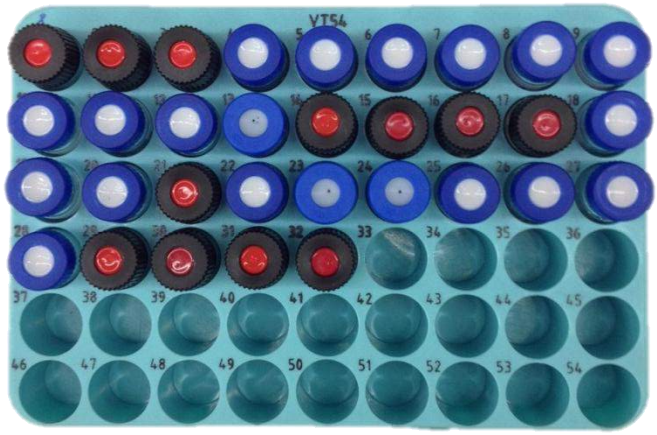
Note: In this Los Gatos Research analysis template, the vials of each local measurement standard and control standard contain ~1 to 1.5 mL of water. Triplicate redundancy of local measurement and control standards is intentional in order to avoid reliance on a single standard vial and to ensure the best 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 daily standard ampoules available to users from the USGS and IAEA (See Appendix 1).

Table 2. Default 20-sample Analysis Template for Picarro Instruments.
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 LL1102i 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).

Sample	Vial Pos	List #	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

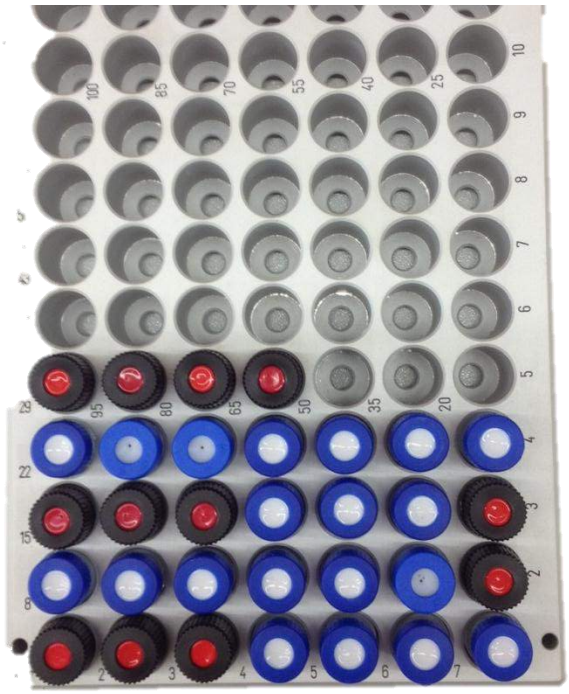
Vial Layout for Default Picarro Analysis Template



Default 20-Sample Analysis Template and vial layout, shown for Picarro CombiPAL 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



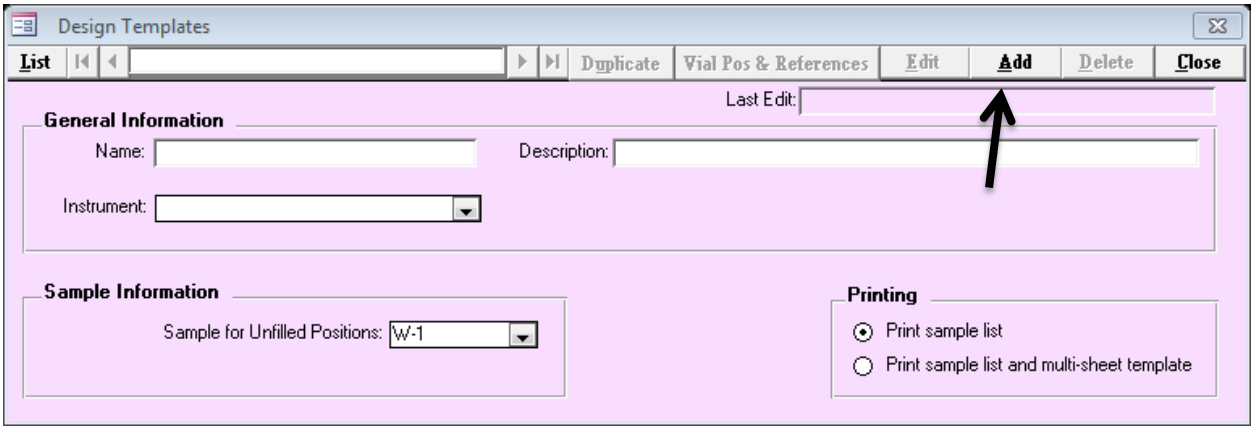
Default 20-Sample Analysis Template and vial layout, shown for Picarro G-2000 Autosampler.

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

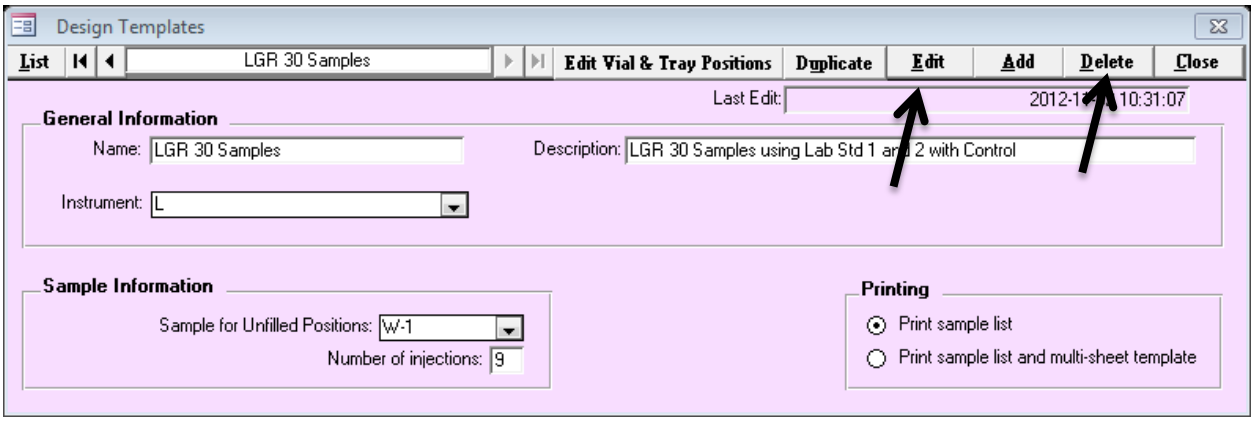
Above: Tray of the Picarro G-2000 Series Liquid Autosampler

8.4 Creating a New Los Gatos Research 30-Sample Analysis Template

1. From the LIMS Main Page, open “Special Features”.
2. Click on “Analysis Templates”.



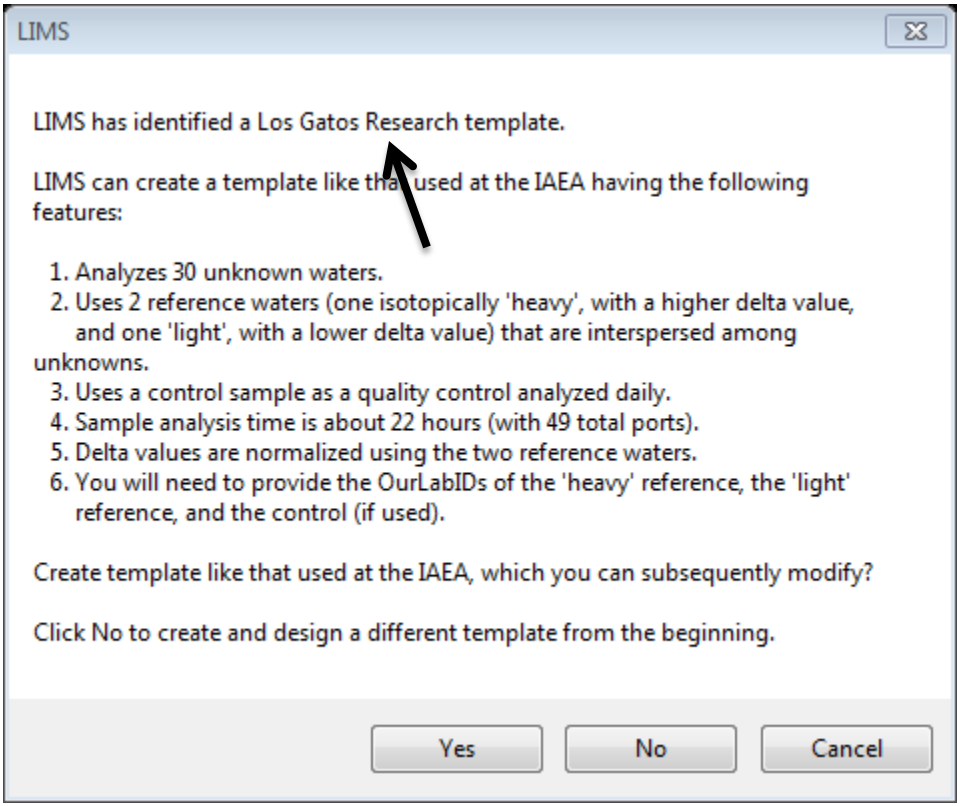
3. Click on “Add”.
4. Under “Name”, type a relevant description (e.g. Los Gatos Research 30 Samples).
5. Under Description – add relevant additional details (e.g. which Standards used).
6. Under Instrument, choose “L” for Los Gatos Research.
7. The “Sample for Unfilled Positions” defaults to W-1 (a dummy 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, 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.



Los Gatos Research Sample Layout and Instrument Run Sequence

The analysis sequence of local measurement standards, control standards and the client samples are set up by clicking the "Vial Pos and References" button. The term "Vial Pos" denotes the vial position of the sample or measurement standard in the tray of the instrument liquid autosampler.

Clicking on "Vial Pos and References" in *LIMS for Lasers* brings up the Los Gatos Research Analysis Template Wizard:



Clicking "No" presents the user with a blank template (if you want to design it from scratch). For now, choose yes.

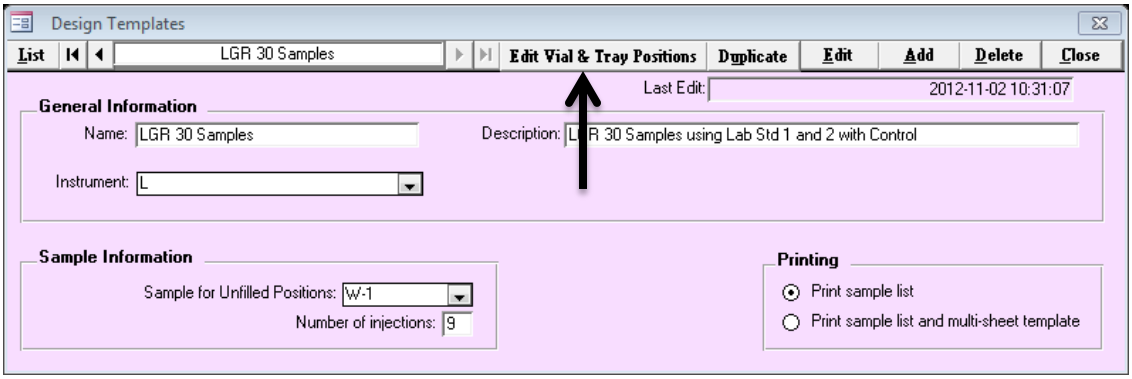
Before going further with template construction, you will need to know the Our Lab IDs of the local measurement standards (and control standard), and their corresponding "W" numbers.

If you do not have these "W" numbers at hand, go back to the View Projects button on the Main Page. The LIMS Project for laboratory measurement standards is called "Lab References" and has Our Lab ID place holders ranging from W-31 to W-69.

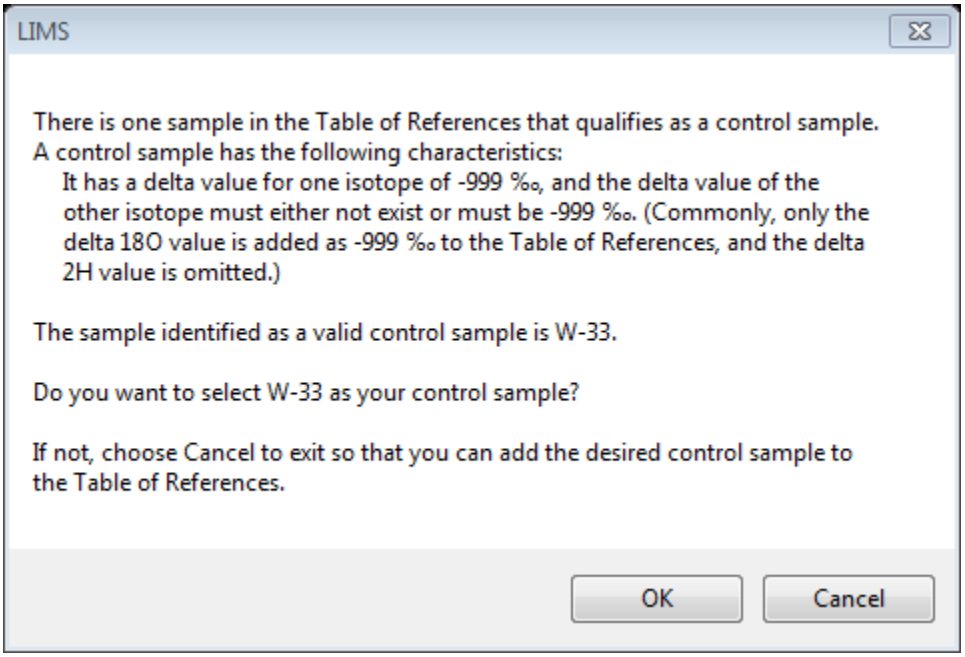
Recall in Chapter 6.4 that we created a high (δ) laboratory measurement standard (W-31), a low (δ) laboratory measurement standard (W-32), and a control standard (W-33). We will use these three laboratory measurement standards as an example for the new Los Gatos Research Analysis Template. Once "W" numbers are noted, proceed to the next step.

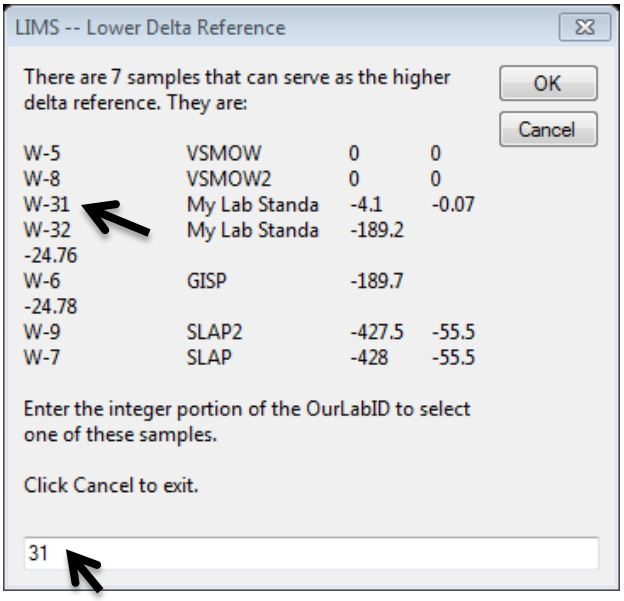
Go back, or stay in, Special Features → Analysis Templates → and choose the Los Gatos Research template to be created from the "List" button.

Click on "Edit Vial and Tray Positions", and then click "Yes" on the Wizard to create a new Los Gatos Research 30-sample template.

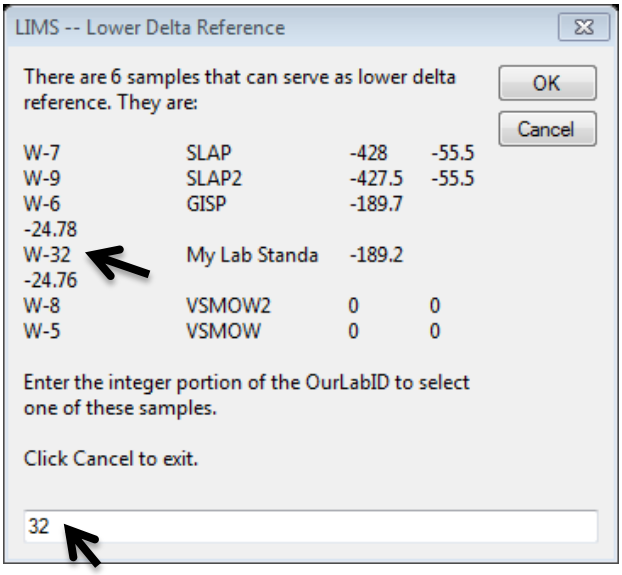


LIMS recognizes we created W-33 as our Control Standard, Click "OK", or cancel if you do not want to add a control standard.

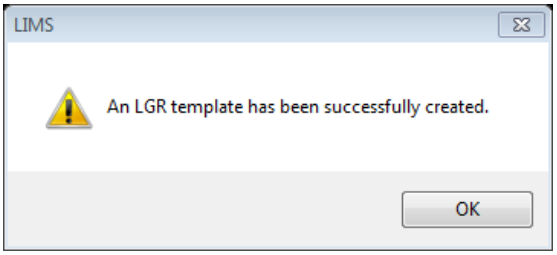




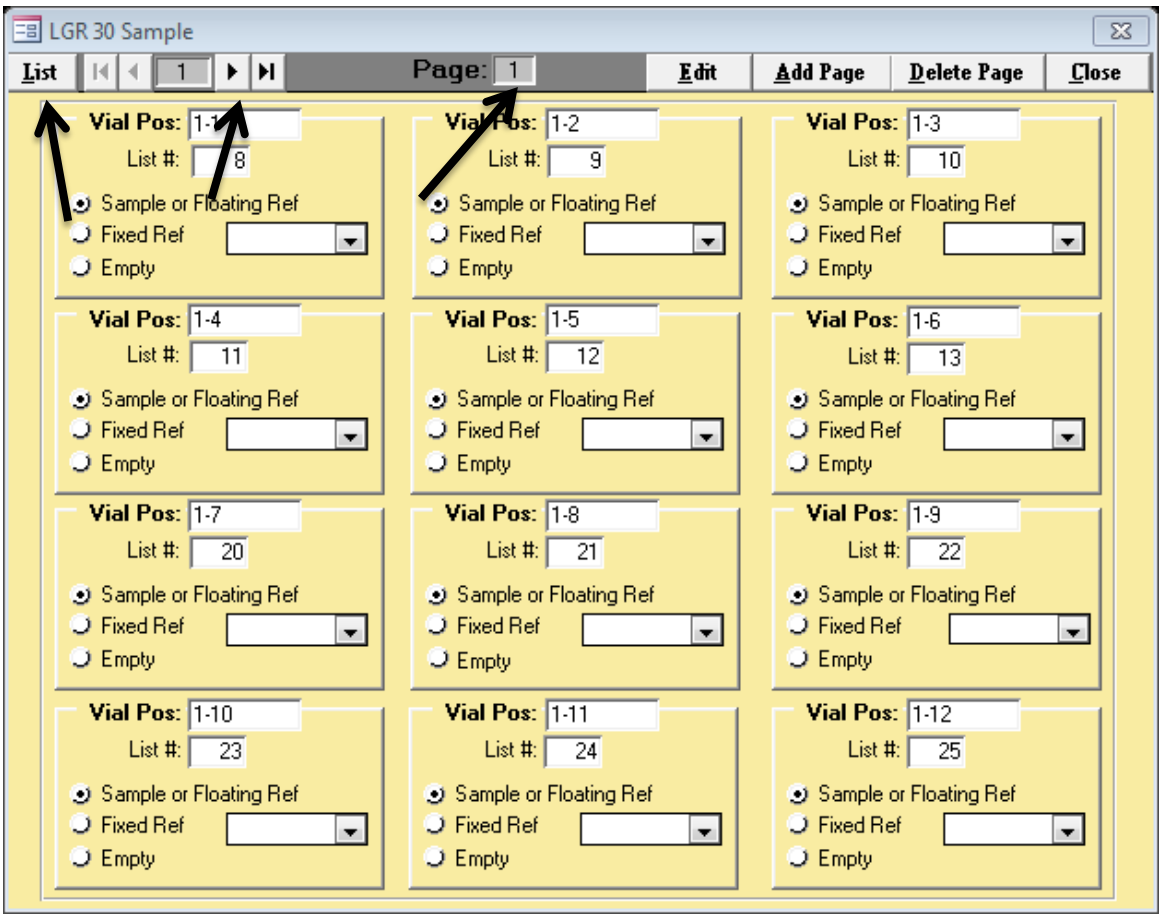
In the above dialog, Lab Standard W-31 is to be assigned as the higher delta laboratory measurement standard. In the box enter “31”, and then click “OK”.



In the above dialog, the lower delta lab standard is W-32. In the box, enter “32” then click “OK”, and a message shows the new Los Gatos Research template has been created.



Click “OK” and the following new template details appear:



There are 7 “pages” in the new Los Gatos Research 30-sample Analysis Template (12 entries per page).

On Page 1, we see 12 samples for Tray 1 along with their vial positions. List # refers to the analysis sequence. Here, the first sample is located in Tray 1, vial position 1, but it is the eighth sample to be measured (after our measurement standards, below).

The Vial Pos and List # correspond to the layout shown in Table 1. By clicking the “right arrow” next to the page number, we find the last sample (Sample 30) occurs on Page 3 (Vial Pos 1-30, List # 61).

From Page 5 onward, we see the entries for local measurement standards, control standards, and DI washes, listed in turn. The list # shows the occurrence in the run sequence (Table 1). The first two samples run in this Template are deionized water samples for instrument conditioning, and they are found on Page 7 (List #1 and #2).

This page layout may seem a bit confusing compared to sequential listings like Table 1; however, this layout is very flexible to later modification. For example, if we wanted to create a

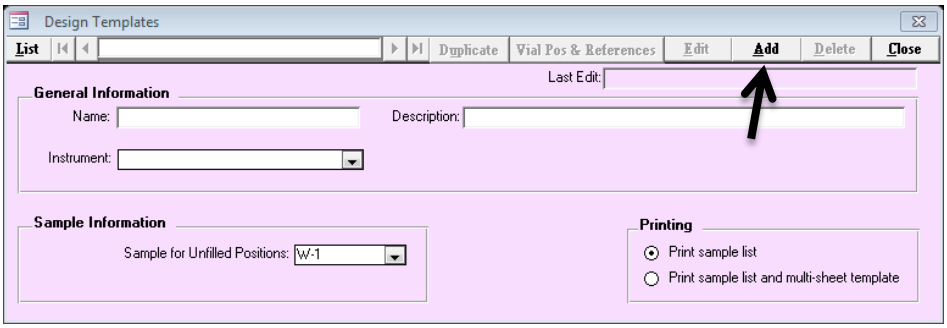
smaller 20-sample template, we only need to click “Duplicate” then delete Page 3 and a few other entries on Page 2 (to List #46) and save it.

The page layout may be constructed sequentially like in Table 1, but it is less flexible since duplication and modification will require complete renumbering of many entries spanning over several pages.

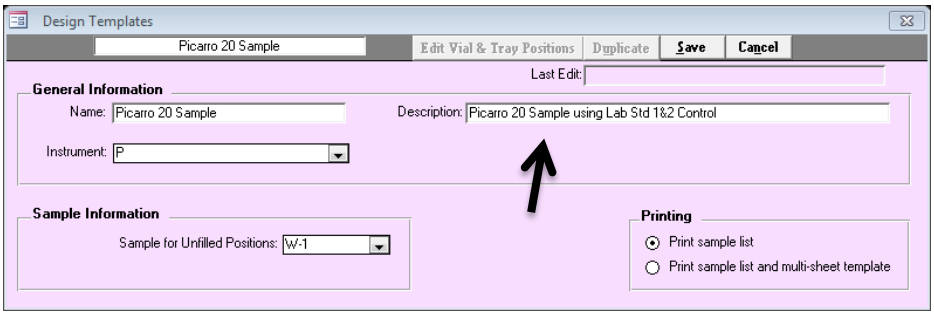
Fortunately, good performing analytical templates, once created need rarely be changed.

8.5 Creating a Picarro 20-Sample Analysis Template

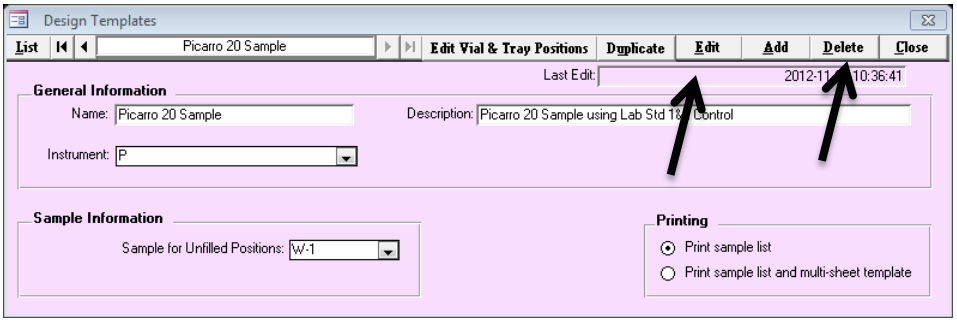
1. From the Main Page, open “Special Features”.
2. Click on “Analysis Templates”.
3. Click on “Add”.



4. Under “Name”, type 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.



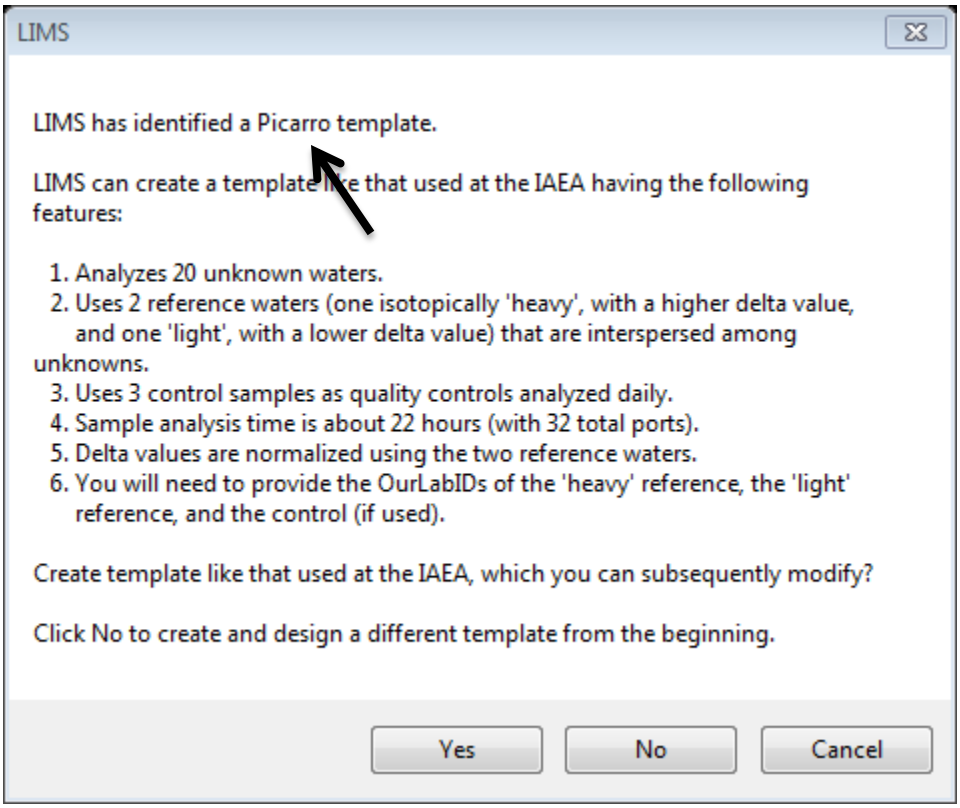
8. Click “Save”.
9. Once saved, the template “Name” cannot be edited, only the description and lower fields can be edited. The template may be deleted or edited if a mistake was made, below.



Picarro Sample Layout and Instrument Run Sequence

The run sequence of all samples, standards, and control standards are set up in the "Vial Pos and References" dialog.

Clicking on "Vial Pos and References" in *LIMS for Lasers* brings up the Analysis Template construction Wizard:

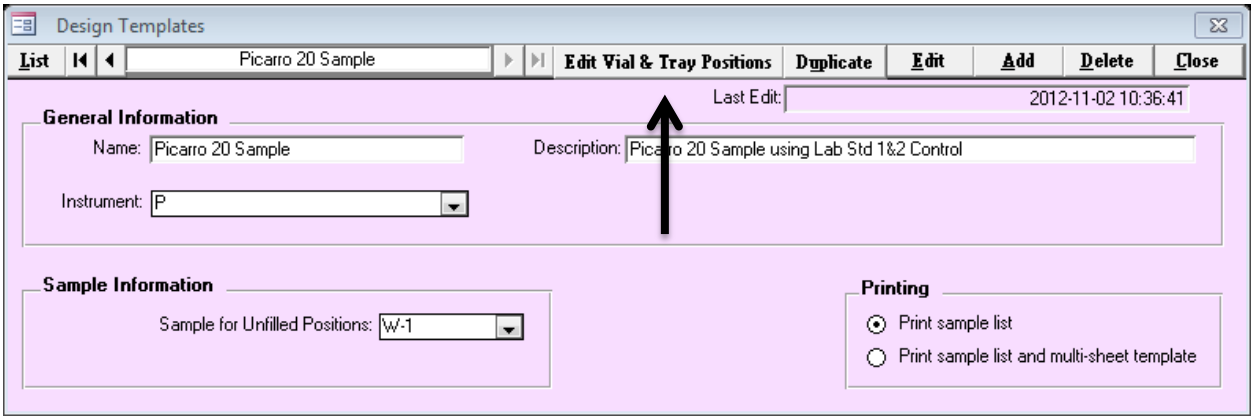


Before going further with the template construction, you will need to know the Our Lab ID or "W" numbers, of the local measurement standards (and the control standard).

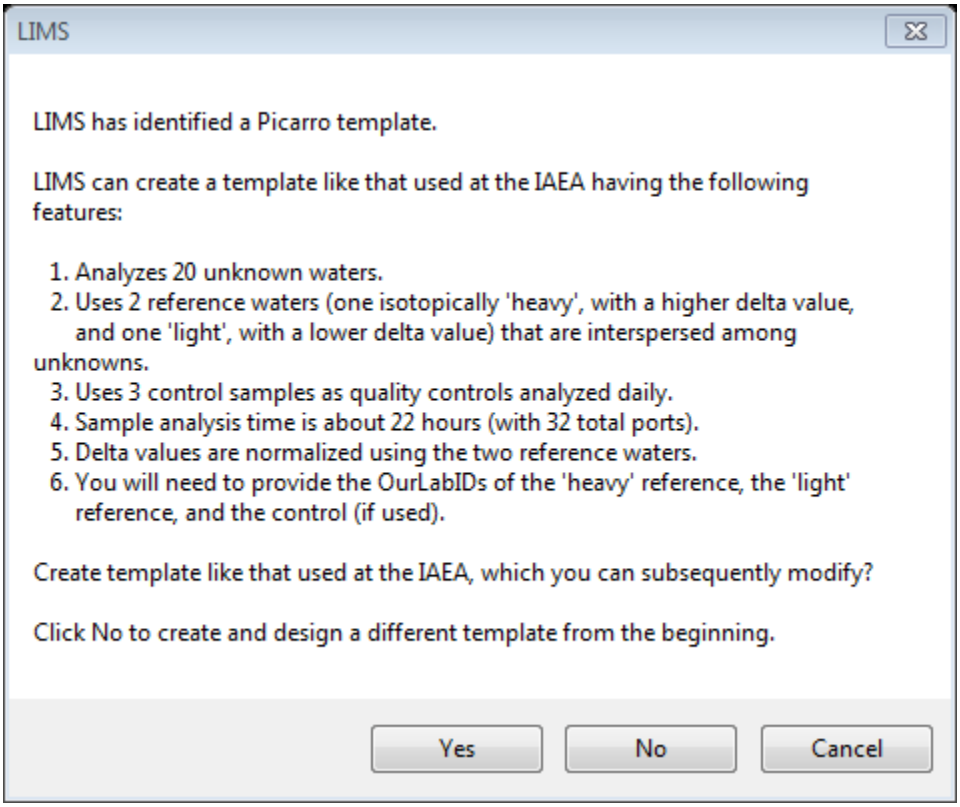
If you do not know the "W" numbers, cancel and go back to View Projects on the Main Page. The project for lab standards is called "Lab References" and contains pre-populated place holders ranging from W-31 to W-69.

Recall in Chapter 6.4, that we created a high (δ value) lab Standard (W-31), a low (δ value) lab standard (W-32), and a control standard (W-33). We will use these three measurement standards as an example for the new Picarro 20 sample template. Once noted, proceed to the next step.

Go back, or stay in Special Features → Analysis Templates → and choose the Picarro template to be created from the "List" button.

