LADR

Software Manual

www.norsci.com/ladr/

Norris Scientific

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Acknowledgements

Introduction

Why LADR?

As per conventional metrology the calculation of an unknown concentration using a calibrated response takes a form that is trivial to calculate using basic spreadsheet software: multiply the observed intensity of the unknown by the known concentration in a reference material and divide by the observed intensity of the signal from that same reference material[1].

$$X_{SAM} = I_{SAM} \times \left(\frac{X_{CAL}}{I_{CAL}} \right)$$

Using this "external calibration" approach for LA–ICP–MS analysis does not generally work. The primary issue is that different materials ablate at different rates resulting in different (and in practice unknowable) variations in the yield from sample to sample. The most direct approach to tackling this complication is to normalise the entire expression for one analyte by that for another. This second analyte is referred to as the "internal standard". Dividing the two expressions and rearranging gives us the following:

$$X_{SAMa} = X_{SAMb} \times \left(\frac{I_{SAMa}}{I_{SAMb}} \right) \times \left(\frac{I_{CALb}}{I_{CALa}} \right) \times \left(\frac{X_{CALa}}{X_{CALb}} \right)$$

This expression is a rearranged form of the equation introduced to the LA–ICP–MS community by Longerich et al. in their paper from 1996. Note that for this expression to be evaluated successfully the concentration of the internal standard element needs to be known in both the reference material and the unknown sample.

Using this "internal standard" approach certainly works, but if data reduction of LA–ICP–MS data could be performed using just this expression then LADR would not exist and most users would simply calculate their own values using basic spreadsheets.

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1   This is not a maths text (phew!) but it is hoped that demystifying the basic calculation demonstrates that computing the concentration is not a difficult task. The true complexity of LA–ICP–MS data reduction stems from the peripheral calculations that are required to ensure high quality results: spike removal, gas blank modelling and subtraction, down-hole fractionation correction, calibration modelling, and so on.

The catch is that calculation of both accurate and precise results requires a number of peripheral calculations and some interpretation from the analyst: the changes to gas blank intensity and instrument yield over time must be modelled, spikes must be removed, down hole fractionation must be modelled, interferences must be removed or at least assessed, and errors must be propagated to the final values.

Furthermore, thanks to automation, a modern LA–ICP–MS laboratory can easily produce thousands of ablations per day with applications varying from trace element analysis in different materials through to quantified isotope ratios for geochronology. Thrown into the mix is the reality that most analysts are using LA–ICP–MS as the analytical tool that it rightly is, and being research scientists in their own, often disparate, fields their primary concern is the production of high quality results in the most straight-forward and error-free way possible...which is exactly what LADR does.

How to Use this Manual

Reading it would be a good start (!) but at 222 pages there is an awful lot of information here for you to soak up! You can try reading just the "Introduction" and the "Glossary", but realistically that is probably not quite enough to get going with the software.

The "Getting Started" chapter offers a very brief walk-through, and also introduces the general concepts behind the software. The walk-through covers the standard workflow which begins with loading data files and finishes with exporting results, but most of the options are omitted from the example. Most users, especially experienced analysts, will find they can use the software successfully after reading only that chapter.

The remaining chapters are each dedicated to a specific section of the software, and arranged in a similar order to the steps along the analytical workflow. While each chapter covers the software operation in depth, they all begin with an introduction section that discusses the philosophy behind the software, and where appropriate, mentions why LA–ICP–MS data should be collected in a specific way if the analyst is to make optimal use of the features available in the software.

The quickest way to get the most out of this manual will be to read the "Getting Started" chapter followed by the introduction section from each of the subsequent chapters. Then, return to each chapter for assistance as you work through the software to process your first project.

Contact LADR support (ladr@norsci.com) if you require additional assistance.

Program Overview

The LADR program follows a basic workflow, introduced in the "Getting Started" chapter. Data files are loaded and the user specifies how the data are to be computed. The user must perform a number of analytical tasks, such as choosing regions to quantify and inspecting the gas blank and calibration models. Finally, the user can compute the results and export the data to spreadsheet software of their choice.

Using pre-defined values a user can calculate useful trace element data from a dataset of any size in approximately five minutes. In more complex projects the time commitment will scale with the number of samples and is mostly dominated by the user checking each analysis to ensure the mineral/material type matches what was expected, or adjusting sample intervals. Where such tasks are unavoidable LADR provides a convenient interface to minimise errors and maximise throughput.

Program name

LADR is derived from "laser ablation data reduction" and is easiest to pronounce as "ladder".

Program version

This manual is written for the current version of LADR released at the time of publication. See the Notices section for the specific version.

Program compatibility

LADR is written in C# and runs under version 4.7 of the .NET framework. It runs on Windows 7, 8, and 10, provided the .NET framework has been installed. If your system is lacking the .NET framework, it can be downloaded from Microsoft here:

> https://www.microsoft.com/net/download/windows

Note: While LADR will run on OSX and Linux under Mono, it is not supported at this time. It is anticipated that full Mono support will be released in mid 2020.

It will be possible to run LADR on any PC, but performance with large projects will be limited by the available system RAM. More than 2GB is recommended, but ≥8GB would be best for large projects.

Note: A large project contains more than one million data points. Under representative conditions (0.5s sweep time, 40 masses, 60s per sample) this equates to loading a project with over 1200 samples.

A minimum display resolution of 800×600 is advised, with 1024×768 or greater preferred. All forms scale dynamically, and all charts support increased fidelity on hi-dpi displays. If working at 4K (or larger) we recommend increasing the Windows display resolution to 125-150% (right click on desktop, Screen Resolution, click "Make text and other items larger or smaller").

Licensing

LADR requires a user and license key to operate. Once entered and saved, the licence keys are preserved indefinitely, but obscured on the registration window to prevent them being exfiltrated from the software. Use the main menu item "Help"→"Registration" to view the current licence details, or to enter new ones.
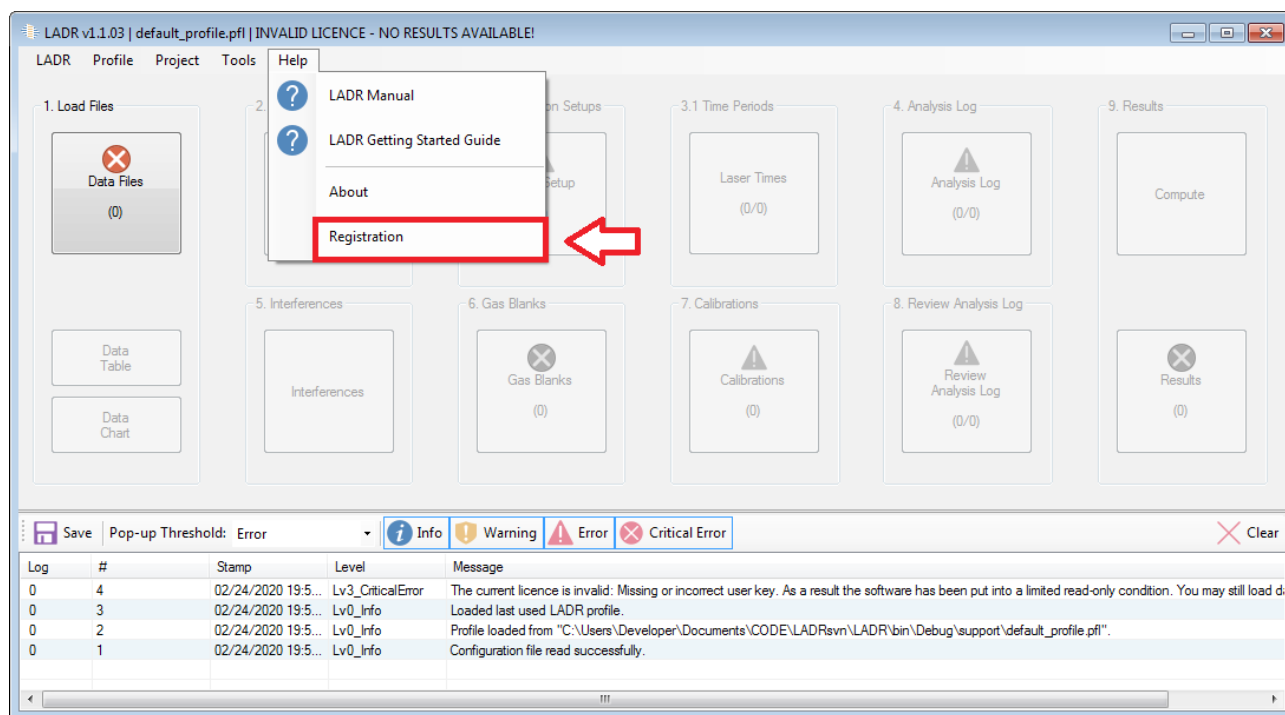
Figure 1: Opening the LADR Registration Window
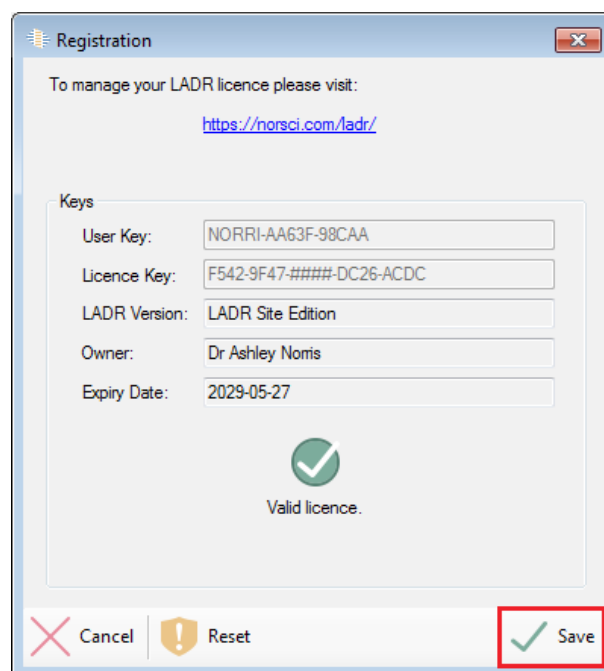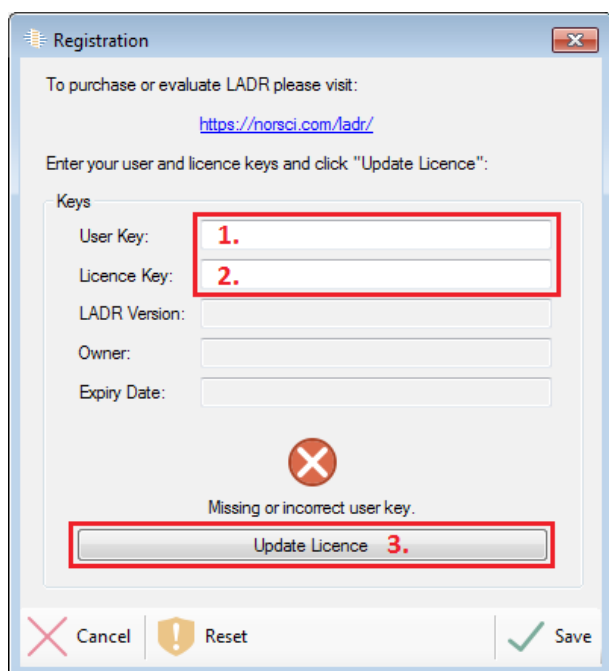
Validation of the registration keys requires an active internet connection, but, please note that ongoing use of LADR does not require an always-active connection to the internet, and an offline grace period is provided.

In those scenarios where the offline grace period has expired then an active internet connection will be required before LADR can operate as normal.

If LADR is executed without a valid license, or the online license check is prevented from running, then LADR will still operate, however the results window will not be available.

Glossary

AMU – Atomic mass unit, approximately equal to the mass of one nucleon.

Analyte – A mass corresponding to an element of interest.

Background – A common synonym for "gas blank". Where possible, the term gas blank is used preferentially throughout this manual and the LADR software.

Calibration Standard – A reference materials containing a known concentration of the analyte and internal standard element.

Counts – The raw output from a mass spectrometer detector due to the detection of ions.

Counts Per Second (CPS) – Integrated counts over one a one second interval. CPS are a direct representation of signal intensity.

Data Point – A single mass spectrometer measurement of a single mass for a specific duration as a specific moment in time. Sequential instruments can only measure one data point at a time.

Detection Limit – The lowest level of a signal that can be regarded as statistically greater than the gas blank signal. A mathematical definition is provided elsewhere in this document.

Dwell Time – The length of time, typically measured in milliseconds, that the mass spectrometer spent counting on an individual mass.

Drift / Instrument Drift –The change in mass bias over time. Drift results in a time–dependent change in the ratio of an analyte to the internal standard. Drift can be corrected by performing regular measurements on a reference material.

Element Fractionation – A "catch all" term to describe any effect that results in a different yield response on a sample compared to the calibration standard. This can be caused by many factors, and can be either time independent (for example matrix mismatch between sample and standard) or time dependent (for example down–hole fractionation).

Gas Blank – The signal measured on the mass spectrometer when there is no sample being introduced to the ICP.

Internal Standard – An analyte chosen for other masses to be normalised to.

Isobars – Different elements that have the same atomic mass (to within 1 AMU).

Jump Time – Length of time the mass spectrometer needs to move from one mass to another.

LADR – The name of this software, derived from "Laser Ablation Data Reduction", most easily pronounced as "ladder".

Laser Fluence / Fluency – Laser light intensity at the surface of the sample, as measured in energy by area. This is conventionally measured in J.cm–2.

Logbook – The logbook in LADR is a table showing the samples in the project. The logbook can be created by hand using the logbook form in LADR, or it can be imported from a logbook file.

Logbook File – A logbook file is a spreadsheet file (typically CSV) that lists the samples that were measured in the project along with the laser conditions, sample type, and the identifier from the ICP–MS. It can be imported into LADR during file loading or on the logbook form.

Mass Bias – The deviation between the measured ratio of two masses, and the true elemental or isotopic ratio of a material due to ICP–MS lenses and mass filtering.

Matrix Correction Factor – A correction to a set of data where an empirically derived offset between a true value and the measured value is consistent and well characterised. See "Secondary Standard Correction Factor".

Polyatomic Ion – A species formed in the plasma or interface of an ICP–MS instrument that consists of multiple atomic ions sharing a single positive charge.

Profile – A profile file (extension ".pfl") contains reference material information, timing templates, and quantification procedures defined and previously created by a LADR user. The information stored within a profile can be loaded and made available for multiple LADR projects which improves the reproducibility of results. When the

software starts for the first time it defaults to a new empty Profile. On subsequent LADR restarts the program will automatically load the most recent profile that was opened.

Project – A project file (extension ".la") is completely self–contained and contains all information required for computing results. Project files contains data files, and the selected pertinent information from the profile including reference materials, timing templates, and quantification setups.

Quantification Setup (QS) – A LADR entity; the QS contains all of the necessary information including standards, internal standard masses, interference corrections, and associated settings needed to fully quantify a specific type of material using a specific method.

Raw Data – Unprocessed data produced by the mass spectrometer, typically reported in counts or CPS.

Reference Material (RM) – A material with known elemental concentrations, and/or isotopic ratios, and/or age. A RM may be used for calibration of signals (see "Calibration Standard") or for determining secondary standard correction factors (see "Secondary Standards"). Values for reference materials can either be entered manually or imported into a LADR profile from multiple external sources or from previous projects and profiles.

Repetition Rate / Rep. Rate. – The frequency of a pulsed laser; measured in hertz.

Sample – Within LADR a sample refers to a time resolved measurement that is defined in the logbook. There may be one sample per file, or many. Each sample must be marked with one (or more) of the following types: calibration standard, secondary standard, or unknown. Most sample measurements contain a gas blank measurement followed by an ablation, but LADR is flexible enough to accommodate any sample arrangement.

Secondary Standard – A RM used for a secondary purpose, thus similar to but not a "Calibration Standard". Typical use can include verification of an analytical method, as well as automatic determination of secondary standard correction factors.

Secondary Standard Correction Factor – An empirically–derived matrix correction factor that can be applied to a set of data to account for analytical biases due to matrix

mismatches between the calibration standard and the unknowns. Applying the factor correctly will improve the accuracy of the results.

Signal Clean Up – Signal processing to remove statistical outliers from a dataset according to a pre–defined set of conditions.

Spot Size – The diameter of the laser beam used to ablate a sample.

Sweep Time – The time taken for the mass spectrometer to complete a cycle through all mass measurements. Typically applied to quadrupole based instruments, but can relate to any sequentially based measurement.

Timing Template (TT) – A LADR entity; the timing template contains essential timing information that is not present in the mass spectrometer data files. Some formats do not require any additional timing information. The combination of timing template and a data file allows all data points to be placed on a common timeline at the time the measurement was made.

Getting Started

Introduction

The best way to get started with LADR is to load some of your data files and process the results. It must be stated here that this will not always be easy for all users in the first instance. The main reason is that reducing any LA–ICP–MS data set can require considerable setup, the most important step being defining the RMs and their compositions.

Furthermore, while LADR supports a wide range of ICP–MS data files, it is not possible to guarantee that all files from all systems will load successfully at the first attempt. In some cases the ICP–MS software settings will have to be changed to conform to a standard output, and in other cases there may be variations in output files that have not been yet been documented and supported in LADR.

For this reason, if you run LADR and are unable to load your data files please do not give up! The first thing to do is to read the error message reported by LADR, then read the "file loading" section of this manual, and then contact Norris Scientific for support.

LADR is distributed as a ZIP folder and does not need to be installed. Simply extract the contents of the ZIP folder to a convenient location, and open the LADR program by double-clicking on the LADR.exe application file.

When executed for the first time the program will go online and check the license information. If you wish to evaluate LADR then trial version licenses are available from the Norris Scientific website (http://norsci.com/ladr/) where full version licenses are also available for purchase.

Profiles and Projects

These are introduced later in more detail, but to get started, please note that a profile is a repository of information that is re-used by multiple projects. This includes reference material compositions, quantification setups (more on those later) and default values for calculation options.

Most users will have their own single profile and work from that, but note that there exist features in LADR that allow profiles to be shared among groups of users. It is even possible to protect a profile and pass it on to another user, which is especially useful

for novice users who are focussing on loading and processing data sets rather than changing quantification options.

A project holds everything required to reduce a single LA–ICP–MS data set, which could be anything from a few hours to a few days of acquisition. It is advised (especially to new users) that a project should be started to coincide with any time the ICP is ignited, which most typically would occur daily. Advanced users could process a week of data, but setting up the project to this level of detail can take more time than is saved by not splitting the projects.

Once set up and saved the project remains a self-contained entity, which also contains the original data files as they were exported by the ICP–MS. A project file can be sent to colleagues, or opened many years later, and the same results will be calculated. Performing new calculations with old projects, such as updating RM values and re-computing is a relatively straightforward process.

It is not possible to run LADR without a valid profile.

Getting Ready

When running LADR for the very first time it is quite tempting to go directly to file loading and bash away at the software until some results fall out. While that is certainly an enthusiastic way to get started, it is highly suggested that users ignore file loading in the first instance, and instead take the time to establish their reference materials.

Reference materials are created, edited, and saved in the profile. They are copied from the profile to the project on an as-needed basis, and they are saved in the project so that opening a project in the future, or under a different profile, will still produce the same results.

When LADR runs for the first time, a default profile is loaded. Go to the main menu "Profile"→"Save As" and choose a convenient name for your profile. It will be reloaded from this location each time LADR runs.

Next, from the main menu, choose "Profile"→"Manage RMs". The default profile contains a single entry for the NIST610 reference glass with the preferred values from

GeoRem[2]. Use the controls to add more RMs as well as edit (or remove!) the entry for NIST610.

There exist controls for importing RM concentration information from the GeoRem database, as well as RM data files from other data reduction programs such as Iolite (both v2/v3 and v4) or Glitter. Those functions are explained in more detail in the "Reference Materials" chapter.

Loading data files also goes hand-in-hand with use of a logbook file. The log book file contains the run table from the analytical session and defines a number of additional parameters that are not present in the ICP–MS data files. Use of a log book file is optional, and LADR provides an interface (the "LogBook" window, page 63) for setting up the logbook entirely within LADR. It is recommended that users set up logbooks using the LADR interface for their first few projects, then migrate to using external log book files.

Your First Project

There are multiple steps within LADR that should be performed in the order specified. These steps are shown sequentially on the main LADR window as individual buttons which each open separate windows.

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2   http://georem.mpch-mainz.gwdg.de/
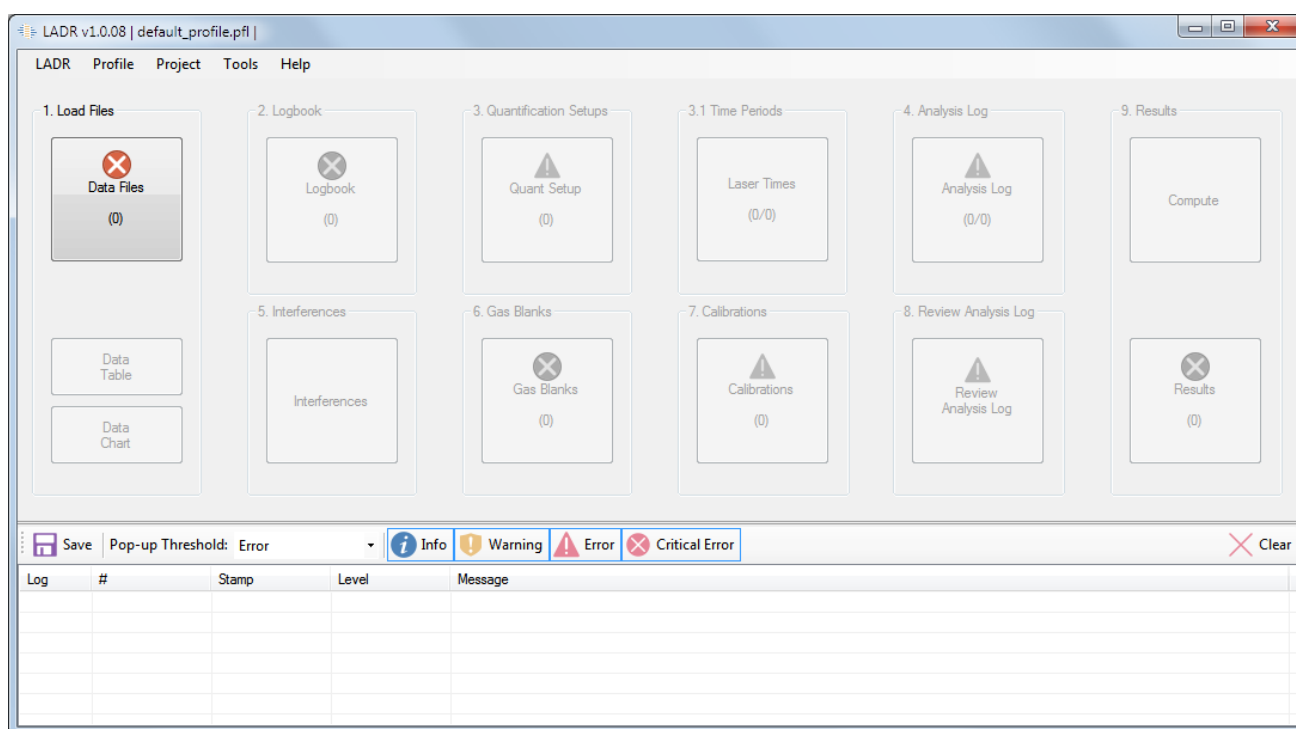
Figure 2: The main LADR window.

Note: After each step has been completed, be sure to click the "Save" button to save the changes and move on to the next step in the workflow. Closing the window using the Windows "X" icon, or ALT+F4, or the ESC key, will cancel the form and discard any changes that were made.

Note: Because projects can hold a lot of data and depending on complexity some require a lot of manual setup, it is advised that users save their projects after each step in the workflow.

The following walk through outlines the minimum steps required to compute results for a very basic trace element project.

1. Click the "Data Files" button:

   • Select the ICP–MS used for data collection, the file type being loaded, and select the files using the "Select New Files" button. If all of the selected files are valid, they are added to the list automatically, invalid files are rejected and the rest must be confirmed. Check the files loaded in the table at right to ensure all of the files were loaded in the order expected. Reorder using the controls at right, if required.