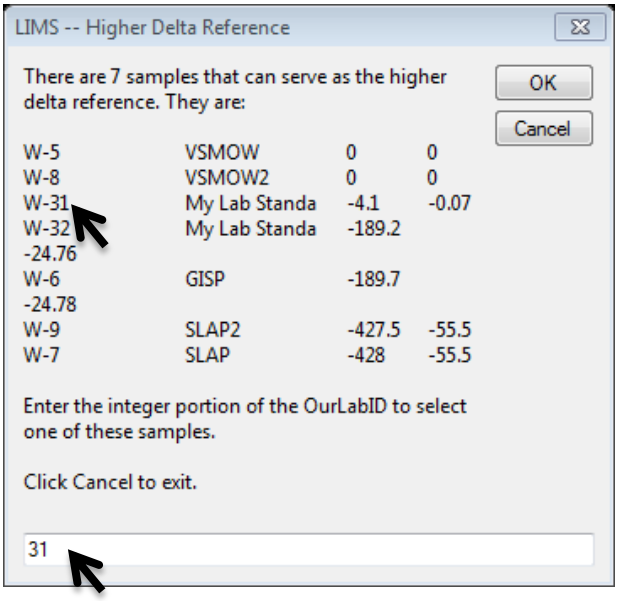


Click on “Edit Vial and Tray Positions”, and then click “Yes” to create a new Picarro 20-sample template:

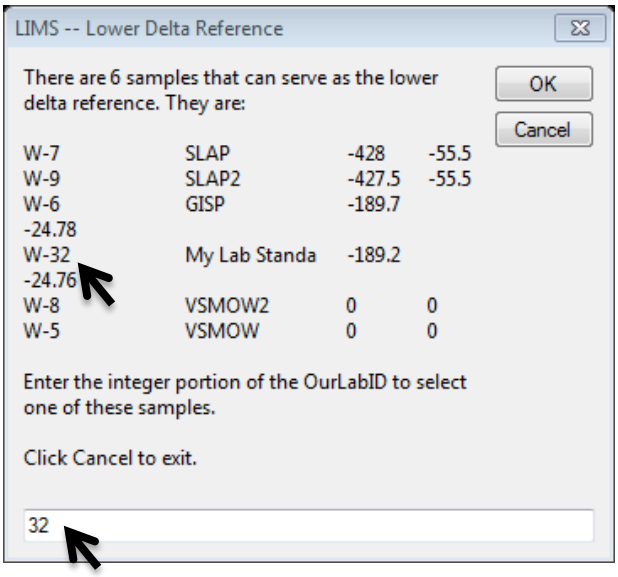


Alternately, clicking “No” presents the user with a blank analysis template (if you want to construct a template from scratch).

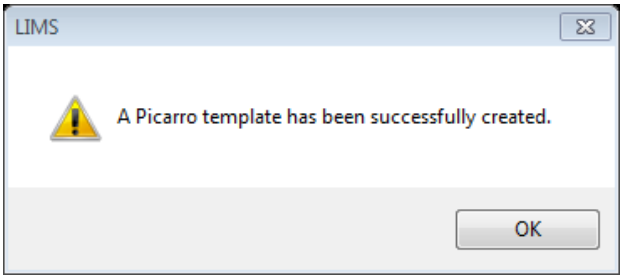
Next, LIMS recognizes that we created W-33 as our optional Control Standard, Click “OK” or click cancel if you do not want to add a control standard.



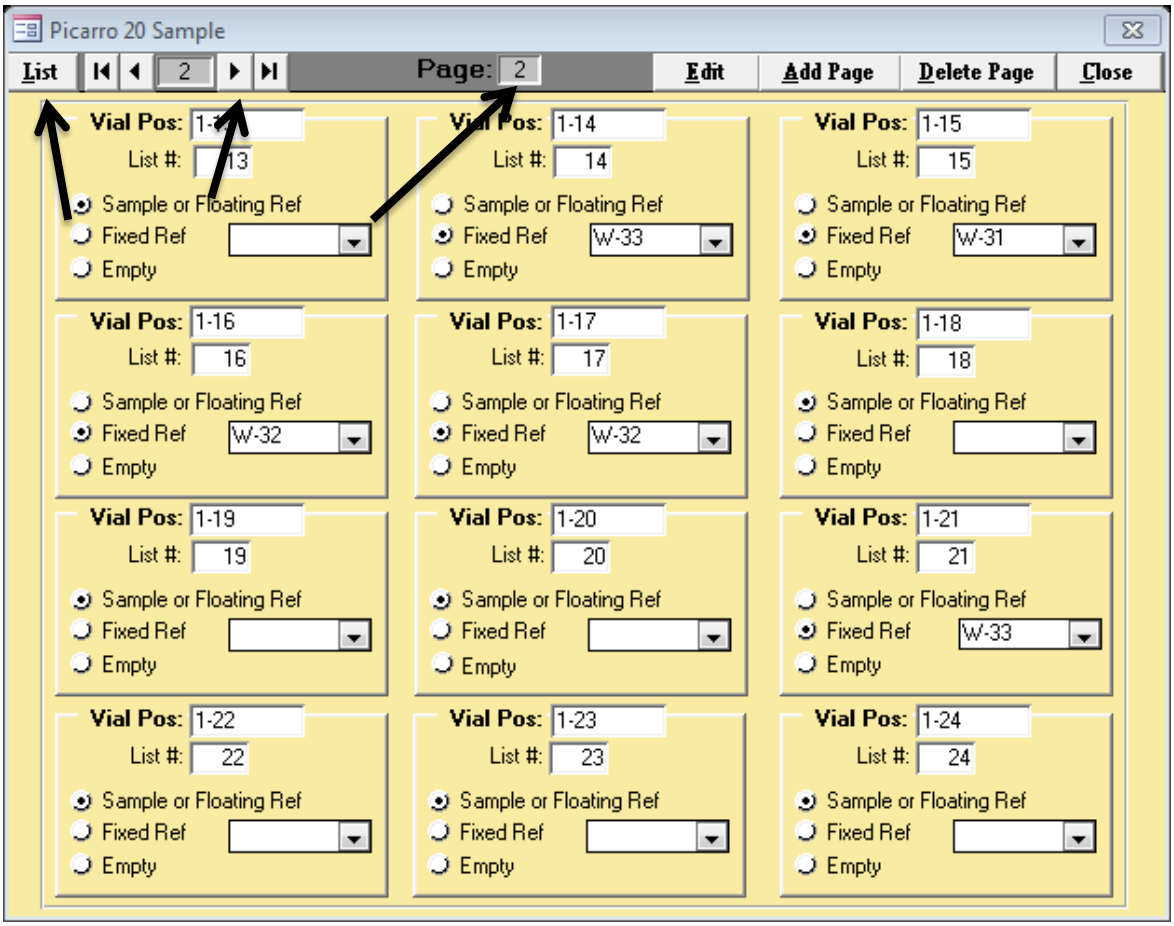
In the above dialog, Lab Standard W-31 is assigned as the isotopically "heavier" standard. In the box enter "31", and then click "OK".



In the above dialog, the "lighter" lab standard is W-32. In the box, enter "32" then click "OK", and a message shows the Picarro template has been created.



Click “OK” and the following new Picarro Analysis template details appear:



There are 3 pages in the Picarro 20-sample Analysis Template (12 entries per page).

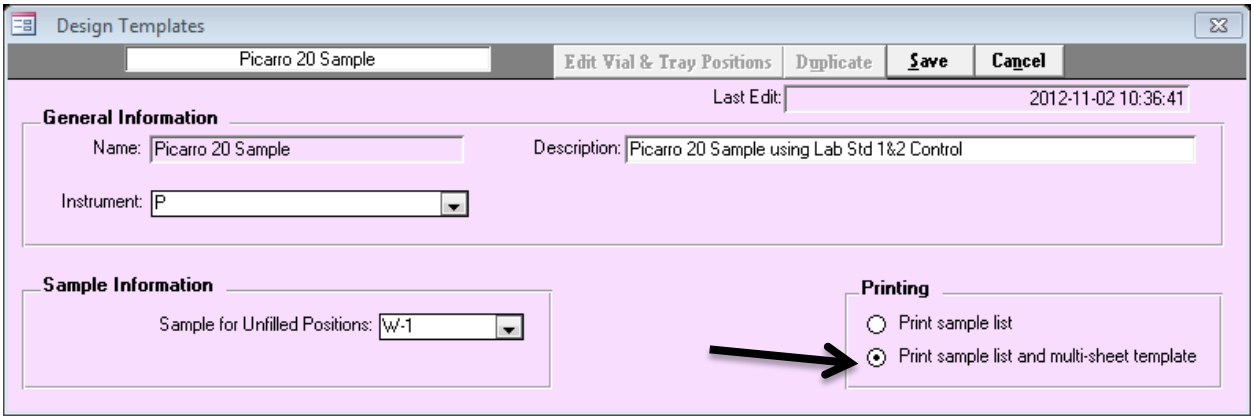
On Page 1, we see 4 lab standards followed by 8 samples located in Tray 1 listed, along with their Vial Position numbers. List # is the analysis sequence.

The Vial Position and List # values correspond to the layout shown in Table 2. By clicking the “right or end arrow” next to page number, we see the last sample is in position 27, and it is the last standard (W-31).

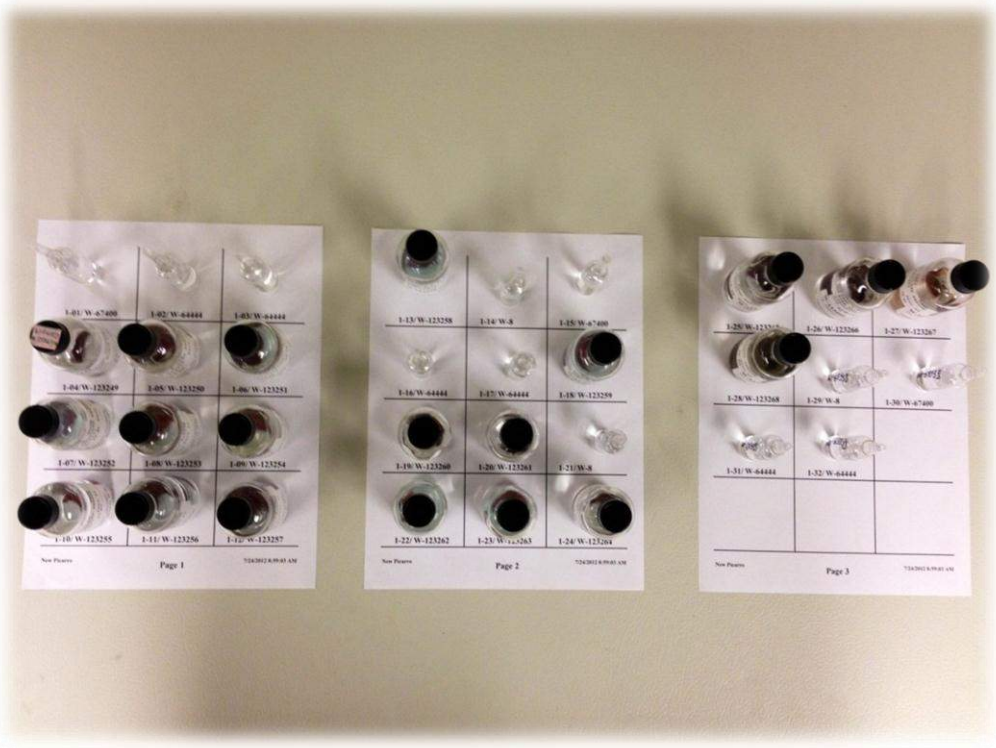
***Tip*:** One useful feature of the Design Template page is the “Duplicate” button. For example, suppose you desire 60-, 30-, and 10-sample Picarro Analysis templates. Start by constructing the largest (60-position) template, and then duplicate it to edit to a smaller template.

8.6 Multi-sheet Sample Layout Printouts

The hands-on organization of the client water sample bottles and the vials in relation to the laser Analysis Template can be aided by using a multi-sheet template printout. This optional setting prints a hard copy of the sequence layout corresponding to the Analysis Template, and it helps staff organize their samples and vials.



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

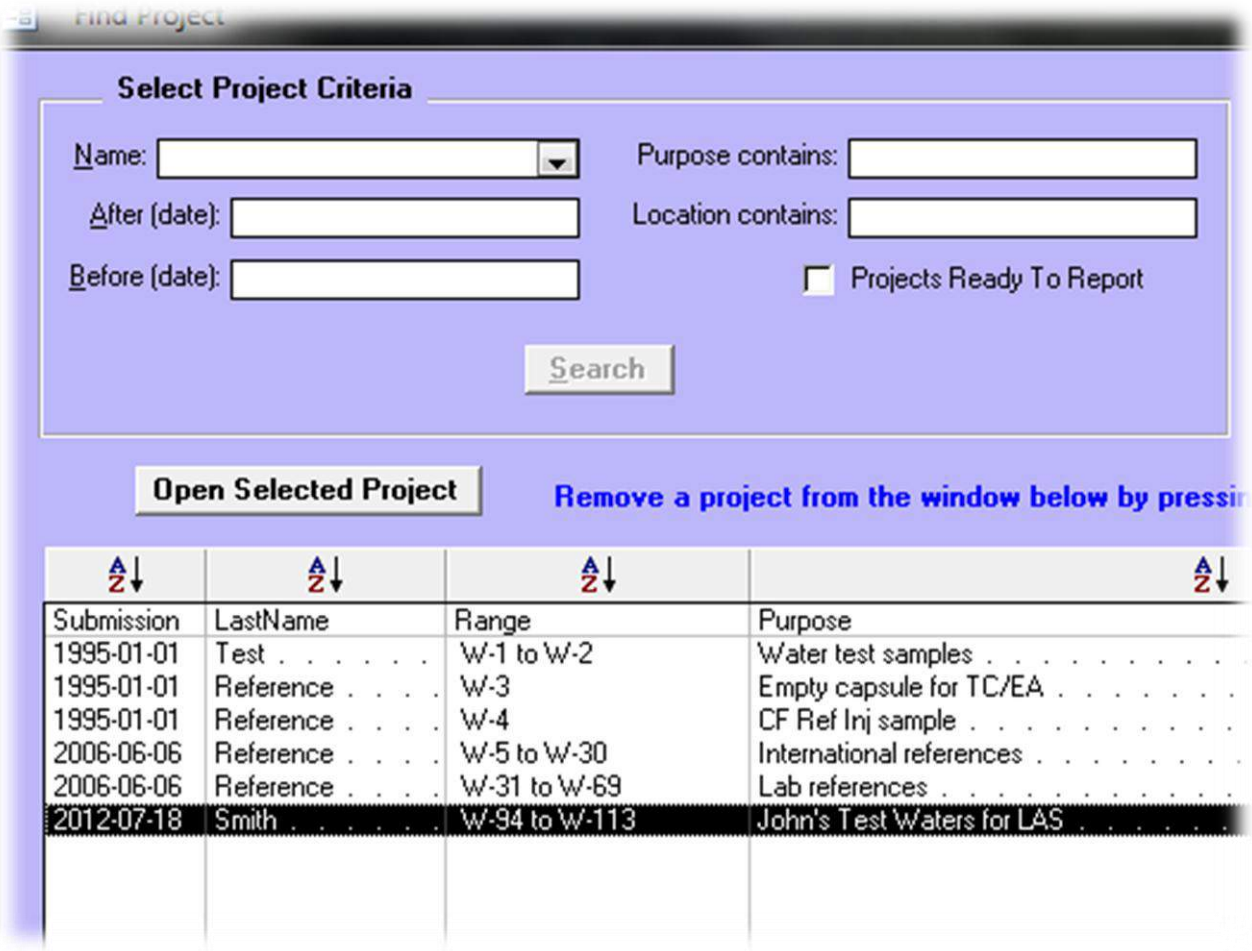


LIMS printed multi-sheet template for sample organization

8.7 Adding Customer Samples to Analysis Templates

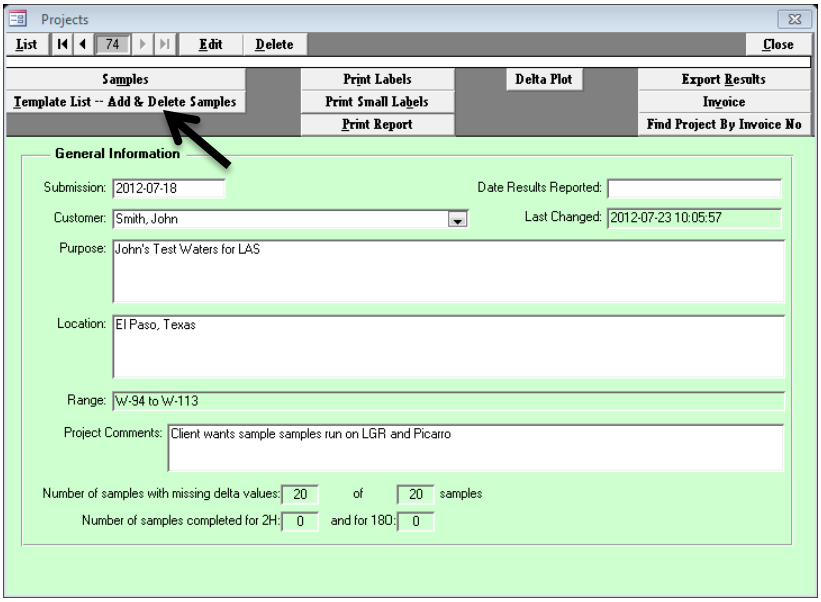
In order to add new samples to a LAS analysis template (or queue), a customer and their project samples must already exist in *LIMS for Lasers* (see Chapter 6.1).

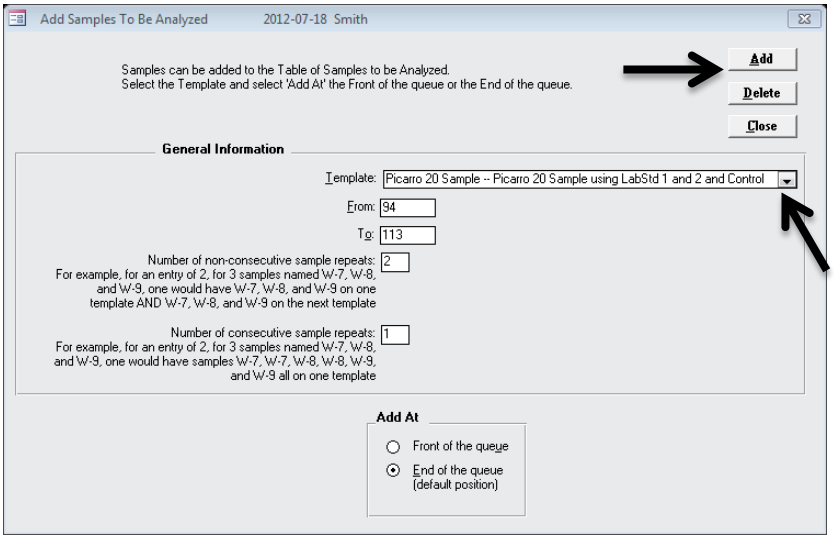
For illustrative purposes, we will analyse the new project containing water samples from John Smith (see Chapter 6). Smith submitted 20 water samples from 4 locations that he wishes to be run on a Picarro instrument (full Template) and a Los Gatos Research (partial Template). His samples span the Our LabID range W-94 to W-113 (below).



8.8 Adding Samples to the Picarro Analysis Queue

1. Open “John’s Test Waters for LAS” from the Project page by double clicking it.
2. Click on “Template List – Add & Delete Samples”.

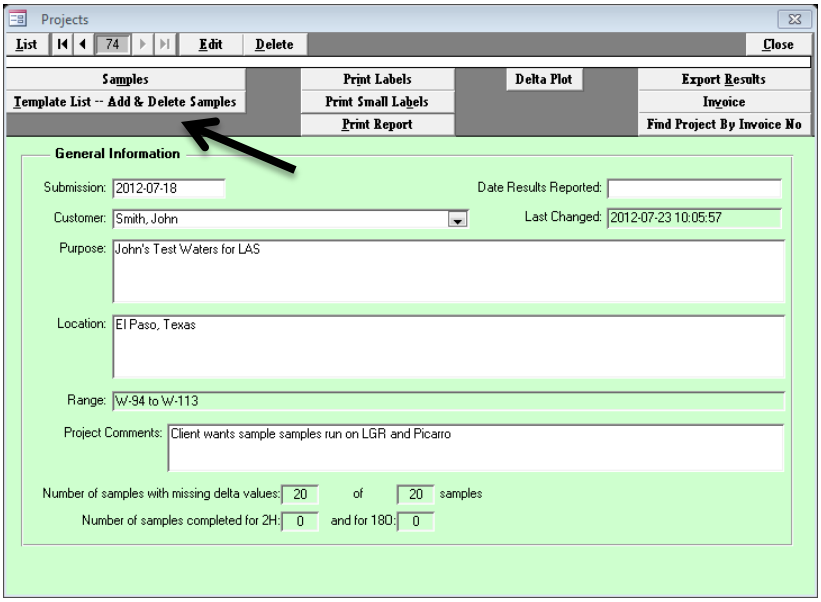


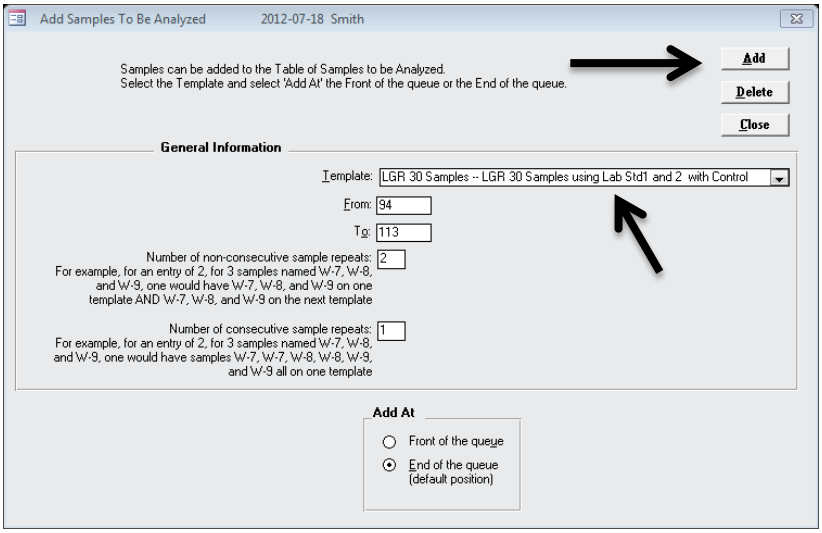


3. From the “Template” pull down, choose “Picarro 20 Sample” and then click on the “Add” button on the top right.
4. The samples are now added to the Picarro 20-sample analysis queue.

8.9 Adding Samples to the Los Gatos Research Analysis Queue

1. Open "John's Test Waters for LAS" from the Project page by double clicking it.
2. Click on "Template List – Add & Delete Samples".





1. From the "Template" pull down, choose "Los Gatos Research 30 Samples..." and then click on the "Add" 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 instrument.

.

8.10 "Add Sample" Options

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

"To and From"

The "From and To" option boxes confirm the LabID range of the samples to be added to the queue. By default, all samples in the customer project are proposed to be added to the queue– all samples of John Smith from W-94 to W-113.

However, if one wanted to choose the first ten of Mr Smith's samples, one would enter "103" in the "To" box.

If one wanted to measure the last ten samples of his Project, one could enter From 104 To 113.

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

The Number of Non-consecutive Repeats is normally set to "2". This means the laboratory will run Mr. Smith's samples *twice in 2 different vials using 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

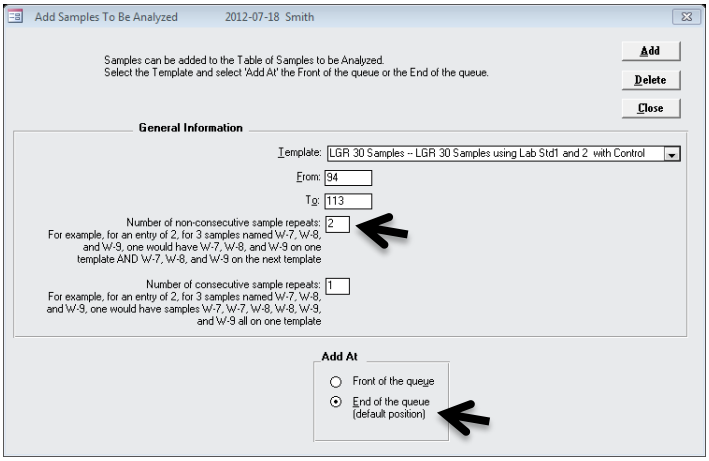
Number of Consecutive Repeats (Default Setting = 1)

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, we 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 outcome is identical.

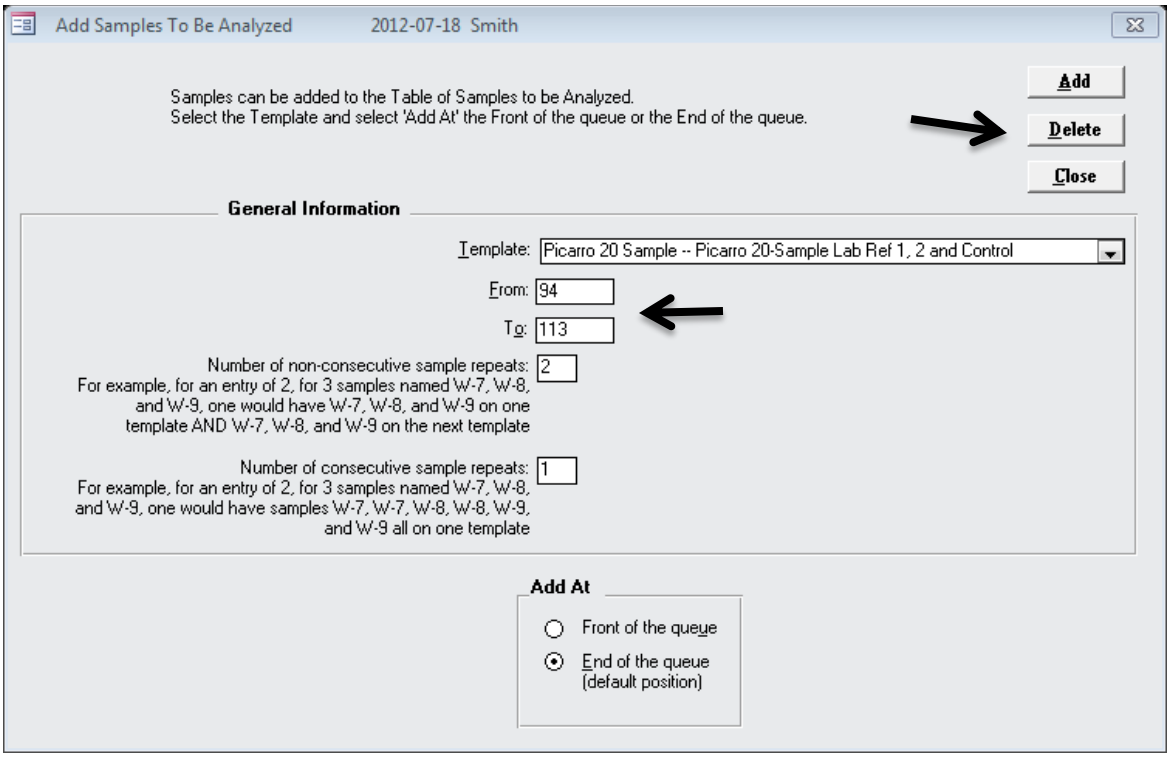
8.11 Removing or Managing Samples Added to the Analysis Queue

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

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

Removing Queued Samples from the Project Page

If you added samples from an entire project to an analysis template queue, you remove them the same way you added them. In the Project pane, click "Template List - Add & Delete Samples". The following window opens – and click "Delete" to remove all of the samples from the specified template queue, or alternately eliminate selected samples using the "From" and "To" boxes.



One-click removal of John Smiths samples from the Picarro analysis queue within his Project.

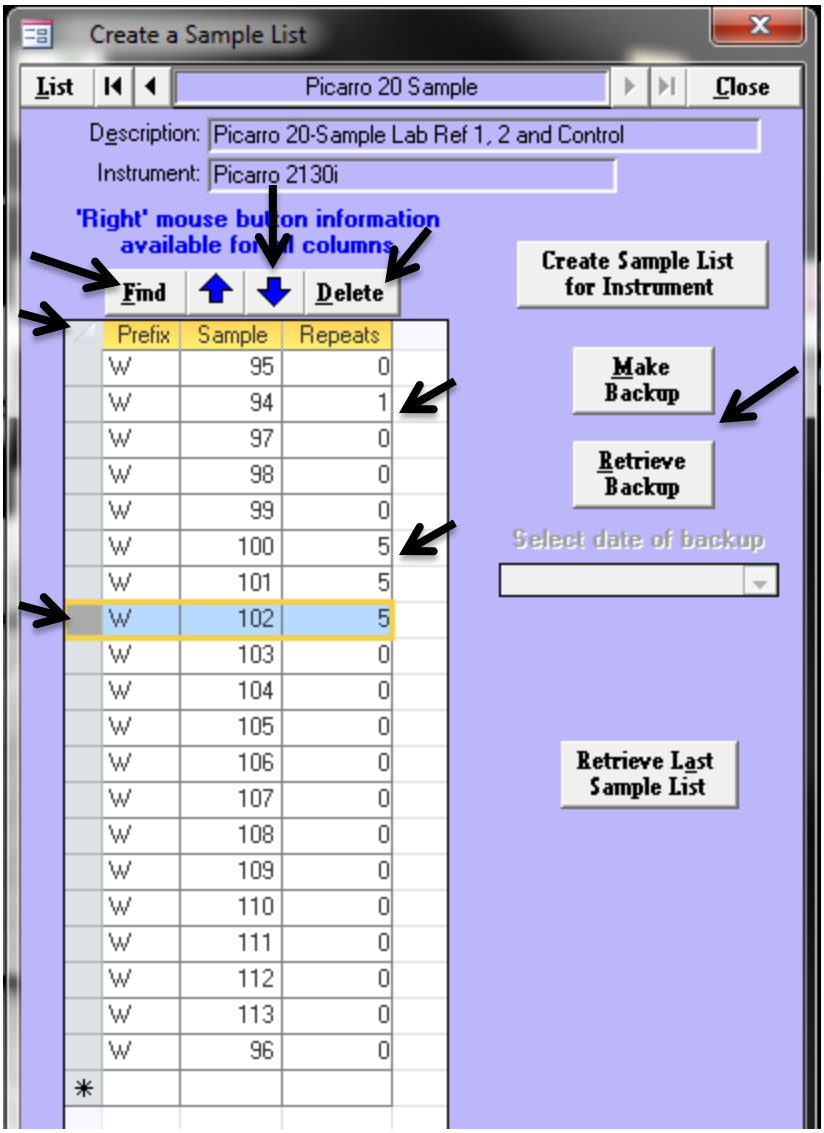
Manual Removal and Editing of Queued Samples in a Template

A second, flexible way to edit a template queue is manually:

1. On Main page, Click on “Create Sample List”.
2. Now choose the instrument Analysis 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 Manual Sample Queue Editing

8.12 Repeated Samples in LIMS for Lasers

LIMS for Lasers default analysis policy is that all samples are measured at least twice. It is good laboratory policy to run two or more repetitions of each sample (using different vials). This policy may be manually overridden (see Chapter 12.5).

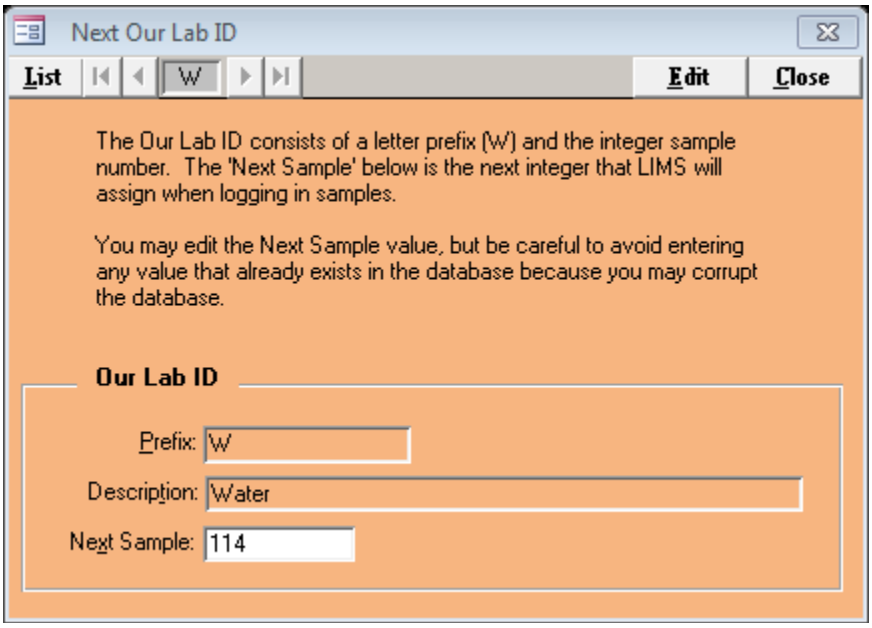
The benefit of having two or more analyses of the same sample promotes good laboratory practice, helps catch vial placement errors, allows the operator to check the consistency between two or more analyses of the same sample, helps identify problematic samples (e.g. poor repeats), and allows one to compare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

8.13 Next Sample Number

The "Next Sample Number" button is located in *LIMS* "Special Features". This optional utility allows one to specify the next Our LabID 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 and sequential W numbers.

For example, by default *LIMS for Lasers* customer samples start at W-1000 (or W-100 in the example). The last default place holder for our lab standards is W-69. This means OurLabID numbers from W-70 to W-999 are 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-114 is the next Our Lab ID.



Suppose we wanted to add 10 new measurement standards, but we want them to sequentially follow the current laboratory standards (e.g. ending at W-69). First – note the last W number shown (here it is W-114) 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 LabID numbers W-70 to W-79.

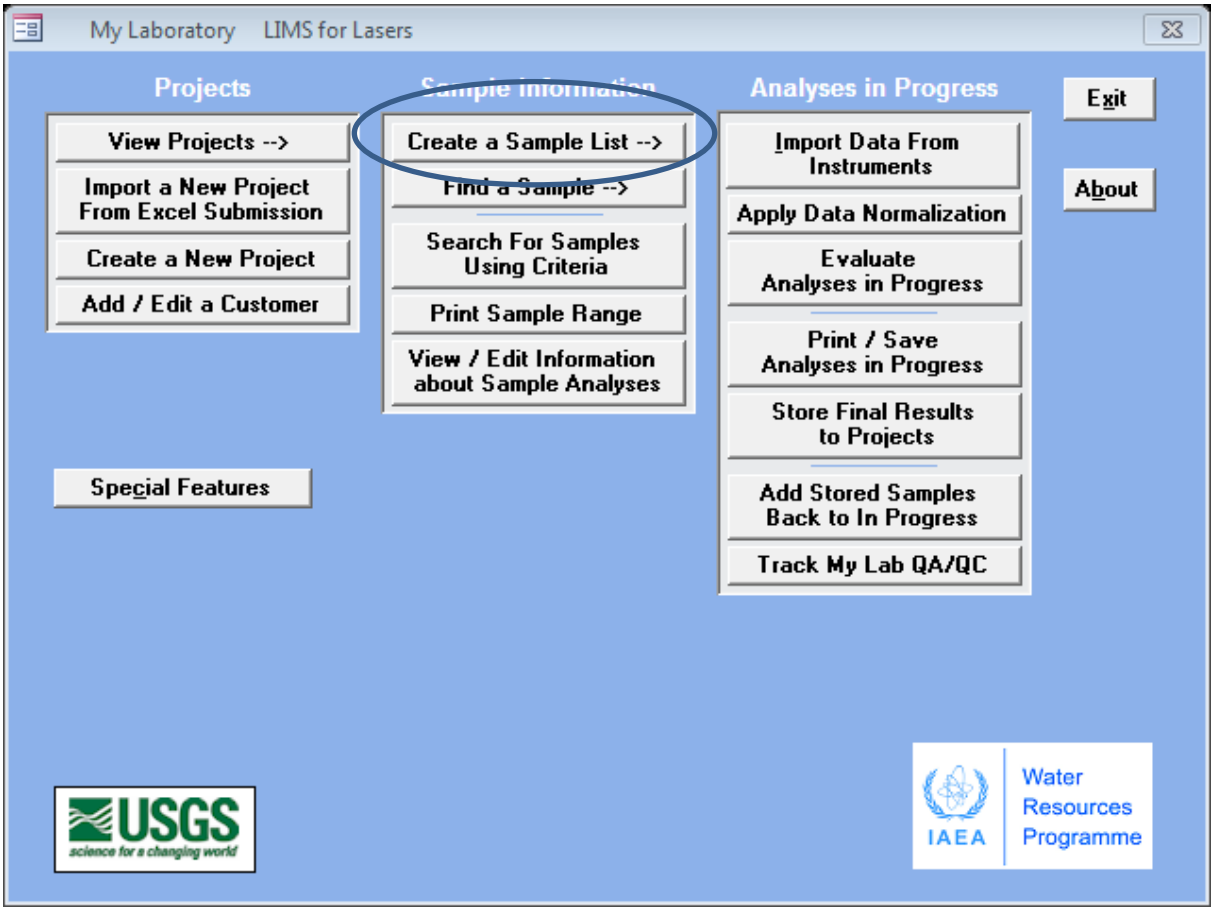
IMPORTANT: Now go back to Next Sample Number option, click edit, and change the number back to what was originally found (here 114). This ensures you do not attempt to overlap pre-existing W numbers.

9

Running Samples on a Picarro Laser

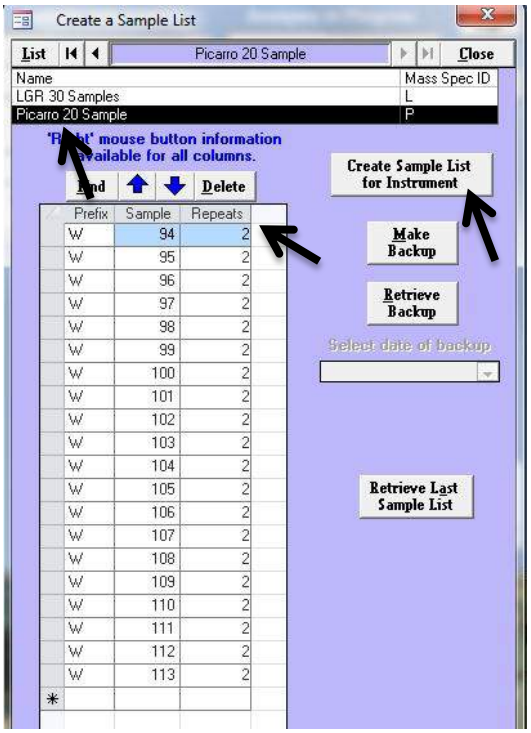
9.1 Creating a Sample List for a Picarro Instrument

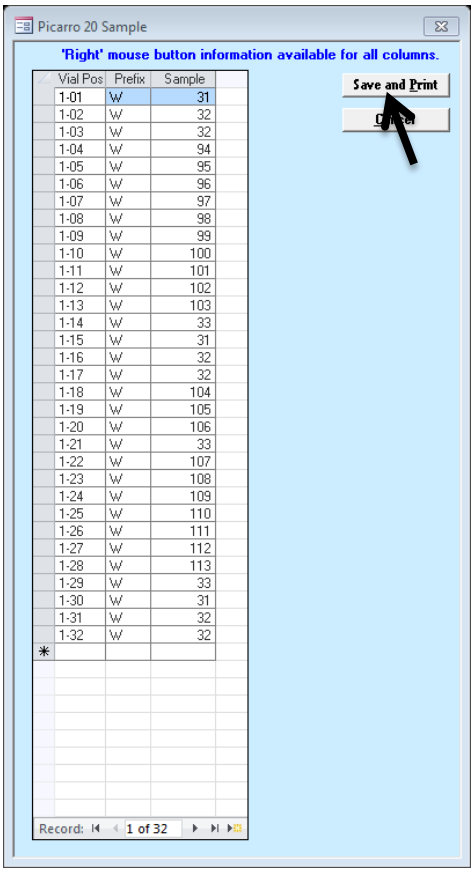
LIMS for Lasers creates Sample Lists (sometimes called sequence files or sample run lists) for Picarro instruments. These sample lists are transferred via a USB stick or network to the Picarro laser instrument for analysis. This action is performed from the "Create a Sample List" button on the Sample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



By an example, we will create a sample list for a Picarro instrument.

1. Ensure John Smith's samples were added to the Picarro queue (see Chapter 8.5).
2. On the Main LIMS Page, click "Create a Sample List".
3. Choose "List" and click on "Picarro 20 Sample", the sample queue opens:

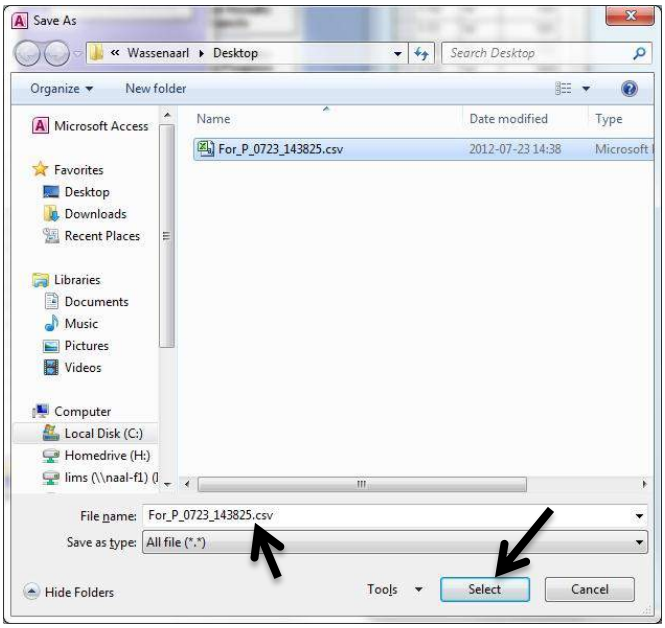




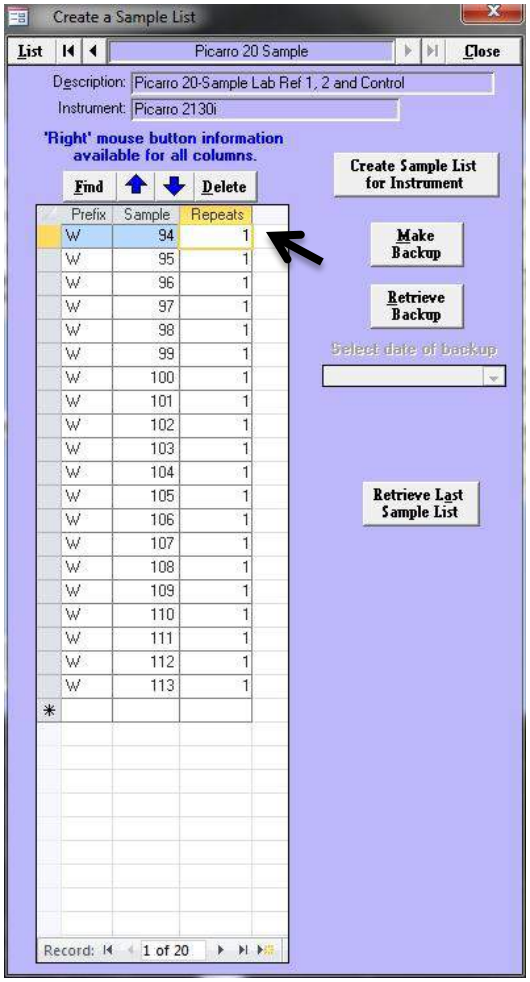
In the sample queue, shown above left, John Smith's entire project (W-94 to W-113) is queued to be run twice (# of repeats = 2).

4. Click on "Create Sample List for Instrument", a dialog box confirms the first 20 of Smith's samples are to be added to the current queue. Click "OK".
5. The run sequence, containing the local measurement standards and control standards assigned in the template and Smith's samples opens (above, right figure).
6. Click "Save and Print".
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 memory stick 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. Note the saved file is in CSV format, whose 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.



9. A Printer dialog box may open, 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.
10. After printing, the queue reopens and we see the sample "repeats" were decremented from 2 to 1 (right). This indicates that the second set of sample repeats are still in the queue for the next run on this instrument template.
11. 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.
12. 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

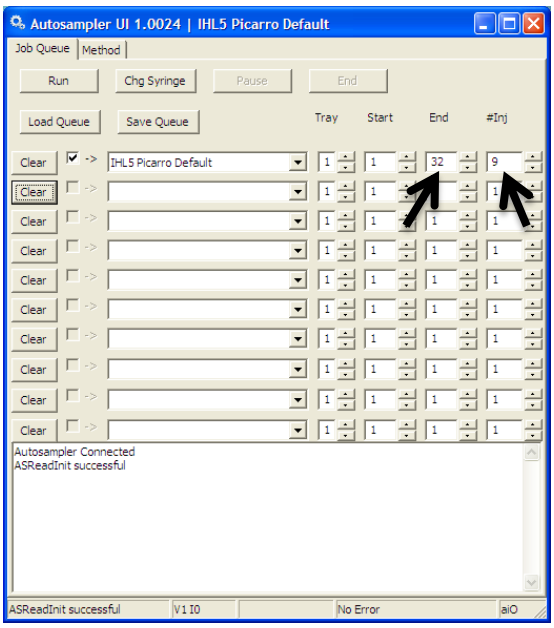
Vial Po	Our Lab ID	Notes	Vial Po	Our Lab ID	Notes
1-01	W-31				
1-02	W-32				
1-03	W-32				
1-04	W-94				
1-05	W-95				
1-06	W-96				
1-07	W-97				
1-08	W-98				
1-09	W-99				
1-10	W-100				
1-11	W-101				
1-12	W-102				
1-13	W-103				
1-14	W-33				
1-15	W-31				
1-16	W-32				
1-17	W-32				
1-18	W-104				
1-19	W-105				
1-20	W-106				
1-21	W-33				
1-22	W-107				
1-23	W-108				
1-24	W-109				
1-25	W-110				
1-26	W-111				
1-27	W-112				
1-28	W-113				
1-29	W-33				
1-30	W-31				
1-31	W-32				
1-32	W-32				

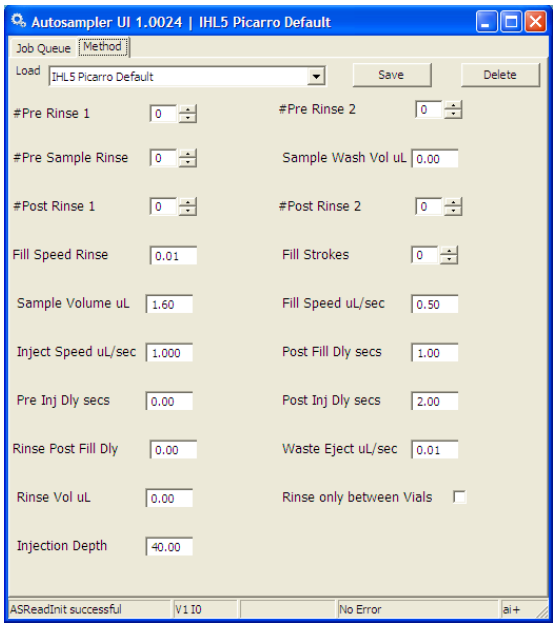
Analysis template report

13. 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), a Picarro G-2000 Autosampler 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 CombiPAL control unit (not shown), the same analysis setup is done 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.





CAUTION: Be aware sample analyses via the Picarro Coordinator data acquisition software are independent of LIMS. There is no coordinated data connection between the instrument and the LIMS sample file. Therefore, ensure that the number of analyses and injections set up on the Picarro Autosampler or CombiPAL *match exactly what the LIMS Analysis Template expects*. Finally, ensure a new Picarro Coordinator output file is started immediately before initiating the autorun to avoid importing data from previous autoruns or conditioning samples.

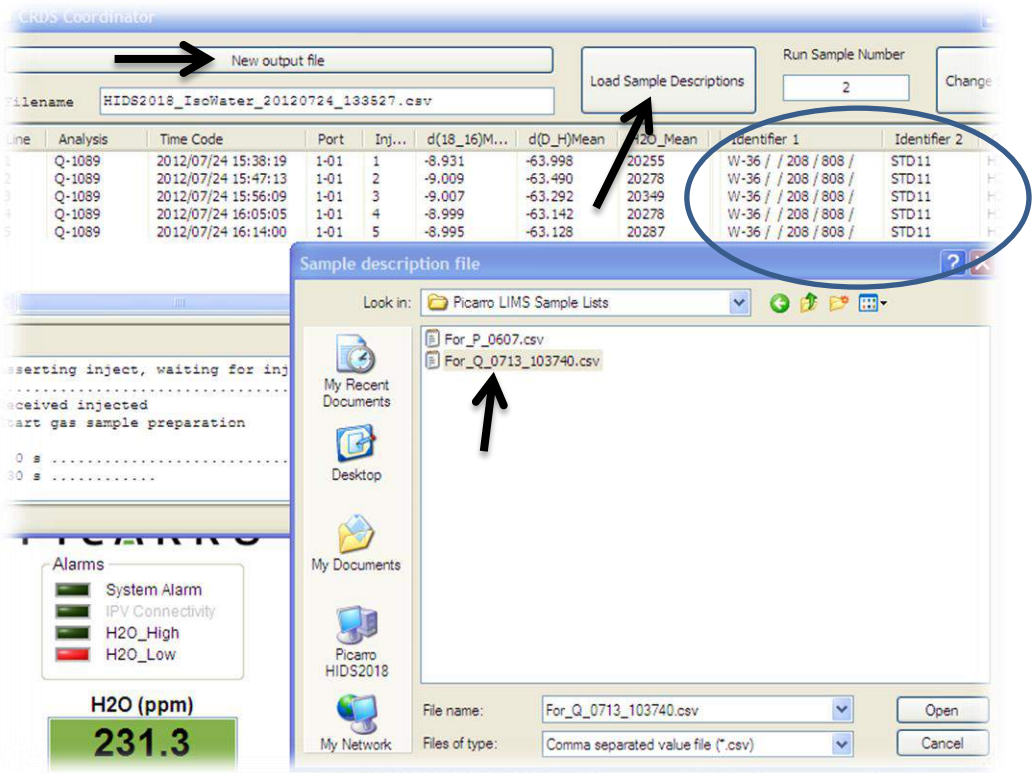
The second panel (above, right) shows the Picarro 2130i default sample injection parameters. Here a 1.6-µL injection achieves the instrumental target of ~20,000 ppmv H_2O. The Autosampler UI parameters shown are found on the CombiPAL controller. See the Picarro instrument user manuals for the autosampler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

On all Picarro instruments, the sample data collection, integration, and processing of measured "delta" values is done by the "CRDS 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 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 7.5.1, can be loaded into the Coordinator **AFTER** one or more lines of analyses results are reported in the Coordinator window. The LIMS sample list can be loaded from the USB stick, or via a network connection. A caution - attempting to load the LIMS sample file into Coordinator *before* isotopic results appear in Coordinator will result in null loading of the required LIMS Identifier fields.

Adding the LIMS Sample List to Picarro Coordinator

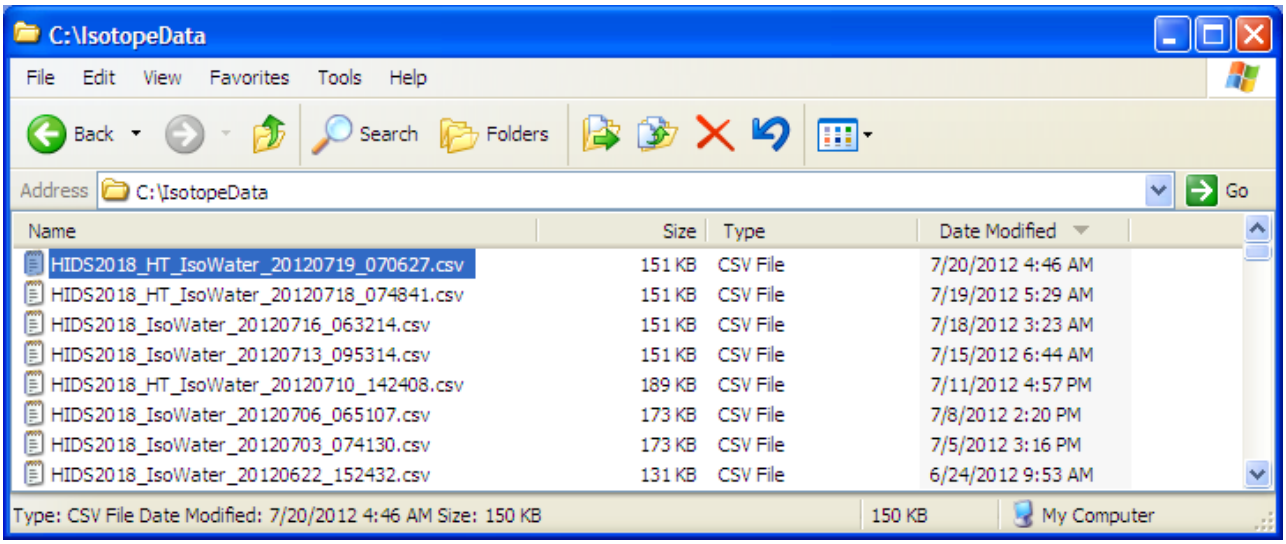
1. Start the Picarro analysis autorun – **important** - wait for one or more sample isotopic results to appear in the Coordinator window (and before the autorun ends), this may take a few minutes following the first sample injection.
2. Next, in Picarro Coordinator, click "Load Sample Descriptions" button.
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 will correspond to those samples and standards being analysed.
5. Allow the analysis autorun to finish (30+ hours for the default template).



9.2 Importing Isotopic Data from a Picarro

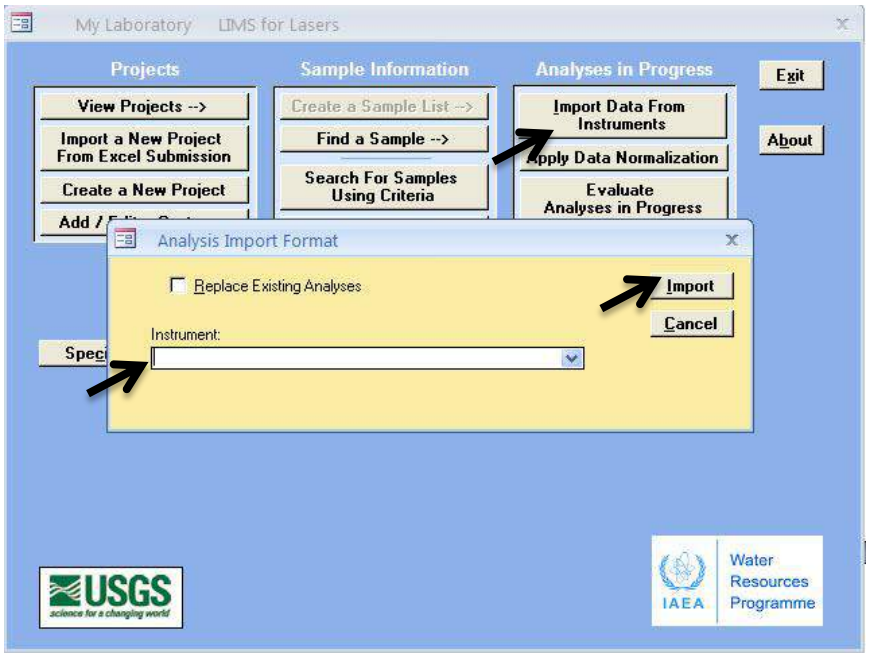
Once a Picarro water isotope analysis run loaded with the LIMS Identifier fields has finished, the final measured isotopic results can be imported into *LIMS for Lasers* for screening, data normalization, processing and evaluation, and final reporting to the customer.

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.

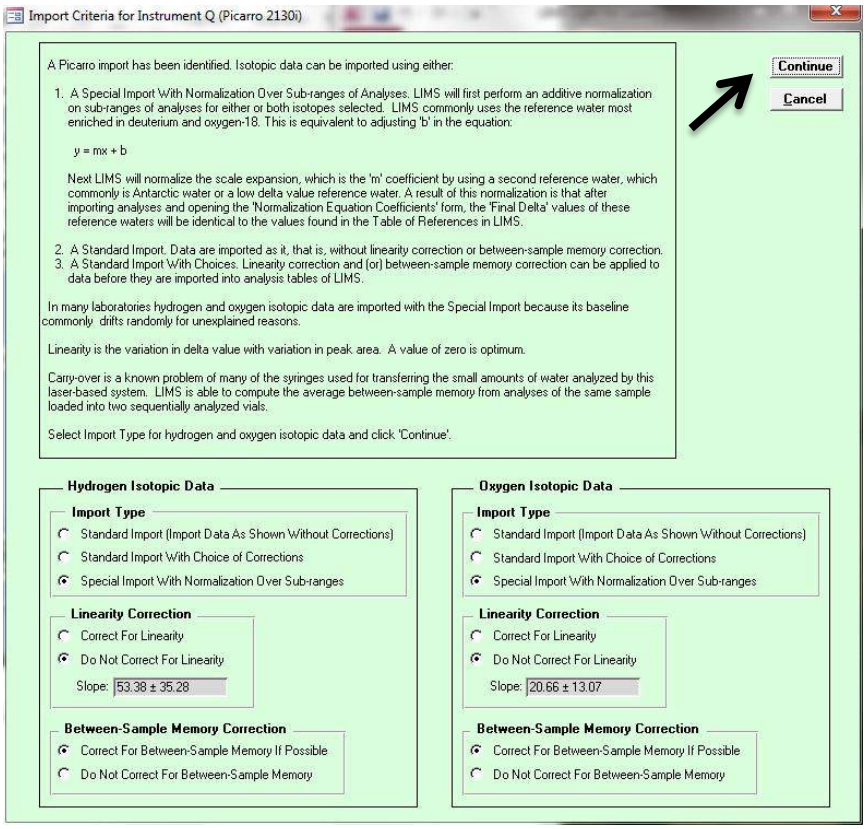


1. Copy the correct Picarro CSV autorun data file to a memory stick, or to a LIMS accessible network location.
2. On the LIMS main page, click “Import Data From Instruments”, choose the Picarro instrument from the pull down menu, and then click “Import”. Choose the appropriate data output file from the 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. The default setting is left unchecked.



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

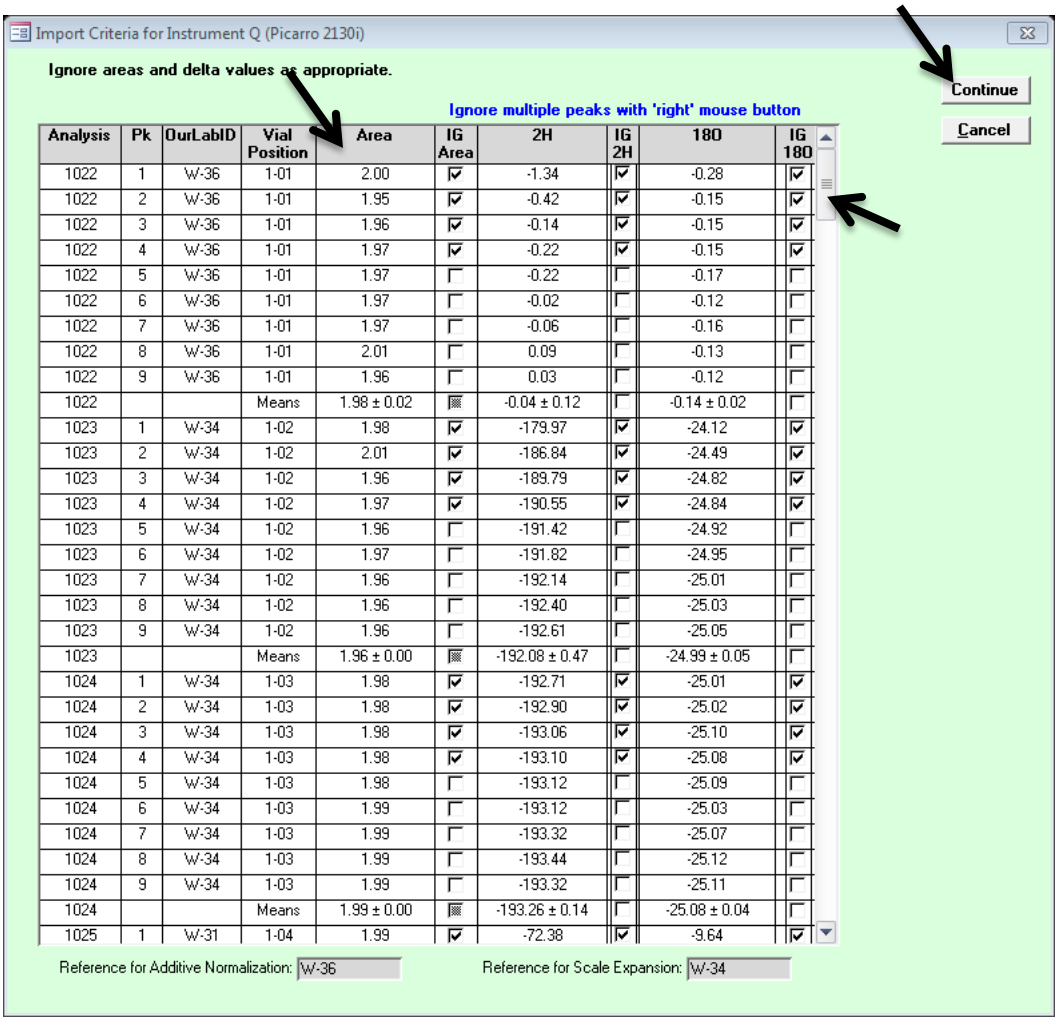


4. On this import screen, accept the default options and click, “Continue”. The various import options available are described later in Chapter 11.1. Accept default for now.

5. A summary of the autorun with all measured δ^2H and δ^{18}O isotopic data and H_2O yield appear with the analysis number, injection number (Pk), Our Lab ID, vial position, analysis data, and the summary statistics (using non-ignored injections) for each sample. Note that *LIMS for Lasers* ignored the first 4 injections per sample, as specified in the Instrument settings for this specific instrument. (note: the Coordinator ignore flag is not used in LIMS).

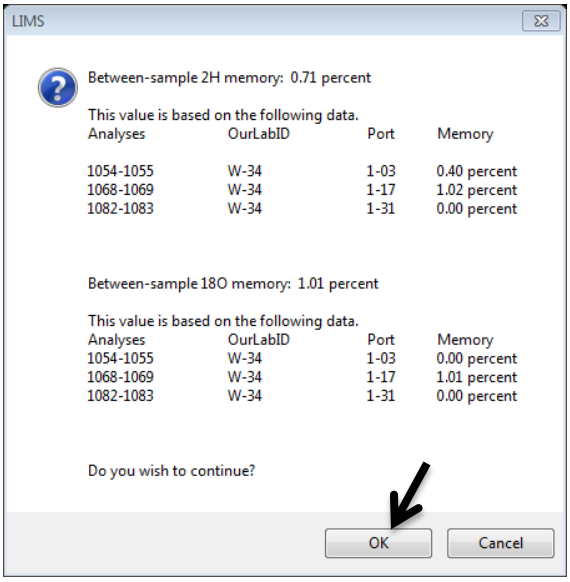
   Before clicking Continue, use the scroll bar to scan for outliers in "Area" (1.97 is a reduced number to represent 19,700 ppmV H_2O in the Picarro instrument) and for any isotopic outliers. Outliers may be ignored by clicking the Ignore box next to each item. Checking "IG Area" automatically checks both the corresponding H and O isotopic data.

   If all of the data appear OK, click on "Continue".

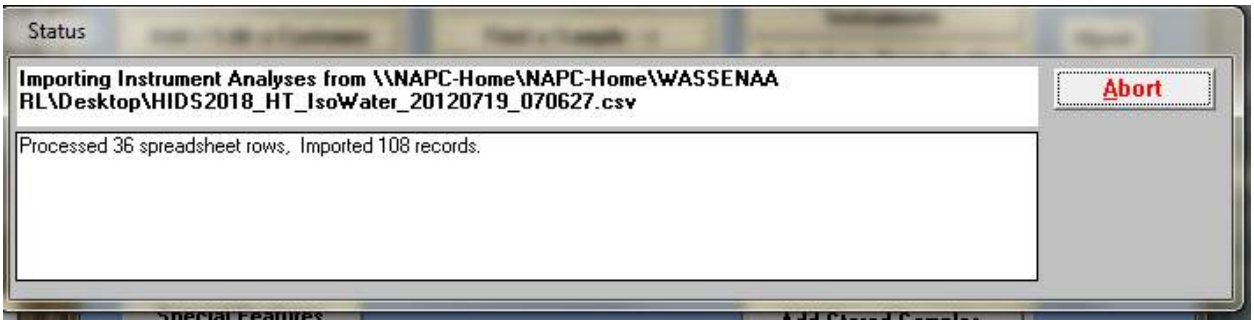


Analysis	Pk	OurLabID	Vial Position	Area	IG Area	2H	IG 2H	18O	IG 18O
1022	1	W-36	1-01	2.00	☑	-1.34	☑	-0.28	☑
1022	2	W-36	1-01	1.95	☑	-0.42	☑	-0.15	☑
1022	3	W-36	1-01	1.96	☑	-0.14	☑	-0.15	☑
1022	4	W-36	1-01	1.97	☑	-0.22	☑	-0.15	☑
1022	5	W-36	1-01	1.97	☐	-0.22	☐	-0.17	☐
1022	6	W-36	1-01	1.97	☐	-0.02	☐	-0.12	☐
1022	7	W-36	1-01	1.97	☐	-0.06	☐	-0.16	☐
1022	8	W-36	1-01	2.01	☐	0.09	☐	-0.13	☐
1022	9	W-36	1-01	1.96	☐	0.03	☐	-0.12	☐
1022			Means	1.98 ± 0.02	▩	-0.04 ± 0.12	☐	-0.14 ± 0.02	☐
1023	1	W-34	1-02	1.98	☑	-179.97	☑	-24.12	☑
1023	2	W-34	1-02	2.01	☑	-186.84	☑	-24.49	☑
1023	3	W-34	1-02	1.96	☑	-189.79	☑	-24.82	☑
1023	4	W-34	1-02	1.97	☑	-190.55	☑	-24.84	☑
1023	5	W-34	1-02	1.96	☐	-191.42	☐	-24.92	☐
1023	6	W-34	1-02	1.97	☐	-191.82	☐	-24.95	☐
1023	7	W-34	1-02	1.96	☐	-192.14	☐	-25.01	☐
1023	8	W-34	1-02	1.96	☐	-192.40	☐	-25.03	☐
1023	9	W-34	1-02	1.96	☐	-192.61	☐	-25.05	☐
1023			Means	1.96 ± 0.00	▩	-192.08 ± 0.47	☐	-24.99 ± 0.05	☐
1024	1	W-34	1-03	1.98	☑	-192.71	☑	-25.01	☑
1024	2	W-34	1-03	1.98	☑	-192.90	☑	-25.02	☑
1024	3	W-34	1-03	1.98	☑	-193.06	☑	-25.10	☑
1024	4	W-34	1-03	1.98	☑	-193.10	☑	-25.08	☑
1024	5	W-34	1-03	1.98	☐	-193.12	☐	-25.09	☐
1024	6	W-34	1-03	1.99	☐	-193.12	☐	-25.03	☐
1024	7	W-34	1-03	1.99	☐	-193.32	☐	-25.07	☐
1024	8	W-34	1-03	1.99	☐	-193.44	☐	-25.12	☐
1024	9	W-34	1-03	1.99	☐	-193.32	☐	-25.11	☐
1024			Means	1.99 ± 0.00	▩	-193.26 ± 0.14	☐	-25.08 ± 0.04	☐
1025	1	W-31	1-04	1.99	☑	-72.38	☑	-9.64	☑

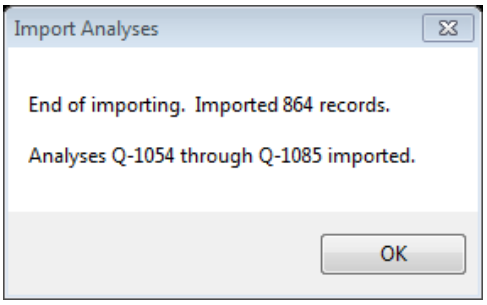
6. The between-sample memory calculations are now quantified and averaged for the entire autorun. These should be less than 1 to 2 per cent. Click OK to continue.



7. The sample drift and memory-corrected data is imported into LIMS. This import step can take several minutes to process the hundreds of lines of instrument data – please be patient.