- Select the "Measurements" tab to see the sample measurements table which also shows additional information about each sample measurement.

- At least one new timing template (TT) called "Auto Template" will be automatically created and assigned to each file entry. To modify the TT please see detailed instructions in the "Selecting and Loading Data Files " chapter on page 53.

- Optional: Load a logbook file at the bottom-right of the upload data window. Otherwise skip this step and define the log book information directly within LADR in the next stage of the workflow.

- Click the save button to load the data.

2. Click the "Logbook" button:

- Click the "Add RMs" button and use the dialogue to add the required reference materials to the project. At least one must be added. If the profile does not yet contain the required reference materials (tut tut, see "Getting Started" above) then stop here and use the "Main Window"→"Profile"→"Manage RMs" window to add reference materials to the profile.

- Use the table to mark each sample as either a "calibration standard", "secondary standard", or an "unknown". When marking an entry as a standard then you must also indicate the RM.

- Use the table to enter the laser ablation parameters. Cells can be edited by double-clicking.

- For convenience there are "fill down" and "fill out" controls accessible via the right-click menu.

- The logbook is valid when it contains at least one calibration standard sample.

- Click the save button to save the log book.

3. Click the "Quant Setup" button:

- For basic quantification of trace elements, do the following:

o   Click the "Add QS" button to create a new QS. The section to the right is used to configure the QS. Enter a meaningful name for your new QS.

o   Click on the "Trace Elements" tab.

o   The table shows each mass in the project and the form requires you to specify an internal standard mass and calibration standard RM for each of them. The available RMs shown are restricted to only those which were added to the logbook for this project, not all of those present in the profile.

o   Choose an internal standard and calibration standard for the first mass in the table. Then right click on it and choose "Set All Masses to Match this One". This is the quickest way to complete the table, but of course may not give the best results.

   Note: Some masses cannot be quantified because they are not characterised in the calibration standard, a common example of this being mercury. In such a case, to keep with the logic of the software, it is still necessary to assign the mass to an RM.

o   Scan down the table and take note of the warnings (if any) shown beside each mass. Extra information can be displayed by hovering the mouse over the icon. The most common warnings will refer to multiple masses per element (affecting the total) and missing element concentrations in the calibration standard. To compute results for your first project both of these messages can be ignored.

- Click the save button to save the new QS. A pop-up warning may appear alerting you to any problems with the QS. Provided all of the masses are assigned to a valid internal standard and calibration standard, it is safe (for now) to ignore the warnings and proceed.

4. Click the "Analysis Log" button:

- The form shows a table at left and a chart at right. Click and drag a time interval on the chart to create a new analysis log entry. Each entry in the table will be quantified to give a set of results, as per the QS assigned to it.

- Right click the newly created entry and choose "Copy Timeperiod to All Samples in Project".

- Use the chart navigation arrows to inspect the samples in the project and to verify that the analysis intervals are in the correct locations.

- Inspect the "QS" column and verify that the QS created in the previous step has been assigned to each entry. Note that reference materials are not assigned a QS.

- Click the "Int. Std. Values" button to enter the internal standard concentration for each sample. Intervals on reference materials will have IS values automatically completed. Use the form to enter IS concentrations for each sample. The table supports copy, paste, and fill down, and can accept, or show, values in different units.

- Click the save button to save the internal standard values. Then click the save button to save the analysis log.

5. Click the "Gas Blanks" button:

- There are three tabs, the first one "Time Intervals" is selected by default.

- Click and drag on the chart to select the first gas blank time interval. The time period is added to the list.

- Right click the newly created interval and choose "Copy Time Period to All Samples".

- Use the chart navigation arrows to inspect the samples in the project and to verify that the gas blank intervals are in the correct locations.

- Click on the "Gas Blank Models" tab then the "Automatic Defaults (All Masses)" button.

- Click the "Mass" button and click the first mass at the top of the list.

- The chart shows the gas blank model that has been automatically assigned to this mass. Where possible the algorithm will attempt to assign a continuous

curve, but if there are excessive outliers, then the curve will be split to interpolate between gas blank time intervals.

- Use the controls (click on each mass in the table, use the next/prev buttons, or "up"/"down" keys) to inspect each mass in the project. The curve type can be adjusted using the buttons along the bottom of the chart, or split manually into multiple sections. The boundaries can be dragged on the chart, and the polynomial order adjusted using the buttons at the top of the chart.

- In general, the automatically assigned gas blank models will be suitable for most users. See the "Gas Blanks" chapter on page 132 for more details.

- Click the save button to save the gas blank models.

6. Click the "Calibrations" button:

- In this basic example, the form will go directly to the "Calibration Models" tab by default because the time intervals on calibration standards were previously set up by the analysis log form. Other tabs will be used for more complex projects.

- With the "Calibration Models" tab selected, click the "Automatic Defaults (All QSs, All Types)" button.

- Click the "Mass" button, then the "Traces" tab, and then click the first mass at the top of the list.

- The chart shows the calibration model that has been automatically assigned to the selected mass.

- Where possible the algorithm will assign continuous curves of an appropriate polynomial order, but will break to separate interpolated intervals if the fitting is unsatisfactory. There are controls for changing the model types, and splitting and merging the models.

- In general, the automatically assigned calibration models will be suitable for most users. See the "Calibrations" chapter on page 145 for more details.

- Click the save button to save the calibration models.

7. Click the "Compute" button, wait for the calculation, then click the "Results" button:

- The table shows the quantified results. Rows can be selected, and CTRL+C will copy them to the clipboard.

- Set the desired display units: PPM or weight percent.

- Use the tool bar to set the number of decimal places.

- Set the desired uncertainty multiplier. This choice will be reflected in the exported file.

- Set the uncertainty level (signal error, full within-lab, full analytical, etc.). This choice will be reflected in the exported file.

- To fully inspect a quantified result, right click the cell and choose "Calculation Explorer" to show all of the details, including the error propagation tree.

- Either use the clipboard to copy and paste values into spreadsheet software, or export the results directly to either a CSV or XLSX file.

- A full description of the results table is given in the "Results" chapter on page 170.

This concludes the brief walk through of the basic project workflow. There are many additional details that remain to be demonstrated, and these are covered in the following chapters: welcome to LADR!

Main Program

Introduction

The main LADR window is highly structured with the workflow clearly indicated by the numbered buttons, The workflow starts at the very left and runs to the very right in two rows of controls. Compare the complete LADR workflow shown in Figure 3 to the interface shown in Figure 4.
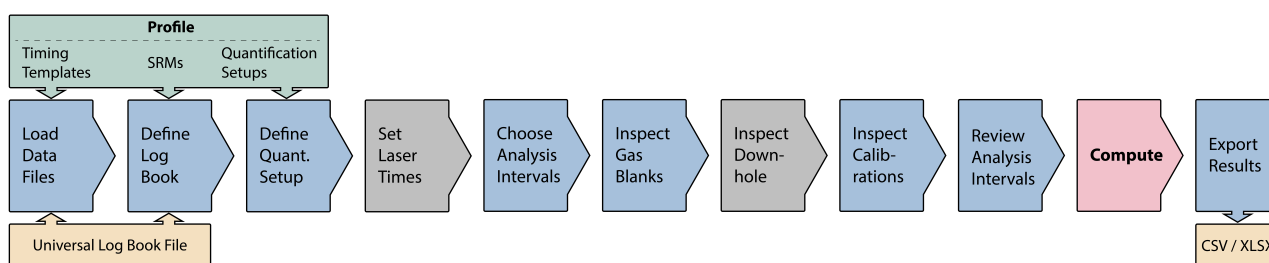

Figure 3: The complete LADR Workflow

Each button on the main form operates a traffic light notification system: if a stage has not been completed then the user is unable to proceed. This feedback ensures the user always knows what stage they are up to and what problems, if any, are present in the project.

To help users get started, on the first run LADR loads the default profile. The default profile contains a single RM, the ubiquitous[3] NIST610 glass, with the trace element concentrations from "GeoRem Preferred". It is recommended that users start by adding reference materials to their profile to ensure they can create and process their projects correctly.

Interface

When the program first opens, and the license key is checked and authorised, the main form (Figure 4) is the only form visible. The form is divided into three basic sections: the main menu along the top, the workflow buttons across the middle, and the action log at the bottom.

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3   Ubiquitous among LA–ICP–MS laboratories. If you haven't heard of it, start here: Eggins, Stephen M., and J. Michael G. Shelley. "Compositional heterogeneity in NIST RM 610-617 glasses." *Geostandards Newsletter* 26.3 (2002): 269-286.

Workflow

Users must follow the strict workflow to ensure each stage is completed properly (Figure 4). Each stage of data reduction will be described in the rest of this manual. Some steps may become unnecessary based on the data imported, and in those situations the button will be disabled.

Note: At the time of writing the "Interferences" button is unavailable, but will be enabled in future versions.
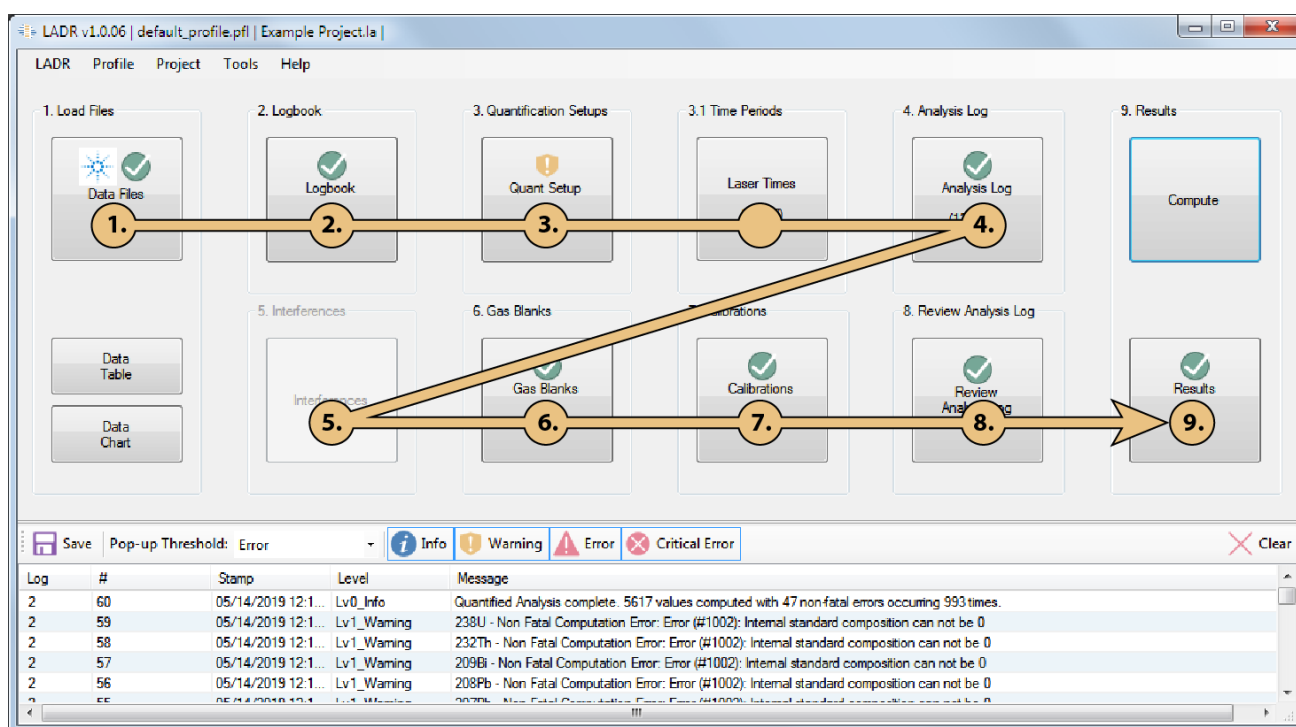

Figure 4 Main form of LADR showing the suggested workflow through each stage of data processing.

Feedback is provided for each stage by a status icon and status message. The icons shown are:

	OK
	Information
	Warning
	Error

Table 1: Status symbols. These are used throughout LADR to highlight potential issues.

If multiple status messages are present, then the icon will show the most severe, where: Error > Warning > Information > OK.

Hovering the mouse over the status icon will show a description of the status message.

Note: Workflow stages showing "error" will prevent the user from continuing.

Note: Workflow stages showing "warning" will allow the user to continue, but the computed results may be incorrect or incomplete!

It may be common to see blue information status messages in your projects. For example, this message is shown when the RM does not contain a concentration for the element and a common situation would involve measurement of 202Hg for monitoring purposes. In this case the blue warning for 202Hg can be safely ignored, and the result table will simply show a column of calculation errors for that mass.

In Table 2 is a list of each step in the data reduction workflow. Each step represented by different buttons on the main screen window has several functions. Some of these functions are optional, and depend on the project (e.g. Trace element analysis versus UPb geochronology).

Step / Button Name	Function
Load Files	Select and load data files.
	Define additional timing information (mass-spec specific).

	Logbook file import.
Logbook	Logbook file import. Define and edit the logbook.
Quant Setup	Import QSs from the profile. Create new quantification setups. Edit existing quantification setups.
Laser Times	Run automatic laser times. Manually define and edit laser times. Run automatic time periods.
Analysis Log	Choose analysis intervals. Spike removal. Define internal standard concentrations (QS specific). View analysis statistics.
Interferences	Interference calibrations (currently unavailable).
Gas Blanks	Select gas blank time intervals. Spike removal. View gas blank statistics. Create and edit gas blank models.
Calibrations	Select calibration time intervals. Spike removal. View RM statistics.

	Common lead corrections (QS specific).
	Down-hole corrections (QS specific).
	Create and edit calibration models.
	View calibration drift.
Analysis Log Review	Change selected time intervals.
	View corrected UPb ages and isotopic ratio results.
	Check internal standard values.
	Live results (coming soon).
Compute	Compute project results.
Results	View and export results table.

Table 2 List of the primary functions available behind each button on the main LADR window.

Main Window Title

The main window title shows:

- Profile name – Name of the currently loaded profile

- Project name – Name of the currently loaded project. This will not be shown if the project has not been saved.

By default the full project path is shown in the form title. There are two options available (see Appendix A – Options) that can be used to control whether the full path, or just the filename, is shown in the title.

The software will periodically check the current license key, and will display "Checking License…" while this takes place.

Action Log

The action log serves as a record of all operations that occurred while a project was created and processed by LADR. The list can be filtered using the buttons, and the log saved to disk by using the save log button. Any individual entry can be inspected by double-clicking the entry in the list. The list can be cleared using the "X" clear button.

Note: at the time of writing the action log is not saved with the project. In the future it will be possible to write the log to write-once storage, allowing LADR to integrate with workflows that guarantee strict data integrity.

The information recorded in the action log includes:

- Log – The log value indicates where the action log message originated. It shows "0" for those from the program, "1" for those from the profile, and "2" for those from the project.

- # – A unique sequential error number.

- Stamp – Time stamp of the error occurrence.

- Level – In order of severity, either "Info", "Warning", "Error", or "Critical Error".

- Message – A helpful message describing the action.

It is possible to control the level of warning required to generate a pop-up box, which can be controlled using the pop-up threshold box at the top of the project change log. There are four levels of pop-ups possible including:

- Info – Information based pop-ups which do not inhibit LADR functionality. Most messages at this level can be ignored.

- Warning – A non-fatal computational error may have occurred. It will still be possible to compute results, but it is possible that the results will be incorrect.

- Error – An error is present that will prevent LADR from computing results.

- Critical error – A program-level error has occurred and LADR will be unable to continue operation. If this error occurs then the program should be restarted.

Main Menu

Many important functions of the LADR software are available in the main menu at the top of the main window. The main functions of each menu option are described in Table 3.

Menu	Functions
LADR	Exit the LADR program.
Profile	New, save, and open profile; manage profile, RMs, QSs, and TTs.
Project	New, save, and open project.
Tools	Reset forms, filter data, edit options, tune flat signal, review spikes, program settings.
Help	Show manual, about, registration.

Table 3 List of functions in the main window menu.

Main Menu – LADR

There is one option under the LADR menu to exit the LADR program. When exiting LADR program will prompt to save the current profile and project.

Main Menu – Profile

Options available under the profile menu for creating a new profile, saving the current profile, and opening a saved profile. The items "Manage Profile", "Manage Reference Materials", "Manage Quantification Setups", and "Manage Timing Templates" are all described in subsequent chapters.

Note: The software must have a profile loaded to work on a project. The profile must contain at least one RM to allow loading of data files.

On first run the software loads the default profile. The default profile contains a single RM, the commonly used NIST610 glass, with the trace element concentrations from "GeoRem Preferred". The default profile must be saved to a new location.

When the software runs it will attempt to load the last-used profile. If the profile cannot be located (file moved, deleted, or unavailable) then the software will initialize

with a new empty profile. To re-load the profile you are working with, choose "Profile"→"Load Profile" and locate your profile file.

LADR profile files have the *.pfl file extension.

Note: Managing the profile allows the user to apply a password which locks profile options for future users. These options will also be expanded in future versions.

Main Menu – Project

A project file is completely self-contained and contains all of the values required for computing results.

As a project is created, options are loaded from the profile, as well as RMs, timing templates, and quantification setups, as required.

Note: Using the profile to save RMs, QSs, TTs, as well as setting default options tailored for your specific LA–ICP–MS instrumentation is an integral part of using LADR effectively.

The project file also contains the original data files, which can be exported as byte-perfect copies of the originals.

When the software starts it defaults to a new empty project.

Note: If the "load data" button is inactive, it means your currently loaded profile does not contain any RMs. The profile must contain at least one RM to continue, either load your profile file, or add RMs to the empty profile and save it for next time.

LADR project files have the *.la file extension.

Main Menu – Tools

Several important LADR options are available in the tools menu. Many of these options significantly affect the functionality of LADR.

Main Menu – Tools – Reset forms

During general use LADR will remember the location and size of every form from when it was last displayed.

Sometimes, typically when monitors are added or removed from the system, some windows will appear off screen. If this happens, use the "Reset Forms" command to return all forms to a default size and location.

If the main LADR window has been "lost", either use the WIN+arrow keys to "walk" the form back onto the main display, or, start LADR while holding the SHIFT key to force a form reset on start up.

Main Menu – Tools – Filter Data

This tool is a general purpose data filter that allows for advanced post-processing of raw data.

It can be used to replace, or delete, data points that fall outside, or within, a specified range. It can, for example, remove all data points from a project that fall on the analogue side of a dual-mode detector.

See "Error: Reference source not found" for an overview of how to use this tool.

Main Menu – Tools – Edit options

The edit options button opens a window showing all program options. All options are displayed in the profile tab, and these options should only be edited when the user desires these edits to pertain to future projects. The project options are populated from the profile when a project is created. The project options should be modified if the user desires the changes to only affect the current project.

Note: Options are discussed in this manual where they are pertinent to the functionality of specific processes. All options identified by the following `"text formatting"` *in this document can be found in the "Edit Options" window.*

Note: Suggested option values are in "Appendix A – Options", page 189.

Each option contains additional information available in the "program options" menu.

- Status is enabled when the option is active in LADR and disabled when the function related to the option is unavailable.

- Behaviour – The behaviour of the option refers to the location the option values are taken from when used in a project.

o   Program – LADR specific options that pertain to program functionality.

o   Profile – Profile options are only visible in the Tools → Edit options → Profile tab. These options generally pertain to quantification of signal and gas blank and file loading options.

o   Profile is Default – These options are in both the profile and project tabs of the Tools → Edit options window. These options are copied from the profile to the project during project creation. Changes must be made in the project tab to take effect in the current project, changes in the profile are used when a new project is created.

o   Profile Is Module Default – These options were copied from the profile to the QS when a QS is created. Each QS has independent options values that must be edited in the QS → General tab to take effect in the current project.

Note: *The default profile options values can be loaded to the project or QS list of options at any time. The profile options values can also be reloaded to the LADR default values.*

- Name – Indicates the step(s) of data reduction where the option is applicable. This field is searchable in the "program options" window.

- Type – Either Boolean for true–false statements, String when several text options are available, Double is for numeric values with a double precision (64 bit), and integer for numbers without a decimal point.

- Value – May be numeric, select from a drop-down menu, or true–false dependent upon the data type.

- Guidance – If data is numeric, the suggested range of values is listed. If the value is selected from a drop-down menu then the options are presented.

- Notes – Short description of the option function.

Manage Reference Materials

Introduction

Reference materials (RMs) are an essential part of LADR, and it will not be possible to load any data files until the profile contains at least one RM entry. RMs reside in the profile, where they can be edited, and are copied into each project as required. Once they are copied into the project they become read-only.

The user can provide as much, or as little, information about each RM as they require. RMs can hold elemental concentrations, isotope systems (currently limited to U and Pb), arbitrary isotope ratios, as well as age.

Importers are provided to conveniently import values from a number of data sources.

Interface

The RM manager provides controls for importing, editing, copying, deleting, and transferring RMs. It is launched from the main menu via "Profile"→"Manage Reference Materials".

Note: On first run the software loads the default profile. The default profile contains a single RM, the commonly used NIST610 glass, with the trace element concentrations from "GeoRem Preferred".
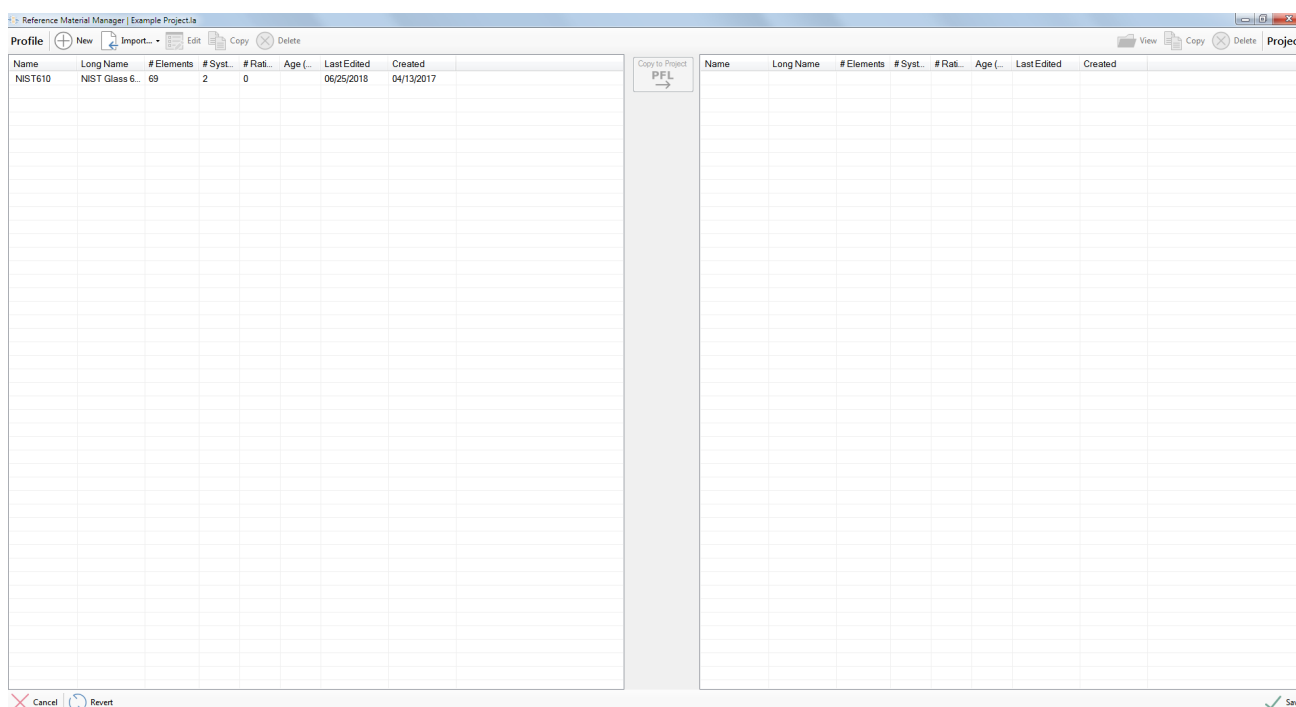
Figure 5 Reference material manager window showing the layout and primary sections.

The reference materials manager displays the reference materials currently in the profile and the project. These RMs can be transferred between the profile and the project but can only be created, edited, or imported from an external resource in the profile. Once added to a project a RM cannot be edited, however it is possible to easily replace a project RM with one from the profile and recompute the project.

Table Column	Description
Name	Reference material name (must be unique)
Long name	Reference material descriptive name
# Elements	Number of elements with concentration information
# Systems	Number of isotopic systems with defined values
# Ratios	Number of isotope ratios with defined values
Age (Ma)	Age of standard
Last edited	When the reference material was last updated
Created	When the reference material was created

Table 4 Reference material information displayed on the reference material manager list.

A new RM can be created by clicking the "Add RM" button which then requires the user to manually input the elemental and isotopic ratio information.

Importing Reference Materials

To import standards into LADR use the import option and choose to load standard information from either the GeoRem website or from another file containing standards (Figure 6).

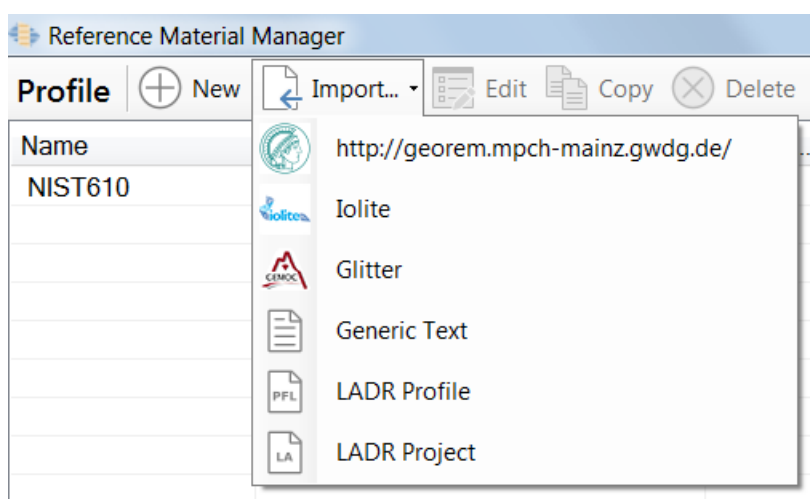Table 5 provides details of each import option currently available in LADR.

Figure 6 Import options for reference materials in the profile window.

Option	Function
GeoRem[4]	Import reference material compositions directly from the GeoRem database. An active internet connection is required.
Iolite[5]	Import RM compositions from your Iolite standard files. If Iolite is installed then the files are located automatically, otherwise manual selection is required.

Ioite RM files from v2/v3 have a *.csv extension while Iolite RM files from v4 have a *.json extension. Both file types are supported by LADR. |

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4   "GeoRem" and the associated logo are trademarks of the Max Plank Institute, Mainz (http://georem.mpch-mainz.gwdg.de/) and are used here in a descriptive capacity only.

5   "Iolite" and the associated logo are trademarks of the University of Melbourne (https://iolite-software.com/) and are used here in a descriptive capacity only.

Glitter[6]	Import RM compositions from your Glitter installation. If Glitter is installed then the files are located automatically, otherwise manual selection is required.
Generic text	Open a plain spreadsheet file, as either XLS, XLSX, CSV, or TXT, from which to load standard concentrations.
LADR Profile	Import RMs contained in a previously saved profile file.
LADR Project	Import RMs contained in a previously saved project file.

Table 5 List of options for importing reference materials into LADR.

When importing multiple RMs the selection dialogue will be shown (Figure 7) which allows the user to choose which RMs to import. Select multiple entries using standard Windows paradigms (SHIFT or CTRL+click) and then toggle the selection using the space bar.
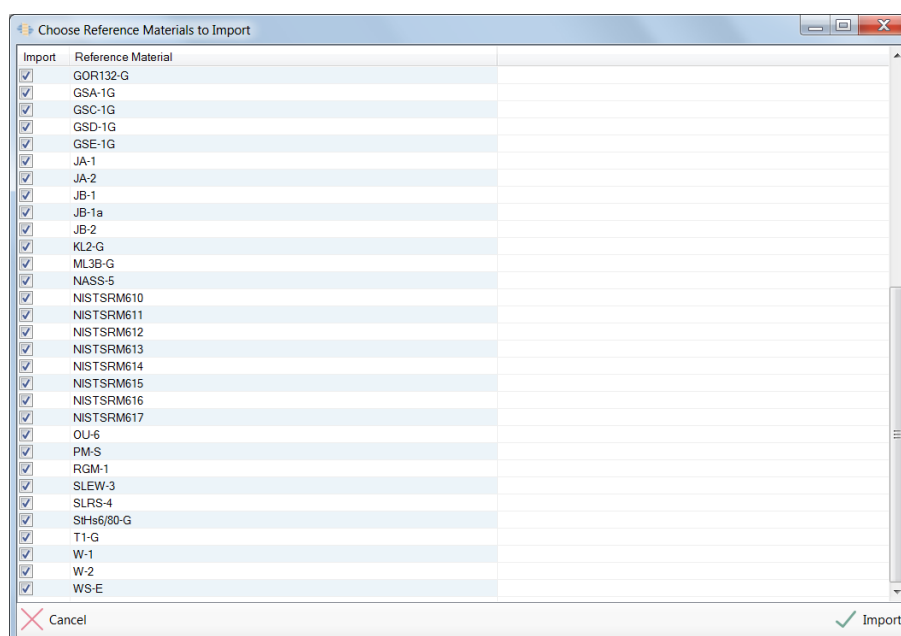

Figure 7: RM selection dialogue

Click "Import" to continue importing RMs into the profile.

Choose a single RM on the profile side of the display and click the "Edit" button.

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6   "Glitter" and the associated logo are trademarks of Macquarie University (http://www.glitter-gemoc.com/) and are used here in a descriptive capacity only.

The form shown in Figure 8 will appear.

Figure 8 The edit reference material window.

Elemental Composition

Elements can be added to the RM by selecting the periodic table button (Figure 8). For each element in the list the following information is displayed:

- Z – Atomic number for element

- Symbol – Atomic symbol

- Element – Full name of element

- Weight% – Concentration in weight% (edit values by double-clicking on this field, all other fields will be updated)

- µg/g – Concentration in PPM (edit values by double-clicking on this field, all other fields will be updated)

- Oxide – The default oxide species according to the default LADR valence information (e.g. SiO2) which cannot be edited here. Note: this value is shown for ease of data entry, and does not indicate the species present in the RM.

- Oxide wt.% – Concentration in oxide weight percent, as per the default LADR oxide species shown in the "Oxide" column. Note: this value is shown for ease of data entry, and does not indicate the species present in the RM.

- Microheterogeneity – Element heterogeneity in the standard which would add an additional source of error to the results. Uncertainty can be established by comparing a large number of microanalytical data from the RM. If present, it is included in the full analytical uncertainty.

   Note: In future versions of LADR this value will become spot-size dependent.

- Comment – Comments such as source of standard concentration, data entry, or reference.

Isotopic Composition

The isotopic composition tab in the edit reference material window handles interconnected isotope systems by defining all of the isotopic abundances, or ratios, for a given element.

Figure 9 Isotopic compositions tab for the edit RM window.

To add an isotopic system to a RM, select the add system button, and modify the isotopic ratios by either atoms or mass (Figure 9).

Note: When an isotope system is added to an RM, ratios will be set at a default natural abundance and must be modified to match the specific RM.

Note: Isotopic system information on the right side of the screen will be updated automatically.

Note: It is recommended that errors are added to isotopic ratios if available. These errors will be propagated through to the results.

Isotope Ratios

Any isotope ratio can be defined in an RM by using the isotope ratio tab of the edit reference material window (Figure 10). Select add ratio and an addition ratio line will be created using hydrogen as the default mass. The "element 1" field can be modified to a different element and the Z column (atomic mass) will be updated automatically. The "mass" (isotope) of the desired element must be defined.

Note: Mass 1 is the numerator and mass 2 is the denominator in the defined ratio.

Figure 10 Isotopic ratios tab of the edit RM window.

Element ratios can be defined by the "compute UPb ratios from age" button. Ratios calculated from the age of the reference material are 207Pb/206Pb, 208Pb/232Th, 207Pb/235U, 206Pb/238U.

Note: An age for the reference material must be provided for these isotope ratios to be calculated.

It is suggested that RMs are imported and modified within the profile before data files are added to the project though this is not strictly necessary. Once the profile contains all of the required RMs, they can be either manually added to the project or they will be automatically added if analysis names match the alias names listed in the standard properties (Figure 8).

Data Tables and Charts

Data tables and charts can be viewed at any stage of data reduction and are located on the left side of the main LADR window, sitting just outside of the main workflow.

These charts and tables allow the user to inspect the raw ICP–MS data.

Data Table

In the data table window, each analysis is shown separately. Data is displayed for each sweep for each element and should match the imported ICP-MS data files. The raw data tables are user editable by double clicking on the desired cell and typing a new value. This is not recommended in the routine LADR workflow.

Note: The "`Profile.AllowDataEditing`" option controls the users ability to modify single sweep information in the table.

Note: Use the "`Profile.UseBackwardFormatForIsotopes`" option to control the order of isotope to element (40K or K40) to suit personal preference.

Figure 11 View/edit raw data window.

The data table can be filtered using the show menu at the top to display several data properties. The options are:

- User Modified – Each cell will display a false if the data cell has not been modified, and a true if the data cell has been modified.

- Time Point – The time during the analytical session each measurement was made. This is a calculated value using the dwell times and jump times included in the project timing template.

- Dwell Time – Mass spectrometer defined dwell time for each mass for each sample analysis.

- Sweep Number – A sweep is defined as the analysis of the lightest through to the heaviest isotope.

- Project Sweep Number – Stacked sweep number of each analysis in the project.

- Counts – The data point value in counts.

Data Chart

The data chart button shows a display of the raw data intensity in counts per second (CPS) over time. Individual samples are displayed on the upper half of the screen, and multiple samples are displayed on the bottom half of the screen. Individual element masses can be selected/deselected and highlighted for viewing on the right side of the window.

Note: Place the mouse cursor over an area of the chart and hold down the CTRL button on the keyboard to zoom into the location of the cursor.

Figure 12 The Data Chart window. Similar charts with common options are shown on various forms throughout the workflow.

The mass list allows the user to choose which masses are shown, their colour, and whether the trace should be highlighted (shown as a thicker line).

Right click the headings above the display elements on the right produces several options for display including:

- The element mass – For example: "23Na".

- The elemental symbol – For example: "Na".

- Possible isotopes – For example: "23Na" (will list other isotopes at this atomic mass).

- The element name – For example: "Sodium".

There are several additional options for the single sample view, which are available by right-clicking on the chart. These options are:

- Save Chart As – It is possible to save the chart area to be imported to a report or presentation. There are three options for saving the report as a bitmap file at

either the current screen resolution, 2x larger, or 3x larger. There is also an option to export the chart in a vector format.

- Scale – Either linear, log, or "symmetric log" can be selected.

- Show – Several options are available for viewing the data including:

  o A cursor can be activated which displays the total time, sample time, and intensity in either counts or CPS of the cursor location. It can also assist with identifying masses.

  o The gas blank grid can be turned on and off.

  o The laser times can be turned on which indicates the beginning of each sample laser signal.

  o An element legend can be shown which highlights all elements currently shown on the graph (these are turned on and in the right-hand list). Note: This legend is shown automatically when saving the chart.

  o Point markers can be turned on and off and show exactly where the data points are located on the chart.

  o The X-axis and y-axis scales can be made visible and invisible.

  o A trace can be added to the graph showing the sum of the data (or total count rate).

  o Ancillary data refers to any additional data that a file may contain. An example of ancillary data would be TOF files reporting the total ion counts, or, vacuum chamber pressure, ICP gas flows, plasma reflected power, or even sample exchange events. The presence of ancillary data is specific to each data file format.

- Masses – Allows the user to toggle on and off the list of masses on the right of the screen. This could be useful if the graph window needs to be larger for easier viewing.

- Data Type – Toggle between counts per second (CPS) and counts.

- View – Choose to view either raw counts or "GB Sub and IS norm and cleaned up from QS" (Gas blank subtracted, internal standard normalised, outlier rejection on ratio applied from QS).

Note: *The appearance of the data chart will be preserved between other forms where it appears.*

Note: *The views of charts and tables in LADR can be adjusted by selecting the column boundaries and moving them to the desired location. LADR will remember the most recent layout when windows are re-opened.*

Note: *The "Profile.Plotting.Legend.HideOffChartMasses" option controls the visibility of all masses in the legend. If set to true then only masses visible on the chart (within range) will be displayed in the chart legend.*

Note: *The "Profile.Plotting.Legend.SortByFinalIntensity" option controls the order of masses in the chart legend.*

Laser Ablation Workflow

Practically all LA–ICP–MS sessions are measured with sample-standard bracketing. Primary standards are measured every 45-60 minutes to calibrate the ICP–MS response and assess drift over time. Secondary standards can be used in a number of ways, as either a quick check that all is working as expected, or quantitatively, to quantify matrix correction factors (at different spot sizes) or measure excess uncertainty. To assess uncertainty it is desirable to place secondary standards half way between calibration standards, where models of instrument drift will be least constrained. Laser ablation control software should provide a convenient interface for sequences to be configured to suit the requirements of the analysis.

The ideal workflow is shown in Figure 13. The optional stage of offline point definition is illustrated for completeness but not considered further. Starting with the laser ablation instrument, once the sample list is defined it is transferred over to the ICP–MS instrument. Ideally this step is automated via a sample list file. Transfer of the sample list to the ICP–MS software ensures that the "data ident" matches between the log book file and the ICP–MS data files. But in addition, all of the sample names and laser conditions are available as well as ensuring the acquisition time for each sample matches between the instruments.
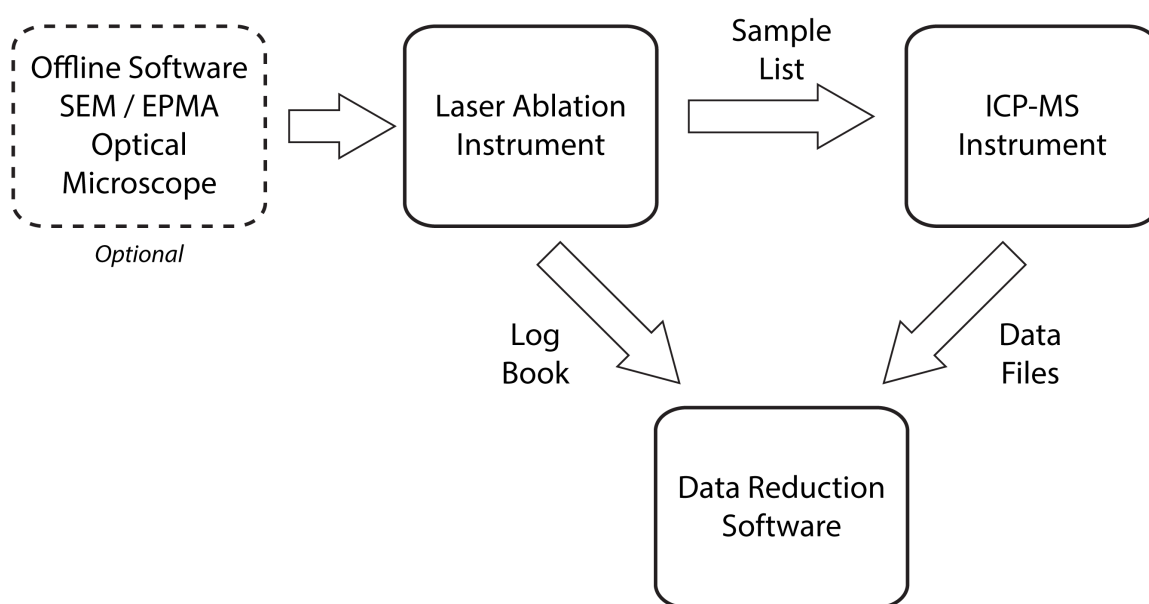
Figure 13: Ideal workflow for LA–ICP–MS.

After the sequence has been ablated, LADR needs information from both instruments: the sample type, quant name, the laser parameters from the laser ablation instrument via the log book file, and the data files from the ICP–MS instrument.

When LADR has all of the information about the sequence, the samples, the laser conditions, and the ICP–MS measurement, the data reduction can be automated as much as possible and the chance of transcription errors between the systems is greatly reduced.

The workflow above is followed by most ICP–MS laboratories but with varying degrees of automation and integration.

File Loading

Introduction

Importing data files from a mass spectrometer output is the first step in the suggested program workflow. Contained within this window are several necessary steps and some optional steps that must be completed before moving on to the next stage of data reduction.

Note: If the "Data files" button is disabled it means the currently loaded profile does not contain any RMs. Add an RM to the profile to start loading data (see "Manage Reference Materials" on page 37).

The workflow for this window requires the user to:

1. Load the desired files by selecting the relevant mass spectrometer file type and selecting data files.

2. Inspect the selected files as a list in the "Files" portion of the "Manage ICP–MS Data Files" window on the right side.

    • Viewable information is file name, type, size, and number of entries.

    • Move, delete, or sort the files appropriately. This may be necessary if files are not loaded using the file creation timestamp.

3. Select the "Measurements" tab of the "Manage ICP–MS Data Files" window on the right side.

    • Set up the Timing Template(s) for the loaded files.

    • Inspect the measurement information such as file name, index, entry name, number of sweeps, number of masses, timing template, timing gap, and timestamp.

4. Optional: Load Logbook file.

5. Save and load data to the current project.
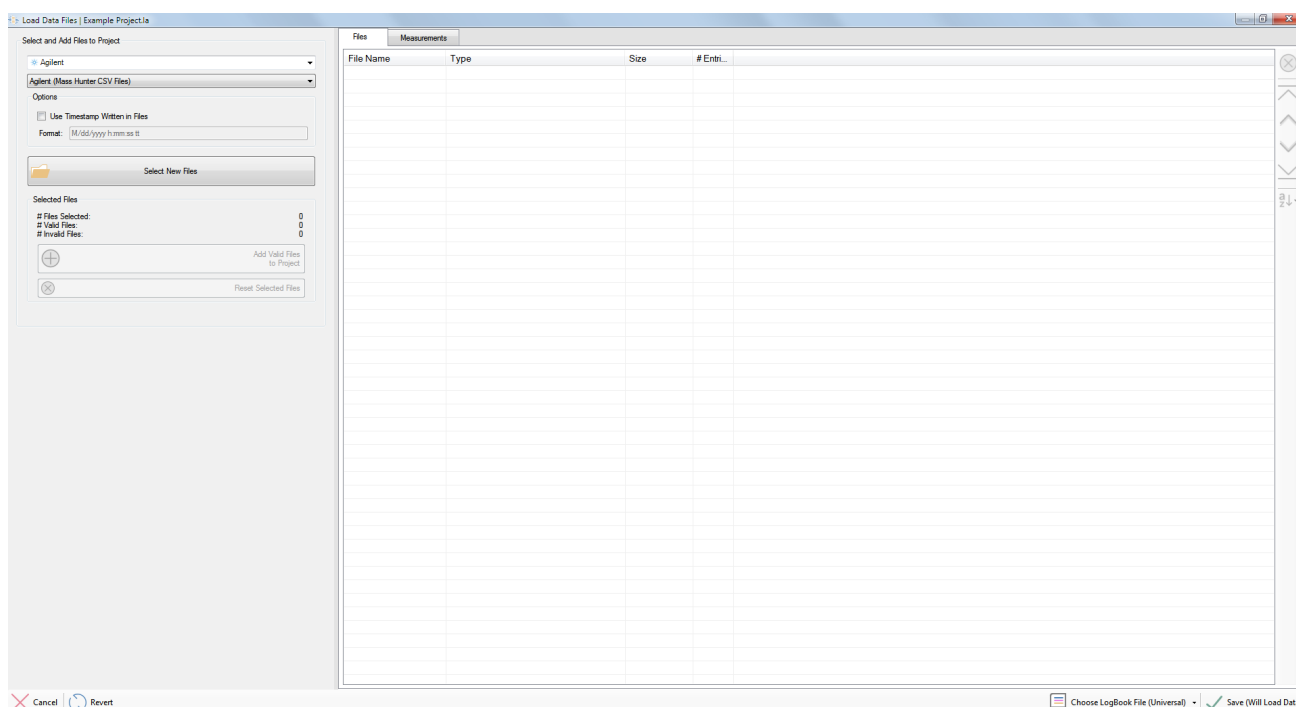
Figure 14 The load data window, with no files loaded.

Selecting and Loading Data Files

To load data files, choose the data file type and set the file loading options (see notes in Table 6 for available options).

Click "Select New Files" and navigate to the desired file directory and highlight the necessary files. The files are inspected by LADR to ensure that they meet the expected file format. If your files do not conform to the expected structure, they will not load.

Note: Contact LADR support (ladr@norsci.com) if you have data files that will not load.

Once the files are processed, if they are all valid then they will be added automatically to the list of files. If a mixture of valid and invalid files were selected, then you must confirm loading the valid files to add them to the list.

Once the files are loaded the file order can be adjusted if necessary using the buttons on the right side of the file list (see Figure 14). Make a selection and use the up and down icons to shift the order. The sort button allows the list to be sorted using either alphabetical, numerical, or file timestamp order.

By right-clicking on a file(s) in the file list, the imported files can be exported to another file (file location, and name can be selected) and the file contents can be viewed in a text editing window.

Instrument Manufacturer	File Type	Notes
Agilent	Chemstation .CSV	Data being in CPS or Counts is read automatically from the header.
	Mass Hunter .CSV	Optional to use file timestamp (check timestamp format) Data being in CPS or Counts is read automatically from the header.
	Mass Hunter batch folder	All parameters are read automatically.
Perkin Elmer	Perkin Elmer .XL	
	Perkin Elmer .REP	
Thermo Fisher	X-series II / PlasmaLab 2	Choose to load CPS or Counts, Timestamp optional
	iCAP-Q/QTegra	Optional to use file timestamp (check timestamp format)
	Element .TXT	
	Element .FIN2	
	Neptune	
Analytic Jena	Analytic Jena .CSV	
	Analytic Jena .PRN	
TOFWERK	Tofware v2	
	Tofware v3	
Nu Instruments	Attom .TRA Plasma II .TRA	NPII files load correctly but in LADR v1.1.01 the faraday detector voltage values are not converted to counts

		in a meaningful way, affecting uncertainty propagation.

Table 6 List of the available data file import types and provided instrument manufacturers.

Defining Additional Timing Information

It is necessary to confirm and sometimes define additional timing information associated with the imported data files. These metadata and timing template(s) are edited by selecting the "Measurements" tab at the top of the Manage ICP−MS Data Files window (Figure 15).

The main purpose of the timing template is to provide additional timing information that is not contained in the data files.

Note: Some data files (e.g. Thermo QTegra CSV files) contain all necessary timing information so editing the timing template is not required. It is a requirement of the software logic that every data file is assigned a timing template, even if the timing template is empty.

Correct ICP−MS timing is important to the functionality of LADR as it allow the user to:

1. Convert between CPS and counts.

    a. Counts are needed so that counting statistics can be correctly applied to the data processing.

    b. CPS are needed to display intensity data on the charts, as well as correctly calculate interference corrections.

2. Place data points on a timeline at the time of the measurement.

3. Calculate accurate isotopic ratios, for UPb geochronology for example.

4. Accurately calculate signal spikes so they can be effectively removed.

If all of the necessary timing information is not provided by the imported ICP−MS files, there are several methods available to provide the additional timing information:

1. If a timing template was previously created and saved to the profile, it can be used in future projects.

2. Loading timing information from additional files, for example importing dwell times from an Agilent AcqMethod.xml file.