8. At the end of the import *LIMS for Lasers* verifies the data has been imported. Click OK.



9. Normalization, evaluation and storing of final results are outlined in Chapter 11.

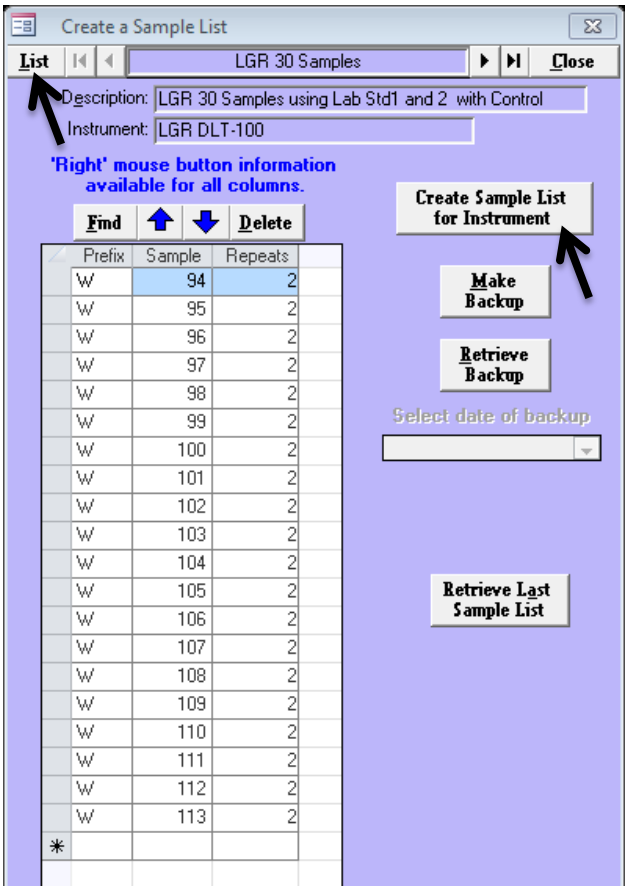
10

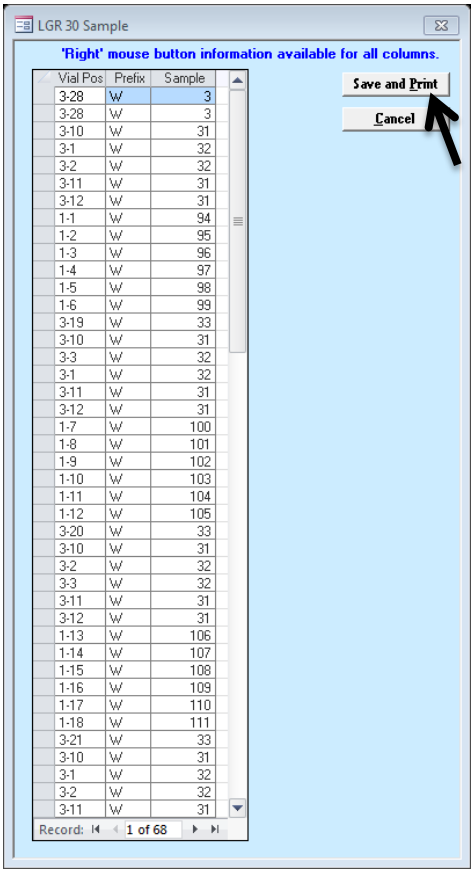
Running Samples on a Los Gatos Research Laser

10.1 Creating a Sample List for a Los Gatos Research Instrument

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

1. Ensure John Smith's samples were added to the Los Gatos Research queue (see Chapter 8.4).
2. In the Main LIMS Page, click "Create a Sample List".
3. Choose "List" and click on "LGR 30 Samples", and the sample queue opens:

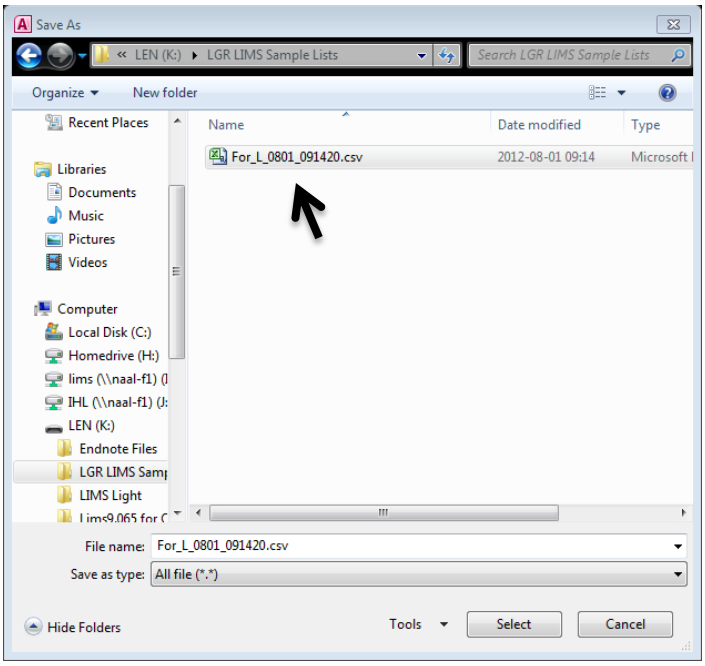




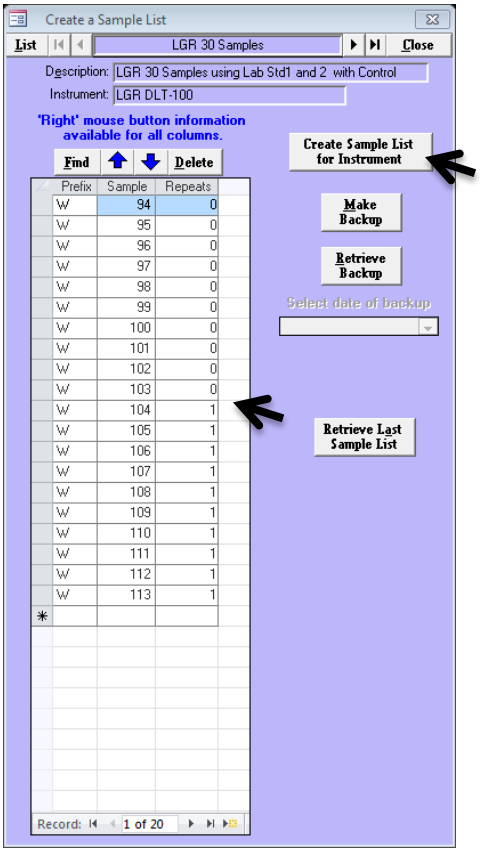
In the Los Gatos Research queue above (left figure), John Smith's 20 samples (W-94 to W-113) are queued to be run twice on a 30-sample template. This leaves 10 extra positions, which will be automatically filled with 10 of his remaining repeats.

4. Click on "Create Sample List for Instrument", a dialog box confirms the first 20 and the 10 of the second set of repeats are in the queue. Click "OK".
5. The run sequence containing the wash samples, local measurement standards, control standards, and Smith's samples opens (right figure).
6. Click on "Save and Print".
7. 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.

8. 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.



9. 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.
10. After printing, the queue reopens and we note the sample repeats have been decremented to 0 and 1 from 2 (right figure). This indicates the first set are in the queue, and because this is a 30-position template and Smith had only 20 samples, the next 10 of his repeats were added to this queue. These samples are now flagged with a “0” since they will have been run twice, albeit within the same autorun.
11. 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.
12. 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.



LGR 30 Sample Samples To Be Analyzed

Vial Po	Our Lab ID	Notes
1-1	W-94	
1-2	W-95	
1-3	W-96	
1-4	W-97	
1-5	W-98	
1-6	W-99	
1-7	W-100	
1-8	W-101	
1-9	W-102	
1-10	W-103	
1-11	W-104	
1-12	W-105	
1-13	W-106	
1-14	W-107	
1-15	W-108	
1-16	W-109	
1-17	W-110	
1-18	W-111	
1-19	W-112	
1-20	W-113	
1-21	W-94	
1-22	W-95	
1-23	W-96	
1-24	W-97	
1-25	W-98	
1-26	W-99	
1-27	W-100	
1-28	W-101	
1-29	W-102	
1-30	W-103	
3-1	W-32	
3-1	W-32	
3-1	W-32	
3-1	W-32	
3-2	W-32	
3-2	W-32	
3-2	W-32	
3-2	W-32	
3-3	W-32	
3-3	W-32	
3-3	W-32	

Vial Po	Our Lab ID	Notes
3-3	W-32	
3-10	W-31	
3-10	W-31	
3-10	W-31	
3-10	W-31	
3-10	W-31	
3-10	W-31	
3-11	W-31	
3-11	W-31	
3-11	W-31	
3-11	W-31	
3-11	W-31	
3-11	W-31	
3-12	W-31	
3-12	W-31	
3-12	W-31	
3-12	W-31	
3-12	W-31	
3-12	W-31	
3-19	W-33	
3-19	W-33	
3-20	W-33	
3-20	W-33	
3-21	W-33	
3-28	W-3	
3-28	W-3	
3-28	W-3	

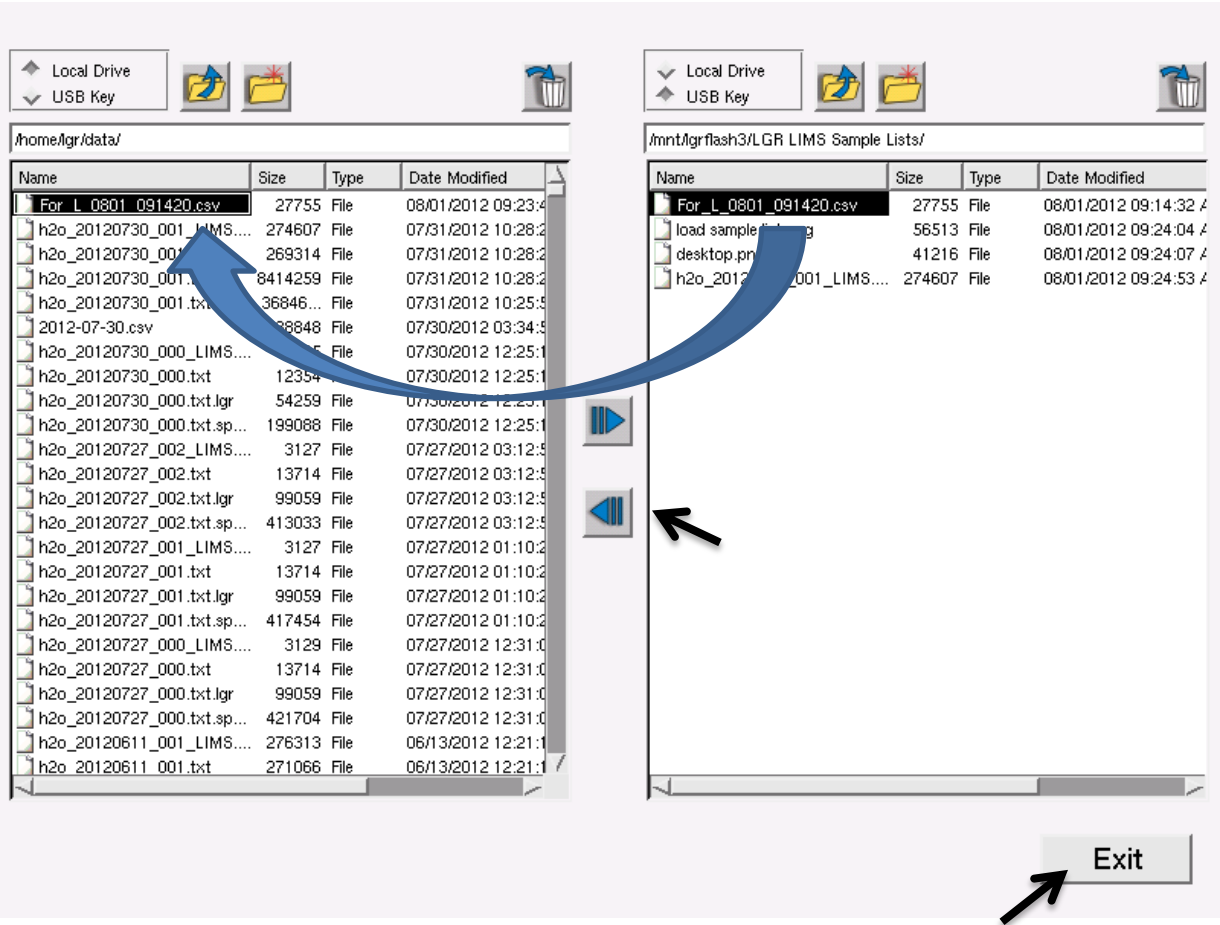
LGR run list report.

13. 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 Instrument

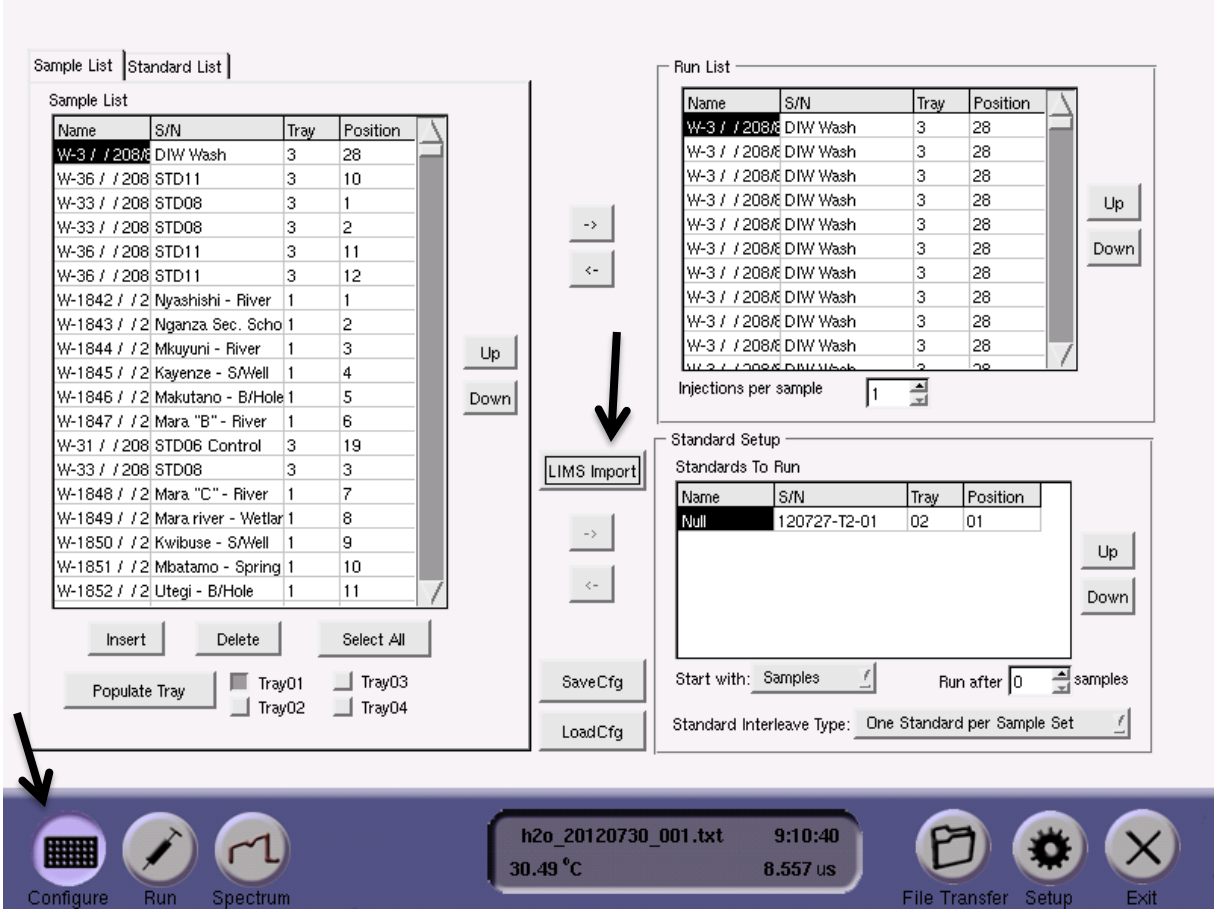
The LIMS generated sample list saved to the flash drive is loaded directly into the Los Gatos Research instrument, and it links sample data to the corresponding LIMS information. The instrument should be ready to run as per manufacturer user instructions:

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 key 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.

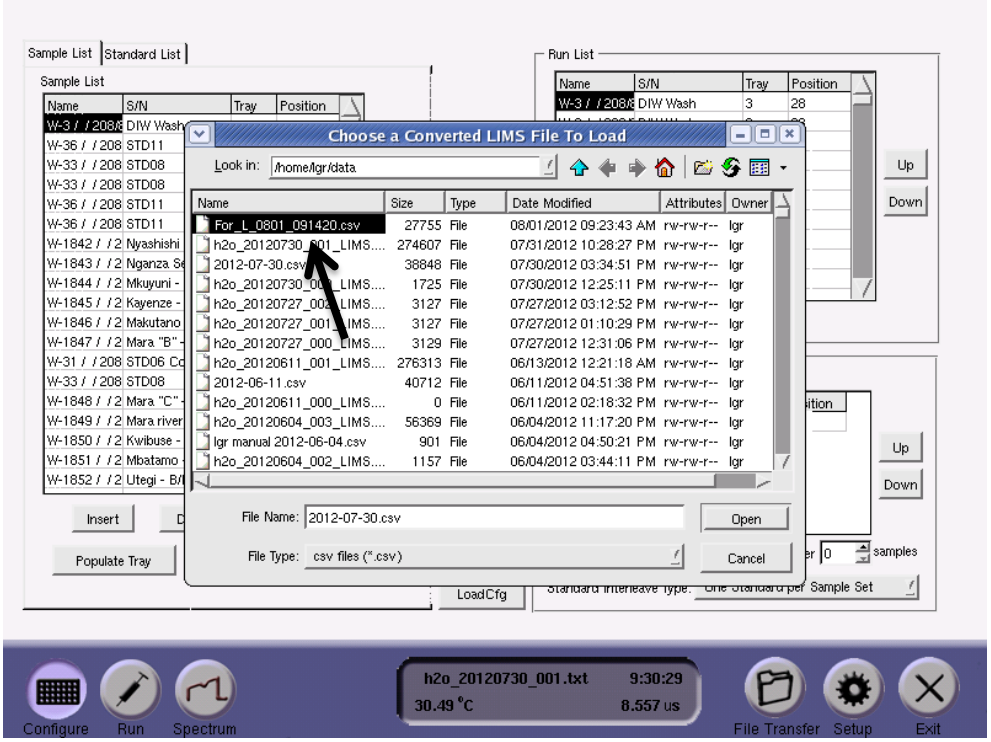


5. The LIMS sample run list can now be loaded into the Los Gatos Research Sample List side in order to start the isotopic analysis.

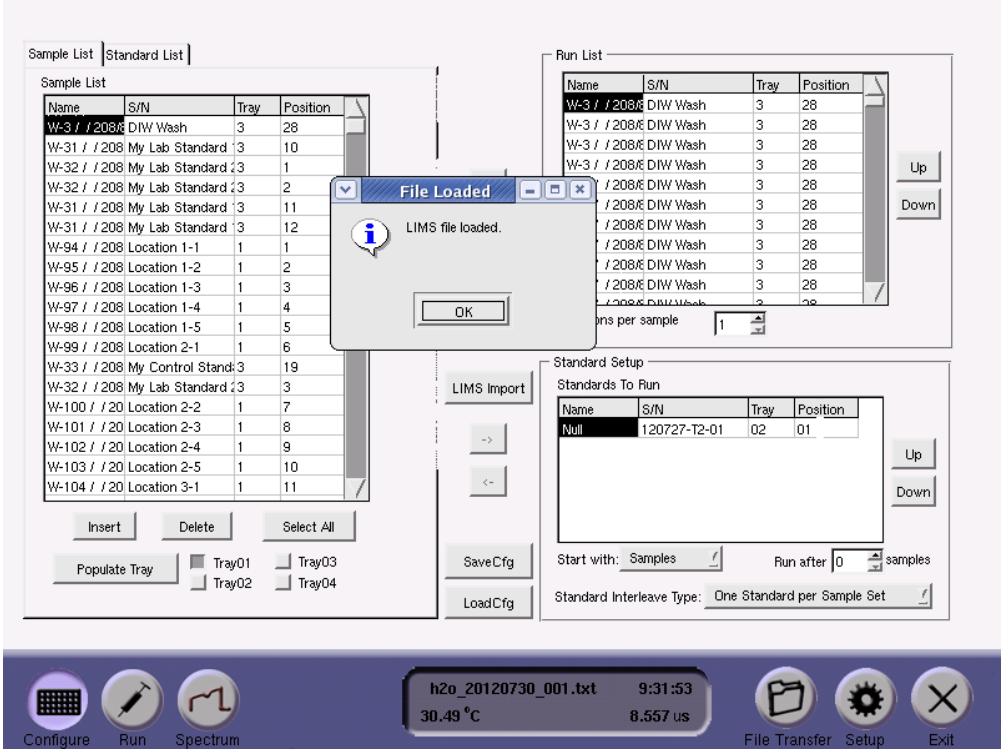
6. In the middle of the Los Gatos Research “Configure” tab, click the “LIMS Import” button.



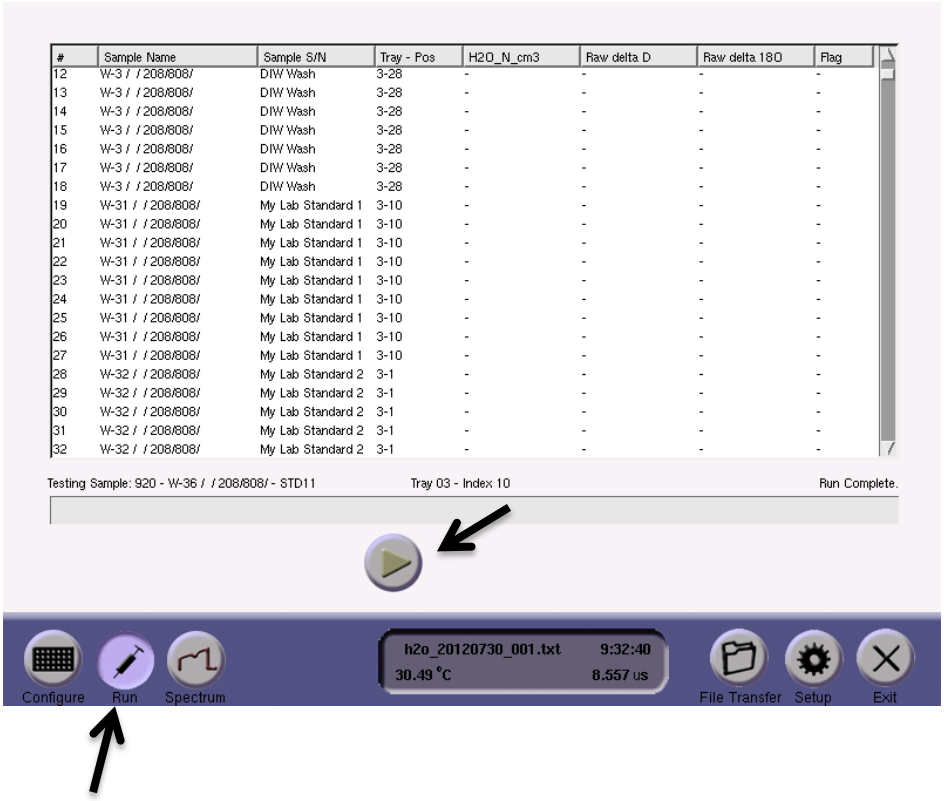
7. Select and double click to open the LIMS sample list CSV file (“For_L_xxxx.csv”) that was copied over to the instrument.



8. The LIMS generated sample run 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).



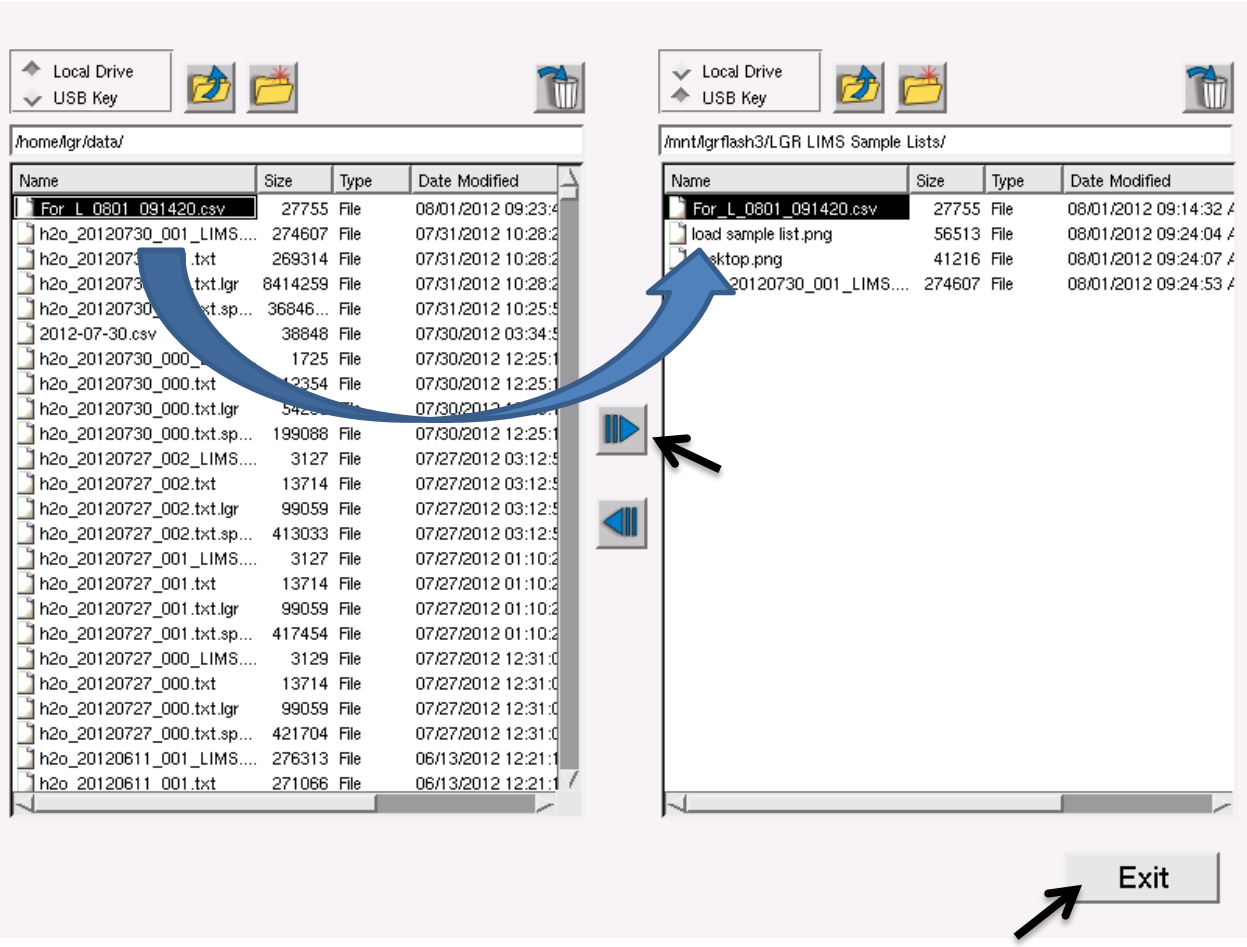
#	Sample Name	Sample S/N	Tray - Pos	H2O_N_cm3	Raw delta D	Raw delta 18O	Flag
12	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
13	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
14	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
15	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
16	W-3 / / 208/808/	DIW Wash	3-28	-	-	-	-
17	W-3 / / 208/808/	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	-	-	-	-

10.2 Importing Isotopic Data from Los Gatos Research

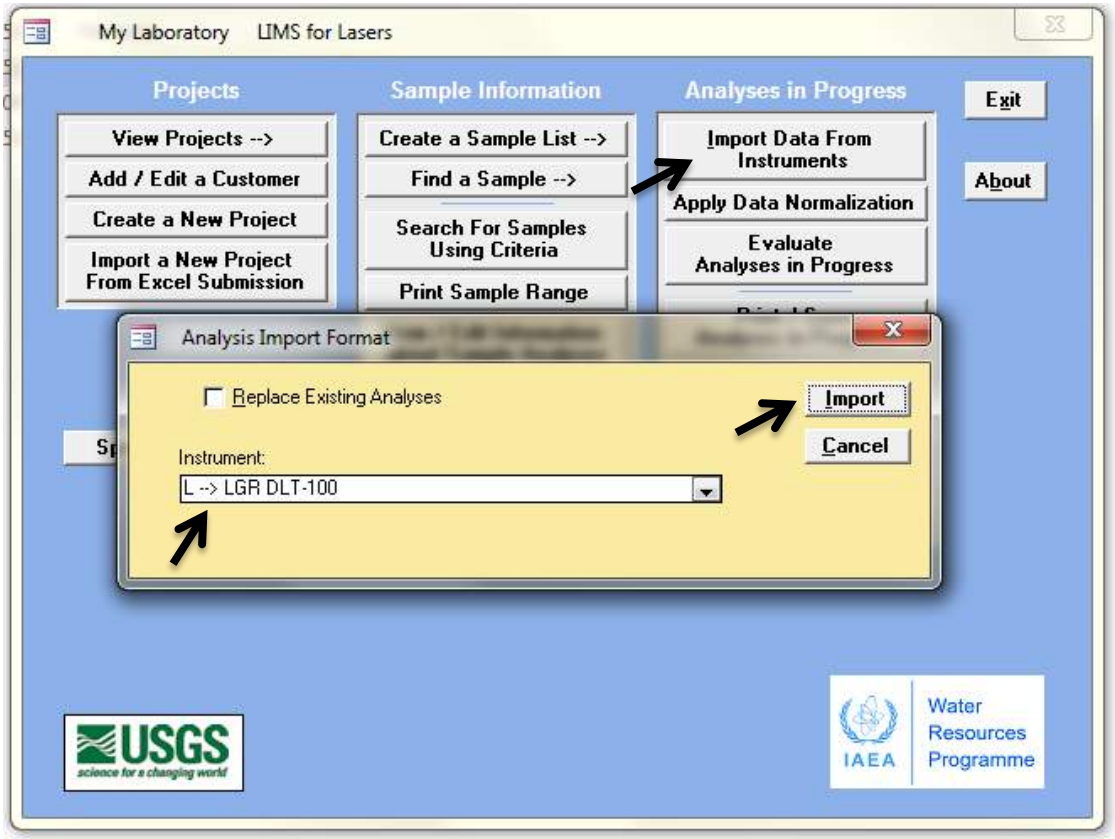
Once the Los Gatos Research autorun is finished, the hydrogen and oxygen isotopic data are imported into *LIMS for Lasers* for data normalization, processing, evaluation and reporting.

The completed autorun file is located in the Los Gatos Research instrument 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.

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 drive using the file transfer button between the two panes.
4. When the file copy is complete, click the "Exit" button. Remove the USB drive and place it into the LIMS computer USB port.

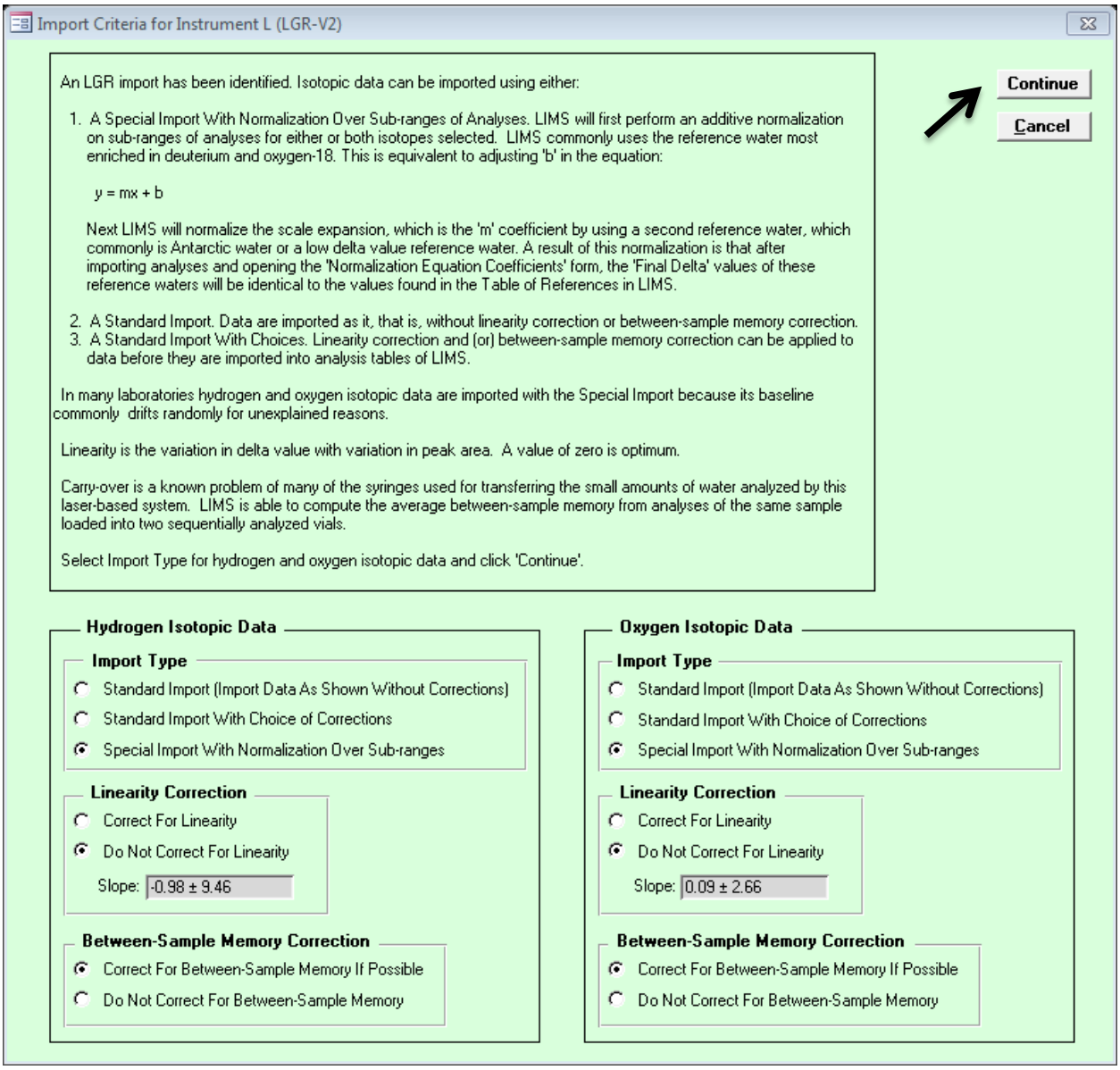


5. On the LIMS main page, click “Import Data From Instruments”. Choose the appropriate Los Gatos Research instrument from the pull down menu and then click “Import”. Select the appropriate instrument data output file from the USB stick.