3. When data are loaded, if no applicable TT exists in the profile, an "Auto Template" will be created assuming all masses have the same dwell time.
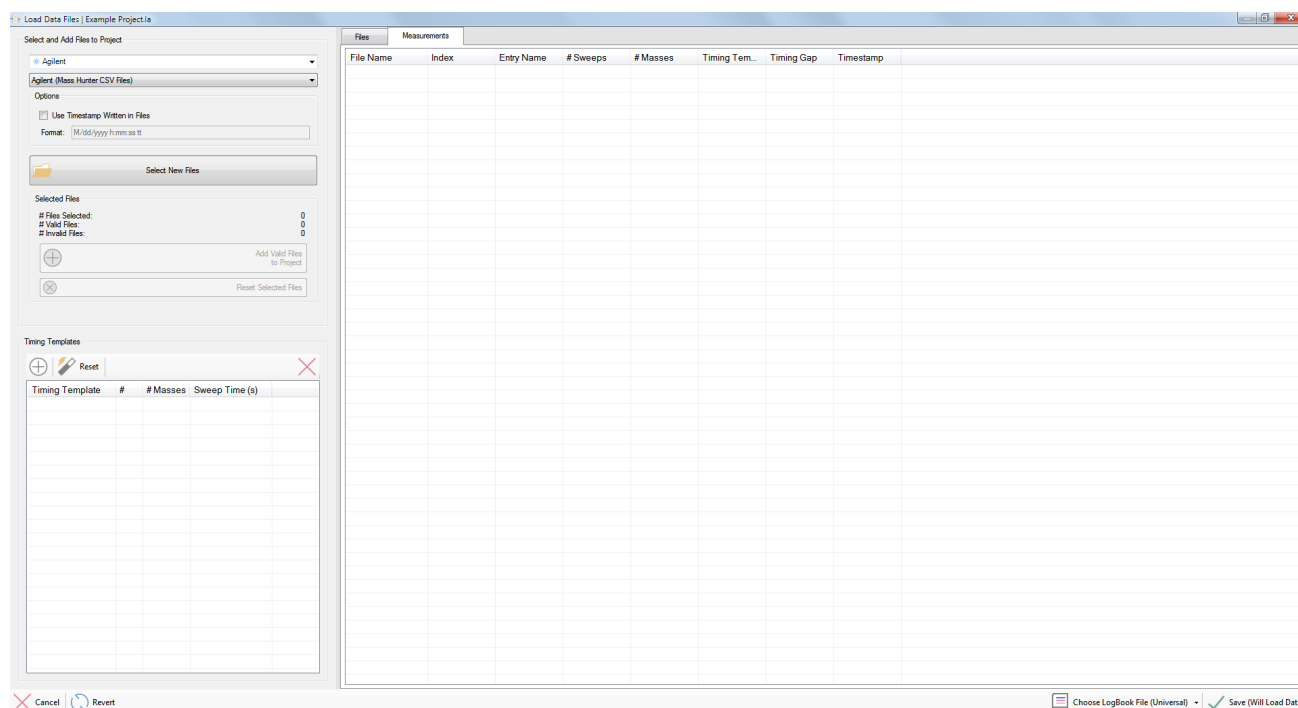
Figure 15. View of the measurements tab on the load data window. Selecting this tab allows the timing template window to be viewed.

Note: To use a saved TT from a profile, the file type, mass list, and timing information, must match the imported data files.

Note: To edit and view the timing templates saved in the profile select "Profile" → "Manage Timing Templates" from the main program window. See "Manage Timing Templates" Page 181 for additional information about timing templates saved to the profile.

Note: You must edit the auto timing template and provide the correct dwell times for data processing to work correctly. If the auto timing template contains estimated values, and you do not review or edit those values, then an additional warning will be shown when you click "Save" to load the data, and the Edit Timing Template window will be shown (Figure 17).

In the measurements tab, there are several additional metadata including the file name, index, entry name, number of sweeps in the file, number of masses contained within the file, allocated timing template, timing gap (time between imported data files), and file timestamp.

Note: If a "multi-entry file type" is uploaded, then the "Files" tab will show a single entry. But the "Measurements" tab will show separate entries for each part of the file.

Several TTs are allowed in a single project and may be required due to changing analytical method, such as analysis of multiple minerals in a single analytical session with different element lists. If multiple TTs are used in a single project, the allocation of a TT to each data file can be modified by double-clicking the desired cell in the TT column. This will produce a drop-down menu where the TT can be changed. The TT can also be changed by highlighting multiple rows, right-clicking and select "fill down timing template". Similarly, it is possible to fill down the timing gap in the same way.

Figure 16 Detailed view of the timing template region of the "Manage ICP–MS Data Files" window.

The timing template section of the Import data window displays the TTs which are being used in the opened project. By right-clicking on the timing template several options become available. These are:

- Edit Timing Template – This opens the edit timing template window (Figure 17).

- Allocate to All Compatible File Entries – Apply this timing template to all imported data files which contain the same element list and sweep time.

- Duplicate Timing Templates – Create a copy of this timing template.

- Replace from Profile – Replace this TT with a suitable TT from the profile.

- Save to Profile – Save this project TT to the profile.

- Delete all Templates from Profiles – This is not recommended.

Right click on the auto template and choose "Edit". This launches the timing template window.

Figure 17 Edit timing template window

In the edit timing template window individual dwell and jump times can be modified by double-clicking the desired cell. Timings can also be filled down by highlighting cells, right-clicking, and selecting "fill down".

You can highlight multiple masses by pressing CTRL + left click on each line that you need to highlight. Then you can right-click and fill down dwell times. The highlighted masses need not be adjacent to each other for this function to work.

Note: Any value that has been determined from the data file will be shown in a pink cell. These values cannot be edited.

Options for calculating dwell and jump times:

- Update Summed Totals – Add all dwell time, jump times, and calculate a sweep time.

- Compute Dwell Times – 95% of the file sweep time is allocated to the total dwell time. The total dwell time is divided amongst the number of masses analysed. All elements are assigned the same dwell time.

- Compute Jump Times (Simple) – The total jump time is calculated by the file sweep time minus the total dwell time. The total jump time is distributed equally among the number of masses analysed.

- Compute Jump Times (Proportional) – The total jump time is calculated by the file sweep time minus the total dwell time. The jump time is distributed based upon the mass difference between masses analysed.

Note: We recommend computing the jump times using the "Compute Jump Time (Proportional)" button.

Note: It is important that the summed sweep time matches the average sweep time reported from the file.

Note: Provided the dwell times were correct (sum of dwell times < sweep time) the jump times will compute correctly.

Save the timing template by clicking the "Save" button.

Give the timing template a memorable name.

Right click on the timing template entry and choose "Save to Profile". This will ensure you can re-use the timing template the next time you load data collected using the same ICP–MS method/conditions.

What is a Mass?

LADR provides considerable flexibility when identifying "masses" in data files. There exists some variation between ICP-MS manufacturers but all mass descriptions can be broken down into three parts:

- Mass number, either an integer or decimal.

- Element symbol.

- Custom string description, e.g. ThO, or Rb86=>104

There are two objectives with how LADR handles masses: can the mass be identified, and can the mass be quantified? The first objective is strictly enforced, while the second is only loosely enforced since there is no reason why every mass must be quantified (e.g. masses such as "ThO", "BKG", or "Ce++").

To meet these objectives LADR has the following requirements for masses:

- All of the masses in a project must be different, so no two masses can have the same values for all three of the components listed above.

- To quantify a mass there must be an element symbol assigned, otherwise it is impossible to get the concentration from the standards.

- Every mass must have a mass number assigned. By default LADR requires mass numbers to be unique, but there is an option to disable this though doing so will mean some features are no longer available.

These rules are enforced during file loading. When the data files contain insufficient information then the periodic table will be consulted to make a best guess (e.g. for mono-isotopic elements) of the missing details. When this approach is ambiguous, then a prompt will be shown asking the user to provide the missing information. The user input is then saved to the "Mass Mappings" in the profile and will be reused when loading subsequent data files.

Mass mappings are saved in the profile for re-use and can be edited or deleted. See the "Manage Profile" section for an overview.

Logbook File Import

The logbook serves a very important role in the software. It assigns operator intent to each sample measurement, as well as additional information about laser ablation conditions and sample composition. The logbook system allows the software to automate many functions.

To load a logbook file first review "Appendix B – Universal Log Book Format" which outlines the expected format. The logbook file will contain an entry for each sample in the project, assign an RM to standard entries, and include meta data from the laser system.

| User | | Data Owner | | Lab & year |
| Date | | Organisation | | C17 |

Filename	Sample Name	Minerals (one or more) eg.pyrite, quartz	Primary Secondary Sample	Spot Size (μm)	Freque (Hz)	Energy (mJ)	Fluence (J/cm2)	Spot Line Image	ICPMS method eg lazirc	Comment
C17SE19A0001	NIST612	Glass	Primary	74μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0002	NIST612	Glass	Primary	74μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0009	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0010	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0011	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0012	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0013	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0014	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0015	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0016	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0017	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0018	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0019	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0020	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0021	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	
C17SE19A0022	Cal-BH17JT011	calcite	Sample	29μm	5Hz	115	3.56	Spot	calcite	

Figure 18 Example of a possible logbook structure.

Note: Loading a logbook file when loading data files is optional, as the logbook can also be loaded at the logbook step of the project workflow.

LogBook

Introduction

The LogBook is a table that defines essential information about the project such as the reference materials analysed during the analytical session, laser ablation analytical conditions (laser beam size, fluence, firing frequency, ablation type and scan rate) and other parameters as described below.

Most importantly the LogBook serves as a record of operator intent[7], which organises the project and greatly assists with project processing.

Laser ablation analytical conditions are referred to in this manual as laser conditions. The current version of LADR supports two ablation types which are also referred to in this manual as analytical modes: "spot" (ablation at a fixed location on the analysed sample) and "line" (ablation of a sample moving under the beam).

LADR is unable to process a project without a valid LogBook.

The LogBook is based on the concept of samples, and each row in the LogBook table is a single sample. In LADR, a sample is defined as a set of data recorded by the mass-spectrometer over a period of time. Samples may contain:

- data acquired during an ablation or part of an ablation; or

- signal acquired from the gas blank; or

- signal corresponding to both the gas blank and ablation;

- or data acquired during several consecutive ablations.

Note: We apologise for any confusion between the use of "samples" in LADR and the common metrological definition of a sample referring to the source material that has been sampled.

Note: Samples cannot overlap in time.

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7   e.g. "this sample was a standard, this one was an unknown…"

Note: *To enable all automation features in the current version of LADR, it is recommended that the samples include a gas blank signal preceding a single ablation.*

Samples can contain multiple time intervals selected for quantification. Such time intervals are named analyses (see "Analysis Log" section for more details). Multiple analyses within a sample can overlap in time.

Only data contained within samples can be processed and quantified.

Data loaded into the project but not included into the periods of time assigned to samples cannot be accessed with LADR.

Samples within LADR must be assigned at least one sample type; the current version of LADR supports three types of samples by default: calibration reference material (shortened to calibration RM); secondary reference material (shortened to secondary RM) and unknown. Throughout this manual it is convenient to refer to all of the unknown samples collectively as *unknowns*. There are three additional types that can be shown in the LogBook table: *maps*, *gas blanks*, and *interference standards*. These will be utilised in future versions of the software.

Icon	Type	Description
C	Calibration Reference Material	Measurement of a calibration RM. The RM will be available for calibration of trace elements, UPb ratios, and quantified ratios.
S	Secondary Reference Material	Measurement of a secondary RM. The RM will be available for secondary standard corrections, and results can be checked against the known concentrations from the RM.
U	Unknown	Measurement of an unknown sample. This is the most common entry type and is the default value.

Table 7 List of possible sample types within LADR.

A single sample can be assigned to both the calibration RM and the secondary RM sample types. This allow the same RM to be used as a calibration RM for quantification

of some unknowns or some chemical elements, and as a secondary RM for other unknowns or other chemical elements.

Note: Samples containing signal acquired from gas blank only must be assigned as an unknown.

A valid LogBook must contain at least one sample of type calibration RM.

Note: A project containing only one sample defined as a calibration RM is a valid LADR project that can be processed to obtain quantified results.

LADR imposes a number of restrictions on the content of a sample:

- Samples cannot include data loaded into the project from multiple file entries.

- If a sample is assigned an RM type (either 'Calibration' or 'Secondary'), the RM needs to be identified by its name, and it is assumed that all ablations within this sample were collected from that same material.

- all ablation of a sample must be acquired using the same laser conditions.

Note: LADR allows for matching of laser conditions between analyses of RMs and unknowns. When this feature is enabled for quantification (see the "Quantification Setup" chapter on page 83), the logbook must contain RMs with laser conditions matching those used for the unknowns, to obtain a result.

Each sample can be assigned a name of the Quantification Setup (QS) which will be used for quantifying the data contained within the sample (see the "Quantification Setup" chapter on page 83). If a QS name is assigned to a sample in the LogBook, this QS will be automatically assigned to every analysis selected within this sample (see "Analysis Log" chapter on page 121).

Note: Assigning QS names to calibration or secondary standard samples is not required as LADR will automatically use them for all relevant Qss.

Glossary of LogBook Terms

The following table serves to clarify the various terms used in relation to the LogBook in LADR.

LogBook	The entity in LADR that describes valid time periods that equate to measurement of samples in the project. The same term is used to describe the window that is opened to edit the LogBook.
Sample	Each entry in the LADR LogBook is a Sample.
LogBook File	A CSV file in the Universal LogBook Format that can be loaded by LADR to complete the LogBook. LogBook Files can be created and editing by hand using spreadsheet or text editing software, or they can be exported directly from laser ablation software such as GeoStar (https://norsci.com/geostar/).
Laser Log File	Existing in a range of formats these files are created by laser ablation software packages. While LADR can load these files, they rarely contain all of the information required to fully populate the LogBook and as such use of the LogBook File is recommended.

Interface

The LogBook form becomes active once valid data are loaded into the project. To open the LogBook Form, press the "LogBook" button on the main LADR window. The LogBook form contains three sections (see Figure 22):

- The LogBook table (left);

- The time-resolved chart showing the measured signal for each mass; and

- The list of masses/isotopes in the project (right).

The information shown in the sample table includes:

- The name of the data file which contains the data assigned to the sample;

- Sample name;

- Three columns corresponding to sample types ("C" for "Calibration RM", "S" for "Secondary RM" and "U" for "Unknown";

- One column for identifying the QS ("Quant Name") which specifies how the measurement is to be quantified (see "Quantification Setup");

- Five columns for laser conditions;

- Comments column; and

- Any columns for internal standard element concentrations if they were specified in a LADR Log Book file (see "Automatically Creating a Valid LogBook").

The data chart shows the time-resolved measurements. For more information on how to modify and adjust the data chart please see the "Data Chart" section on page 46.

Each section of the window can be adjusted in size and configured to display the relevant information. The list of masses is linked to the time-resolved chart and can be used to adjust the masses shown and/or highlight the masses of interest. Use the right-click menu on the chart to show/hide the mass list.

All common LogBook controls are available as buttons across the top of the form. The items are:

- Add Reference Materials – Add reference materials to the project. This is only needed when creating a LogBook manually. If loading a LogBook File or a Laser Log File then reference materials are copied into the project automatically.

- LogBook menu (see Figure 19):

  - New Empty Log Book – Create a new blank LogBook. This would only be performed if created a LogBook manually.

  - Allocate From Source Files – Create a new LogBook where each sample corresponds to each data file.

- Log Book File menu (see Figure 20):

  - Replace LogBook File – Show a file browser and replace the current LogBook File with a new one. This will cause the entire LogBook to be reset and

replaced with the contents of the LogBook File, including copying reference materials into the project from the profile. A copy of the new LogBook File is also saved in the project.

○ Change Format – Choose the LogBook file format to use. Note that the recommended format is "Universal".

○ Reload Log Book File – Use the saved copy of the LogBook file to recreate the LogBook. This would typically be used if manual editing of the LogBook has caused problems.

○ Save Log Book File – Export the saved LogBook File to disk. Please note that this command only exports a previously-imported file, and does not create a LogBook File from the current LogBook.

○ Remove Log Book File – Remove the saved LogBook File from the project. This will also cause the LogBook to be reset.

- Laser Log File menu (see Figure 21):

○ GeoStar CSV Laser Log File – Use a GeoStar CSV Laser Log File to create the LogBook. Note that the LogBook will require further editing before it is correct and complete.

○ GeoStar Verbose LOG File – Use a GeoStar Verbose LOG File to create the LogBook. Note that the LogBook will require further editing before it is correct and complete.
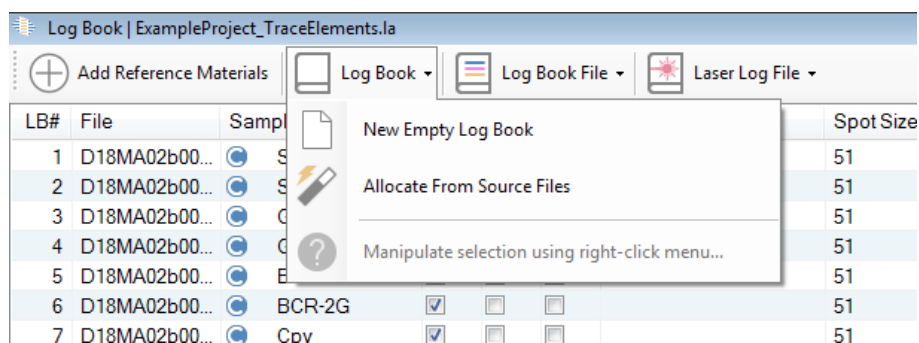
Figure 19: The Log Book drop-down menu.
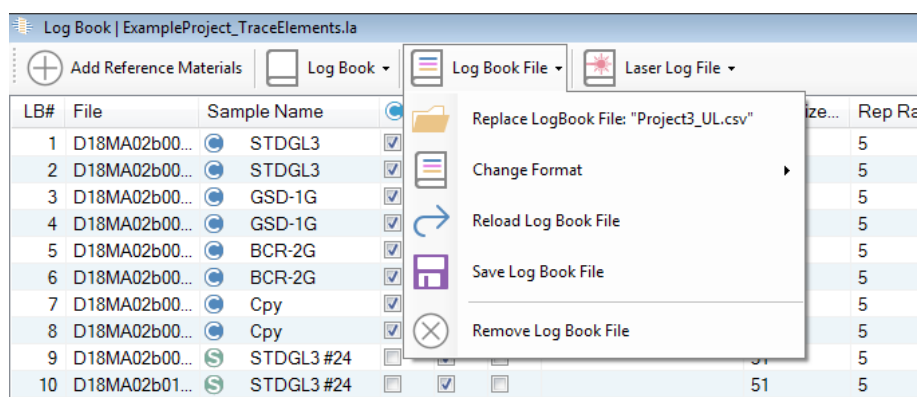
Figure 20: The Log Book File drop-down menu.
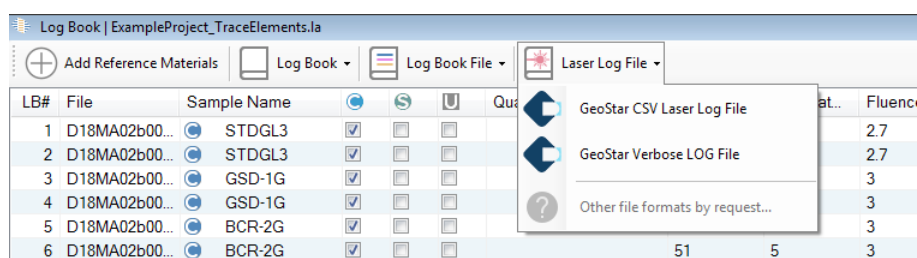
Figure 21: The Laser Log File drop-down menu.

Manually Creating a Valid LogBook

The following examples show different ways to set up the logbook when a LogBook file is not used. This way is fully supported and is feasible for most projects, but the recommended way is to use a LogBook File (see "Automatically Creating a Valid LogBook").

Data Acquired as Separate Measurements for Each Ablation

Figure 22 presents the default appearance of the LogBook form for the case where each file contains only one measurement.

When multiple files are loaded, each containing a single measurement, LADR automatically assigns each file to a sample. Sample names are assigned as file names. All samples are assigned the unknown sample type, all numerical laser conditions are set to 0 and the ablation type is set to "spot". This is the default LogBook that will be created if no LogBook File is chosen during file loading or using the controls on the LogBook form.

This default LogBook is not valid as at least one of the samples must be assigned the *Calibration RM* type. An invalid logbook cannot be saved and clicking the save button in the bottom right corner of the form will trigger an error message explaining the issue.

To exit the logbook form which contains an invalid logbook, press the cancel button in the bottom left corner of the form. Any changes made to the logbook will be lost, but exiting the form in this way allows access to the "Manage Reference Materials" form which may be necessary if, for example, the profile does not yet contain the required reference materials.
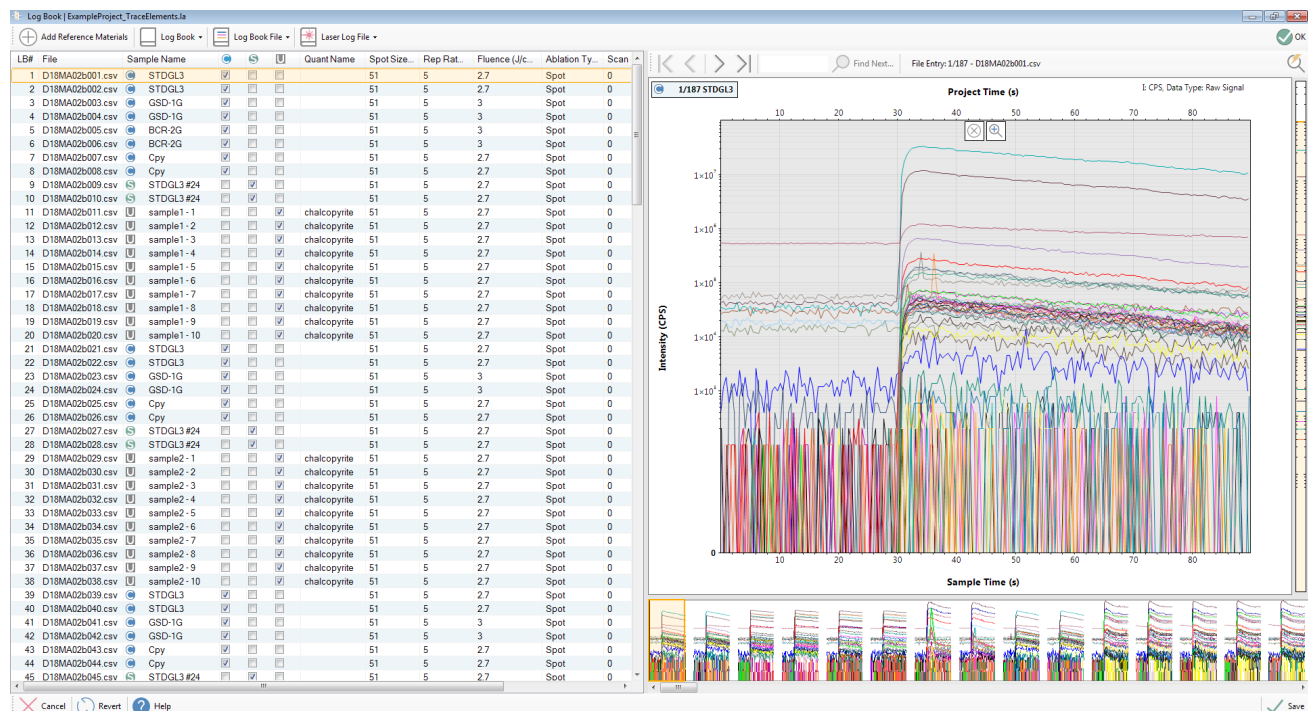
Figure 22: Default appearance of the Logbook form when loaded files contain a single Measurement and a single ablation.

The logbook table contains extra columns which can be made visible, and most of the columns shown by default can be made invisible. To change the appearance of the table right-click anywhere on the headings row and select the columns as required (Figure 23).

Figure 24 presents the default appearance of the Logbook form for the case when each file contains several measurements (e.g., Analytik Jena and X-series II store data in this format; see "File Loading" on page 52). When such data file(s) are loaded, LADR automatically assigns each measurement to a sample. Sample names are assigned as measurement names identified in the data file(s).

To generate a valid LogBook, a Calibration RM type needs to be assigned to at least one sample. Press the "Add Reference Materials" button at the top-left corner of the form to bring up the Reference Material Manager form. Select the required RM(s) in the Profile shown in the left side of the form. Selection can be made using conventional Windows selection paradigm, such as CTRL+click to select multiple items. Press "Copy to Project" button in the central part of the form to copy the selected RM(s) into the Project. Click Save (bottom right corner of the form) to save changes and close the form.

Figure 23: Pop-up window to change the appearance of the LogBook table. To activate the pop-up, right-click anywhere within the heading row of the LogBook table. Click anywhere outside the pop-up to implement changes and close it.
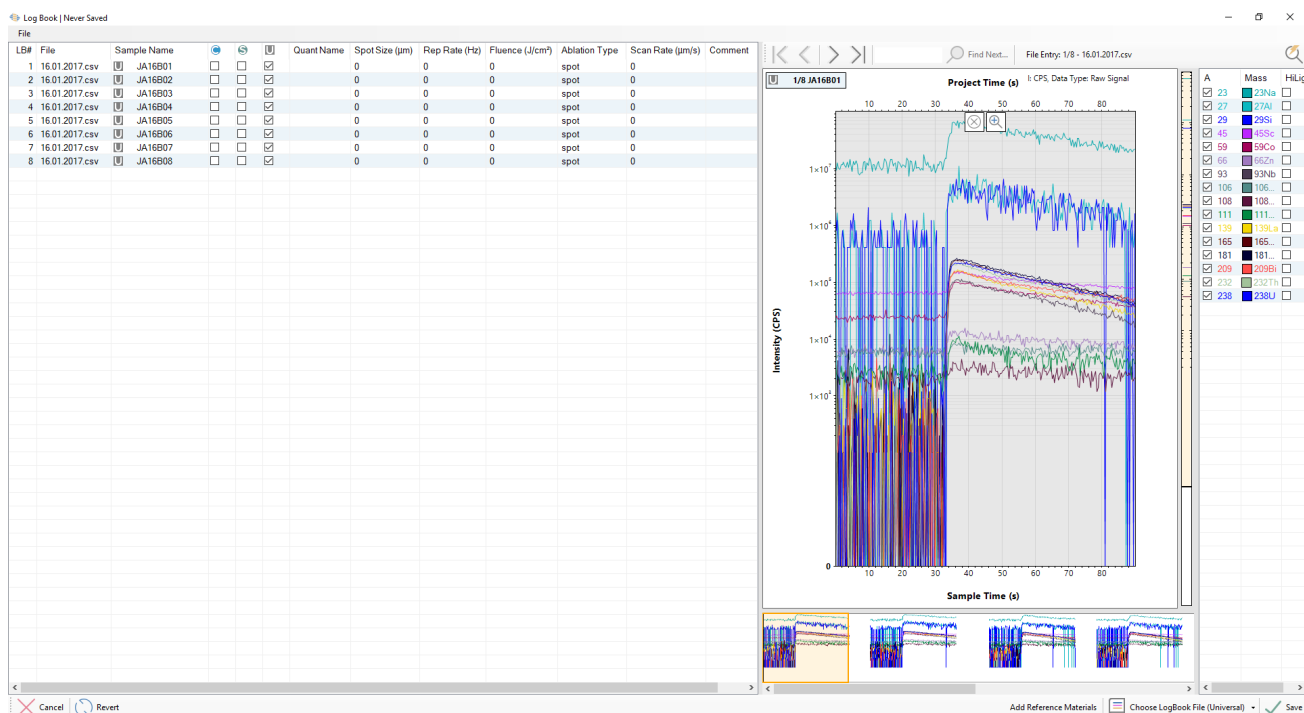
Figure 24: Default appearance of the LogBook form when loaded files contain multiple single measurements and a single ablation in each measurement.
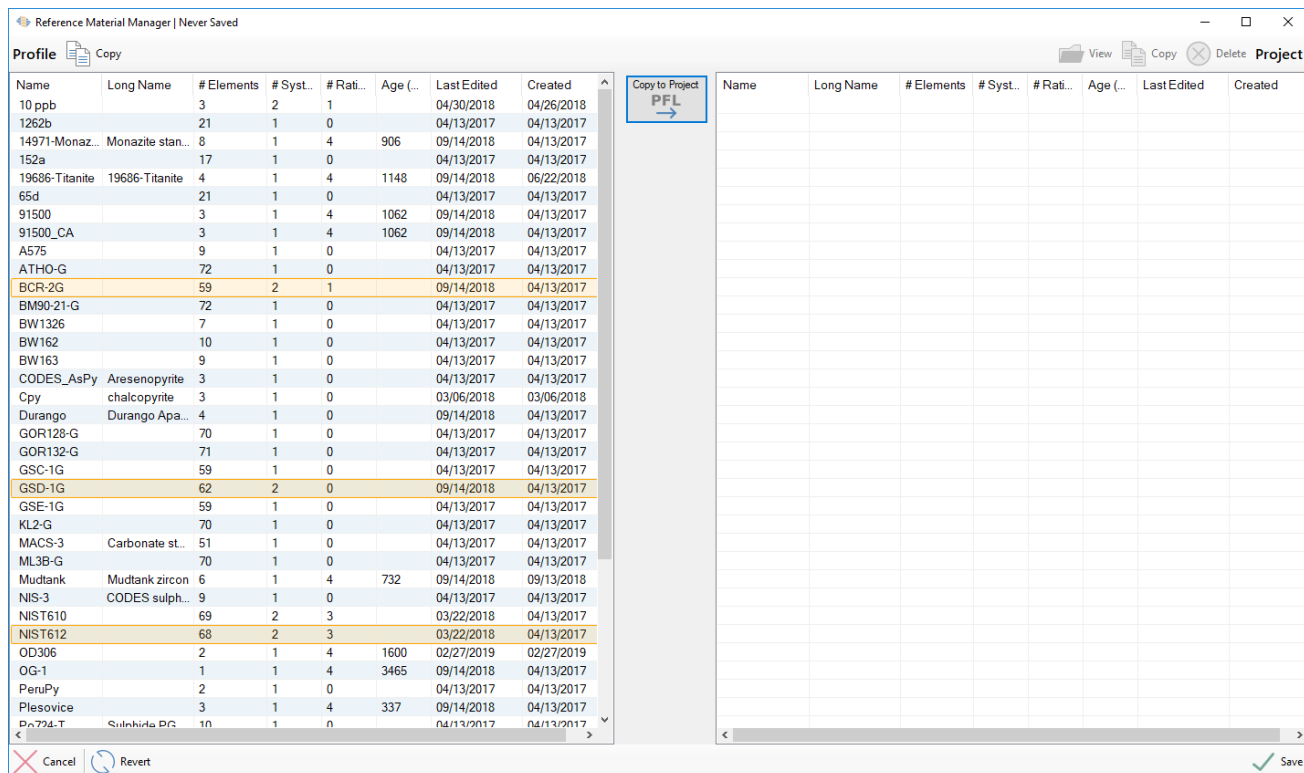
Figure 25: The Reference Material Manager form used to bring required RMs from the profile to the project.

Now click on the 'C' checkbox for the sample which corresponds to ablation of the selected Calibration RM(s). If more than one reference material is present in the project then a pop-up form will appear (Figure 26). Click on the "RM" drop-down list to select the required RM and click "Save". The name of the selected sample is changed to the name of the chosen RM, the icon of the 'Sample Name' field changed to 'C' and the 'C' check box has been checked. Enter the laser conditions used when analysing this RM (Figure 27).

Note: To reverse the selection, click on the 'U' check box and the type for the sample will be changed back to unknown and the original sample name will be restored.
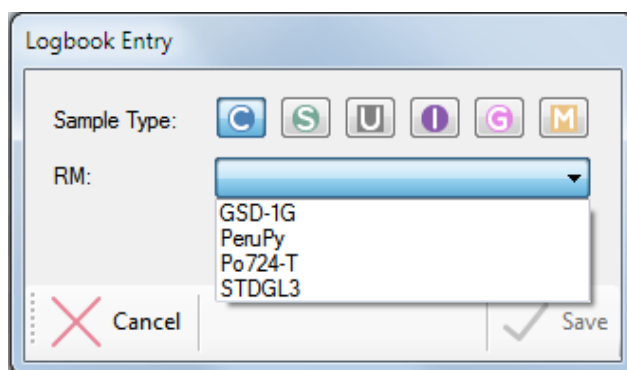
Figure 26: Pop-up form to assign the appropriate RM to a Calibration RM sample in the LogBook. The same form is used to assign RMs to Secondary RM samples.

To assign the same RM to other samples in the project, either repeat the steps above, or select all relevant samples using standard Windows selection paradigms (SHIFT+click or CTRL+click), including the one already edited, and right-click on one of the selected samples. A pop-up menu will appear. Click on the "Fill down (To Selected Rows)" item and choose "Everything". The change made to the first sample will be made to all selected samples (Figure 28).

Repeat the same steps to assign other RMs as required, and also laser conditions, sample names and QSs to the rest of the table (Figure 28). Note that for many (but not all) projects the laser conditions will be constant throughout. To easily fill these in: add the laser conditions to the top row of the table, use CTRL+A to select all of the rows, right-click to bring up the context menu, and use the "Fill Down"→"Laser Conditions" to complete the table.

Once the Logbook table is complete, click the "save" button at the bottom right of the form to save changes. It is recommended to save the project after the LogBook has been completed.

If QSs assigned in the logbook to samples have been previously defined and stored in the profile, they will be automatically copied into the project from the profile on saving the LogBook, providing the loaded data conforms to the definitions of the QSs stored in the profile (refer to the "Quantification Setup" chapter on page 83 for details).
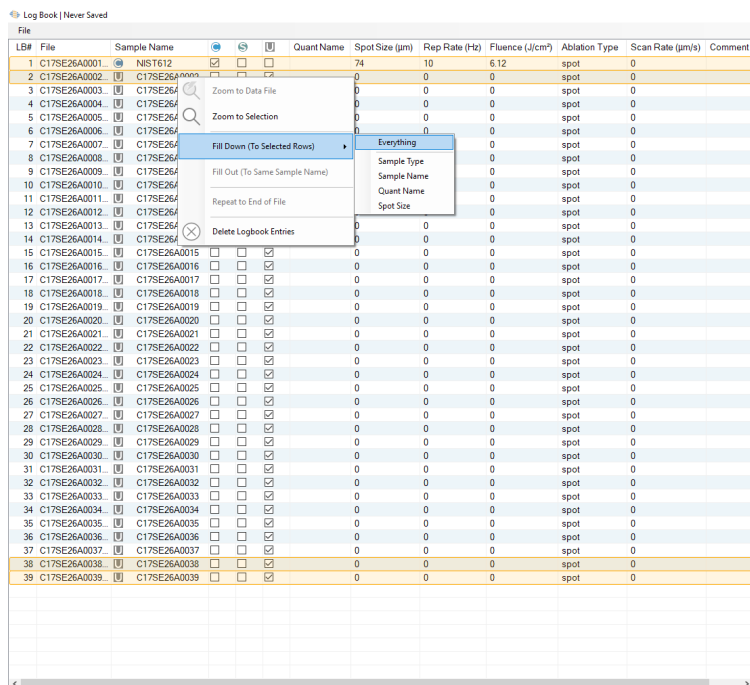
Figure 27: LogBook table menu options for copying parameters defined on one sample to other selected samples.
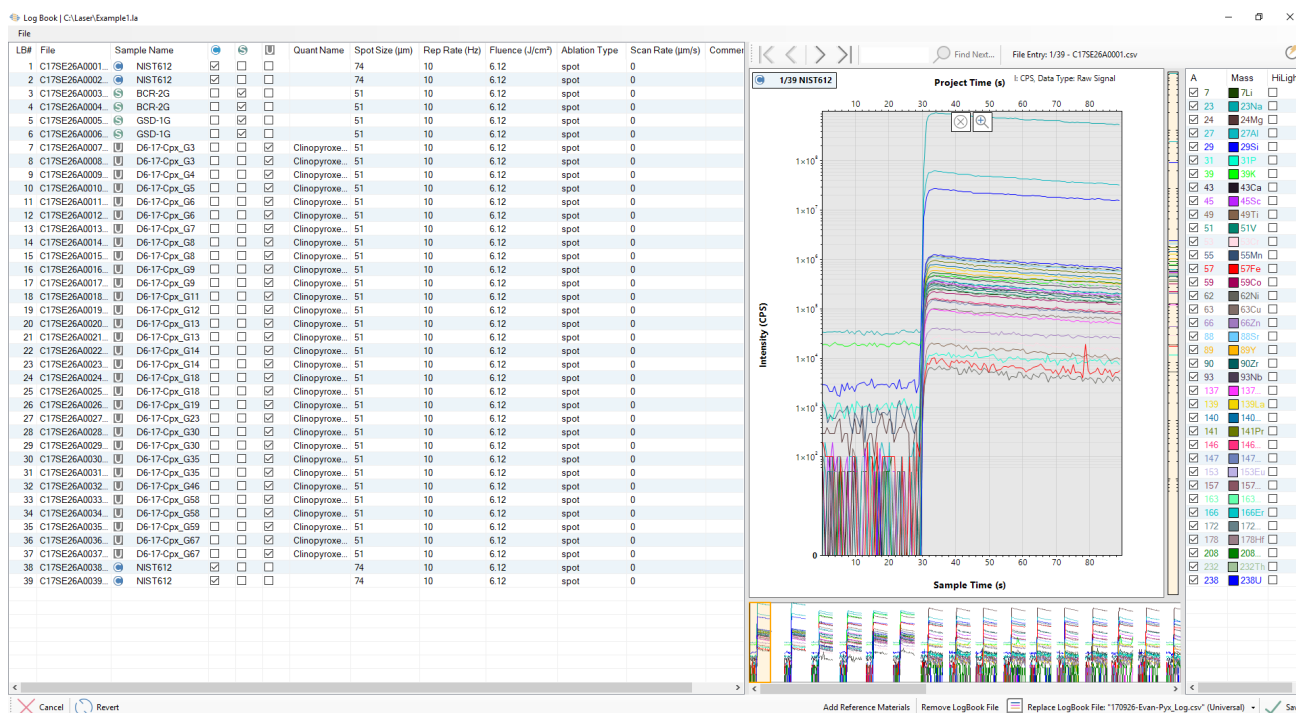
Figure 28: An example of a complete and valid logbook.

LADR offer options for automating LogBook generation by importing a LogBook File.

Data Acquired in a Single Measurement

Note: It is recommended to read the previous section of the manual even if it does not describe how the imported data were recorded.

When data are acquired in a single continuous mass-spectrometer file, or measurement, LADR does not populate the LogBook, and the LogBook table remains empty (Figure 29).

To facilitate populating the LogBook table, zoom in on the first few ablations in the project by holding the ALT key and dragging over a rectangular area on the time-resolved plot to define a region to enlarge (Figure 29). The enlarged part of the project is shown on Figure 31. To define samples corresponding to ablations of RMs and unknowns, click on the time-resolved plot at a time corresponding to the start time of a sample and drag over the time period corresponding to this sample, then release the mouse. A new sample entry will appear in the LogBook table (Figure 31). This action can be repeated to select additional samples (Figure 31). All samples created in this way will have the same default name "New Sample" and will be assigned the unknown sample type.

To delete a sample from the LogBook either press the cross icon shown in the middle of the time period as shown on the time-resolved plot, or right-click on the sample in the logbook table and select "Delete Logbook Entries" from the menu.
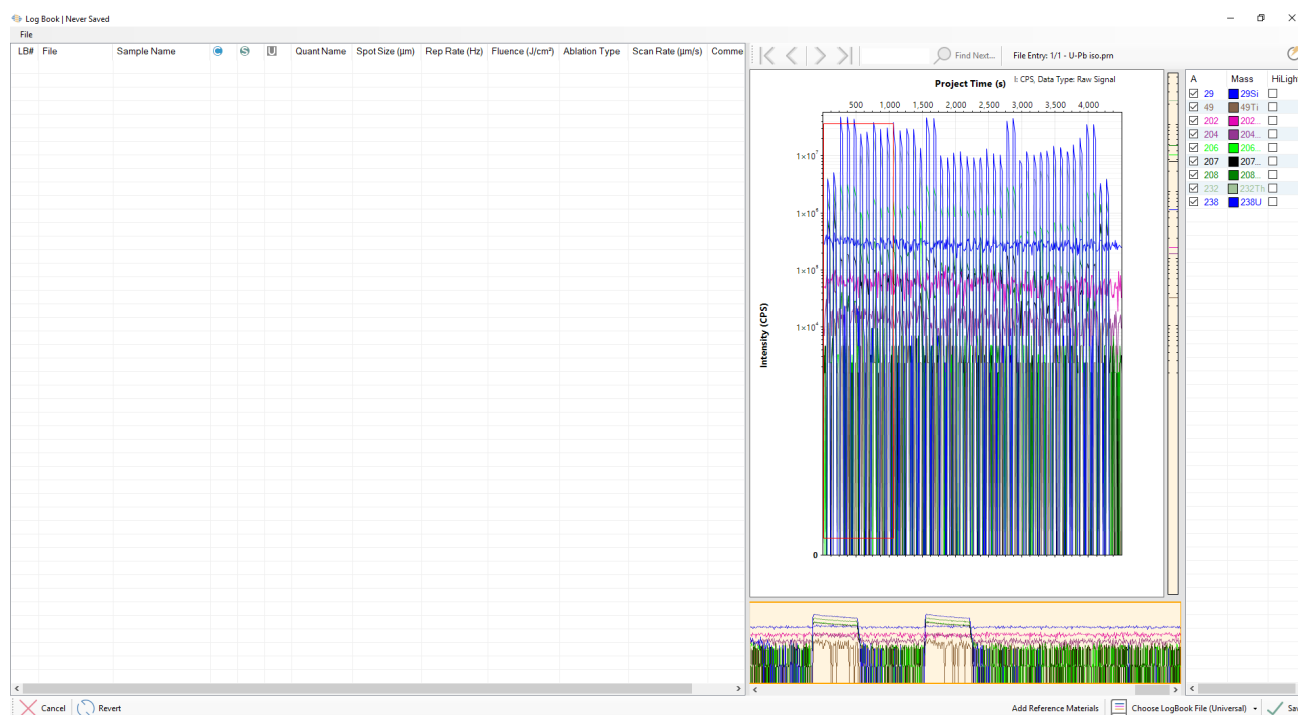
Figure 29: The appearance of the logbook when loaded data were all recorded in a single measurement on the mass-spectrometer. The red rectangle on the time-resolved plot shows the area which the plot will zoom to, as shown on Figure 31.

To facilitate accurate selection and editing of time periods assigned to samples, LADR allows zooming in to a single sample: right-click on the row in the logbook table corresponding to the sample being adjusted, and choose "Zoom to Sample" from the menu. The time resolved plot will zoom to show the selected sample (Figure 32). Adjust the duration of the sample by dragging the start and end times to the desired position (Figure 33).

To select other samples when zoomed in to a single ablation, slide the scroll bar at the bottom of the time-resolved plot section of the form. It is also possible to expand the shown part of the project to include several ablations by adjusting the length of the orange area in the bottom section of the time-resolved plot section of the form.

It is also possible to move the chart by either holding down the space bar and dragging with the left mouse button, or to click and drag with the middle mouse button if your mouse has one.

LADR offers additional tools for defining the logbook for continuously acquired data, all of which are accessed using the right-click "Modify" sub-menu (see Figure 30).
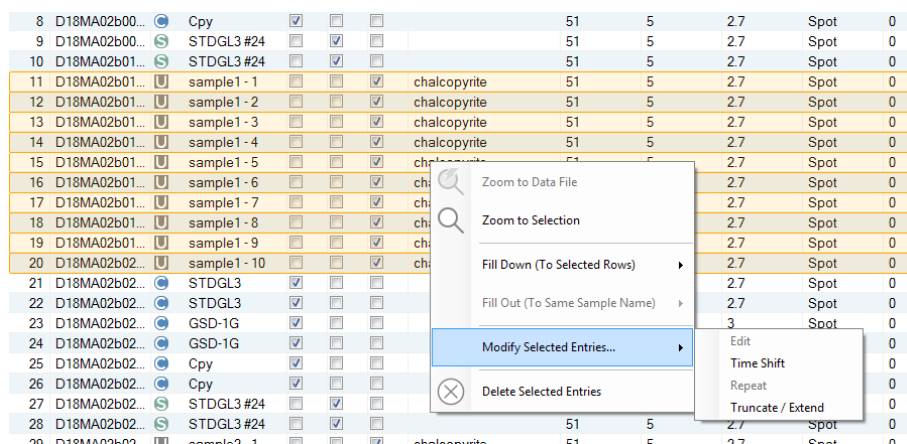
Figure 30: The "Modify" sub menu for editing LogBook entries.

Edit

With a single sample selected, the Edit window allows the start and end times, and/or the duration to be edited using absolute project time, or time relative to the source data file.

Time Shift

With one or more samples selected, the Time Shift window allows them to be moved forwards or backwards in time by the specified amount.

Repeat

With a single sample selected, the Repeat window has options for how the sample should be repeated, including the addition of a gap (e.g. for washout or pre-ablation) if desired.

Truncate / Extend

With one or more samples selected, the Truncate / Extend window allows the start and/or end times of the samples to be modified by the specified amounts.