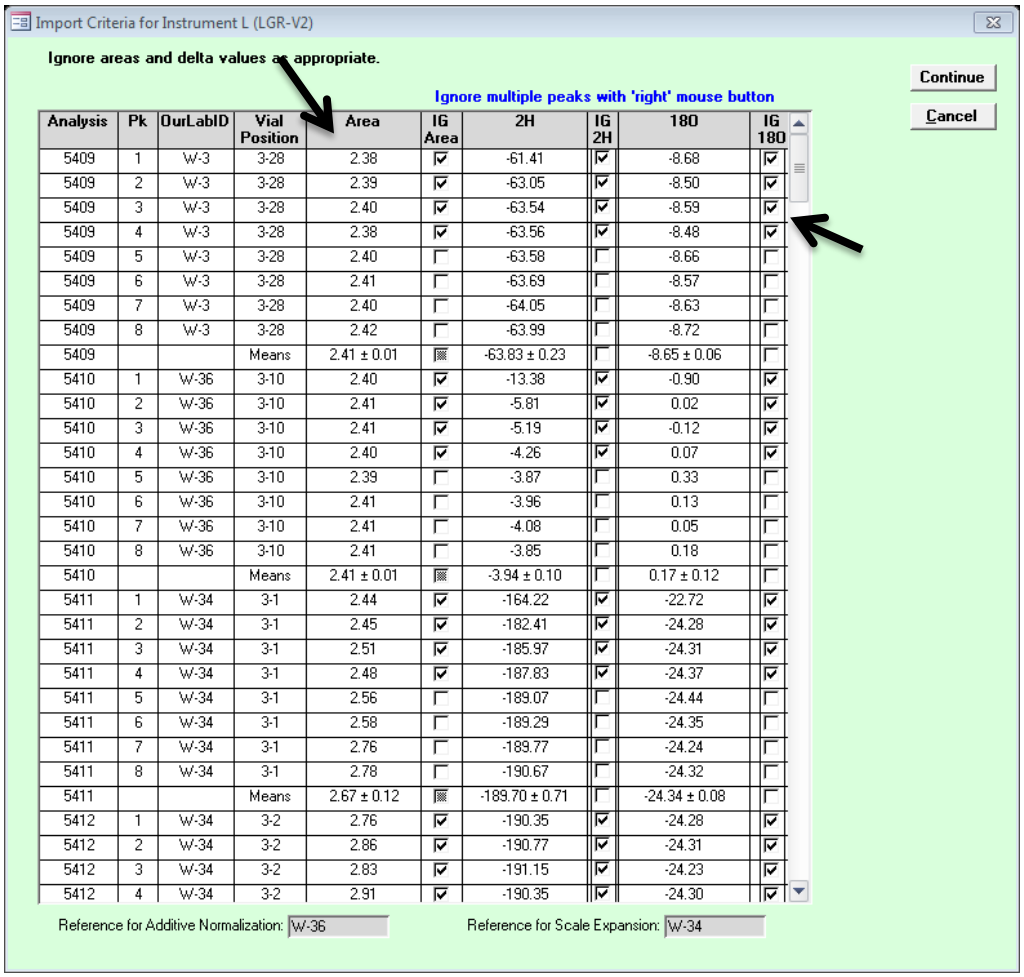
Note: The “Replace Existing Analyses” option check box will overwrite the previous import of the same data file *provided that data was not normalized or stored*. This can be useful if you wish to import the same data several times to examine the impact of different import options described in Chapter 11 or wish to correct a mistake. The default setting is unchecked.

6. If no import warnings appear (see Chapter 7.6), the following screen appears:



7. On the import criteria screen, accept the default options and then click, “Continue”. The import options available are fully described in Chapter 11. Accept default settings for now.

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



Import Criteria for Instrument L (LGR-V2)

Ignore areas and delta values as appropriate.

Ignore multiple peaks with 'right' mouse button

Continue

Cancel

Analysis	Pk	OurLabID	Vial Position	Area	IG Area	2H	IG 2H	18O	IG 18O
5409	1	W-3	3-28	2.38	☑	-61.41	☑	-8.68	☑
5409	2	W-3	3-28	2.39	☑	-63.05	☑	-8.50	☑
5409	3	W-3	3-28	2.40	☑	-63.54	☑	-8.59	☑
5409	4	W-3	3-28	2.38	☑	-63.56	☑	-8.48	☑
5409	5	W-3	3-28	2.40	☐	-63.58	☐	-8.66	☐
5409	6	W-3	3-28	2.41	☐	-63.69	☐	-8.57	☐
5409	7	W-3	3-28	2.40	☐	-64.05	☐	-8.63	☐
5409	8	W-3	3-28	2.42	☐	-63.99	☐	-8.72	☐
5409			Means	2.41 ± 0.01	▩	-63.83 ± 0.23	☐	-8.65 ± 0.06	☐
5410	1	W-36	3-10	2.40	☑	-13.38	☑	-0.90	☑
5410	2	W-36	3-10	2.41	☑	-5.81	☑	0.02	☑
5410	3	W-36	3-10	2.41	☑	-5.19	☑	-0.12	☑
5410	4	W-36	3-10	2.40	☑	-4.26	☑	0.07	☑
5410	5	W-36	3-10	2.39	☐	-3.87	☐	0.33	☐
5410	6	W-36	3-10	2.41	☐	-3.96	☐	0.13	☐
5410	7	W-36	3-10	2.41	☐	-4.08	☐	0.05	☐
5410	8	W-36	3-10	2.41	☐	-3.85	☐	0.18	☐
5410			Means	2.41 ± 0.01	▩	-3.94 ± 0.10	☐	0.17 ± 0.12	☐
5411	1	W-34	3-1	2.44	☑	-164.22	☑	-22.72	☑
5411	2	W-34	3-1	2.45	☑	-182.41	☑	-24.28	☑
5411	3	W-34	3-1	2.51	☑	-185.97	☑	-24.31	☑
5411	4	W-34	3-1	2.48	☑	-187.83	☑	-24.37	☑
5411	5	W-34	3-1	2.56	☐	-189.07	☐	-24.44	☐
5411	6	W-34	3-1	2.58	☐	-189.29	☐	-24.35	☐
5411	7	W-34	3-1	2.76	☐	-189.77	☐	-24.24	☐
5411	8	W-34	3-1	2.78	☐	-190.67	☐	-24.32	☐
5411			Means	2.67 ± 0.12	▩	-189.70 ± 0.71	☐	-24.34 ± 0.08	☐
5412	1	W-34	3-2	2.76	☑	-190.35	☑	-24.28	☑
5412	2	W-34	3-2	2.86	☑	-190.77	☑	-24.31	☑
5412	3	W-34	3-2	2.83	☑	-191.15	☑	-24.23	☑
5412	4	W-34	3-2	2.91	☑	-190.35	☑	-24.30	☑

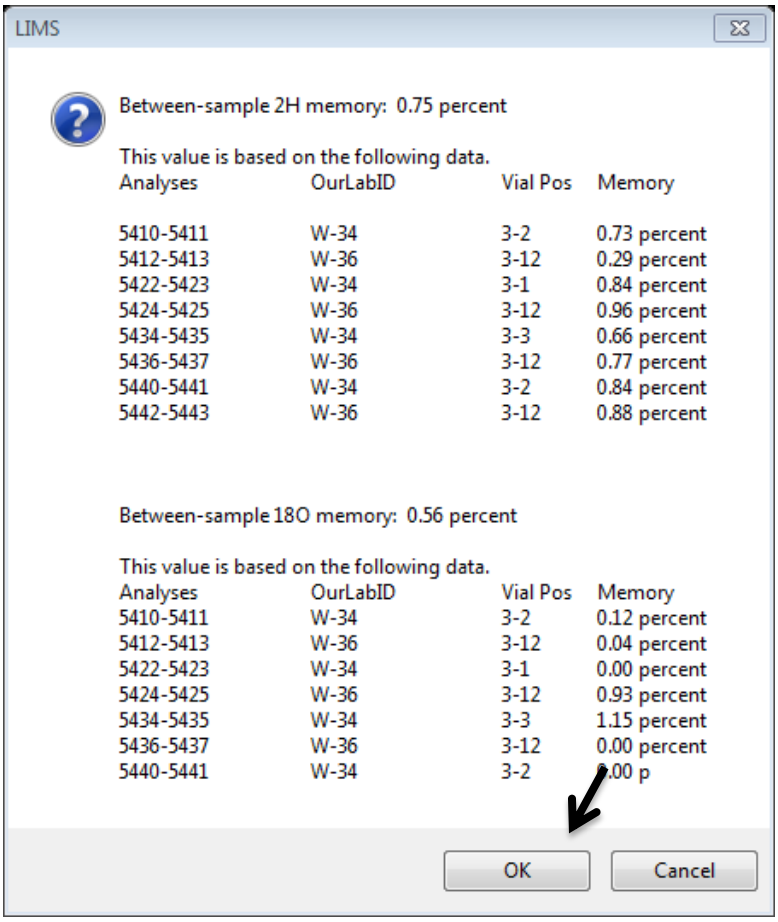
Reference for Additive Normalization: W-36

Reference for Scale Expansion: W-34

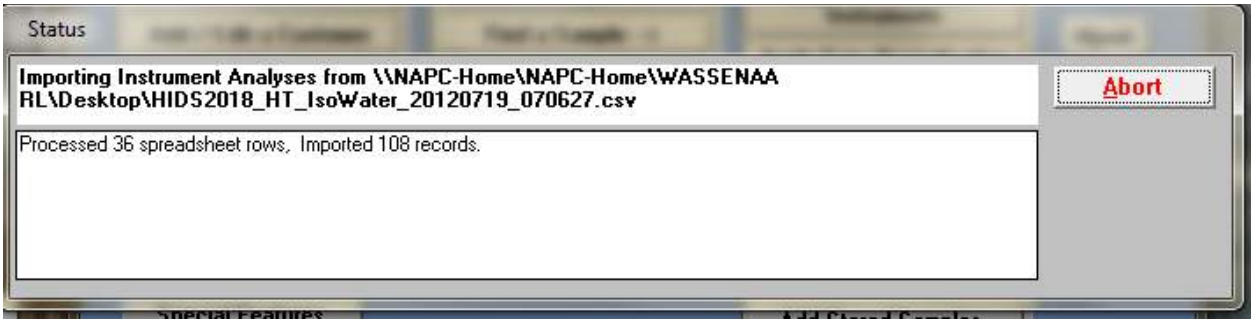
9. Before clicking Continue, use the scroll bar to quickly scan for outliers in "Area" (2.38 is a reduced number to represent 2.38×10^{16} H_2O molecules as reported by the Los Gatos Research instrument) and any isotopic outliers. Outliers may be ignored by clicking the Ignore box next to the item. Checking "IG Area" also checks the corresponding H and O isotopic data.

   If all of the data appears 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 Los Gatos Research data is now imported into LIMS for final processing. This import step can take several minutes to process hundreds of lines of instrumental data – please be patient!



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

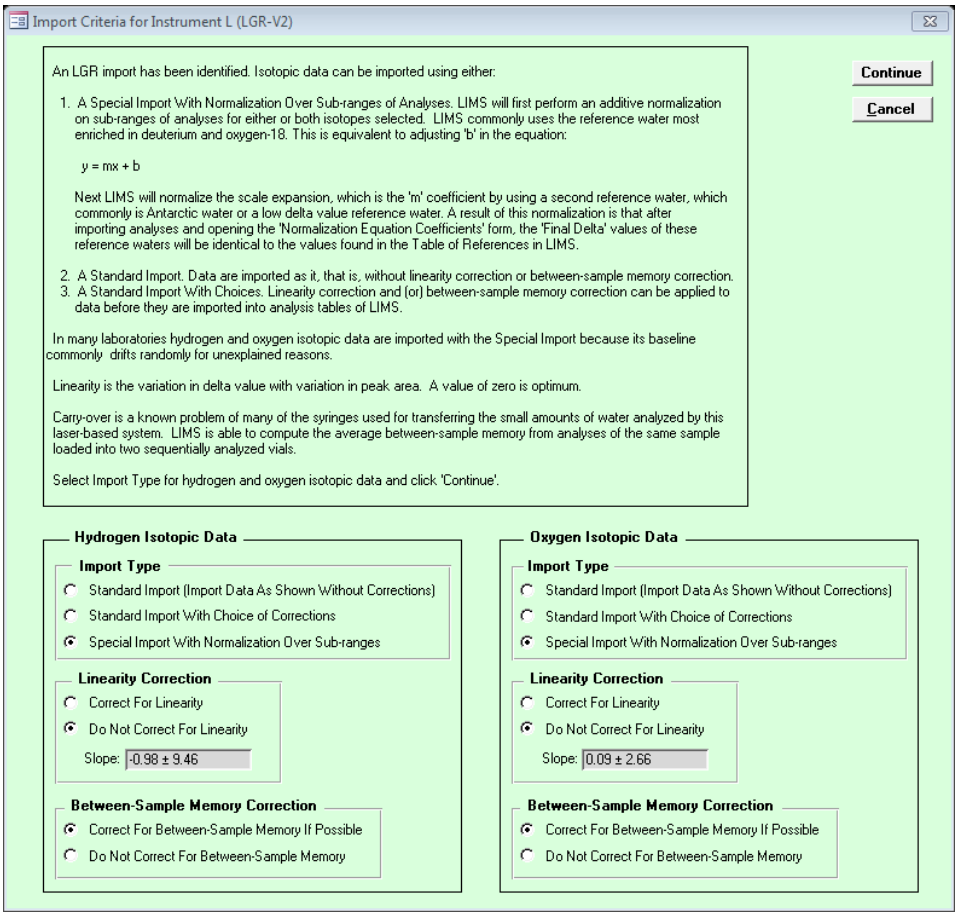
13. Normalization, evaluation and storing final data is outlined in Chapter 12.

11

Data Import - Options and Errors

11.1 Data Import Options Explained

There are several LAS import options available in *LIMS for Lasers*. Notably, be aware that import and correction options are managed for the O and H isotopic data separately. These options are described in detail below.



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

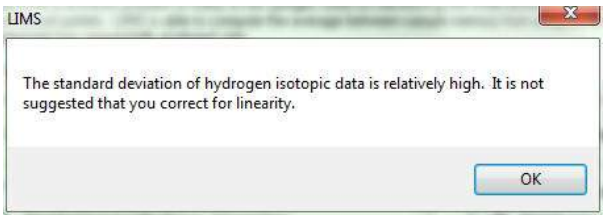
Standard Import – The isotopic data from the laser CSV file are simply imported as-is with no corrections applied. No instrumental drift or memory corrections are applied during the data import, and the other options are greyed out. After the import, drift corrections may be applied when the measurement 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 is 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.

Special Import with Normalization Over Sub-ranges – also known as "bracketed normalization". This is the recommended default import option in *LIMS for Lasers*. 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.

Linearity (Linear Drift) Correction (default = Do not correct)

This option enables the user to correct (adjust) data over the course of the autorun that has clearly exhibited a strong linear drift correlated with the number of samples analysed. This is rarely the case, as typically shown by a high error on the slope of the regression. One can check this option, but one usually obtains the following message:



Between-Sample Memory Correction (default = correct)

This option makes use of the *LIMS for Lasers* 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 delta 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:

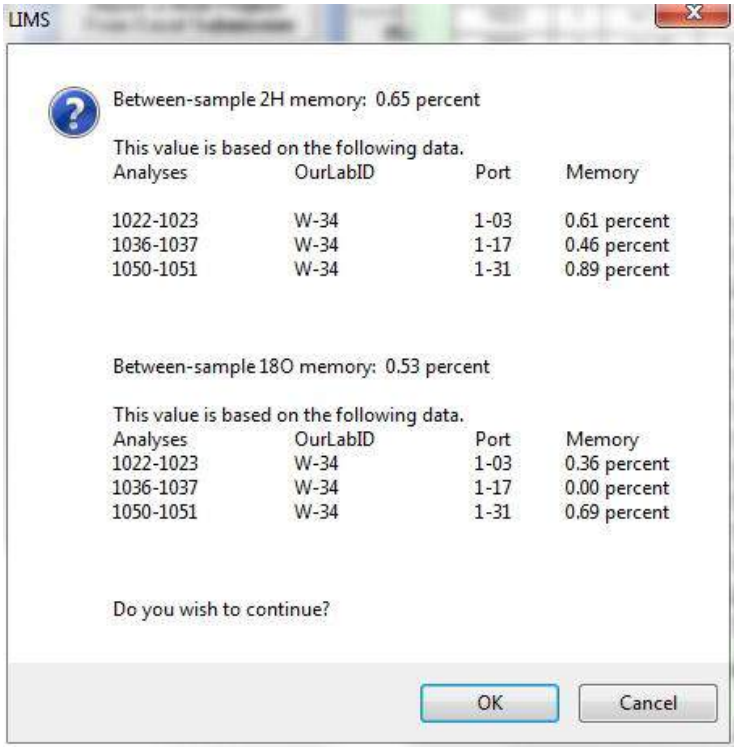
Between-sample memory (%) = (avg LowStd1 – (avg Low Std2)) / avg (HighStd – (avg Low Std2))

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)



LIMS

Between-sample 2H memory: 0.65 percent

This value is based on the following data.

Analyses	OurLabID	Port	Memory
1022-1023	W-34	1-03	0.61 percent
1036-1037	W-34	1-17	0.46 percent
1050-1051	W-34	1-31	0.89 percent

Between-sample 18O memory: 0.53 percent

This value is based on the following data.

Analyses	OurLabID	Port	Memory
1022-1023	W-34	1-03	0.36 percent
1036-1037	W-34	1-17	0.00 percent
1050-1051	W-34	1-31	0.69 percent

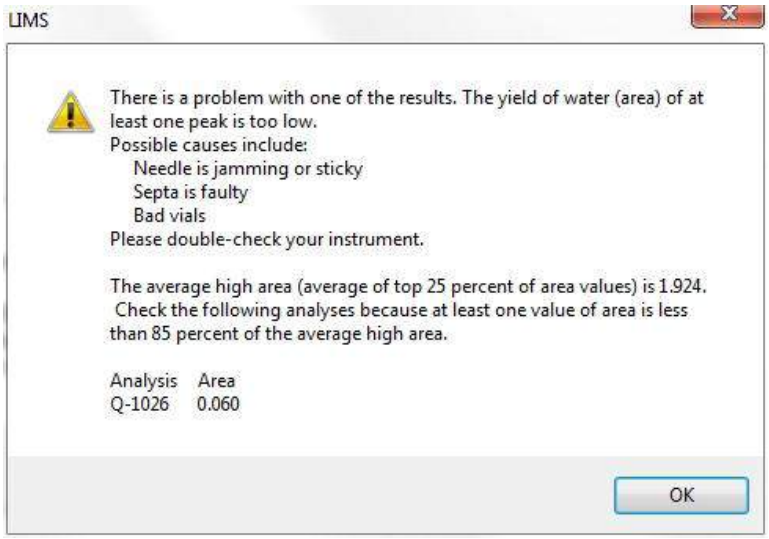
Do you wish to continue?

OK Cancel

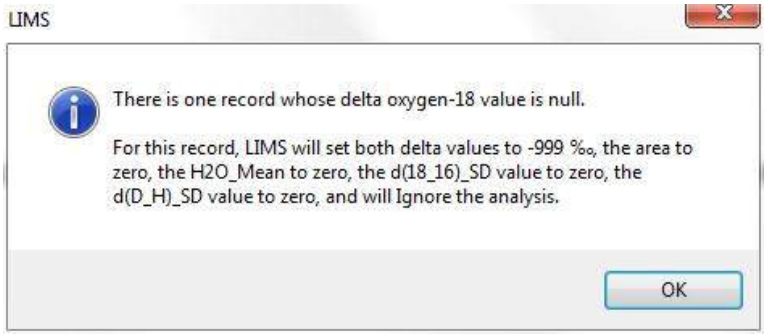
11.2 Data Import Error Messages

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 may 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 do 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 warns the user which sample was problematic.



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

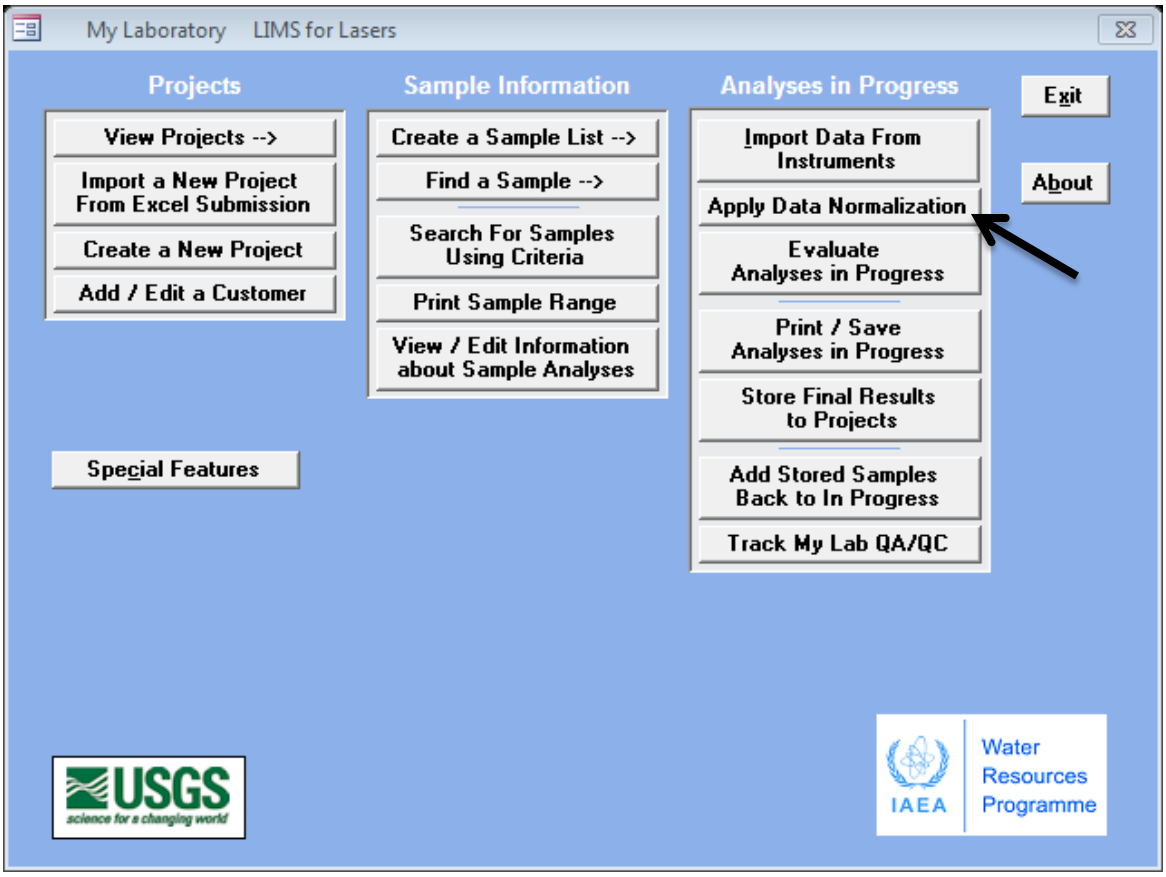
12

Normalizing, Evaluating, and Storing Results

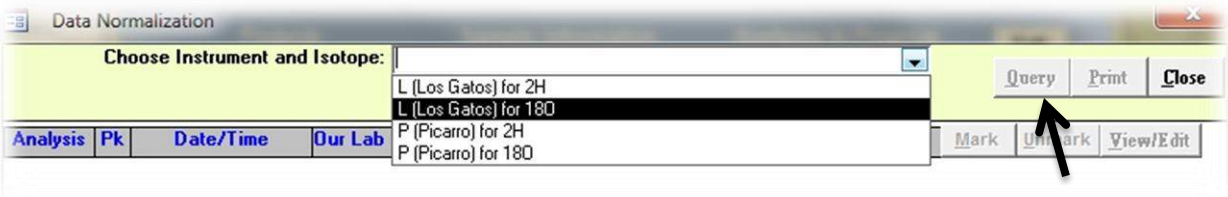
12.1 Normalizing Data to the VSMOW and VSLAP Scales

In this chapter we illustrate data normalization and evaluation. Because the identical procedure applies to both Los Gatos Research and Picarro instruments, and is repeated for ^{18}O and ^{2}H, the process will be shown only once using examples.

1. After data files have been successful imported from a laser instrument (Chap 9 and 10), on the main page of *LIMS for Lasers*, 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 to be processed. Remember: this procedure is performed twice - once for ^{2}H and once for ^{18}O. Choose one instrument and isotope, and click on "Query".

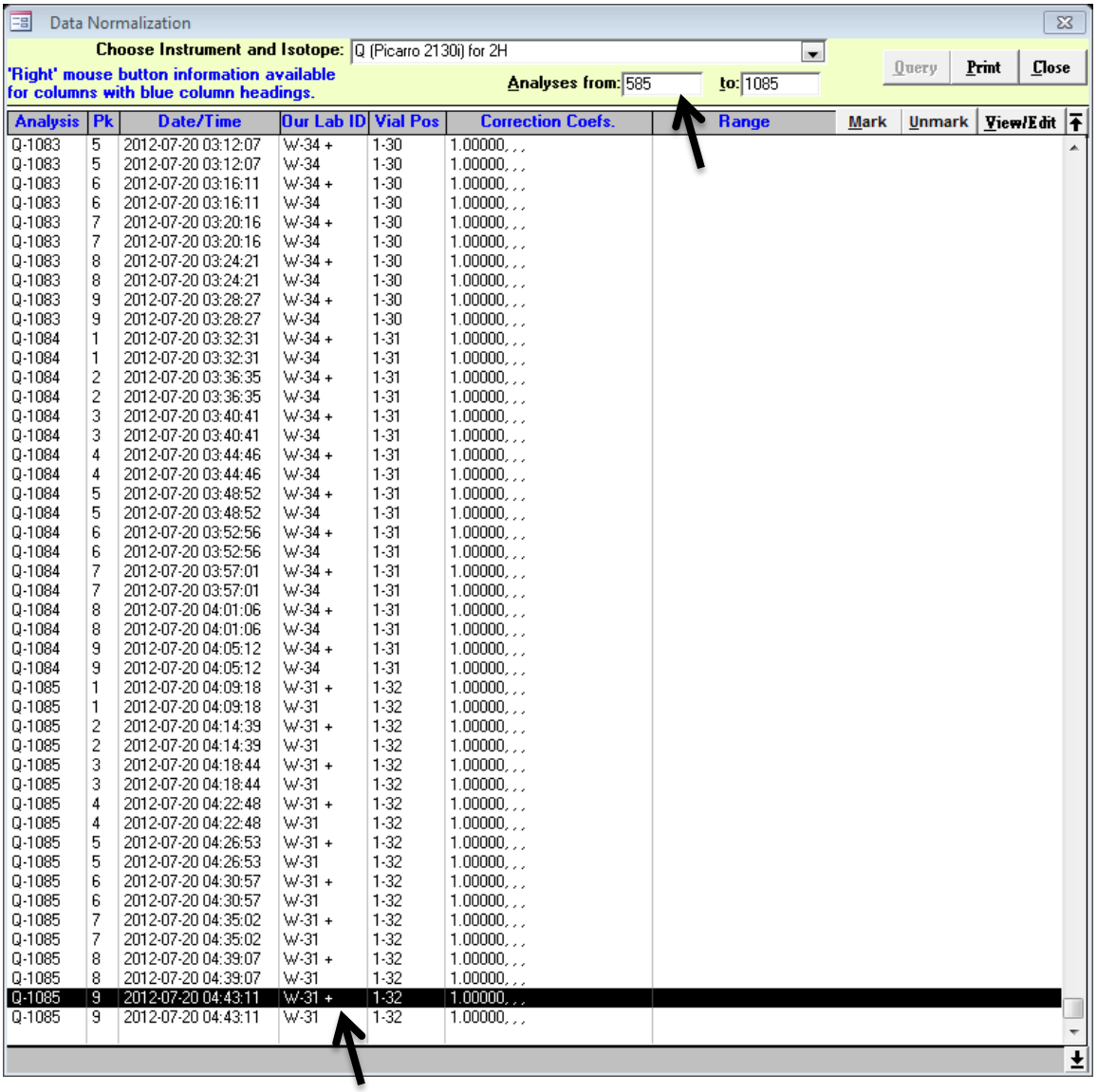


In the window that opens (below), the last 500 analyses for the selected laser instrument will be shown. The analysis list is sorted by date; the most recent samples are shown first. Older data

can be viewed by lowering the analysis numbers “from and to” fields, and then re-querying the database.

The data fields shown are:

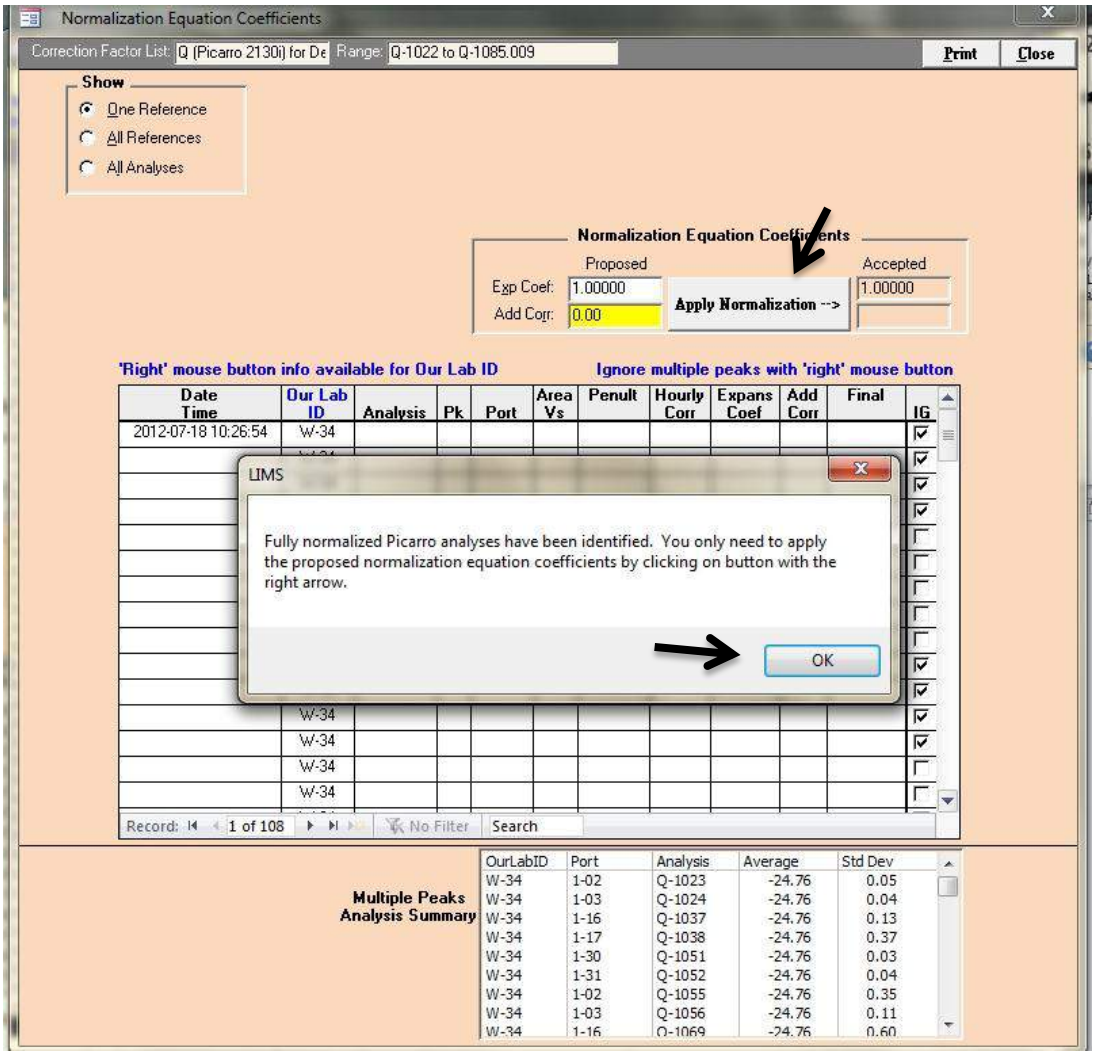
Analysis – The instrument prefix and its counter (L, P, etc.), as provided by the laser instrument.
Pk (Peak) – This is the sample injection number. Here each single sample is comprised of nine injections. There are two instances of each peak number– one is ^{2}H and the other is ^{18}O.
Date/time – 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 selected in Step 2 to be normalized (here ^{2}H on a Picarro).
Vial Pos – The autosampler tray position of each sample.