Please note that editing samples using these controls can create invalid samples that fall outside the time periods of the source data files. If this occurs, an additional column will appear automatically in the table showing those samples which are invalid. There is also an indicator at the top-right showing the overall validity of the samples in the LogBook. The user is encouraged to rectify these issues manually before clicking Save, however, once Save is clicked any invalid samples will be truncated to the time periods defined by the source data files.
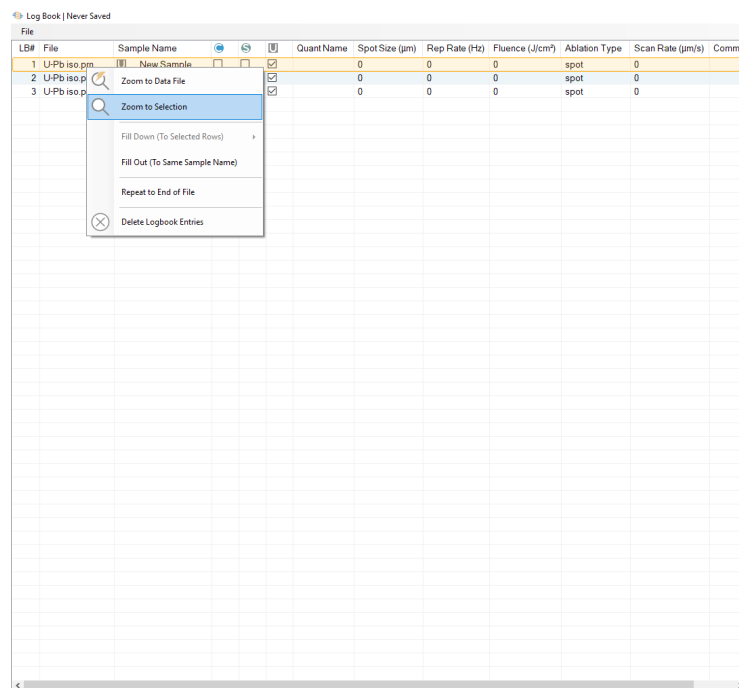
Figure 31: The appearance of the Logbook form showing a zoomed in view of the data, corresponding to the red rectangle on Figure 29. Also shown are three samples selected manually over three different ablations and the right-click context menu which allows the chart to zoom to a sample of interest.
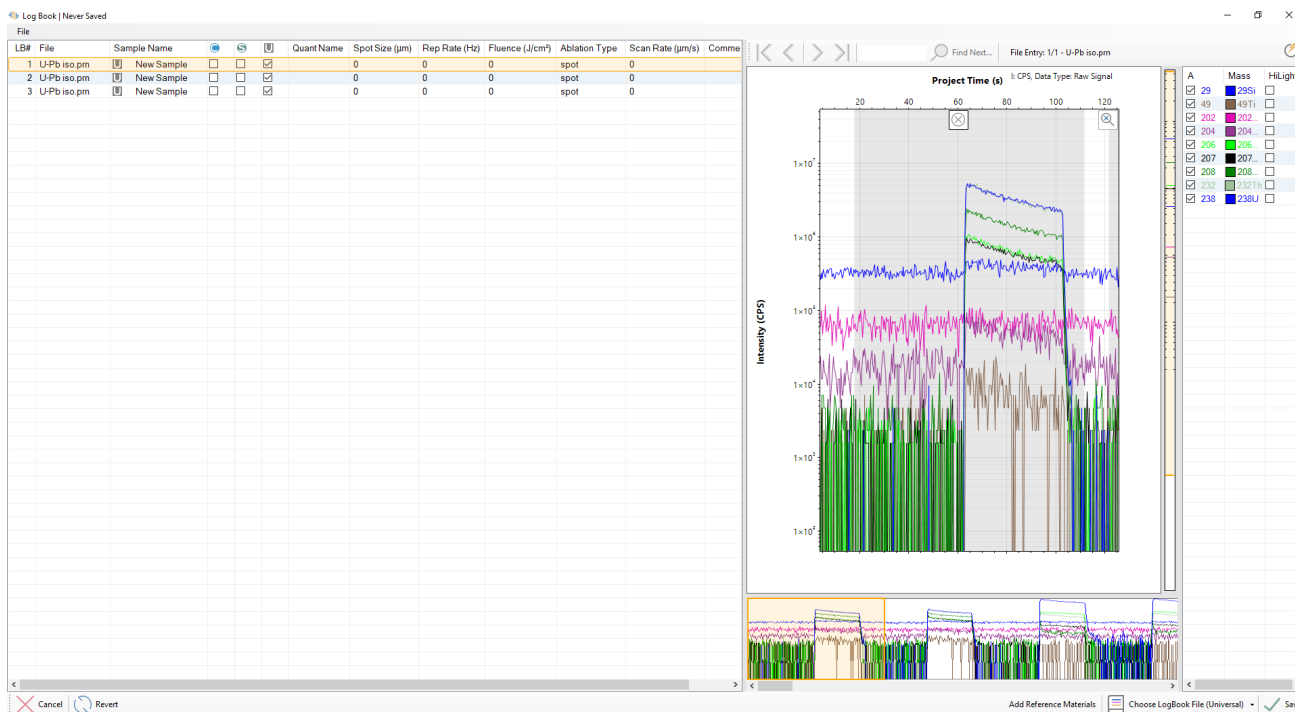
Figure 32: The result of zooming to the selected sample on Figure 25. The time period of the sample can be adjusted by dragging the left and right edges of the sample as desired.
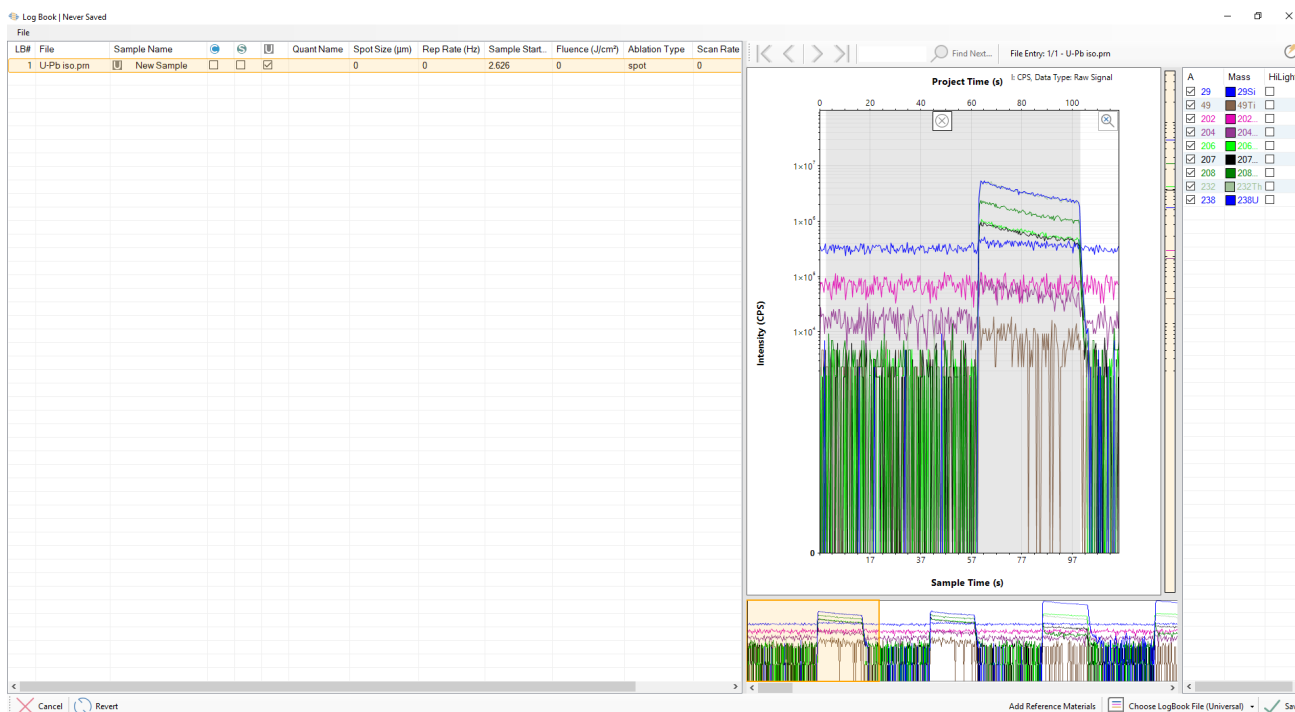
Figure 33: Edited start and end times of the sample shown on Figure 26. The end of the sample has been chosen to coincide with the end of the ablation, and the start of the sample has been chosen to include approximately 60 seconds of gas blank signal.
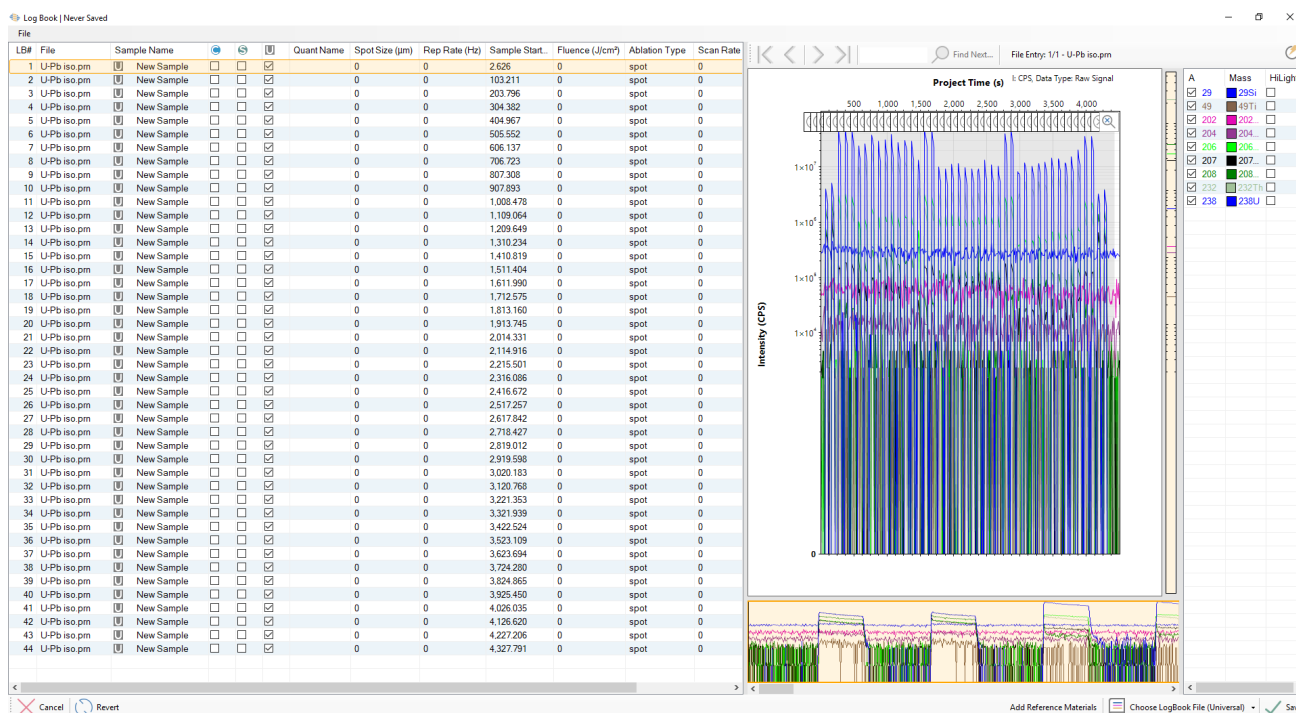
Figure 34: An example logbook generated for the entire project by repeating the sample to the end of the data file.

Once the LogBook table is complete, sample types, laser conditions and QS names can be assigned manually in the same way as described in the preceding sections.

Loading a Laser Log File

The commands to use a Laser Log File to set up the LogBook are accessed from the Laser Log File menu (see Figure "21"). Additional Laser Log File formats will be added here on request.

The use of a Laser Log File still falls under the "Manual" LogBook setup since these files do not contain all of the information required to fully populate the LogBook. See the "Automatically Creating a Valid LogBook" section for a description of how to entirely automate this step.

Be aware that when setting up samples on a single data file using a Laser Log File there will always be an initial offset present, since the Laser Log File does not contain information about when the mass spectrometer was started. To remove this offset, use the chart to determine how long the offset is, then select all samples (CTRL+A) and use the "Modify" sub-menu to "Time Shift" the samples by the required amount. Depending on how long the mass spectrometer collected data for, it is common for the final entry (or multiple entries if the mass spectrometer stopped to early) to overflow

the measured data. Clicking "Save" will truncate the invalid entries to the time span of the data file.

Automatically Creating a Valid LogBook

LADR provides automated generation of the LogBook through loading of a LogBook File.

In the current version of LADR the automatic logbook generation is supported for the cases when data were acquired as either separate mass-spectrometer files or measurements for each ablation.

If measuring data in a single continuous file, then review the "Loading a Laser Log File" section for a workflow supporting partial automation of LogBook creation.

Note: There are plans to fully automate LogBook creation with this style of data collection, and if this is of interest to you then please let us know.

The structure of the Universal LogBook File is described in "Appendix B – Universal Log Book Format" on page 210.

When data files are loaded that use a separate mass-spectrometer file for each ablation, the "DataIdent" column in the LogBook File must correspond to the file name of the corresponding data file.

When data files are loaded that contain multiple measurements, with each containing a single ablation, then the "DataIdent" column in the logbook file must correspond to the measurement name recorded in the mass-spectrometer file. If no measurement name is supported by the file format then the entry index should be used as the "DataIdent" value.

The LogBook File can be specified during data file loading ("Logbook File Import" on page 62). Alternatively, the LogBook File can be loaded from within the LogBook window by clicking on the "Choose LogBook File" button in the drop-down menu.

When the LogBook File is processed, the file contains sufficient information to fully populate the LADR LogBook, and in most cases it will not be necessary to perform and editing using the LogBook window.

The most common issue encountered when using the LogBook File is the matching of reference material names to the reference materials stored in the LADR profile. The following pointers may be of some assistance:

- Ideally, name the sample in the LogBook File the same as the reference material name in the LADR profile.

- Be consistent with naming, however use of the "aliases" field in the LADR reference materials editor provides additional flexibility. This can be used to provide a comma separated list of aliases to match against, for example: "SRM610, NIST610, 610".

- If a typo is present in the LogBook File then the RM will most certainly not match. The best way to correct this issue is to fix the root problem and to edit the LogBook File accordingly. This could involve going back to GeoStar (for example) and editing and exporting the LogBook File a second time, or, simply opening the LogBook File in a text editor and editing it directly.

- The default behaviour is to perform strict matching of the RM names. This will, however, not work for sample entries given numbering prefixes or suffixes (for GeoStar users see "Automatic Numbering" in the GeoStar software manual), such as "NIST610 – 1", "NIST610 – 2", "NIST610 – 3", etc… In this case, if there remains a good reason to number reference materials in this way, then you need to change the RM matching from "strict" to "loose". Do this using the Options (see "Appendix A – Options") and change the profile option: "Profile.LogBookMatchForRMs". Be careful when using "loose" matching as it can cause unwanted behaviour if RM aliases or names are quite short.

- If the RM name does not match in any way. For example, suppose the user called a sample "NIST612" by mistake when actually they ablated "NIST610". The preferred way to fix this is to edit the LogBook File with a text editor since it is very quick to perform a find/replace on these labels. However, the other way is to use the "Fill Out" option in the LogBook form. Take the first entry in the table and assign the correct RM (as well as any other properties that need to be edited) then select the sample, right click, and choose "Fill Out". This will match against both the newly assigned RM name (to continue the example, "NIST610") as well as the old sample name (e.g. "NIST612"), completing the LogBook setup with ease.

Quantification Setup

Introduction

LADR is designed to facilitate planning of analytical sessions to include analyses of different matrices[8] using matrix-specific analytical conditions, which can then be processed simultaneously. Within LADR this is implemented through the concept of Quantification Setups (QSs) which store parameters for defining data processing schemes applied to the raw data to produce analytical results. Multiple QSs can be used in a single project and the same analysis can be quantified using different QSs.

The current version of LADR allows for the following three data processing schemes within a single QS, all of which can be applied simultaneously to the same data:

- Quantification of elemental concentrations ("Trace Elements" scheme);

- U–Th–Pb geochronology ("UPb Dating" scheme);

- Quantification of arbitrary isotope ratios ("Quantified Ratios" scheme).

LADR allows for interference corrections to be applied during calculations. Defining an interference correction involves specification of the interfered mass, the interfering mass, and the interference production rate, and requires that the intensities of both the interfered and interfering masses have been measured during the analytical session.

LADR also allows for mass substitutions (called "Filtering"). These can be used when more than one isotope is measured during the analytical session and are aimed at avoiding signal intensities which are above a specified threshold. They involve substituting the measured signal of the more abundant isotope with the signal calculated based on the less abundant isotope, using the known isotopic proportions. When enabled, substitutions apply to each data processing scheme. In the current version of LADR this option is limited to substituting 238U counts with counts calculated from U235, and is used to automatically discard 238U counts that were measured in the analogue region of the detector.

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8   *Matrix* is used here in a very general sense to refer to the both the structure and composition of the material being analysed.

Because LADR provides a great deal of flexibility when designing application-specific quantification procedures there may be a tendency for users to turn on certain options because "LADR can do it". While LADR will do as much as it can to assist you, the software will not always prevent you from choosing options that will result in poor quantification. As such, users are encouraged to refer to published best practices to inform decisions.

Once defined, QSs can be saved to the profile to be reused for data reduction in the future.

Note: Storing QSs in the profile is recommended when it is expected that data acquisition will be repeated using the same analytical method.

Trace Elements Scheme

The trace elements quantification scheme allows for a single set of ICP–MS calibrations to be used for quantification of different matrices analysed using different laser conditions (refer to the "LogBook" chapter on page 63 for a description of laser conditions).

This is achieved through the concepts of "secondary standard corrections" and matrix- and element-specific correction factors ("matrix-mismatch factors"). This approach allows for choosing reference materials (RMs) for calibrations based on the range of certified elements available in the RMs, and their concentration levels, rather than based on matrix matching between the RMs and the unknowns.

LADR allows for an unlimited number of calibration RMs to be used for quantification of a single analysis. At one extreme a single RM is used for all masses, but at the other it is possible to quantify every element using a different RM, providing that all RMs have been analysed during the analytical session at least once. Not only does LADR make this possible, but the software has been designed to intrinsically support this feature.

LADR allows for an unlimited number of internal standard elements (ISs) to be used for quantification of a single analysis. As for RMs, at one extreme a single IS can be used for all masses, but at the other it is possible to quantify every element using a different IS, providing that the concentrations of all ISs in the sample are defined by the user for each sample being quantified using the QS. Of course the astute reader will notice that

the extreme case of using every mass as an IS for every other mass is useless and would negate the entire point of performing the analysis.

LADR allows for quantification to a specified sum of concentrations of all analysed elements ("analytical total"), instead of providing concentrations for the ISs. This quantification to an "analytical total" feature requires that only one IS mass is specified in the trace elements scheme in the QS, but no concentration is required for the associated element in the analysis.

LADR allows for reporting of concentrations either in the form of elemental concentrations or in the form of compound concentrations. In the current version of LADR the following compound anions are defined: O_2^-, S_2^-, S^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, SiO_4^{4-}, As^-, $(SAs)^{2-}$, Cl^-, F^-. These anions can be combined with measured values using arbitrary stoichiometry, and there is also support for substitutions: for example As and Se substituting for S in sulfide minerals.

LADR allows for the concentrations computed using the calibrations defined on calibration RMs ('primary calibrations') to be adjusted based on the analyses of 'secondary RMs' (refer to the "LogBook" chapter for a description of different sample types supported by LADR). This approach is illustrated by the following example:

Example: *During an analytical session the same matrix (e.g., the same material, mineral type, etc.) was analysed in the 'Spot Mode' (refer to the "LogBook" chapter for a description of different analytical modes supported by LADR) using a range of laser beam sizes ("spot sizes"). Such an approach may be needed when analysing samples with different grain sizes from the matrix of interest so as to avoid using the smallest spot size on all grains. The well-known spot size dependence of the extent of elemental fractionation during LA–ICP–MS would require that analyses performed at different spot sizes are quantified using different calibrations. LADR offers an approach to quantification which allows for all such analyses to be quantified on a single "primary calibration" defined using a single spot size, providing that that the secondary RMs have been*

| Conventional | Problematic | LADR |

Primary standard measured using large spot size to produce good counting statistics for all masses.

PRIMARY

PRIMARY

PRIMARY

Limited to same size spots on the primary standard and the unknown.

Using a different spot size on the unknown will affect the results for some elements.

Secondary standard measured using same spot size as unknown; the matrix correction factor is applied to the primary calibration.

SECONDARY

UNKNOWN

UNKNOWN

UNKNOWN

Unknown measured with spot size appropriate for the material and application.

Figure 35: Use of secondary standards to compute matrix correction factors.

UPb Dating Scheme

The UPb dating quantification scheme allows for using the U-Th-Pb system to produce an estimate of the age of the analysed sample using a common geochronological approach[9]. The current version of LADR provides graphical tools for identification of analyses affected by mixing with common Pb and also Pb loss, such as concordia diagrams and time-resolved graphs of 206Pb/238U, 207Pb/206Pb, 208Pb/206Pb and 208Pb/232Th values during an analysis, however no tools for performing common Pb corrections are currently available.

To enable the UPb dating quantification scheme it is required that masses 206Pb and 238U are present in the analytical method and that a calibration RM with a known age is analysed at least once during the loaded analytical session. In practice it is recommended that the following masses are also present in the analytical method: 202Hg, 204Pb, 206Pb, 207Pb, 208Pb, 232Th, 235U, 238U.

Note: A correction for the isobaric interference of 204Hg on 204Pb can be applied during quantification, providing that 202Hg was included in the analytical method.

LADR allows for automatic matching of samples and unknowns analysed at the same laser conditions by using matching masks. Given the well-known impact of analytical conditions on the UPb values, it is strongly recommended that all masking parameters are applied.

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9   For more information (or if UPb geochronology by LA–ICP–MS is new to you) then the following references are a good place to **start**:

- Davis, Donald W., Thomas E. Krogh, and Ian S. Williams. "Historical development of zircon geochronology." *Reviews in mineralogy and geochemistry* 53.1 (2003): 145-181.

- Gehrels, George E., Victor A. Valencia, and Joaquin Ruiz. "Enhanced precision, accuracy, efficiency, and spatial resolution of U-Pb ages by laser ablation–multicollector–inductively coupled plasma–mass spectrometry." *Geochemistry, Geophysics, Geosystems* 9.3 (2008).

- Solari, Luigi A., et al. "U-Pb zircon geochronology with an integrated LA-ICP-MS microanalytical workstation: Achievements in precision and accuracy." *Geostandards and Geoanalytical Research* 34.1 (2010): 5-18.

- McFarlane, Chris RM, and Yan Luo. "UPb geochronology using 193 nm excimer LA-ICP-MS optimized for in-situ accessory mineral dating in thin sections." *Geoscience Canada* 39.3 (2012).

Note: When matching masks are enabled, only those unknowns which match the analytical conditions used for the primary calibration(s) will be processed.

To facilitate selection of shorter integration time periods on the unknowns compared to the calibration RMs, LADR allows for down-hole fractionation correction to be automatically applied to any of the measured ratios. Use of down-hole correction requires laser times to be defined on the project.

Note: Application of the down-hole fractionation correction restricts the time spans on the unknowns to fall within the time spans selected on the calibration RMs, all relative to the laser aerosol arrival time.

LADR allow for excess uncertainty to be added to each of the quantified ratios to compensate for any factors contributing to the total uncertainty budget which are not accounted for in the current implementation of the quantification scheme. Whether or not an excess uncertainty is required can be assessed using the following approach:

> When an RM with a defined isotope ratio is analysed multiple times within an analytical session, assessment of the need for, and size of the excess uncertainty, can be assessed by calculating the value of the MSWD[10] for the weighted average of all analyses of this RM within the session. The MSWD should be calculated using the "Within-run analytical precision" uncertainty values obtained during quantification (see the "Results" chapter for details on different levels of analytical uncertainty). If the obtained MSWD is > 1, this indicates that the reported "Within-run analytical precision" is too low, and excess uncertainty needs to be added to bring the MSWD closer to 1. An alternative approach, which can be used when MSWD calculations are not available, involves comparing the RSD[11] of the average of all RM analyses in the session to the average "Within-run analytical precision" of all RM analyses in the session. If the RSD of the average is larger, an excess uncertainty is required.

The UPb scheme can also be configured to remove common lead from measured values on reference materials. This is achieved by using the known age of the reference material to compute a radiogenic lead composition, and with a known common lead composition, the common lead component can be calculated and removed. There are

_____

10   Mean square weighted distribution (https://en.wikipedia.org/wiki/Reduced_chi-squared_statistic).

11   Relative standard deviation.

three ways to compute the common lead component, and three ways to define the common lead composition.

Quantified Ratios Scheme

The quantified ratios quantification scheme allows for quantification of ratios of any two isotopes, providing that at least one calibration RM with the known value for each ratio is analysed at least once during the project.

LADR allows for automatic matching of samples and unknowns analysed at the same laser conditions by using matching masks. Given the well-known impact of analytical conditions on the extent of down-hole fractionation, it is strongly recommended that matching masks are applied when isotopic ratios between different elements are being quantified (e.g., 85Rb/86Sr, 232Th/238U). Application of masks is much less critical for accurate quantification of isotopic ratios of the same element (e.g., 206Pb/204Pb).

Note: When matching masks are enabled, only those unknowns which match the analytical conditions used for the 'primary calibration(s)' will be processed.

Note: Interference corrections can be applied to any isotope involved in isotope ration quantification.

LADR allows for down-hole fractionation correction to be automatically applied to any of the measured ratios. Use of down-hole correction requires laser times to be defined on the project.

Note: Application of the down-hole fractionation correction restricts the time spans on the unknowns to fall within the time spans selected on the calibration RMs, all relative to the laser aerosol arrival time.

Validity of QS

QSs stored in the profile can be reused when the same analytical method has been used. Whether or not a stored QS can be used with the loaded data is determined by the following criteria:

1. All 'Calibration RMs' and 'Secondary RMs' used in the stored QS have been analysed in the analytical session being processed;

2. All masses defined as ISs in the QS have been measured in the analytical session being processed; and

3. All masses measured in the analytical session being processed are defined in the QS.

Note: Those data being processed can include fewer masses than those included in the saved QS, as long as all ISs defined in the QS have been measured in the analytical session being processed.

Interface

The QS form becomes accessible once a valid logbook is generated (see "LogBook" chapter for details on generating project Logbook). The QS form can be used to generate new QSs; to edit, copy or delete existing QSs, to copy QSs from the project into the current profile, and to bring valid QSs from the current profile into the current project.

To open the form press the "Quantification setup" button on the LADR main window.

If on logbook generation no QSs have been automatically copied from the User Profile into the Project, an empty QS form would appear (Figure 36, top-left panel).