Analysis	Pk	Date/Time	Our Lab ID	Vial Pos	Correction Coefs.	Range
Q-1083	5	2012-07-20 03:12:07	W-34 +	1-30	1.00000, , ,	
Q-1083	5	2012-07-20 03:12:07	W-34	1-30	1.00000, , ,	
Q-1083	6	2012-07-20 03:16:11	W-34 +	1-30	1.00000, , ,	
Q-1083	6	2012-07-20 03:16:11	W-34	1-30	1.00000, , ,	
Q-1083	7	2012-07-20 03:20:16	W-34 +	1-30	1.00000, , ,	
Q-1083	7	2012-07-20 03:20:16	W-34	1-30	1.00000, , ,	
Q-1083	8	2012-07-20 03:24:21	W-34 +	1-30	1.00000, , ,	
Q-1083	8	2012-07-20 03:24:21	W-34	1-30	1.00000, , ,	
Q-1083	9	2012-07-20 03:28:27	W-34 +	1-30	1.00000, , ,	
Q-1083	9	2012-07-20 03:28:27	W-34	1-30	1.00000, , ,	
Q-1084	1	2012-07-20 03:32:31	W-34 +	1-31	1.00000, , ,	
Q-1084	1	2012-07-20 03:32:31	W-34	1-31	1.00000, , ,	
Q-1084	2	2012-07-20 03:36:35	W-34 +	1-31	1.00000, , ,	
Q-1084	2	2012-07-20 03:36:35	W-34	1-31	1.00000, , ,	
Q-1084	3	2012-07-20 03:40:41	W-34 +	1-31	1.00000, , ,	
Q-1084	3	2012-07-20 03:40:41	W-34	1-31	1.00000, , ,	
Q-1084	4	2012-07-20 03:44:46	W-34 +	1-31	1.00000, , ,	
Q-1084	4	2012-07-20 03:44:46	W-34	1-31	1.00000, , ,	
Q-1084	5	2012-07-20 03:48:52	W-34 +	1-31	1.00000, , ,	
Q-1084	5	2012-07-20 03:48:52	W-34	1-31	1.00000, , ,	
Q-1084	6	2012-07-20 03:52:56	W-34 +	1-31	1.00000, , ,	
Q-1084	6	2012-07-20 03:52:56	W-34	1-31	1.00000, , ,	
Q-1084	7	2012-07-20 03:57:01	W-34 +	1-31	1.00000, , ,	
Q-1084	7	2012-07-20 03:57:01	W-34	1-31	1.00000, , ,	
Q-1084	8	2012-07-20 04:01:06	W-34 +	1-31	1.00000, , ,	
Q-1084	8	2012-07-20 04:01:06	W-34	1-31	1.00000, , ,	
Q-1084	9	2012-07-20 04:05:12	W-34 +	1-31	1.00000, , ,	
Q-1084	9	2012-07-20 04:05:12	W-34	1-31	1.00000, , ,	
Q-1085	1	2012-07-20 04:09:18	W-31 +	1-32	1.00000, , ,	
Q-1085	1	2012-07-20 04:09:18	W-31	1-32	1.00000, , ,	
Q-1085	2	2012-07-20 04:14:39	W-31 +	1-32	1.00000, , ,	
Q-1085	2	2012-07-20 04:14:39	W-31	1-32	1.00000, , ,	
Q-1085	3	2012-07-20 04:18:44	W-31 +	1-32	1.00000, , ,	
Q-1085	3	2012-07-20 04:18:44	W-31	1-32	1.00000, , ,	
Q-1085	4	2012-07-20 04:22:48	W-31 +	1-32	1.00000, , ,	
Q-1085	4	2012-07-20 04:22:48	W-31	1-32	1.00000, , ,	
Q-1085	5	2012-07-20 04:26:53	W-31 +	1-32	1.00000, , ,	
Q-1085	5	2012-07-20 04:26:53	W-31	1-32	1.00000, , ,	
Q-1085	6	2012-07-20 04:30:57	W-31 +	1-32	1.00000, , ,	
Q-1085	6	2012-07-20 04:30:57	W-31	1-32	1.00000, , ,	
Q-1085	7	2012-07-20 04:35:02	W-31 +	1-32	1.00000, , ,	
Q-1085	7	2012-07-20 04:35:02	W-31	1-32	1.00000, , ,	
Q-1085	8	2012-07-20 04:39:07	W-31 +	1-32	1.00000, , ,	
Q-1085	8	2012-07-20 04:39:07	W-31	1-32	1.00000, , ,	
Q-1085	9	2012-07-20 04:43:11	W-31 +	1-32	1.00000, , ,	
Q-1085	9	2012-07-20 04:43:11	W-31	1-32	1.00000, , ,	

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* is "bracketed normalization", LIMS has already pre-processed and normalized all of the isotope 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 isotope (e.g. ^{18}O). LIMS has used bracketed (memory and drift corrected) measurement standards to normalize sample H or O isotope data to the VSMOW and VSLAP scales. Next, we can evaluate the results as outlined in Chapter 12.3.



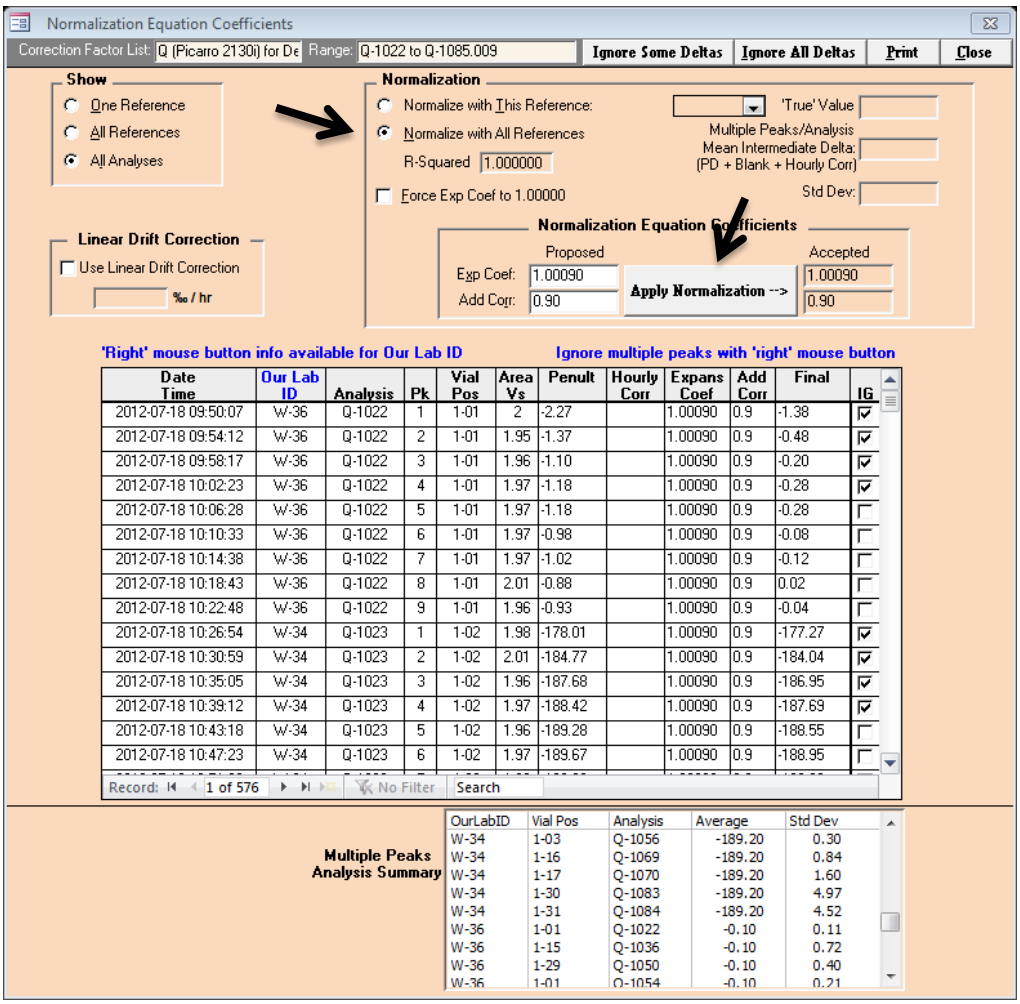
***Note*:** To avoid confusion, normalize ^{18}O and ^{2}H results from each autorun *before* importing the next autorun. This avoids unintentional combining of datasets from different autoruns.

12.2 Normalizing Data (Without Bracketed Normalization)

If you imported your laser isotopic data using the optional "Standard Import" or "Standard Import with Choice of Corrections", the data is treated as a single batch, and more normalization options, like linear drift correction, can be applied after following Steps 1-3 in Chapter 12.1.

1. Click "Normalize with All References". The calculated R^2 value should be >0.99.
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 (e.g. ^{18}O). Then evaluate your results (Chapter 12.3).

Note: LIMS reveals our ignored injections as set in LIMS 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.

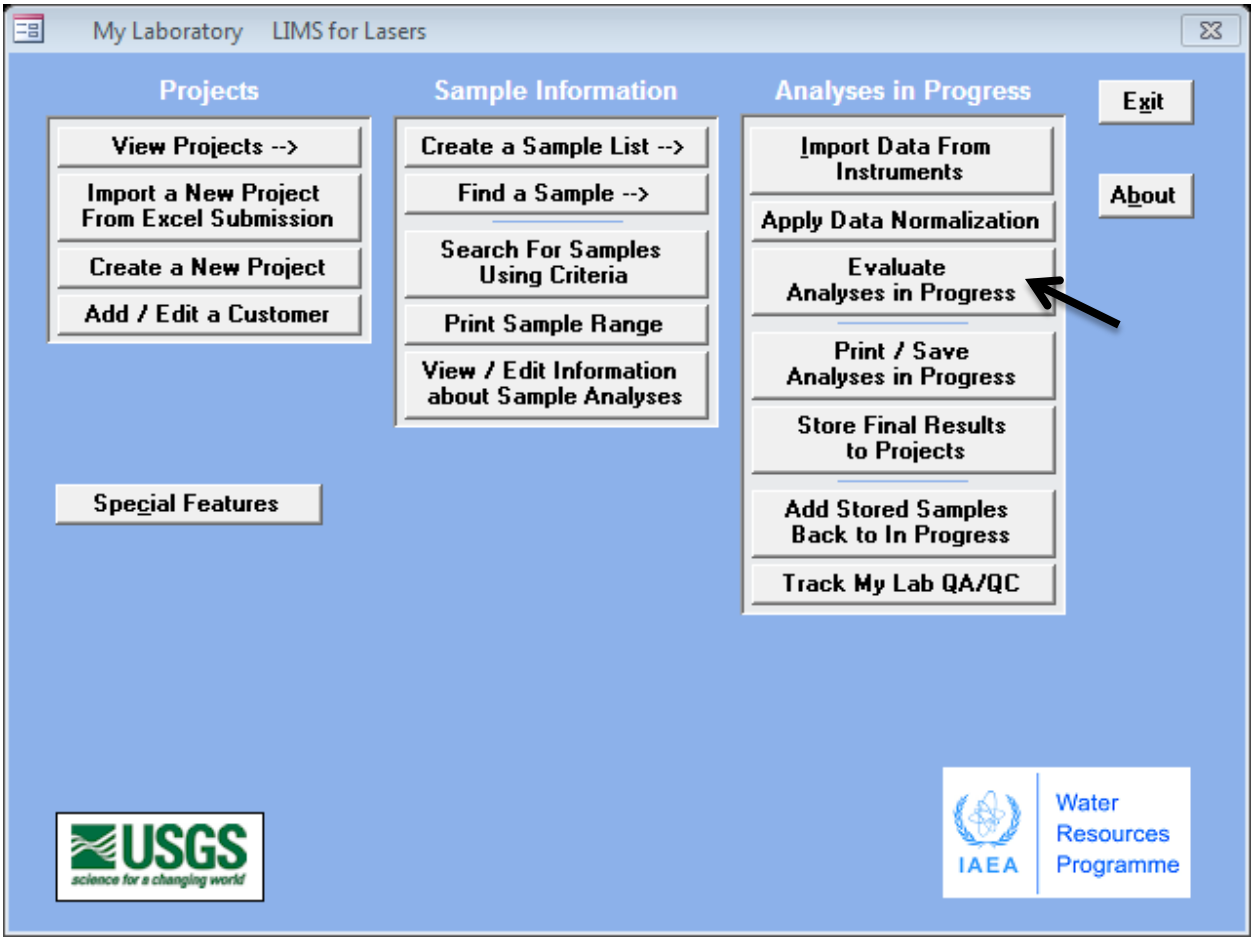


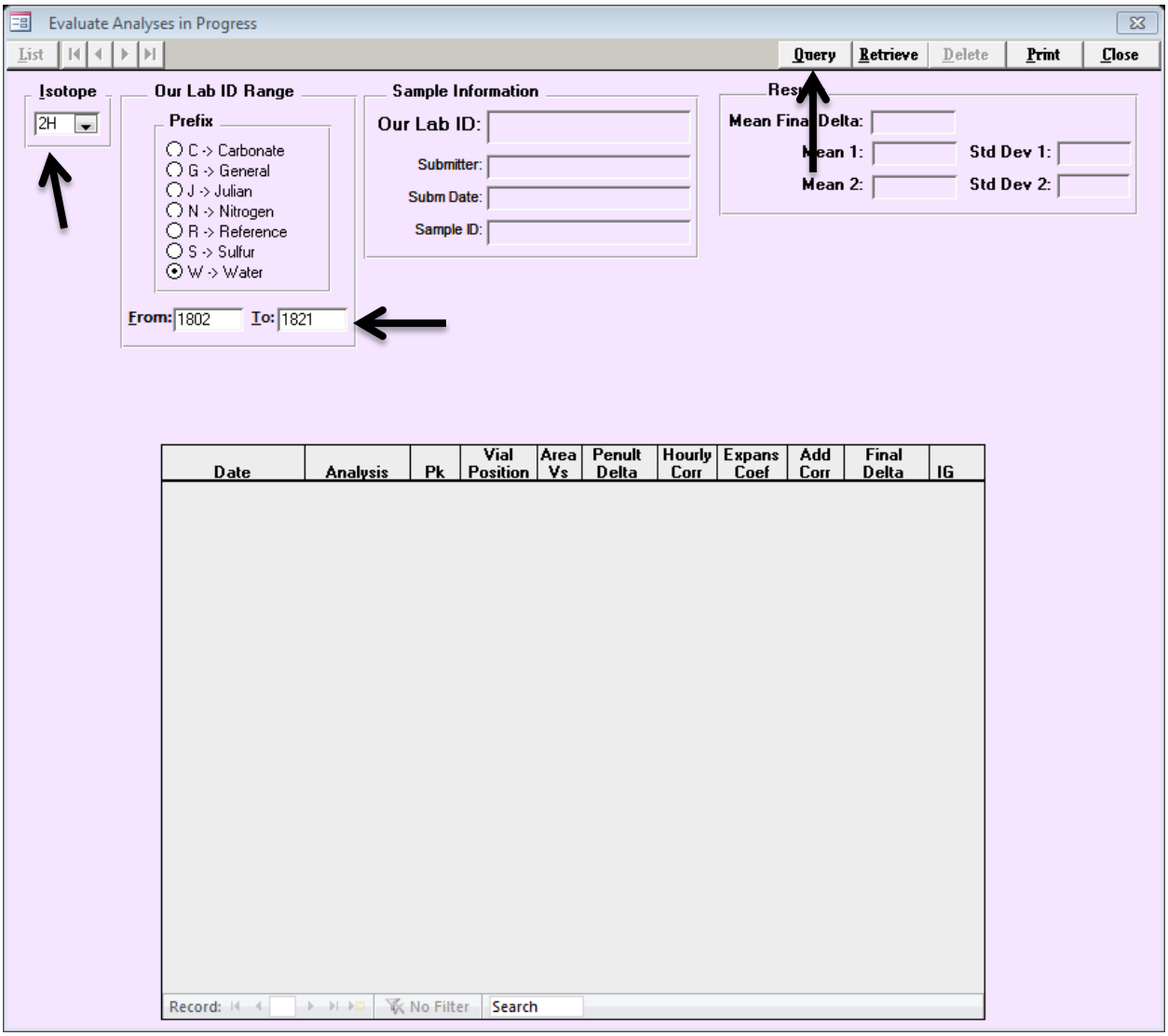
12.3 Evaluating Analyses in Progress

Once customer samples have been measured twice and all of the data are 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.

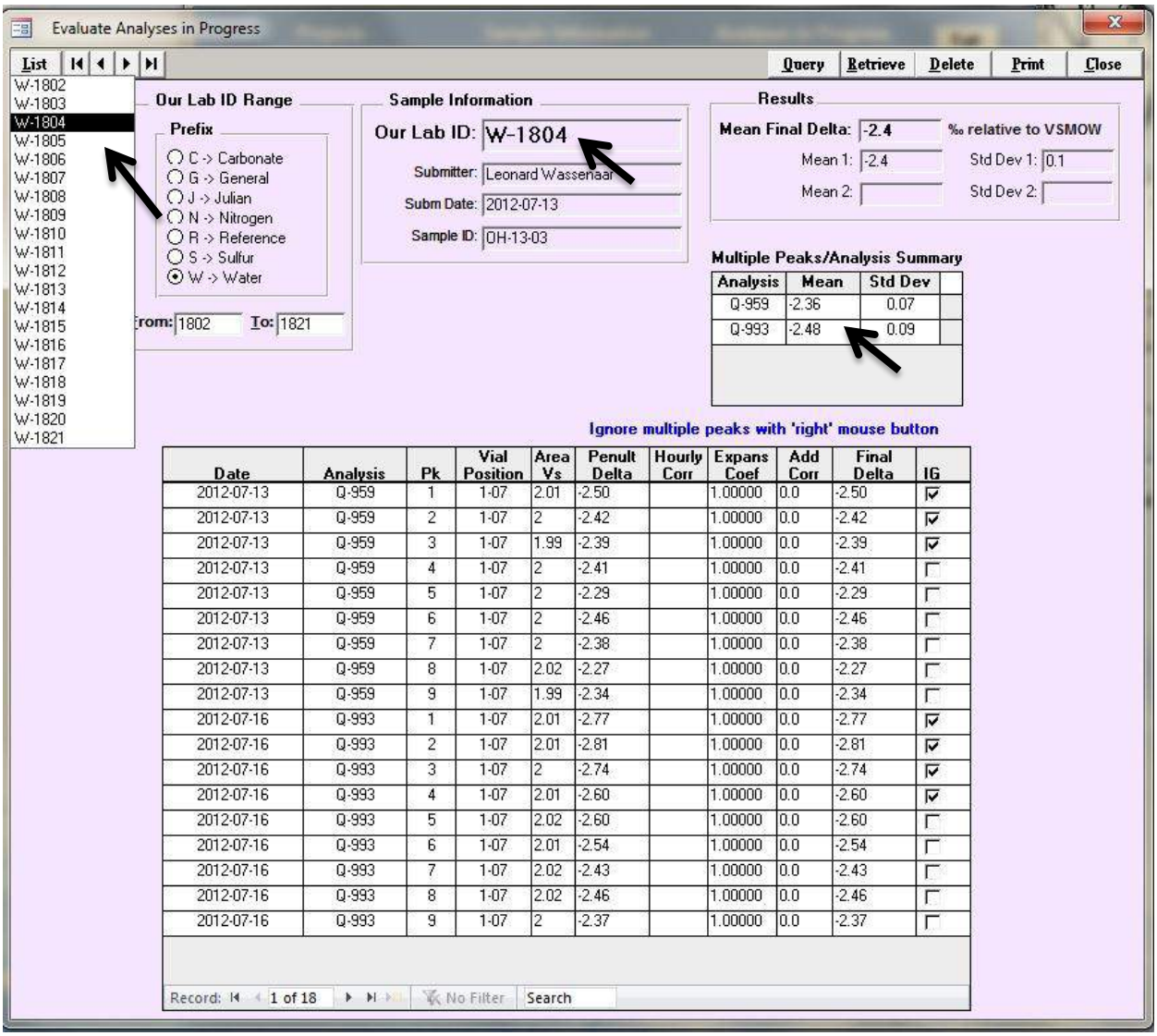
The *LIMS for Lasers* data evaluation consists of two parts: (1) checking the repeatability of all normalized samples that were measured at least twice, and (2) checking the performance of control standards included in each autorun, and over time (see Chapter 12.7).

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





2. Choose one isotope – such as ^{2}H - that you want to evaluate from the pull down menu located in the upper left (remember to repeat this procedure for ^{18}O).
3. The available Prefix in *LIMS for Lasers* 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, 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 can view individual samples to examine the measurement result(s). In the example, the sample with Our LabID W-1804 was selected for δ^2H.

This window displays the Sample Information (ID, customer, analysis date) and a summary of the normalized results (Mean and StdDev). Here, we note sample W-1804 was analysed twice as Analyses 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, 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.

Where there is a significant disagreement between the H or O isotope outcomes of two different assays of the same sample, that sample should be measured a third time. If two of the three results agreed well, one can reasonably 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. The judgement takes into consideration the required level of precision needed, and the accuracy that the instrument used can reasonably achieve.

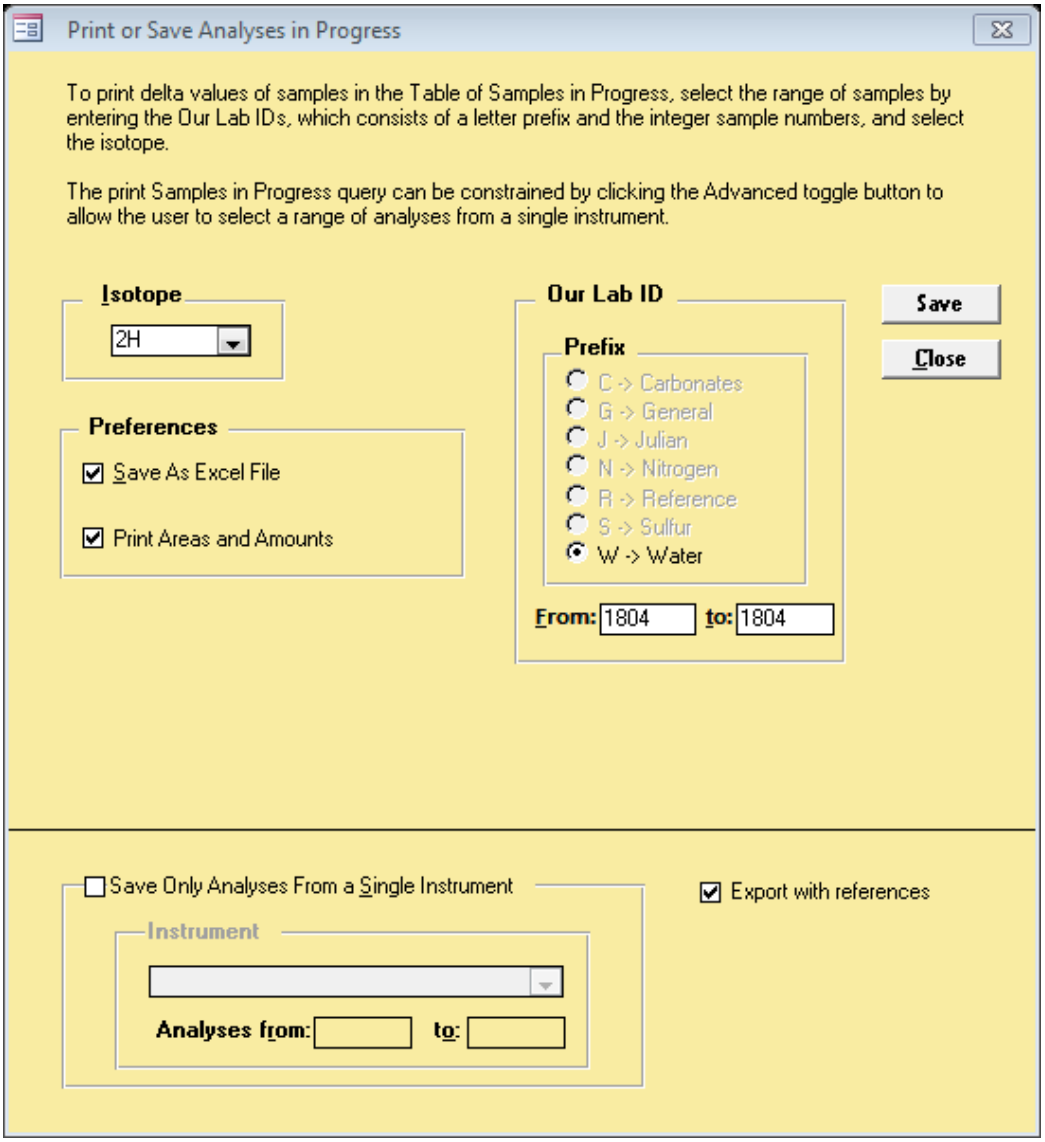
As a first suggestion (and this is instrument specific), δ^2H repeats that repeat within 1.5 ‰ of each other are generally considered acceptable for hydrological studies. For δ^{18}O, repeats that lie within 0.2 ‰ of each other are generally considered acceptable. This assessment, however, remains for each laboratory to decide on its own, and thereby becomes the 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).

Very Important! If a sample has been run three or more times and there is a clear outlier, in Evaluate Analyses in Progress is where that outlier must be manually "Ignored". In the bottom window, check the IG (ignore) boxes for that outlier sample (e.g. all instances having the same analysis number). It will disappear from the Multiple Peak Summary window, and these bad results will not be used in calculating the mean reportable final results for that sample.

Be careful - if you do not ignore bad results, they will be included in the final reported mean value!

12.4 Print or Save Analyses in Progress

Some analysts (and clients) prefer to see and evaluate individual analyses offline using Excel, or view print-outs of detailed summaries and the statistics for individual samples and injections before they are stored. This is facilitated with the "Print/Save Analyses in Progress" button on the main LIMS page, which opens the form below.



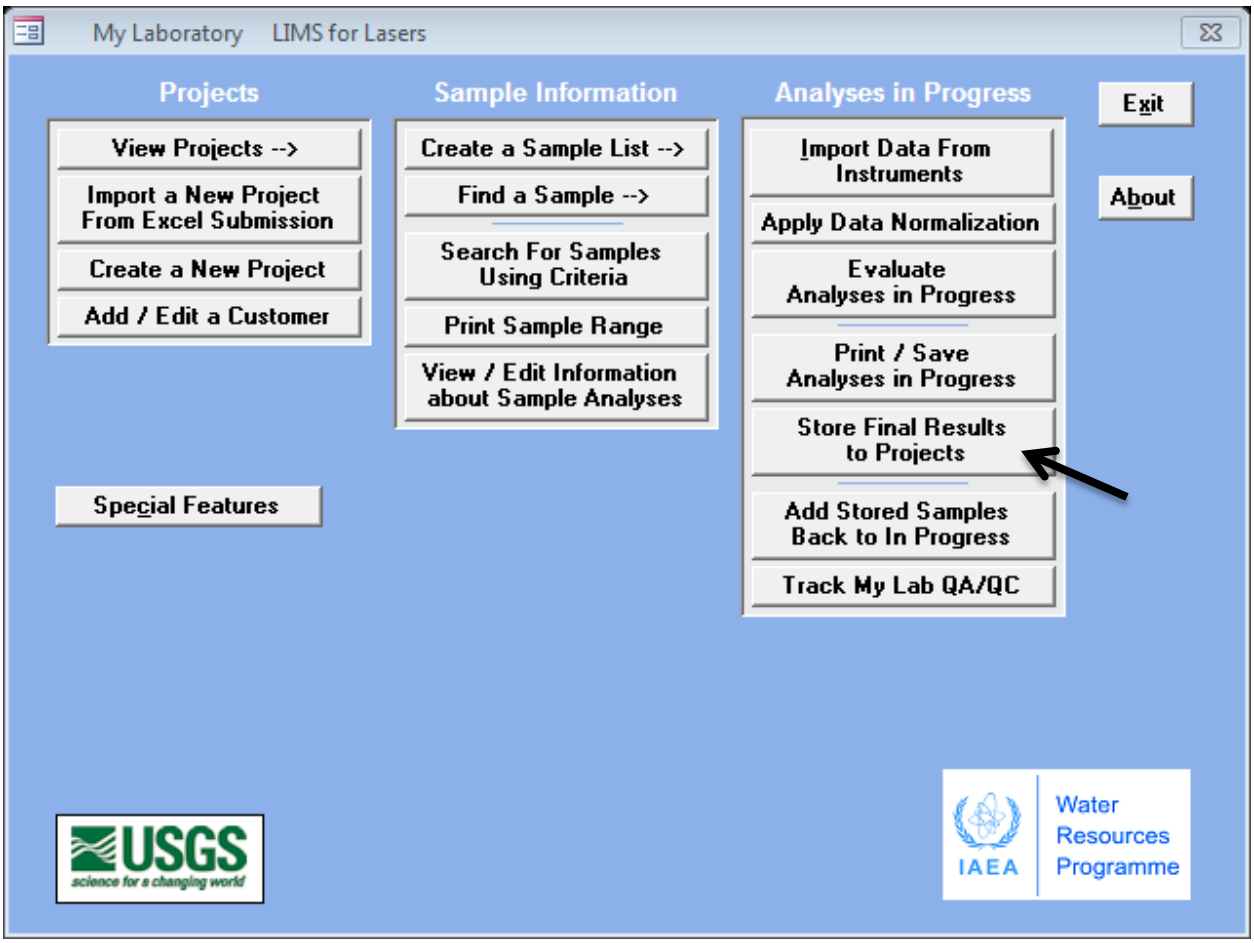
In the above example, all δ^2H analyses of W-1804 can be printed or "Saved" to a spreadsheet for offline analysis. Optionally, one may select analyses from only one instrument, or include the reference data that accompanied the samples, and include the water amounts (areas) recorded in the laser cavity.

Many clients to do not request this level of detail and this section can often be skipped.

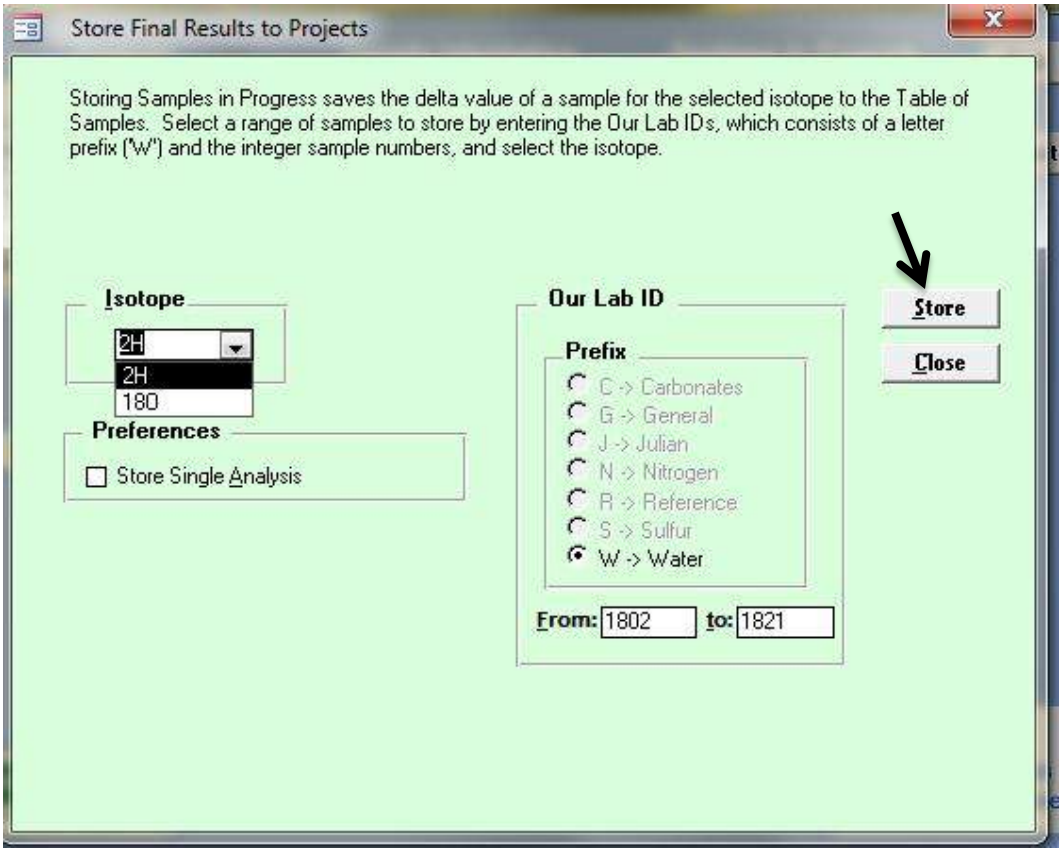
12.5 Store Final Results to Projects

The action of "storing" final results to a Project means that the laboratory analyst has normalized all of the samples or controls that were measured in replicate, and is satisfied their results agree with their specified laboratory evaluation criteria.

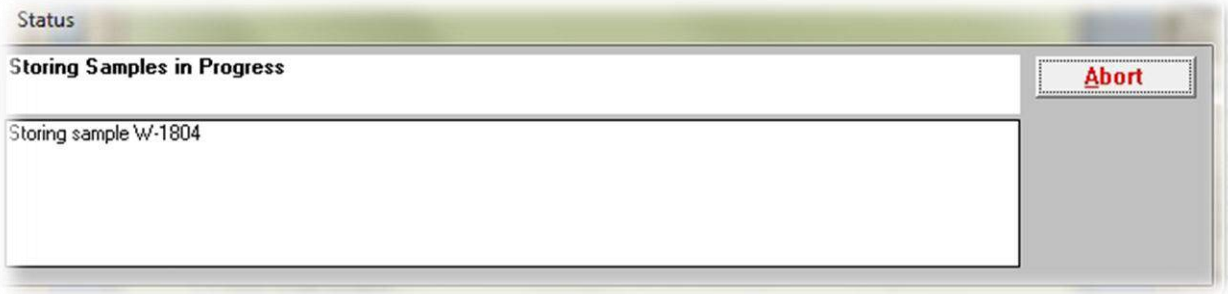
The final step is to "Store" the final results of the samples into the customer Project for reporting purposes.



1. Click on the "Store Final Results to Projects" button.
2. In the window that opens, chose the isotope (^{2}H or ^{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 accepted δ^2H results for samples W-1802 to W-1821 are selected to be "Stored".
4. Click on "Store" and LIMS shows the samples being stored, and a message indicates its completion.



5. Repeat the same process for ^{18}O by from the pull down menu. Then close the Store Samples page.
6. All H and O isotope samples for the selected range are now stored back to the Projects for final reporting (Chapter 13).

***Important*:** By default, *LIMS for Lasers* does not store final data unless samples have been analysed twice, or more. To override this, check the "Store Single Analysis" box – only then will samples analysed once be stored. This 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 where stored data need to be placed back "in progress" again. This could be for a few reasons:

- Mistaken storage of singly run 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.

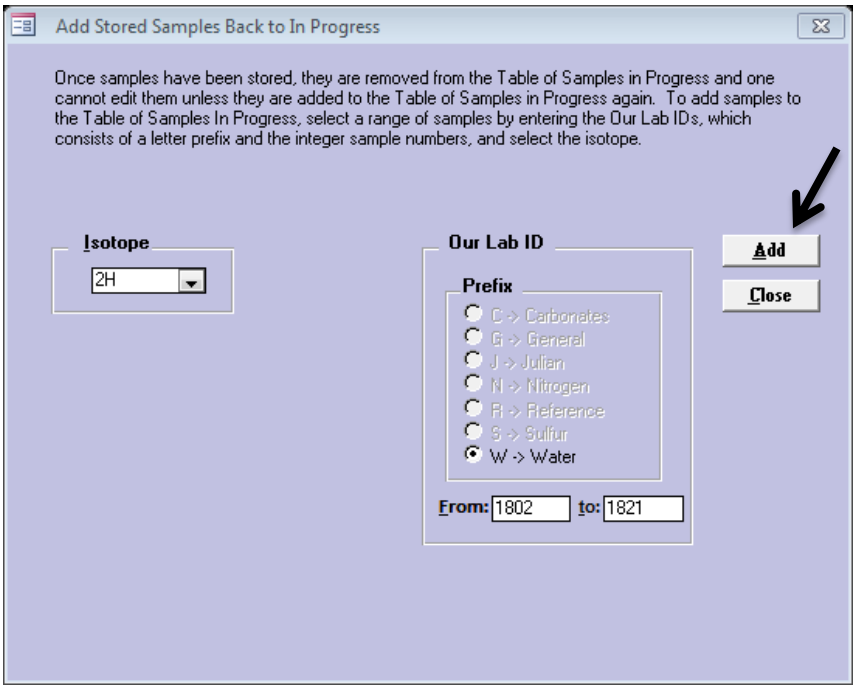
Adding samples back to "in progress" allows the analyst re-process data, correct or ignore errors, or remove faulty data from the client's project. Note that if a sample was already stored and is re-analyzed, *LIMS for Lasers* automatically loads that sample back to "In Progress".

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

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



Note: Be sure to "Store" updated data once corrections are made, or the Project will retain the incorrect data that was previously stored.

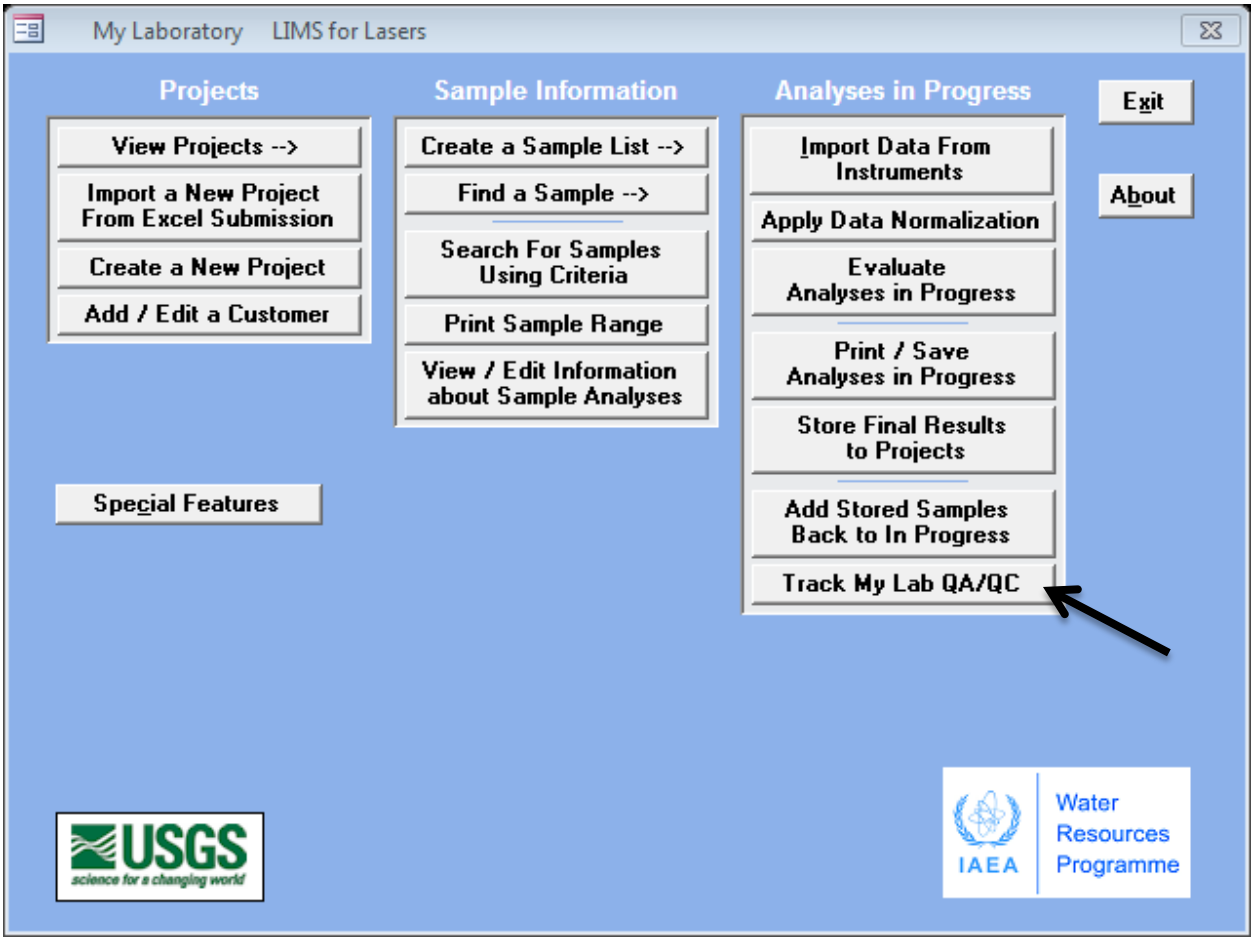
12.7 Track My Lab QA/QC

The second part of robust data evaluation is to examine the results of control standards included in each autorun with the known value or results of those control standards over time (usually before storing final results). This QA/QC evaluation can is made through the systematic use and monitoring of laboratory control standards, as recommended in the default *LIMS for Lasers* analysis templates.

Following each autorun, *LIMS for Lasers* facilitates evaluating the performance of the control standards. Over time, this assessment provides the operator with realistic metrics of LAS instrumental precision, and this strategy allows one to quickly spot unexpected changes in the control outcomes.

Gradual or abrupt changes in the δ values of a control standard can arise from factors like improper storage of the Control water sample (e.g. inadvertent evaporation), or by 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 analyses, or define a range of analysis dates.
4. Optionally, select a specific instrument if the control standard is measured on several instruments (e.g. multiple LAS).
5. Click "Create Graph". *LIMS for Lasers* 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.

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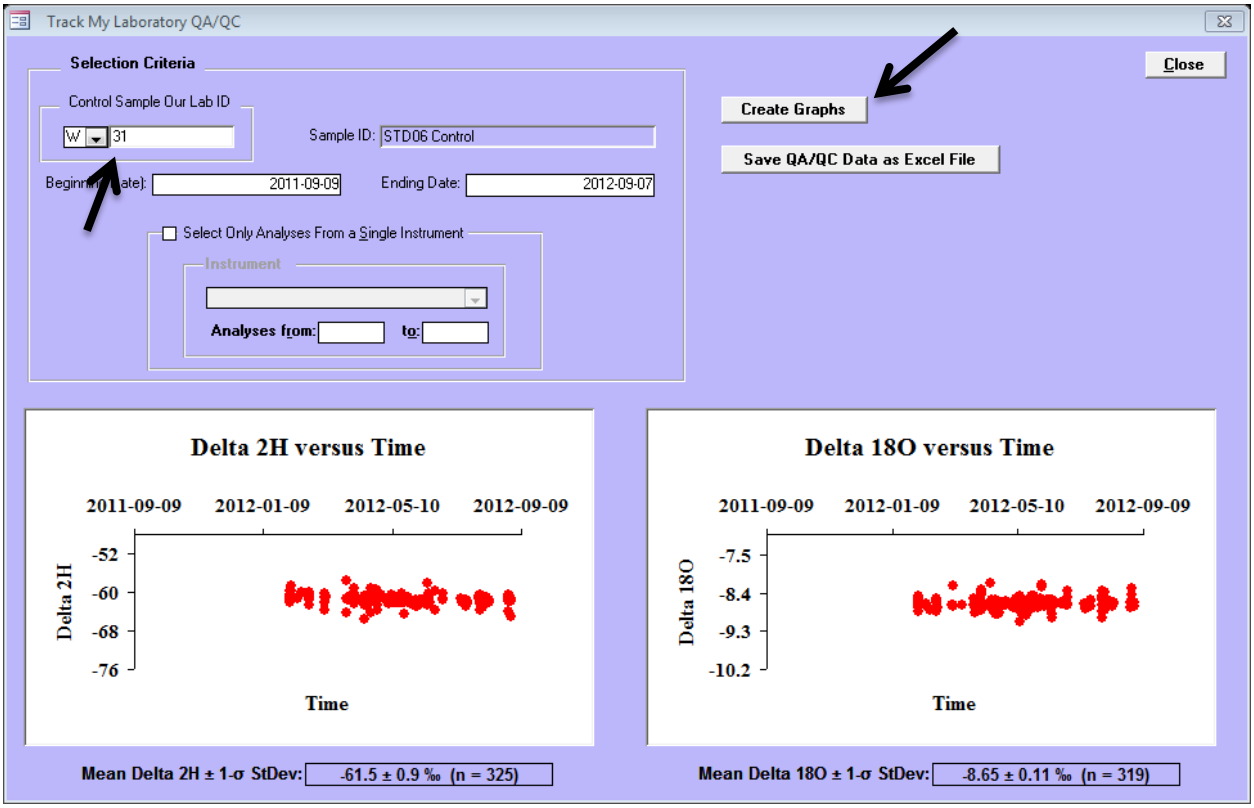


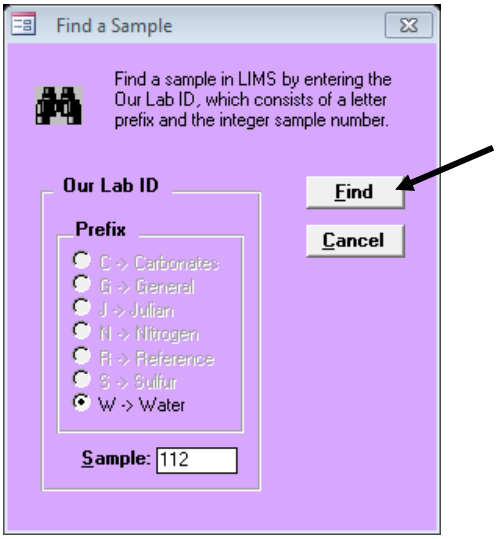
LIMS for Lasers monitors laboratory performance through the use of control standards.

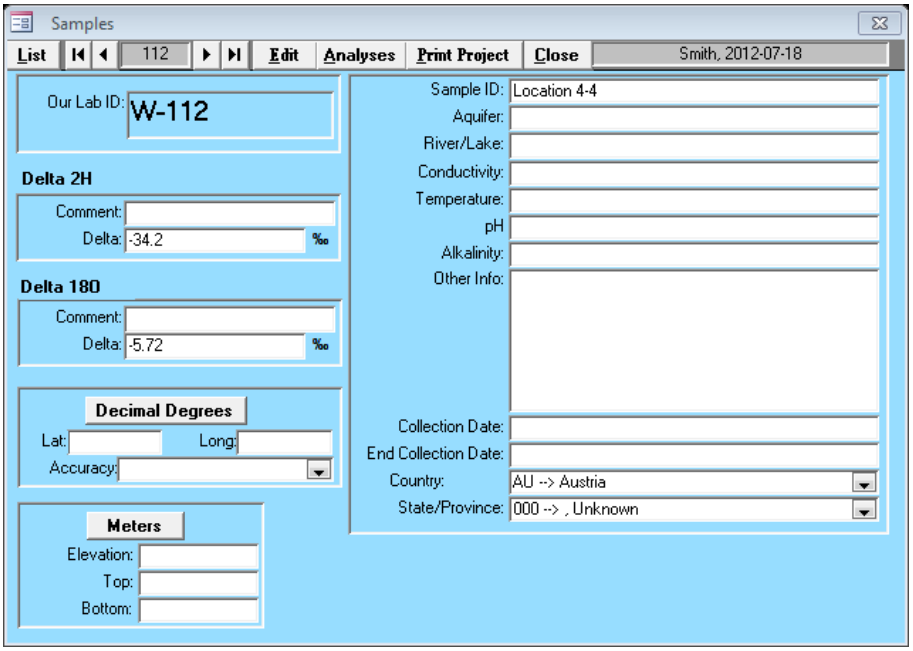
12.8 Querying and Editing Sample Results and Information

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

Find a Sample

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



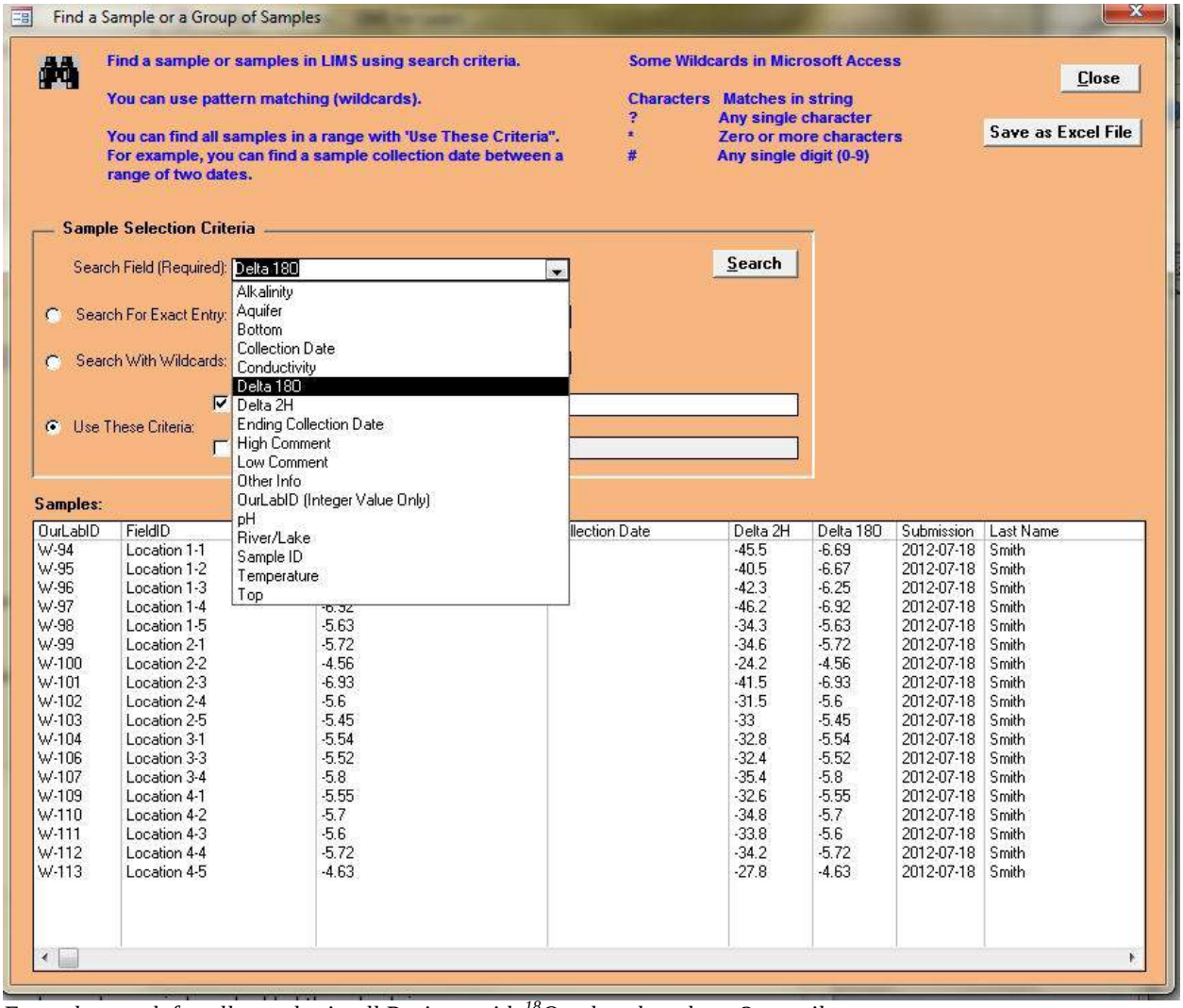


Results of Find a Sample

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 isotopic values or dates.

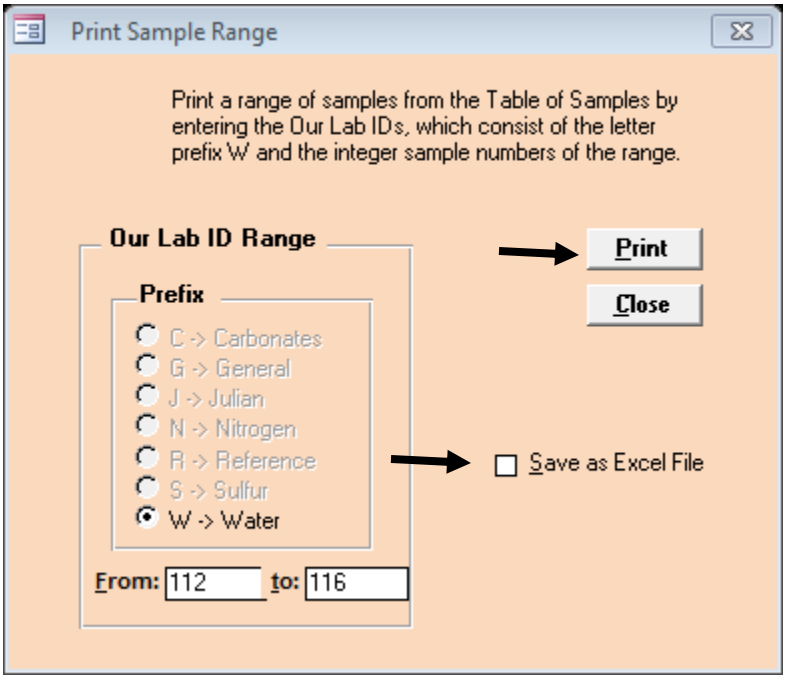
For example, one can quickly locate all data or samples from a specific region, aquifer, or formation regardless of the client, provided the sought information was supplied with the project. These search findings can be saved to Excel.

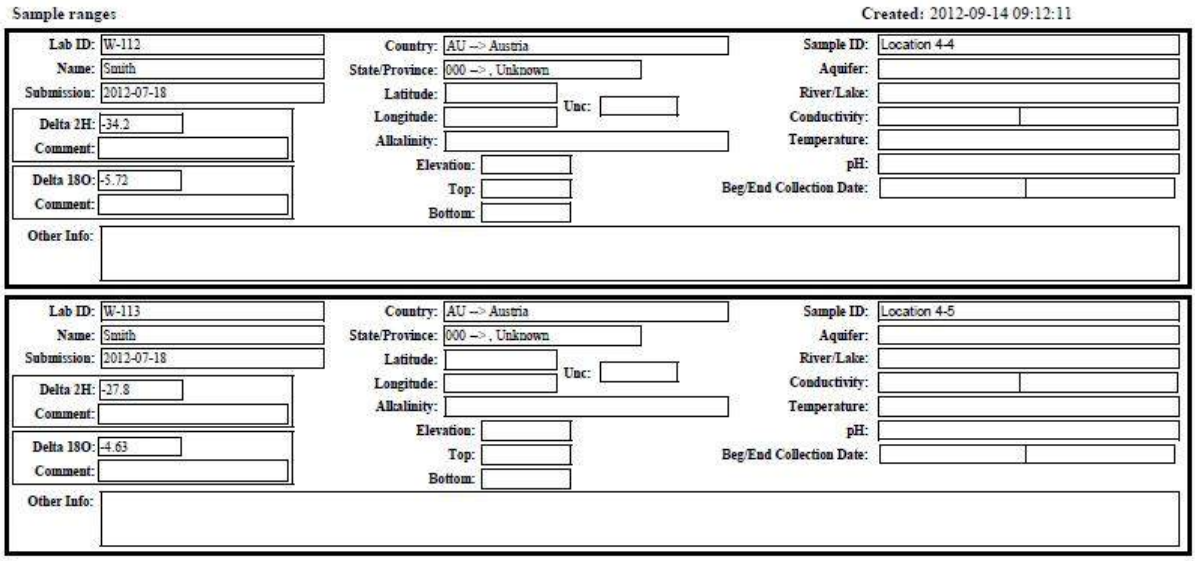


Example search for all samples in all Projects with ^{18}O values less than -2 permil.

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.



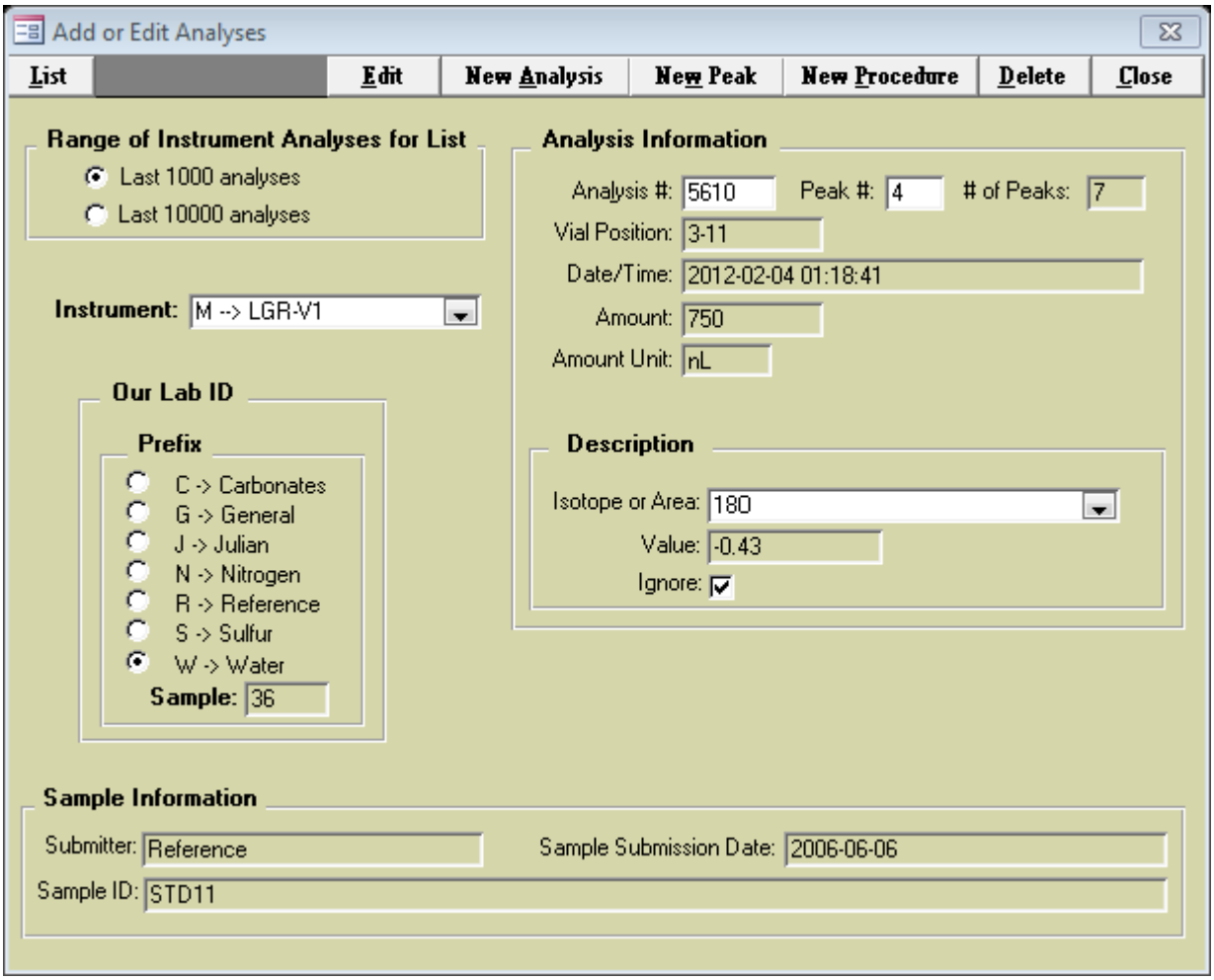


Example of a one-page printout of a Sample Range

View / Edit Information About a Sample

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

In the example, we can see the 4th injection (Peak #4) of Analysis #5610 for ^{18}O on an LGR instrument with Prefix ID "M", and corresponding to sample W-36, a laboratory measurement standard. We also see it was ignored, being one of the first 4 peaks.



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*:** These 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 repeated entirely, than manually edited. *In short, manual editing of sample results is rarely used under normal operations.*

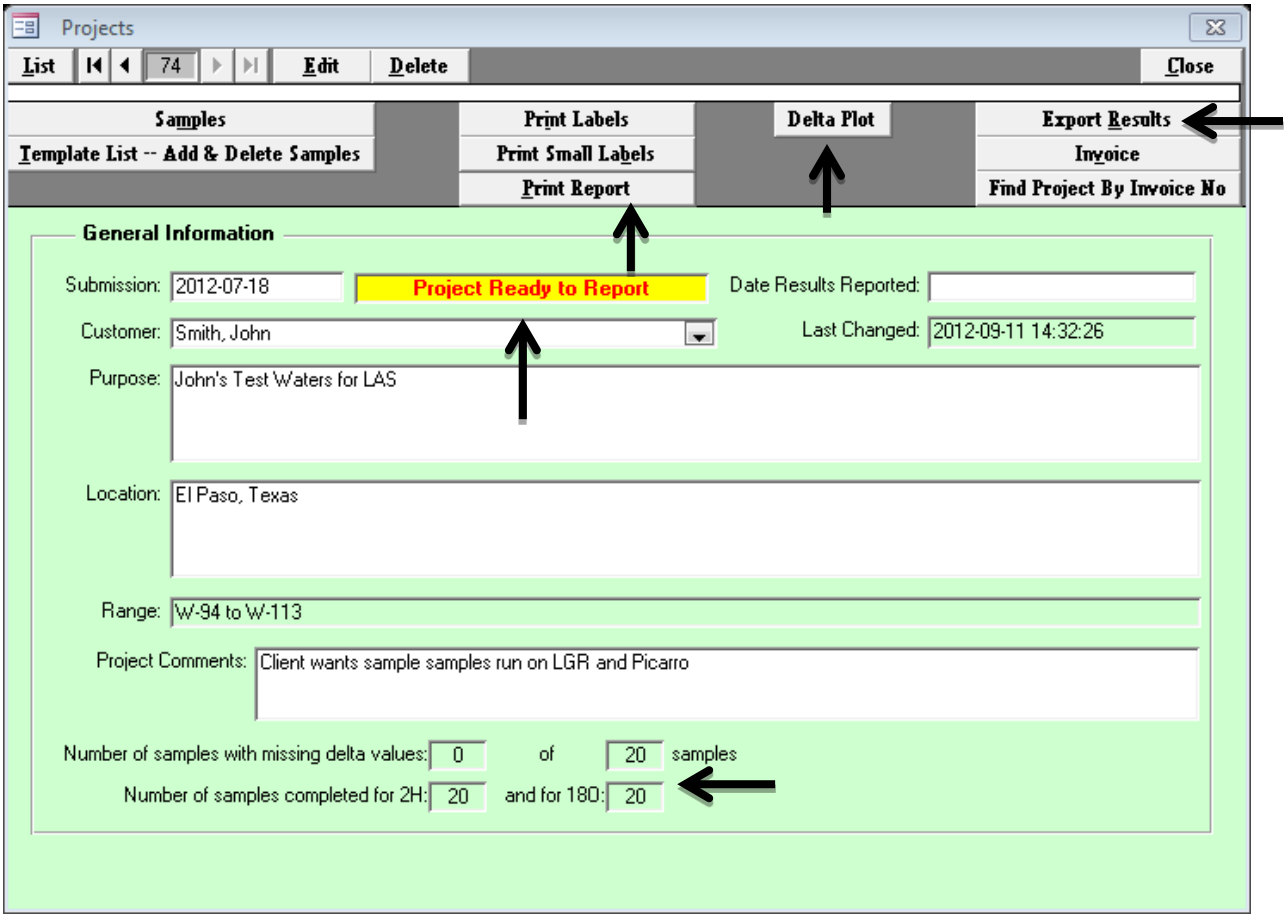
13

Reporting Customer Results

13.1 Reporting Final $\delta^{18}O$ and $\delta^{2}H$ Results to the Customer

The reporting of final stored $\delta^{18}O$ and $\delta^{2}H$ results to the customer is done from the Projects Page. *LIMS for Lasers* 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 the results in an Excel spreadsheet.

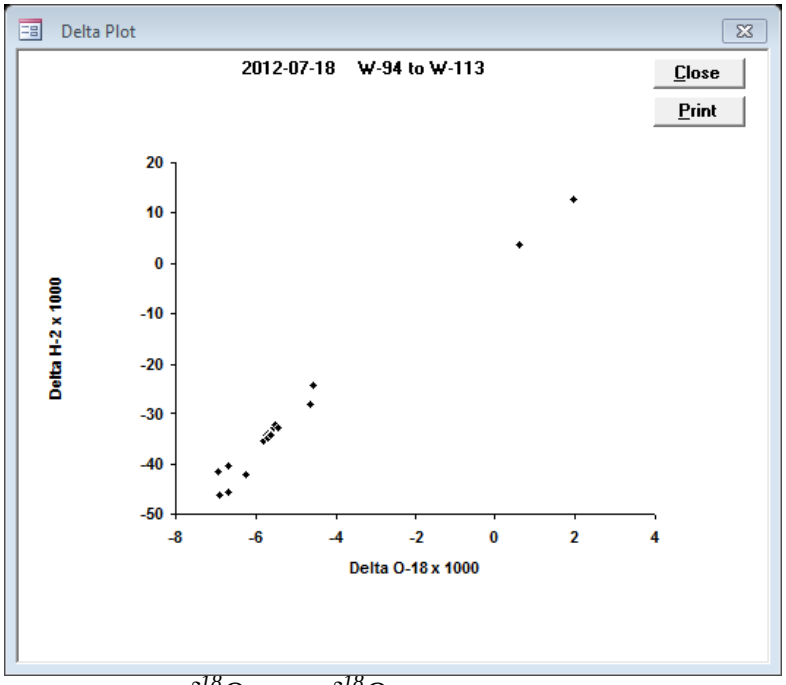
1. On the main LIMS page, click on View Projects, then double click on the completed project to be reported. In this example, double clicking on Smith's project gave the following screen:



2. Because Smith's samples were all measured twice, evaluated, accepted, and stored by the analyst, the project status is now shown highlighted in yellow as "Project Ready to Report". The bottom panel of the window shows that none of the 20 samples are outstanding for $\delta^{18}O$ or $\delta^{2}H$.

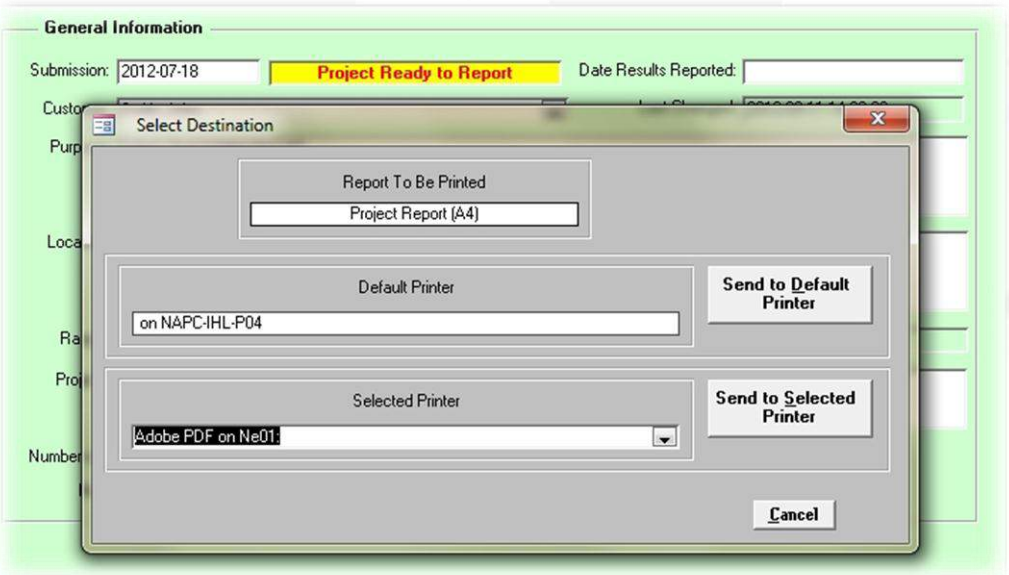
3. Before reporting the final results, one last step is to examine the project results using the "Delta Plot" feature. Clicking on the "Delta Plot" button produces a $\delta^{2}H$ versus $\delta^{18}O$ cross plot for the Project samples. Be aware the data axes will scale according to the project data. This plot provides a quick means of visualizing the correlation between the two isotopes arising from "meteoric relationship". Outliers that fall far away from a linear relationship

may be suspect, or they may be OK. Non-linear relationships on this plot may result from added isotopic tracers distorting the correlation, or when there is little to no isotopic variation in the project samples (axis scaling artifacts).