If the profile contains valid QS(s) which can be imported into the current project, the "Profile Quant Setup(s) Available" label will appear within the top toolbar (Figure 36, bottom-left panel);

Note: When a valid QS(s) available in the User Profile have not been automatically brought into the project when a valid Logbook was saved, this indicates that the name of the QS(s) did not match the entries into the 'Quant Name' Column of the logbook.

When compatible QSs are available in the profile, mouse right click within the table in the left side of the form brings up a pop-up menu for copying QSs from the profile into the current project (Figure 36, bottom-right panel).
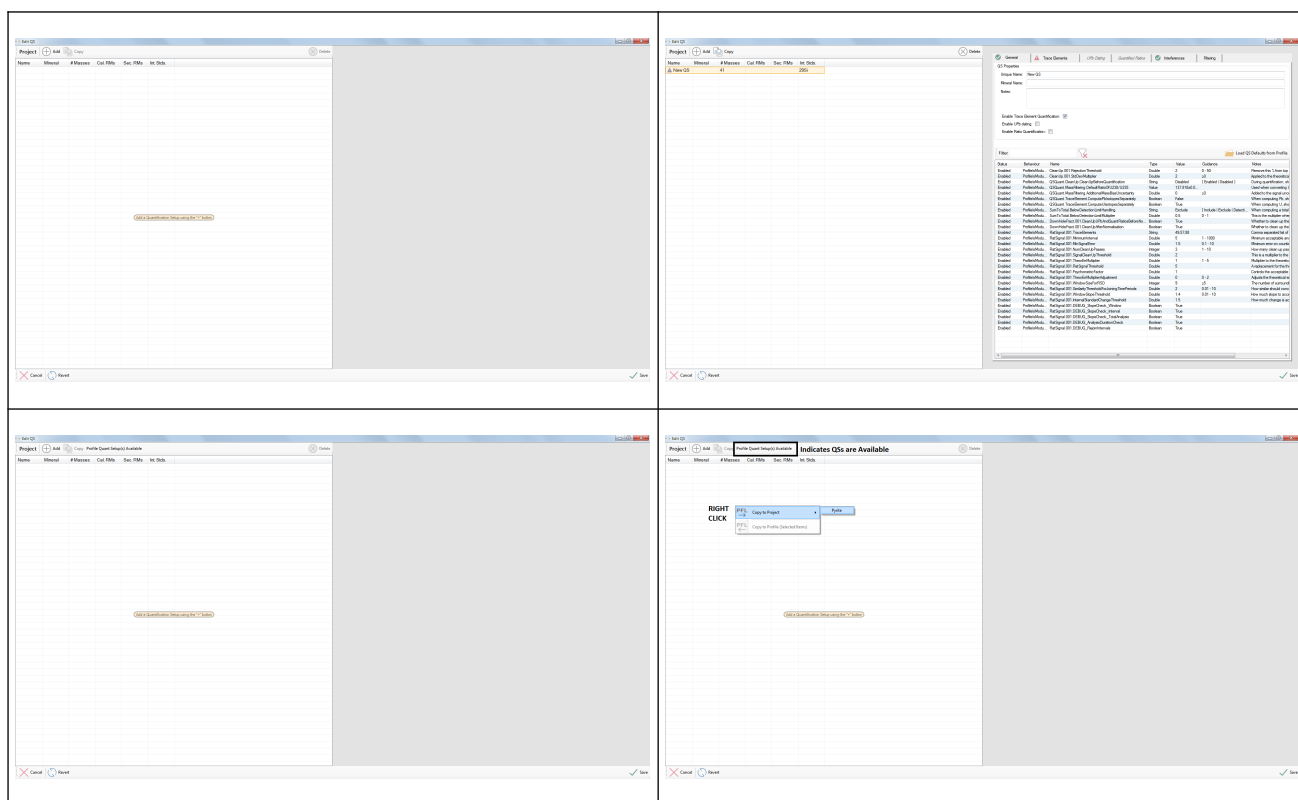
Figure 36: The appearance of the QS form when no QSs has been defined in the project.

Automatic Addition of QSs to the Project

When the logbook is created by a logbook file you can set the QS name (column header "QuantName") on each sample measurement, and if the name matches a QS in the profile then it will be added to the project automatically after logbook creation.

Creating and Editing QSs

Pressing the "Add" button on the top panel of the form will generate a default new QS (Figure 36, top-right panel). The new QS will have only the trace elements quantification scheme enabled, and one of the isotopes would be assigned as an IS by default, but is probably unsuitable for the application. As such, the default QS is not yet complete, and requires user input to set it up as a valid, and useful, QS.

Note: It is also possible to add a new QS to the Project using the "Manage Quantification Setups" window, shown by using profile down menu from the main LADR window.

Once a valid QS is configured, it can be saved to the profile for future use by right clicking on it in the list of QSs and choosing "Save to Profile".
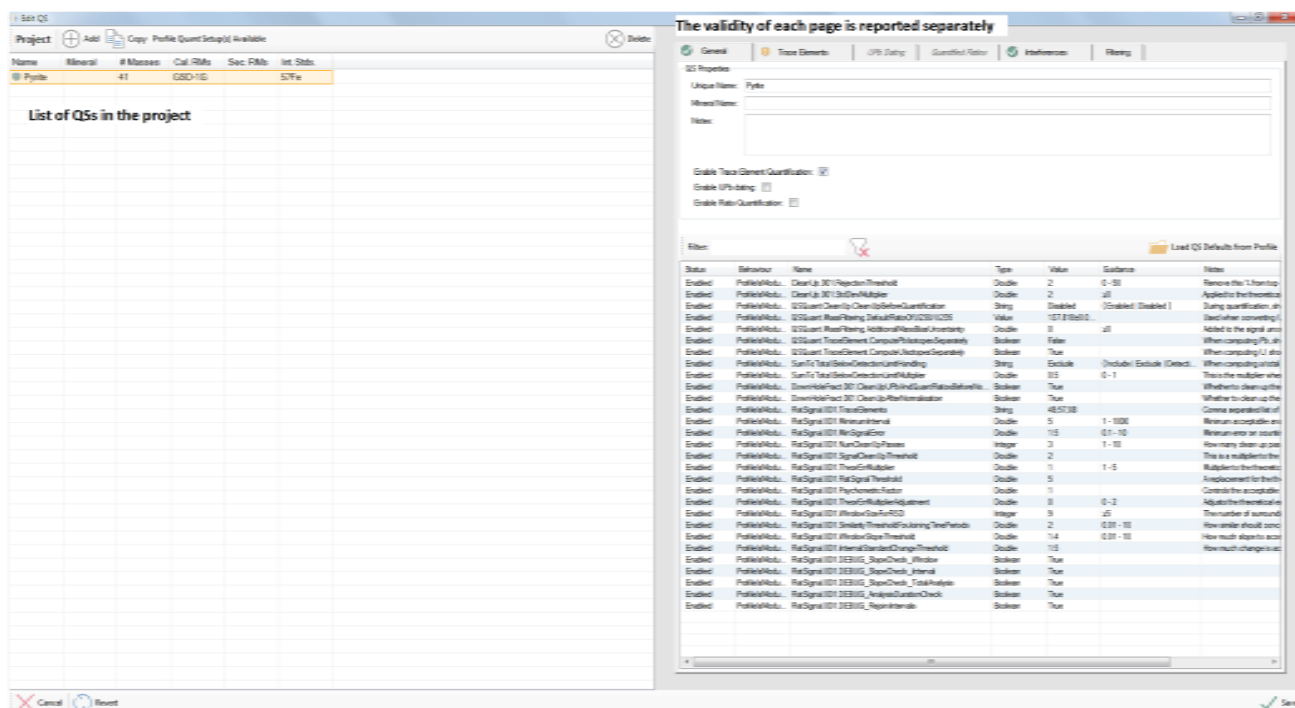
Figure 37 Editing a QS.

It is possible to create a project containing multiple QSs. This is useful if, for example, multiple minerals were analysed, and a single analytical method would not apply to all materials. If there are multiple QSs, the corresponding QS must be defined for each analysis in the "analysis log" window.

The different tabs in the "Edit QS" view show different configuration options:

- "General" for overall QS information, and advanced options.

- "Trace Elements" for setting individual-mass quantification options for trace elements.

- "UPb Dating" for setting the options for each UPb ratio.

- "Quantified Ratios" for setting up isotopic ratio quantification.

- "Interferences" for setting mass interference correction expressions.

QS Settings – General

The unique QS name can be set and will need to match the QS in imported logbooks for the QS to be automatically uploaded to a future project. The mineral name and notes are included to aid the user to keep track of multiple QSs.

If trying to name a QS to match another in the project, the edit will be rejected, or "_N", where "N" is the lowest number required to make the name unique, will be automatically appended to the end of the name.

To enabled different quantification schemes use the check boxes on the general page. This will make the different tabs enabled so the settings there can be modified.

Note: Trace elements are turned on by default.

Note: List of options on "General" tab will be discussed where they are applicable to the functionality of LADR.

Use the "Quant.PairingStrategy" in the options menu to change the method of internal standard production for each data point. The options are: "interpolate", "closest distance", "closest time", and "same sweep". The default value of "interpolate" is recommended for most applications.

QS Settings – Trace Elements

The trace element tab shows all of the relevant details about how to quantify trace element data. The minimum requirement to quantify trace elements is to set the internal standard (IS) element and assign a calibration RM to each mass.

There are two types of quantification available including:

1. Using an internal standard – An internal standard element is chosen for each mass analysed. The concentration of the internal standard element will be defined later (see Analysis Log, page 121).

   Note: In routine LA–ICP–MS analysis a single element is chosen for all masses, but this is not strictly necessary as users may choose to quantify elements by matching the element to an internal standard element with similar ablation characteristics.

2. Using normalisation to a total, with internal standard – An internal standard element is still defined for each mass, but it is not necessary to provide an internal standard element concentration. A total wt.% to normalise the masses to can be defined and negates the necessity for an externally measured IS concentration. The total will only apply to the measured cations in the sample unless anions or anion complexes are assigned to each cation (see "Element Stoichiometry" tab below.

Note: The normalisation with internal standard method should only be used if all major and minor elements are measured. If an element/component cannot be measured (for example, water in hydrous minerals) the total wt.% must be adjusted to account for the difference.

Note: Primary calibration standards and secondary standards are always quantified using the internal standard element value defined in the RM.

There are several options available for controlling how data below detection limit are used when calculating a total. The "SumToTotal.BelowDetectionLimitHandling" option allows the user to include the detection limit value, exclude the data point entirely from the total, or apply a below detection limit multiplier, to use, for example, half the detection limit. The "SumToTotal.BelowDetectionLimitMultiplier" option allows the user to change that multiplier if that was the chosen method in the previous option.

Group quantification by laser parameters is an optional step which is useful if laser parameters were modified during an analytical session. The details of spot size, repetition rate, fluence, type, and scan rate can be added to an imported log book file and this allows for quantification of samples run with different laser parameters (e.g. spot size) in the same laser session.

QS Settings – Trace Elements – Quantification

The quantification window allows the user to change the internal standard element, calibration standard, exclude elements from any calculated element total, and apply a matrix correction factor between standards and unknowns if this has been previously derived (Figure 38).
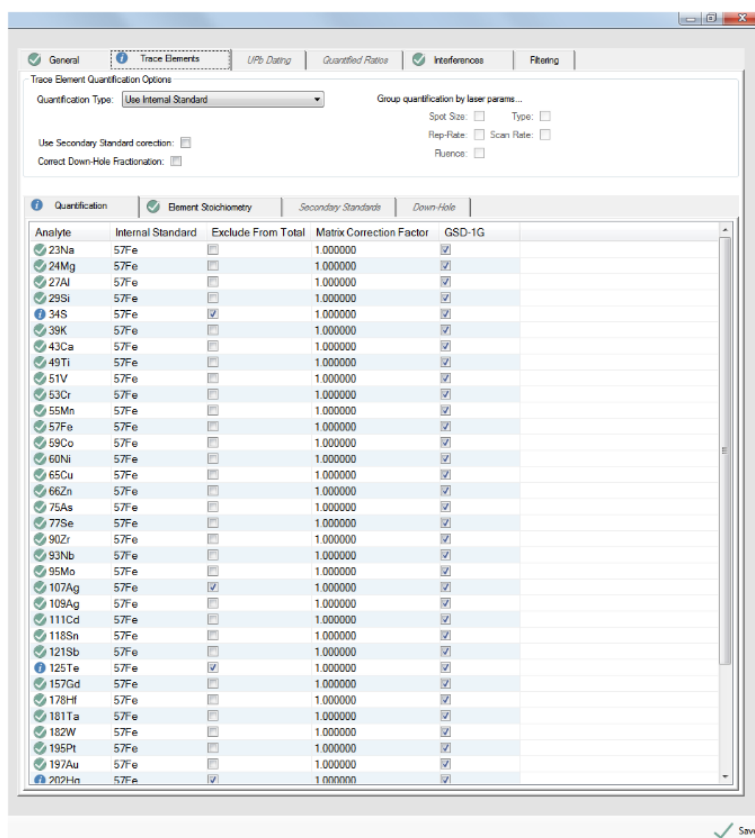
Figure 38 Quantification of trace elements window. The top portion of the screen is duplicated on all the lower tabs.

3. Analyte – An analyte is a mass corresponding to an element. This list is updated directly from the masses in the imported ICP–MS files.

4. Internal Standard – The internal standard is a mass chosen by the user. It is used to both normalise the count rate of the analyte, and to provide a known concentration in the unknown as a correction for varying ablation rates. In general, the internal standard element should:

   a. have a moderately high concentration in both the unknown and the calibration standard;

   b. have a relatively high count rate, since noise on the internal standard propagates to every analyte;

   c. not be subject to any spectral interference;

   d. be homogeneously distributed in the materials, and

e. not be readily affected by changing laser conditions;

f. have an externally measured concentration on the unknowns, which is input in the "Analysis Log" stage of the LADR workflow.

5. Exclude from total – The total is always computed, but will only be of interest when "Use Normalisation with Internal Standard" is selected, or the analyst wishes to export a meaningful total with the results. It is common practice to measure multiple isotopes for some elements, and when this occurs it is not logical to add the elemental concentration from each analyte to the total. Use this option to exclude an analyte from the total.

Note: Masses must be excluded if they are not present in the primary standard (e.g. 13C in NIST glasses), or if several isotopes of the same element are analysed (e.g. 206Pb, 207Pb, and 208Pb) unless the option to calculate isotopes independently has been checked (only applies to U and Pb isotopes).

6. Matrix correction factor – If a material and a RM have a consistent systematic offset in some or all masses, this factor allows the user to correct for this offset. This matrix correction factor is typically derived externally to the project and is laboratory specific.

7. Choice of calibration standard – Calibration standards are necessary to quantify the unknowns. Several calibration standards can be used in a QS, but only one can be applied to each element. Note: multi-standard calibrations will be made available to users in the near future.

When choosing a calibration standard important factors include the concentration of the elements in the standard, the potential for a mass interference which effects the standard more/less than the sample, homogeneity of an element in a standard, reliability of externally determined standard concentrations. While the choice of calibration standard falls well beyond the scope of this manual, users are encouraged to read the literature and engage the LA–ICP–MS community to ensure their analytical methods follow best practices.

Note: Every mass must be assigned to a calibration RM, even if you know the RM will not quantify the element. This is to ensure logical consistency throughout the software. Those masses not in the RM (see 13C in the example above) will be marked with a blue

information level notification to remind you that it will not be quantified, hover over the status indicators (anywhere) to see the status messages.

QS Settings – Trace Elements – Element Stoichiometry

The element stoichiometry tab is used to assign anions to cations with defined ratios. These cation/anion pairs will be normalised to the total, and shown in the results. When using the "Use Normalisation with Internal Standard" quantification type the stoichiometry page becomes essential for any samples other than metal alloys. However, it can also be used with the "Use Internal Standard" quantification type as the compounds will be shown in the result along with the analytical total.

No Stoichiometry

Analyte	Compound	Analyte/Compound Ratio	Formula
23Na			Na
24Mg			Mg
27Al			Al
29Si			Si
34S			S
39K			K
43Ca			Ca
49Ti			Ti
51V			V
53Cr			Cr
55Mn			Mn
57Fe			Fe
59Co			Co
60Ni			Ni
65Cu			Cu
66Zn			Zn
75As			As
77Se			Se
90Zr			Zr
93Nb			Nb
95Mo			Mo
107Ag			Ag
109Ag			Ag
111Cd			Cd
118Sn			Sn
121Sb			Sb
125Te			Te
157Gd			Gd
178Hf			Hf
181Ta			Ta
182W			W
195Pt			Pt
197Au			Au
202Hg			Hg

Monosulphides

Analyte	Compound	Analyte/Compound Ratio	Formula
23Na			Na
24Mg			Mg
27Al			Al
29Si			Si
34S			S
39K			K
43Ca			Ca
49Ti			Ti
51V			V
53Cr			Cr
55Mn			Mn
57Fe	(S,As,Se)	1.000	Fe(S,As,Se)
59Co	(S,As,Se)	1.000	Co(S,As,S...
60Ni	(S,As,Se)	1.000	Ni(S,As,Se)
65Cu	(S,As,Se)	1.000	Cu(S,As,Se)
66Zn	(S,As,Se)	1.000	Zn(S,As,Se)
75As	(S,As,Se)	-1.000	
77Se	(S,As,Se)	-1.000	
90Zr			Zr
93Nb			Nb
95Mo	(S,As,Se)	1.000	Mo(S,As,S...
107Ag	(S,As,Se)	2.000	Ag2(S,As,...
109Ag	(S,As,Se)	2.000	Ag2(S,As,...
111Cd	(S,As,Se)	1.000	Cd(S,As,S...
118Sn	(S,As,Se)	1.000	Sn(S,As,Se)
121Sb	(S,As,Se)	0.667	Sb2(S,As,...
125Te	(S,As,Se)	1.000	Te(S,As,S...
157Gd			Gd
178Hf			Hf
181Ta			Ta
182W	(S,As,Se)	0.500	W(S,As,S...
195Pt	(S,As,Se)	1.000	Pt(S,As,Se)
197Au	(S,As,Se)	2.000	Au2(S,As,...
202Hg	(S,As,Se)	1.000	Hg(S,As,S...

Oxides

Analyte	Compound	Analyte/Compound Ratio	Formula
23Na	O	2.000	Na2O
24Mg	O	1.000	MgO
27Al	O	0.667	Al2O3
29Si	O	0.500	SiO2
34S	O	0.333	SO3
39K	O	2.000	K2O
43Ca	O	1.000	CaO
49Ti	O	0.500	TiO2
51V	O	0.667	V2O3
53Cr	O	0.667	Cr2O3
55Mn	O	1.000	MnO
57Fe	O	1.000	FeO
59Co	O	1.000	CoO
60Ni	O	1.000	NiO
65Cu	O	2.000	Cu2O
66Zn	O	1.000	ZnO
75As	O	0.667	As2O3
77Se	O	0.333	SeO3
90Zr	O	0.500	ZrO2
93Nb	O	0.400	Nb2O5
95Mo	O	1.000	MoO
107Ag	O	2.000	Ag2O
109Ag	O	2.000	Ag2O
111Cd	O	1.000	CdO
118Sn	O	0.500	SnO2
121Sb	O	0.667	Sb2O3
125Te	O	1.000	TeO
157Gd	O	0.667	Gd2O3
178Hf	O	0.500	HfO2
181Ta	O	0.400	Ta2O5
182W	O	0.333	WO3
195Pt	O	2.000	Pt2O
197Au	O	2.000	Au2O
202Hg	O	2.000	Hg2O

Figure 39 The "Element Stoichiometry" page allows different stoichiometry values to be entered. The figure gives examples of a QS with no stoichiometry (left), monosulfide stoichiometry (middle), and oxide stoichiometry (right). Of course the stoichiometry chosen should match that in the sample.

For each mass in the project a compound can be selected. The ratio of the number of analytes to the number of compounds is added to the "analyte/compound" ratio (Figure 39). Analytes not predicted to be in the target unknown can be excluded from

the total calculation by leaving the compound blank. This may be useful if several masses are only analysed as monitors of mineral mixtures.

Options for compound anions are: O, S, SO_4, CO_3, PO_4, Cl, F, and SiO_4.

Note: Support for additional compounds can be added on request.

By right-clicking on the element stoichiometry window it is possible to fill down to:

- Set all masses to match this one – All masses will be set to the same compound and analyte/compound ratio as the mass selected.

- Fill down the top one selected to others selected – When multiple masses are highlighted the top mass will be filled down to the rest.

- Load defaults – Automatically set a compound and analyte/compound ratio for all sample(s) highlighted. Available compounds for this function are oxides, monosulfides, bisulfides, carbonates, and orthosilicates.

Note: The user must predict the oxidation states for certain elements (e.g. Fe) and this is best done using prior knowledge of the material (e.g. presence of Fe^{2+} instead of Fe^{3+} in olivine).

Note: Masses are greyed out in the element stoichiometry window if "exclude from total" option is selected in the quantification tab.

QS Settings – Trace Elements – Secondary Standards

Secondary standard corrections may be necessary when the primary standard does not have the same ablation characteristics as the unknown, or the calibration standard was analysed using different laser settings from the unknowns, see Figure 35. Secondary standard corrections are optional in LADR and are application specific. Figure 40 shows the secondary standard window.

To use secondary standard corrections the checkbox "Use Secondary Standard Corrections" (in the top section of the window) must be checked, and at least one secondary standard from the project must be assigned to at least one analyte in the table.

By default, measurement of secondary standards must match the laser conditions of the unknowns (spot size, laser fluence, etc...).

Note: Secondary standard choices must consider the concentration of the element in the standard, the potential for a mass interference which effects the standard more/less than the sample, homogeneity of an element in the standard, and reliability of externally determined element concentrations.

Use the "`Quant.SecondaryCorrection.AveragingStyle`" option to control the method of combining corrections from multiple secondary standards. The "AverageAllRMs" option averages all RM concentrations. The "AverageEachRMSeparately" option averages each standard first, then averages the averages.
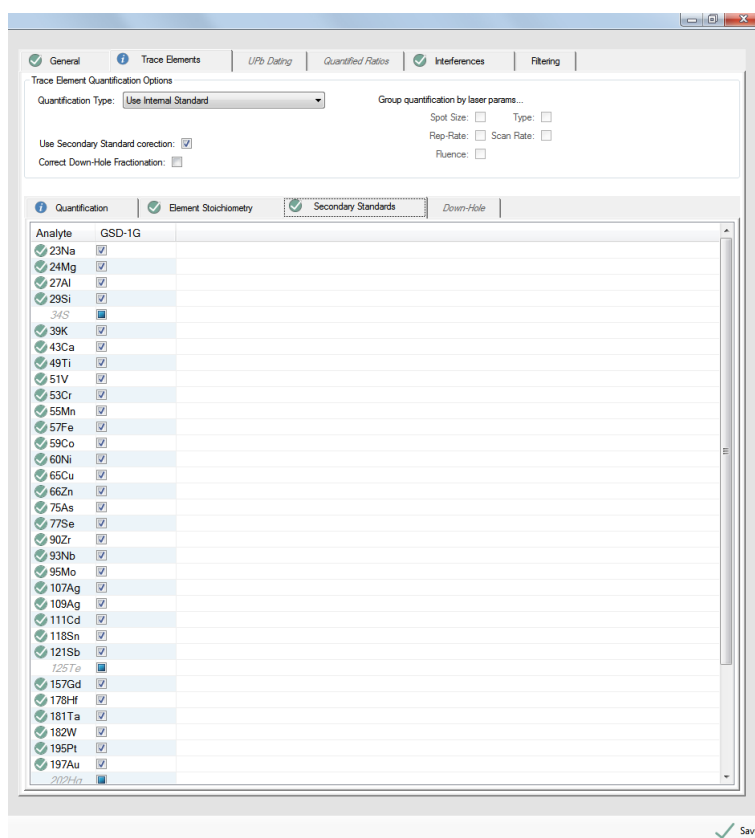
Figure 40 Secondary standard selection for trace element quantification.