LIMS for Lasers $\delta^{18}O$ versus $\delta^{18}O$ cross plot of results

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



LIMS for Laser Example Final Report to the Customer

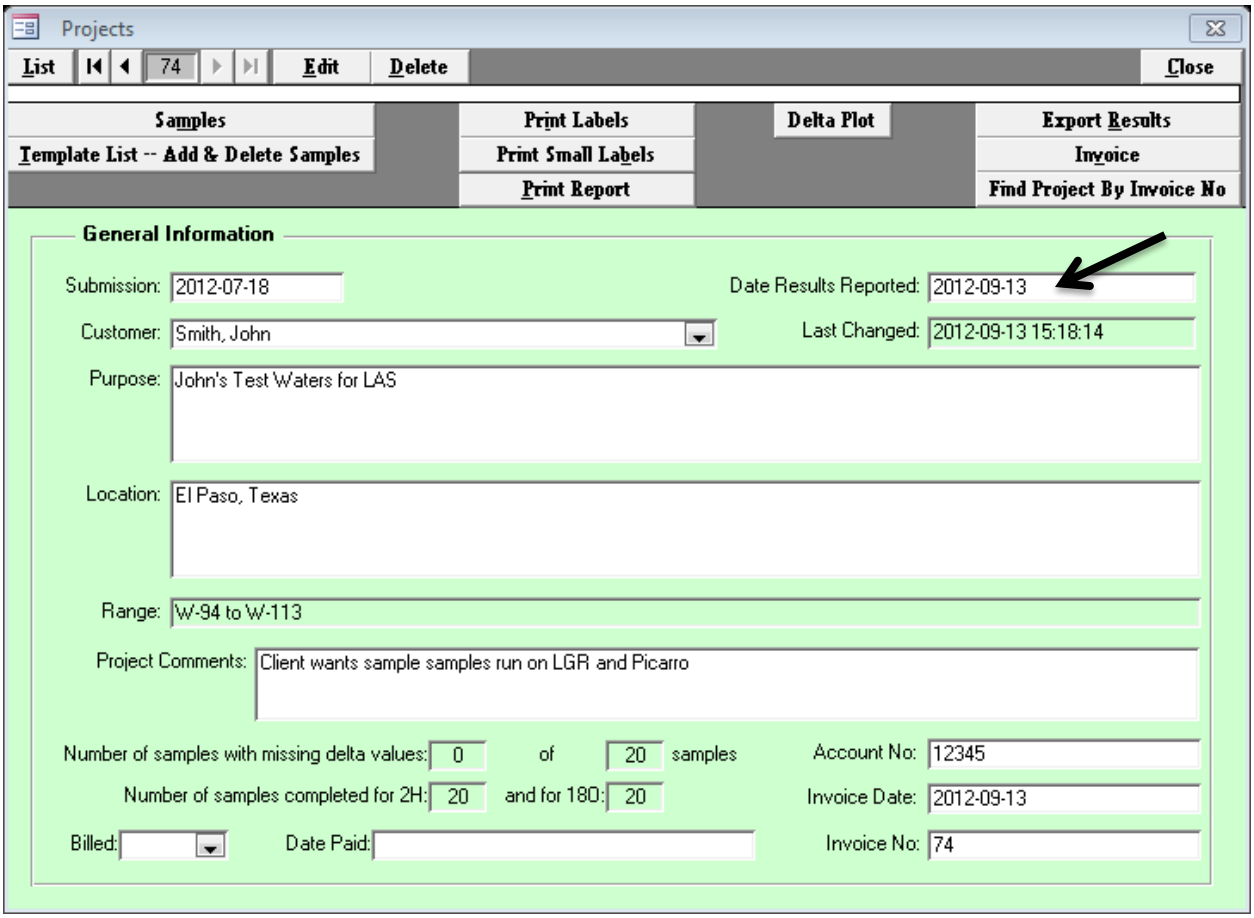
Submission: 2012-07-18 Smith, John **W-94 to W-113** 2012-09-11

Purpose: John's Test Waters for LAS

Location: El Paso, Texas

Sample ID:	Collection Date	Our Lab ID	$1000\,\delta^2H_{VSMOW}$ Value	Comment	$1000\,\delta^{18}O_{VSMOW}$ Value	Comment
Location 1-1		W-94	-45.5		-6.69	
Location 1-2		W-95	-40.5		-6.67	
Location 1-3		W-96	-42.3		-6.25	
Location 1-4		W-97	-46.2		-6.92	
Location 1-5		W-98	-34.3		-5.63	
Location 2-1		W-99	-34.6		-5.72	
Location 2-2		W-100	-24.2		-4.56	
Location 2-3		W-101	-41.5		-6.93	
Location 2-4		W-102	-31.5		-5.60	
Location 2-5		W-103	-33.0		-5.45	
Location 3-1		W-104	-32.8		-5.54	
Location 3-2		W-105	3.8		0.60	
Location 3-3		W-106	-32.4		-5.52	
Location 3-4		W-107	-35.4		-5.80	
Location 3-5		W-108	12.7		1.96	
Location 4-1		W-109	-32.6		-5.55	
Location 4-2		W-110	-34.8		-5.70	
Location 4-3		W-111	-33.8		-5.60	
Location 4-4		W-112	-34.2		-5.72	
Location 4-5		W-113	-27.8		-4.63	

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-94.XLS for Smith Project). This file can be emailed to the customer.
5. LIMS will automatically fill in the “Date Reported” field of the Customer Project.


Projects
List
74
Edit
Delete
Close
Samples
Print Labels
Delta Plot
Export Results
Template List -- Add & Delete Samples
Print Small Labels
Invoice
Print Report
Find Project By Invoice No
General Information
Submission: 2012-07-18
Date Results Reported: 2012-09-13
Customer: Smith, John
Last Changed: 2012-09-13 15:18:14
Purpose: John's Test Waters for LAS
Location: El Paso, Texas
Range: W-94 to W-113
Project Comments: Client wants sample samples run on LGR and Picarro
Number of samples with missing delta values: 0 of 20 samples
Account No: 12345
Number of samples completed for 2H: 20 and for 18O: 20
Invoice Date: 2012-09-13
Billed:
Date Paid:
Invoice No: 74

13.2 Combining and Reporting Results from Multiple Projects

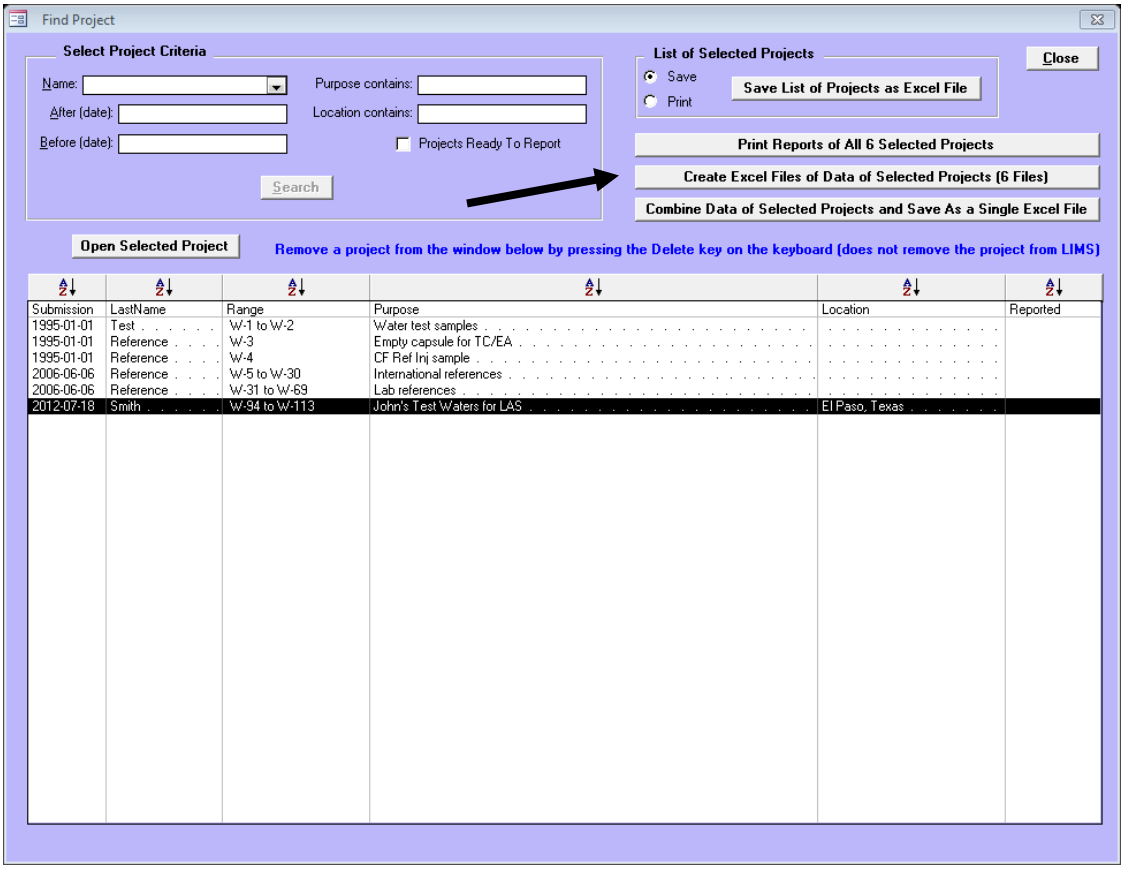
Occasionally, a customer may have several projects, or may request results of their projects in a single Excel file, rather than in multiple spreadsheets or printed reports.

Once *LIMS for Lasers* accumulates several 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-34.xls).

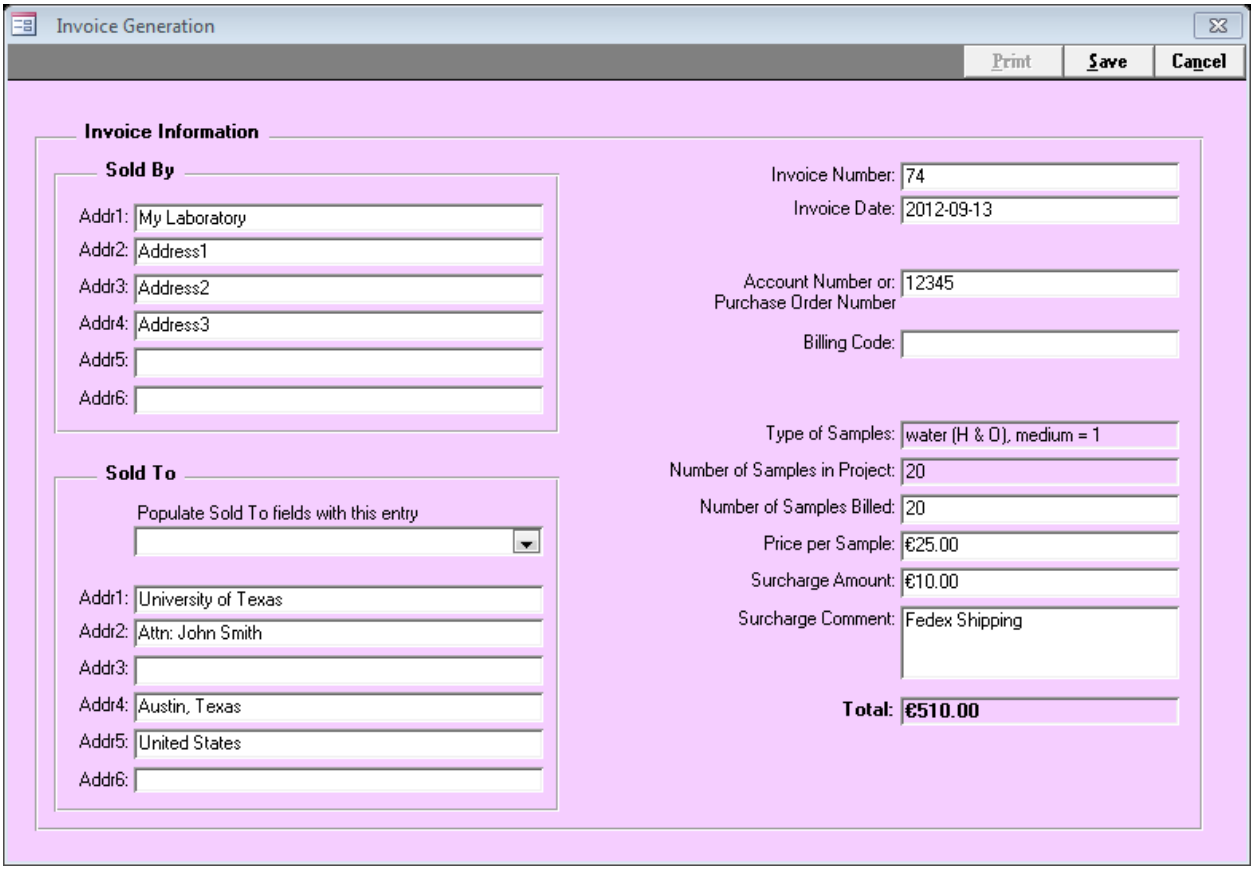


***Note*:** To delete a Project from a search result, highlight it and enter the delete key. Only the search result is deleted, not the Project itself.

13.3 Project Invoicing

Some laboratories may wish *LIMS for Lasers* to generate a Customer invoice.

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.*
4. Complete the Sold By and Sold To fields. Enter the price per sample.
5. Print the invoice.



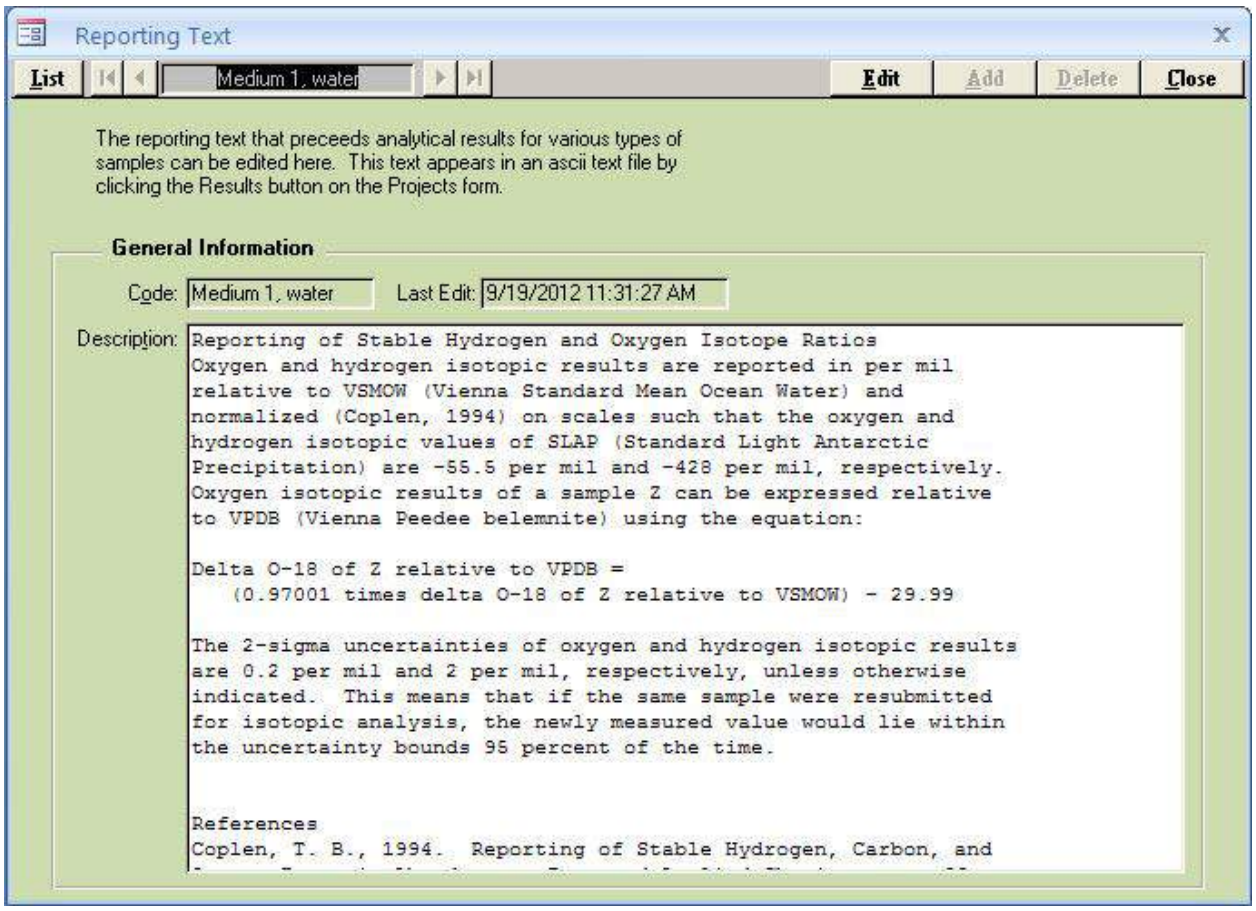
***Note*:** The currency reported on this form is derived from the Windows regional settings on your computer.

13.4 Exporting to ASCII file with Reporting Text

On the Project page, clicking on “Export” results also 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 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 Isotope Reference Materials

VSMOW2 and SLAP2 are the 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 milliliters of calibrated secondary daily-use measurement standards. The recommendation is that ampoules with two substantially different isotopic compositions be opened daily and used for data normalization and a third intermediate delta value water can be used as a control. 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)

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 comes 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* 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 with these isotopic reference standards in order to provide sufficient data to determine measurement uncertainty. It is good practice to have other laboratories test and measure your proposed laboratory standards for external verification, before assigning their final delta values in the *LIMS for Lasers* 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 & VSLAP2) 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 run.

Sample	Vial Pos	List #	LIMS for Lasers 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/VSLAP (or VSMOW2/VSLAP2) 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 run.

Sample	Vial Pos	List #	LIMS for Lasers 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

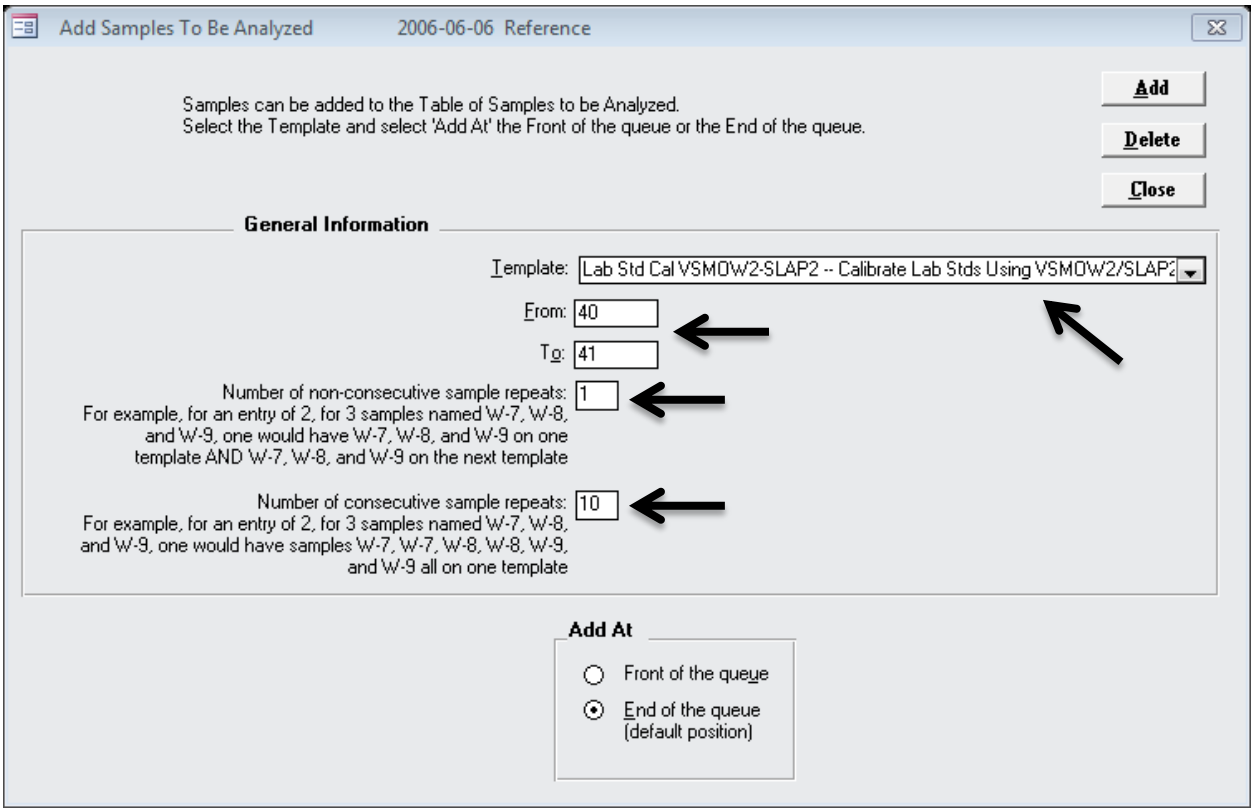
14.4 Calibration Template Procedures

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

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

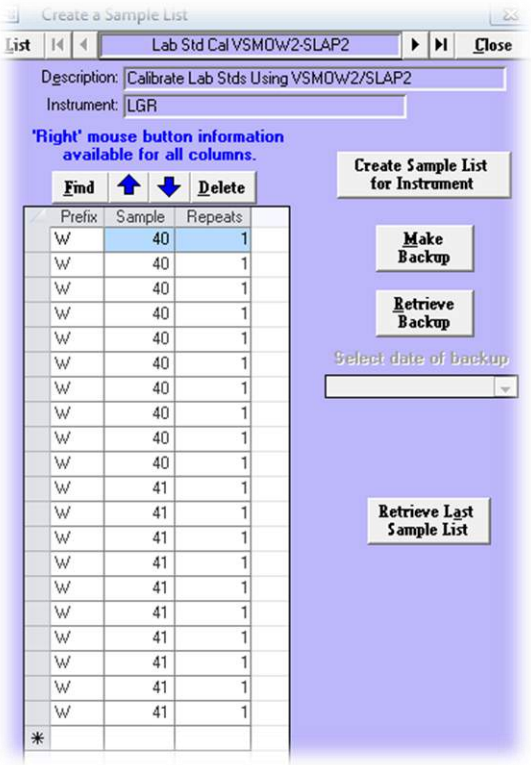
For Los Gatos Research Instruments:

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

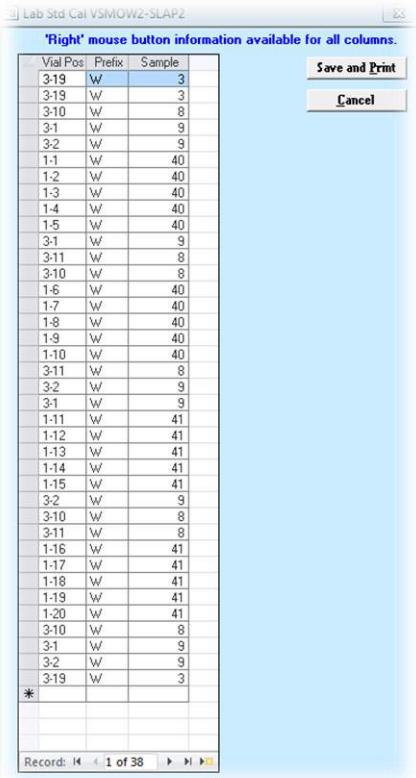


4. We will calibrate local laboratory standards W-40 and W-41 using the VSMOW2 and SLAP2 primary reference waters. From the template pull down menu (see above), choose the VSMOW2-SLAP2 Analysis Template (or VSMOW/SLAP if using those primary reference materials).
5. In the From and To boxes, type From 40 To 41.
6. Set the number of non-consecutive repeats to 1 (each will be run once).

7. Set the number of consecutive repeats to 10 (each sample will be run 10 times in a row as shown in Table 3).
8. Click “Add”, then “Close”.
9. On the *LIMS for Lasers* Main Page, Click “Create A Sample List”.
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 run 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. Normalize, evaluate, and store the results, as fully described in Chapters 10 to 13.
14. Once completed, and you are satisfied your local measurement standards have been sufficiently characterized, you may assign their isotopic values to the Table of References (Chapter 7.3)



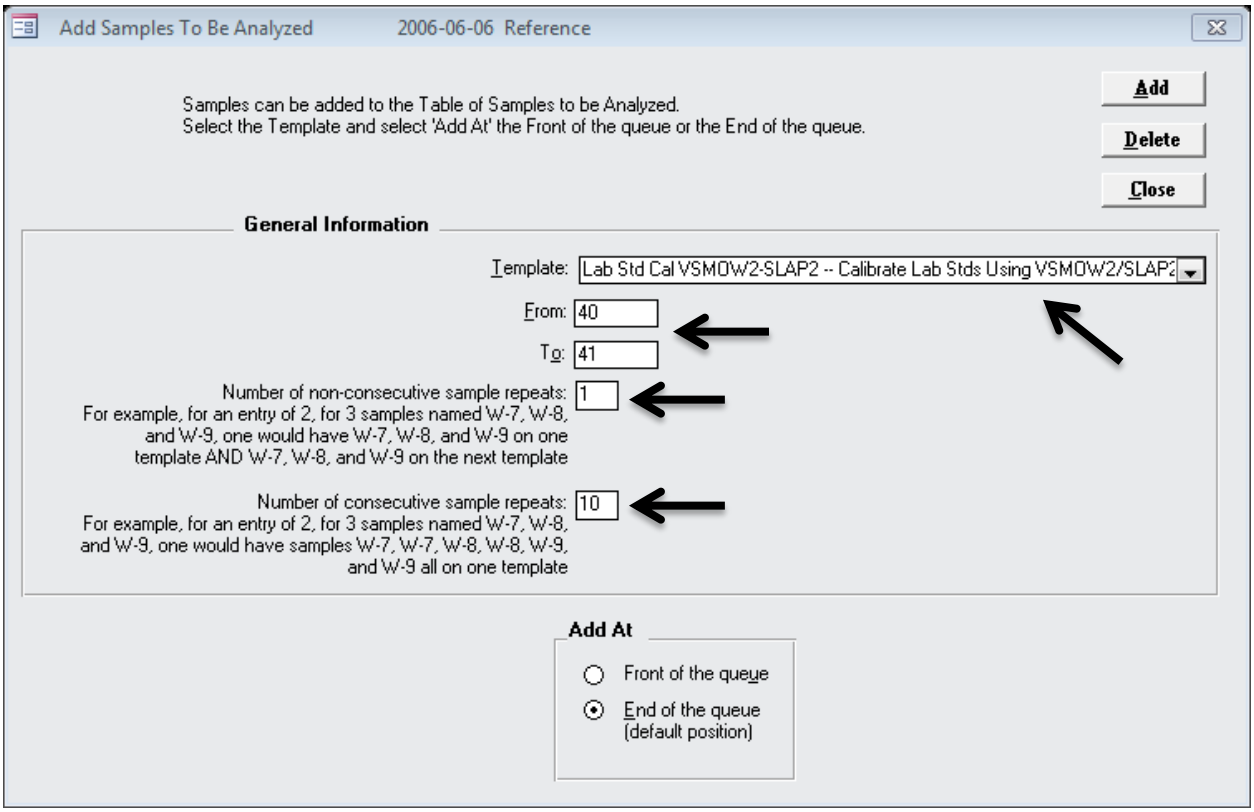
15. Create new analysis templates for sample based on your new local laboratory measurement standards (Chapter 8)



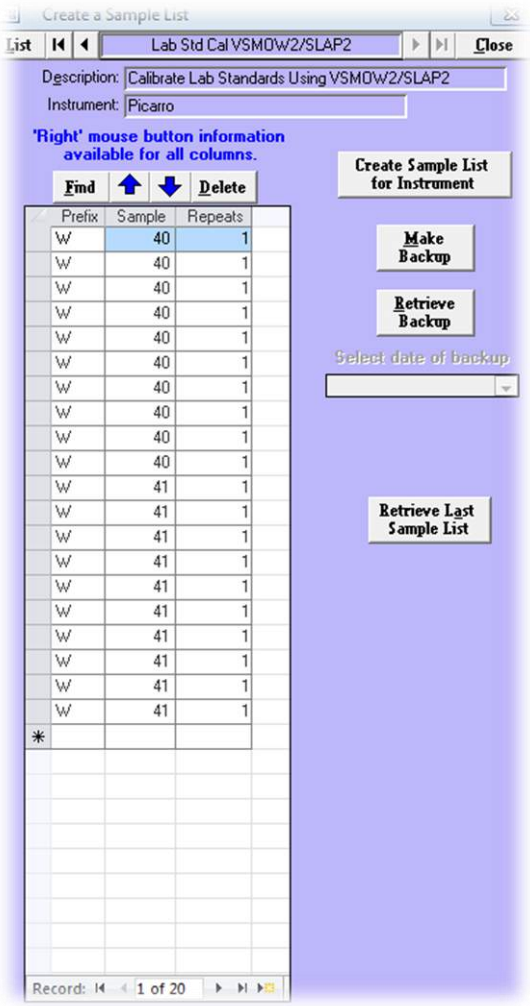
Proposed laboratory measurement standards to be analysed against VSMOW2 (W-8) and SLAP2 (W-9) using a Los Gatos Research instrument. The measurement sequence on the right matches the Analysis Template in Table 3. W-3 is a wash or conditioning sample.

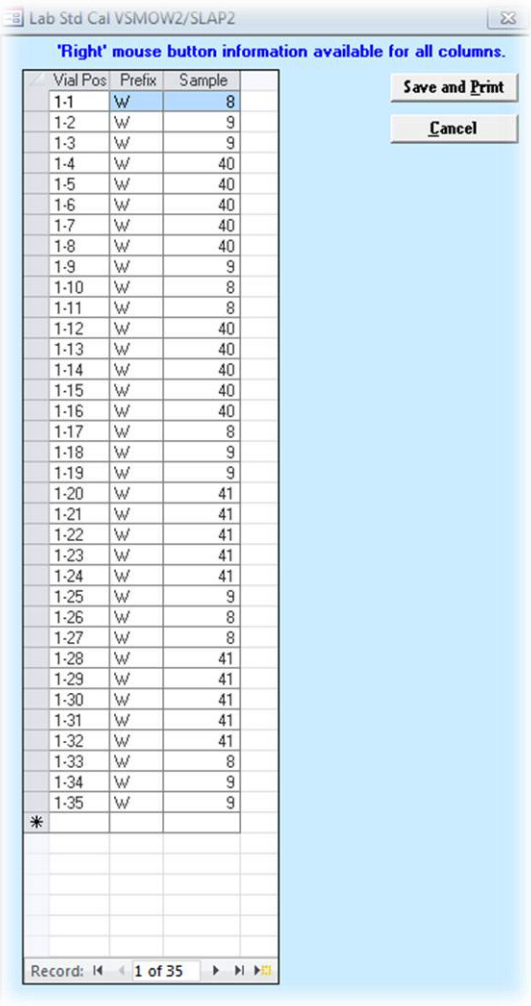
For Picarro Instruments:

1. On LIMS Main Page, 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, pick the Lab Std Cal VSMOW2-SLAP2 analysis template.
5. In the From and To boxes, type 40 to 41.
6. Set the number of non-consecutive repeats to 1 (each will be run 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* Main Page, Click "Create A Sample List".
10. From the pull down menu, choose the VSMOW2/VSLAP2 Analysis Template.
11. On the window that opens, we see W-40 and W-41 are queued to be run 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, normalize, evaluate and store the final results, as described in Chapters 9, 12-13.
14. Once completed, and you are satisfied your new local standards are sufficiently characterized, you may assign their established isotopic values to the table of references (Chapter 7.3)
15. Create new measurement templates using your new laboratory standards (Chapter 8)





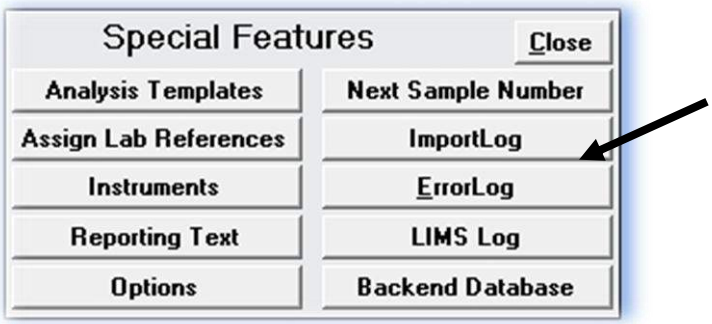
Proposed laboratory measurement standards to be analysed against VSMOW2 (W-8) and SLAP2 (W-9) on a Picarro. The measurement sequence on the right matches the Analysis Template in Table 4.

15

Logging and FAQs

15.1 Log Files

Under the Special Features tab, LIMS keeps track of all Imports, Errors and general logging. Each of these logs can be viewed by clicking on the Log file. This information may useful for troubleshooting.



15.2 Frequently Asked Questions

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

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

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

Q. Why is it recommended to run every sample twice? This seems very unnecessary.

The default approach of running each sample twice is a conservative approach that will allow you to assess the reproducibility of every single unknown that is measured, not only the control 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 local laboratory 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 instrument manual recommends 5 injections, ignoring only the first 2.

As noted in Chapter 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 the outcomes differ significantly can be tested by comparing default *LIMS for Lasers* recommendations with those of the same run but using fewer injections and fewer ignored injections. Using fewer injections you may find precisions are worse and between-sample memory percentage higher. Ultimately, each lab must decide what will be their acceptable performance standards.

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

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 to ZIP and email your backend database (in confidence) so that we can troubleshoot to what is going wrong.

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