QS Settings – Trace Elements – Down-Hole

A down-hole correction accounts for the change in the ratio between the internal standard and any analysed mass with increasing laser drill depth. This tool is primarily used for spot analyses where the dill depth can cause element ratios to change (element fractionation). The predicted down-hole curve is modelled after the defined

calibration standard. The correction is applied to the unknowns and requires the laser times to be defined (see "Laser times" on page 111 for more information).

To use down-hole corrections the checkbox "Correct Down-Hole Fractionation" (in the top section of the window) must be checked, and at least one model type other than "none" assigned to at least one analyte in the table.

Several line fit functions are available for defining the down hole correction curve. The down hole correction models can be inspected in the calibrations window (see "Calibrations" on page 144).

Figure 41 Down-hole correction for trace element quantification.

The down-hole correction options are:

- None – No correction will be applied to this mass.

- MiddleNormLinear – A linear down-hole correction is applied to the mass, normalising the down hole fractionation to the middle of the ablation.

- MiddleNormPoly2 – A second order polynomial down-hole correction is applied to the mass, normalising the down hole fractionation to the middle of the ablation.

- MiddleNormPoly3 – A third order polynomial down-hole correction is applied to the mass, normalising the down-hole fractionation to the middle of the ablation.

QS Settings – UPb Dating

The "UPb Dating" page (Figure 42) shows the options available for the UPb dating scheme. This tab becomes active when the "UPb Dating" box is checked in the "General" tab. The scheme consists of UPb ratios (only those valid for the current project are shown in the list) and minimum configuration of the scheme requires the user to choose a calibration standard for each ratio.

Figure 42 UPb dating tab of the "edit QS" window.

In the "Calculated UPb Ratios" region is an option to compute 207Pb/235U from 207Pb/238U – This calculation is done using the 238U/235U ratio defined in the QS options (default is 137.82 from Hiess et al. 2012).

The options for filtering of U238 applies to all measurements of U238 in all schemes, and so is available on the "Filtering" page.

A RM must be selected for each ratio. LADR allows users to choose different reference materials for each ratio. For ratios of different elements, it is important to use matrix matched RMs because of element fractionation during laser ablation. For ratios of the same element (e.g. 207Pb/206Pb) a non-matrix matched standard may be used to obtain better counting statistics on the calibration standard.

Several line fit functions are available for defining the down hole correction curve. The down hole correction models can be inspected in the calibrations window (see "Calibrations" on page 144).
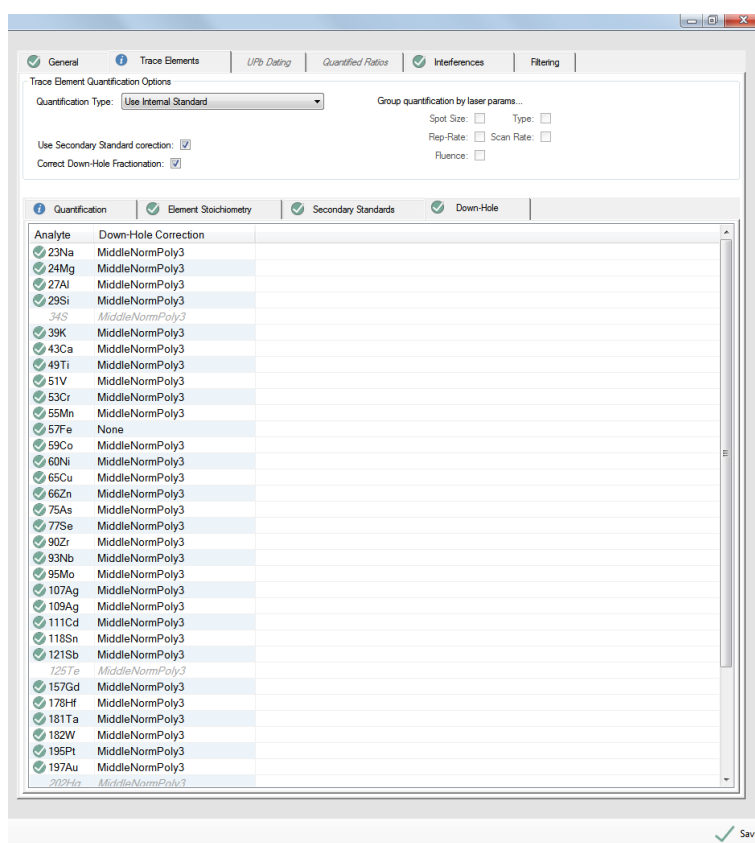
The down-hole correction options are:

- None – No correction will be applied to this mass.

- MiddleNormLinear – A linear down-hole correction is applied to the mass, normalising the down hole fractionation to the middle of the ablation.

- MiddleNormPoly2 – A second order polynomial down-hole correction is applied to the mass, normalising the down hole fractionation to the middle of the ablation.

- MiddleNormPoly3 – A third order polynomial down-hole correction is applied to the mass, normalising the down-hole fractionation to the middle of the ablation.

An excess uncertainty factor is sometimes applied to LA–ICP–MS geochronological data sets and accommodates any additional sources of uncertainty which may be present in the analyses. Please see the "Introduction" section for more information.

Common Lead Removal

There is an option to remove common lead from measurements on the calibration RMs. This is only possible because the age of the RM is known, and the common lead composition is either known or can be estimated.

To use common lead removal choose one of the removal methods:

- 206/207 – The age of the RM is used to compute the radiogenic 206/207 ratio. The difference to the measured ratio is taken to be common lead and the amount of common lead is computed.

- 208 – The measured 208Pb is assumed to be all common lead. This does not work if there is 232Th present, and if this removal method is chosen then 232Th must also be measured and the measured value will be checked for intensity on the RM.

- 204 – The measured 204Pb is assumed to be all common lead. This is performed after interference corrections, so that 204Hg can be removed, typically via measured 202Hg.

Note: The 206/207 method is the recommended default because the signal intensities for these isotopes is typically higher than for 208 or 204.

Once the amount of common lead is known, it is subtracted from all lead isotope measurements on the standards using the defined common lead composition. The common lead composition is defined by either:

- Stacey and Kramers 1975 using the age of the RM.

- Stacey and Kramers 1975 using a custom age, entered on the form.

- A custom common lead composition entered using the table.

The common lead corrected measurements are used for all isotope ratios in the UPb module.

QS Settings – Quantified Ratios

Any quantified isotopic ratio can be produced from masses included in the analytical element list and this tab becomes active when the "Quantified Ratios" box is checked in the "General" tab.

Isotopic ratios are defined in the ratios tab with "Mass 1" as the numerator and "Mass 2" as the denominator of the ratio. Many of the additional quantification options are identical to the quantification of trace elements.

In the "Quantification" tab the calibration standard is defined.

In the "Secondary Standards" tab, one or many secondary standards can be chosen for each ratio.

Note: Secondary standards for quantified ratios are currently disabled, but will be enabled in a future version of the software.

The down-hole correction tab allows the user to select a line of fit for the down-hole curve including: none, linear, 2nd order polynomial, and 3rd order polynomial; similar to what is described above.
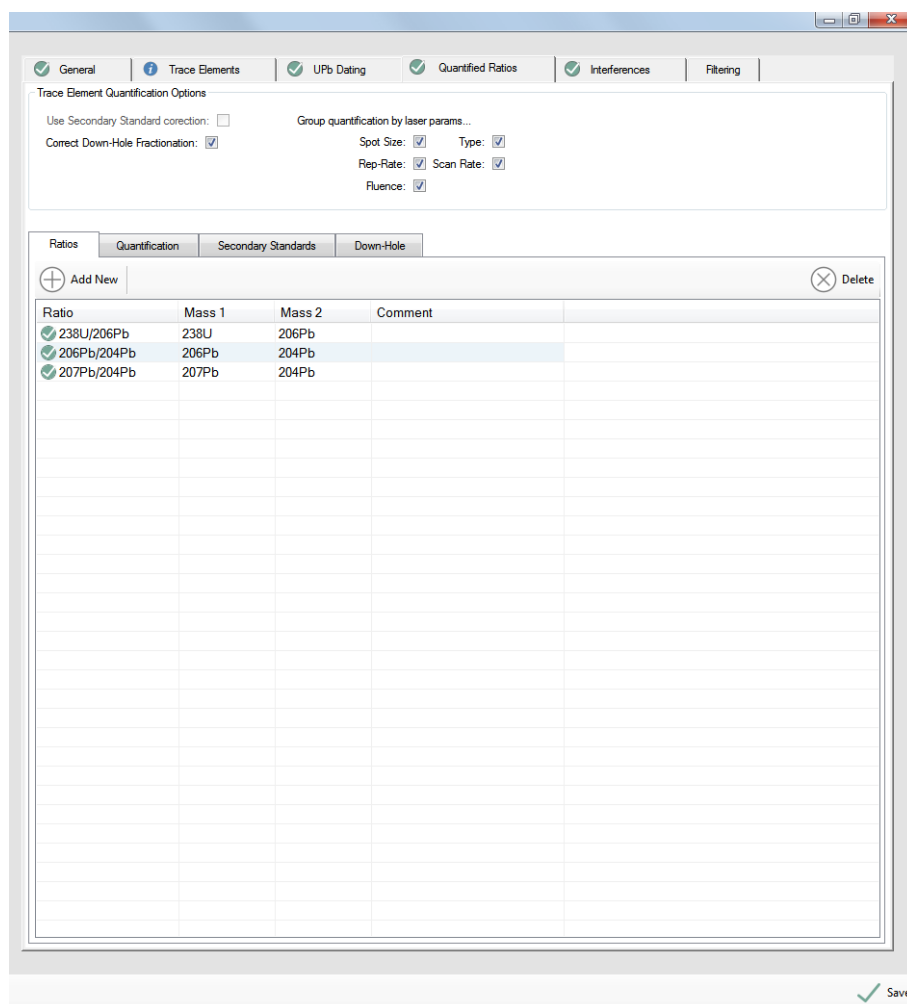
Figure 43 The quantified ratios tab of the edit QS window.

QS Settings – Interferences

The interference tab of the edit QS window allows the user to correct data for interferences present in the signals that would cause inaccurate results (Figure 44).

There are two main sources of interferences in ICP–MS:

1. Isobaric mass interferences in which two elements have the same nominal mass (e.g. 204Hg and 204Pb). These interferences can be corrected using the automatic overlaps button in the interferences tab. In the 204Pb-204Hg

example, another isotope of mercury (e.g. 202Hg) must be analysed to use the isotopic natural abundance ratio to calculate the 204Hg concentration, and contribution to the signal intensity at mass 204.

2. Polyatomic and doubly-charged ions can provide a significant source of interference on measured elements. To correct for these, select the "Add New" button to the interference list, and input all necessary factors to produce a correction equation. Remember that the "Source Mass" value refers to a mass as measured by the ICP–MS, but there is no requirement that this equates to an elemental species.

Note: While interference corrections do work, it is regarded as best practice to avoid them where possible. Avoid the most likely polyatomic interferences by understanding the mineral major element composition and selecting element masses which are least likely to contain a significant interference.

Figure 44 Interferences tab from the edit QS window. An example is displayed of the isobaric interference of Hg and Pb.

- Target mass – The mass being interfered on; the desired element mass exported in the final results.

- Source mass – The mass providing a measurement of the interference intensity, either a monitoring mass used to calculate an isobaric interference, or a mass whose intensity is proportional to a polyatomic species.

- Operation – The default is to subtract any potential interference from the mass of interest.

- Multiplier – This is the interference production rate with values, in general, ranging from 0 to 1, with 0 being no interference production and 1 being 100% interference production. The interference rate can be independently calculated using certified RMs or single element materials.

Note: *Please see a discussion in the ICP–MS community literature[12] pertaining to oxide and argide production rates in different sample matrixes.*

- Mass bias – If there is a known mass transmission efficiency difference between the target mass and interference mass this information can be provided here.

- Equation – Display of the equation for the correction of interferences based upon the values provided. This field allows the user to directly view the correction that will be applied to the final results.

Note: *This interference correction is applied to all calculated values within the QS.*

QS Settings – Filtering

The option here allows the QS to compute 206Pb/238U from 206Pb/235U when 238U has a count rate above a count rate threshold. The purpose of this filtering is to provide greater flexibility during analysis, without introducing a reduction in analytical accuracy caused by the pulse-analogue calibration of the detector. In other words, this filtering approach works when the ratio of U238 to U235 is known better (for a given sample) than the pulse-analogue calibration factor.

This option is particularly useful when 238U has high intensity in the sample, or the user is working with larger spot sizes to meet other analytical constraints. Without this option, the ability to accurately measure the 206Pb/238U ratio in analyses with 238U in one mode of detection, while the calibration standard is in another mode, would then be dependent upon the accuracy of the pulse-analog calibration, which is quoted by instrument manufacturers as 1-2%. This function removes this detector mode uncertainty by using 235U, which would be in the same detection mode as the primary standard. For this option to work, both 235U and 238U must be measured.

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12 Some references to **start** with:

- Guillong, Marcel, et al. "The effect of quadrupole ICPMS interface and ion lens design on argide formation. Implications for LA-ICPMS analysis of PGE's in geological samples." Journal of Analytical Atomic Spectrometry 26.7 (2011): 1401-1407.

- Vroon, P. Z., et al. "Problems in obtaining precise and accurate Sr isotope analysis from geological materials using laser ablation MC-ICPMS." Analytical and bioanalytical chemistry 390.2 (2008): 465-476.

The count rate threshold should be set to just below the transition (in CPS) between the pulse and analog detector modes on the ICP–MS. For most instruments this occurs around 1,000,000 CPS, but you should always check the manual for your specific instrument.

QS Settings – Options

Presented in the QS "General" tab are the options which pertain to the creation/modification of a QS, flat signal calculations, and clean-up of the laser signal. The QS options menu are duplicated from the profile setting options at the time of QS creation. These options can then be transferred with a QS between projects and multiple settings are possible within a project because multiple QSs can exist within a project and a change in one QS will not affect others. These values can be re-set at any time by selecting the "Load QS defaults from profile" button in the "Edit QS" window, "General" tab (Figure 37). For a discussion of the different columns presented in the options please see the section on "Edit options", page 35. For a list of the suggested values see "Appendix A – Options", page 189.

Note: When a new QS is created the default option values are taken from the profile. If you wish to change the default values for all future QSs then go to the main options and set the defaults in the profile.

UPb Dating Options

These options are available for the user to define the 235U/238U ratio and the error associated with that ratio. The default values are from Hiess et al. 2012 (137.82). This is the ratio used for the "compute 207Pb/235U from 207Pb/238U" calculation option in the UPb tab of the edit QS window. These options apply to the QS and thus to the analysis entries on the unknown samples. Any measurements that take place on reference materials will use the 235U/238U ratio from the RM. If not defined, then this default value is used.

- `"QSQuant.UPb.DefaultRatioOfU238/U235"` – Used when converting U235<=>U238. The default value provided is taken from: Hiess et al. 2012.

- `"QSQuant.UPb.AdditionalMassBiasUncertainty"` – Added to the signal uncertainty when converting U235<=>U238 on unknown samples. Enter as relative percent.

Trace Element Options

Lead and uranium isotopes can be calculated in the trace elements tab as either "Total" elemental concentrations, or as separate isotopes. To use this feature, the elemental concentration must be specified on the RM, the isotope system must be specified on the RM, and all of the isotopes in the system must be measured in the project.

Note: While this feature is currently limited to only U and Pb, if you have a requirement for a similar feature in the isotopic system of your choice please contact us to discuss implementation details.

- "QSQuant.TraceElement.ComputePbIsotopesSeparately" – When computing Pb, should isotopes be computed separately? To use this, the RM must have the Pb isotopic composition defined, and as a minimum the Pb isotopes 206, 207, and 208 must be analysed in the project.

- "QSQuant.TraceElement.ComputeUIsotopesSeparately" – When computing U, should isotopes be computed separately? To use this, the RM must have the U isotopic composition defined, and the U isotopes 235 and 238 must be analysed in the project.

Results View Options

For QSs that add elements by stoichiometry, if the element is also measured and quantified (typically as a marker or quality control measure) then the measured value is hidden in the results. This is because if they are shown it is unclear to the user what value they are looking at. Turn this value on to show the measured values, which is only of use when debugging new methods, or when the stoichiometry defined on the QS doesn't match the stoichiometry in the sample: i.e. it's the wrong mineral!

- "Results.DisplayMeasuredStoichCompoundConcentration" – False == Do not show measured values.

Below Detection Level Options

The treatment of below detection level data when calculating the analytical total can be set here.

- **"SumToTotal.BelowDetectionLimitHandling"** – When computing a total, how should concentrations below detection limit be handled? There are three options available: include, exclude, or use a DetectionLimitMultiplier.

- **"SumToTotal.BelowDetectionLimitMultiplier"** – This is the multiplier when using "DetectionLimitMultiplier" option to compute a total. Use this option when it is beneficial to identify the low concentration data, but a multiplier is used such that these values are not associated with the above DL data. Multiplier may be between 0 and 1.

Down-Hole Fractionation Options

These options pertain to the order that the down-hole fraction and clean up functions are completed.

- **"DownHoleFract.001.CleanUpUPbAndQuantRatiosBeforeNormalisation"** – Whether to clean up the mass and IS raw signals before normalisation. For UPb and quantified ratios only. This option is always true for trace elements.

- **"DownHoleFract.001.CleanUpAfterNormalisation"** – Whether to clean up the mass/IS ratio before fitting the model.

Signal Clean-Up Options

When the signal clean up is enabled the mass/IS ratios will be processed and outliers rejected. This improves precision for ratio measurements.

- **"CleanUp.001.RejectionThreshold"** – Remove this % from top and bottom of data. Basic outlier rejection.

- **"CleanUp.001.StdDevMultiplier"** – Applied to the theoretical standard deviation. Basic outlier rejection.

- **"QSQuant.CleanUp.CleanUpBeforeQuantification"** – During quantification, should data be cleaned-up before quantification? Applies to UPb, and quantified ratios. Support for traces will be added in future versions.

Laser Times and Automatic Time Periods

Introduction

Throughout the software the term "laser times" refers to the "aerosol arrival time", and the "stable signal time". For convenience, "laser time" is used to refer to the "aerosol arrival time". The "rise time" is the time between the aerosol arrival time and the stable signal time. For regular work, with good equipment and a plasma well-tuned to the material being abled, the rise time is effective fixed.

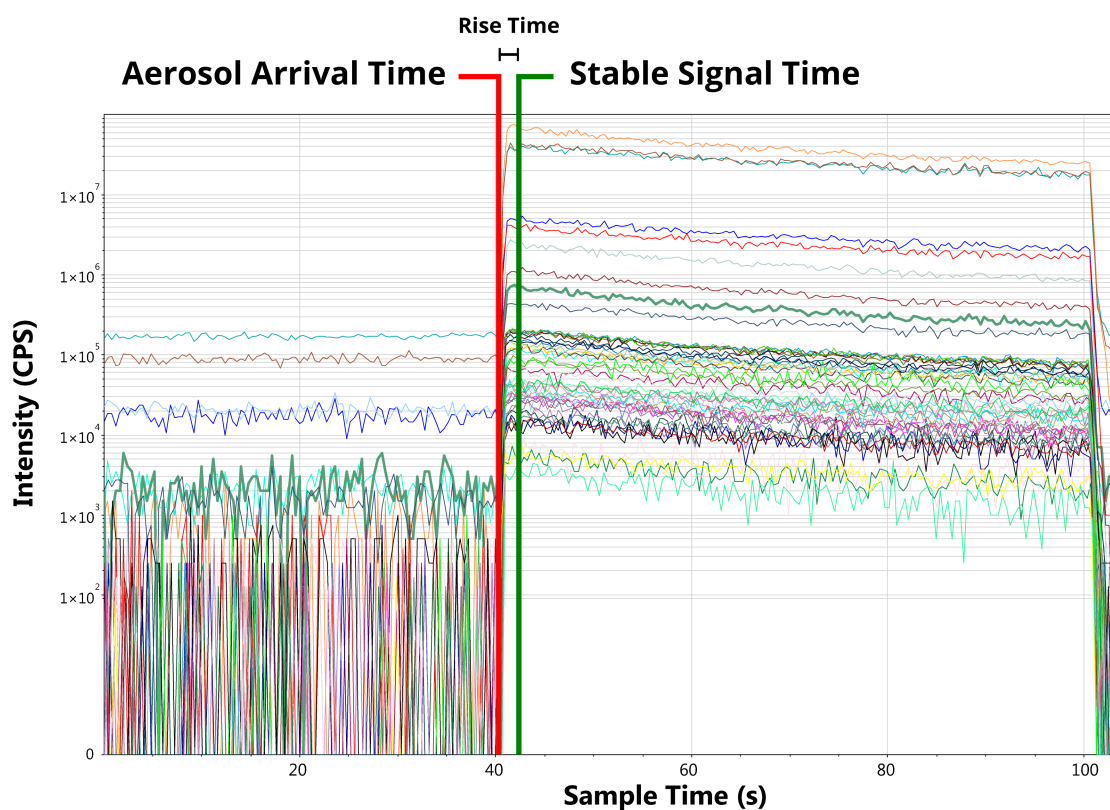*Figure 45: Laser times.*

Defining the aerosol arrival time allows for down-hole fractionation models to be generated on the standards and applied to the unknowns. See the "Quantification Setup" chapter on Page 83 for more information about down-hole corrections.

The stable signal time is used, in conjunction with the aerosol arrival time, to create automatically create time periods in the project:

- By counting backwards from the aerosol arrival time it is possible to place a gas blank interval, provided the gas blank was measured immediately prior to the ablation.

- By counting forwards from the stable signal time, for either a fixed duration, or until the end of the sample, it is possible to create a default analysis entry.

Note: The default analysis entry created in this way is guaranteed to fall where the ablation signal is expected to be, however there is no guarantee that the signal is appropriate for the analysis: i.e. may contain inclusions, or ablate different phases.

Note: At the time of writing LADR does not automatically detect the end of the ablation signal, for example if the ICP–MS measures for longer than the gas blank and ablation combined. The new algorithm that does so will be made available to users in the near future.

Example: During a typical LA–ICP–MS analysis the laser system triggers the ICP–MS to start collecting data, and depending on the model, it either collects data for a fixed period of time, or it receives a command to stop acquiring data. When the laser starts firing the aerosol travels down the transfer line (of arbitrary length) to the ICP where it is vaporised and analysed by the MS. Even if the laser system logs a record of when the laser fires (and most do) there is no reliable record (in the time frame of the ICP–MS) of when the aerosol started to arrive at the ICP. Furthermore, some laser systems[13] can introduce delays between when they command the laser to fire and when the laser light actually starts ablating the sample.

The rise time is typically fixed, but changes in plasma tuning can alter signal intensity, resulting in a longer period of time before the signal becomes stable. In general this should not happen, since the mass of material introduced into the plasma during LA–ICP-MS is considerably less than during solution analysis. However, we mention it here for completeness in case you start to notice variable rise times in your measurements.

Interface

The laser times form has two tab pages: one for setting up laser times, the other for running the "Automatic Time Periods" function.

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13 Especially those that use a beam stop to control the laser light reaching the sample.

Laser times are only required when a down-hole correction function is used for trace elements, UPb dating, or isotope ratios. When and why a user might choose to use the down-hole correction option is discussed in the "Quantification Setup" chapter on Page 83.

Automatic time periods can be created using this window and is a great convenience, especially if most/all of the samples analysed are of homogenous materials.

Both pages of the laser times window have been designed to allow for rapid inspection of all samples. If you have a large monitor, ensure this window is maximised, and use the "More Plots" button to show as many charts as you are comfortable viewing. The "Prev" and "Next" buttons will move the charts in pages, allowing for rapid inspection of even large projects.

Laser times

Time periods allows the user to automatically locate the end of the gas blank signal and the beginning of the sample signal. Laser times are automatically defined when the laser times window is opened. On the left-side of the screen if the program has failed to recognize the correct laser times for samples they will be listed for review.

Add an aerosol arrival time by double-clicking on the chart. Add the stable signal time by holding CTRL and double-clicking on the chart.

Times can be moved by clicking and dragging the coloured vertical lines.

Note: There is a red and a green shading on each graph which represents the median relative laser time for the project ± a standard deviation value set in the laser times options. Any laser time that falls outside this shaded region is regarded as anomalous and should be checked by the user.
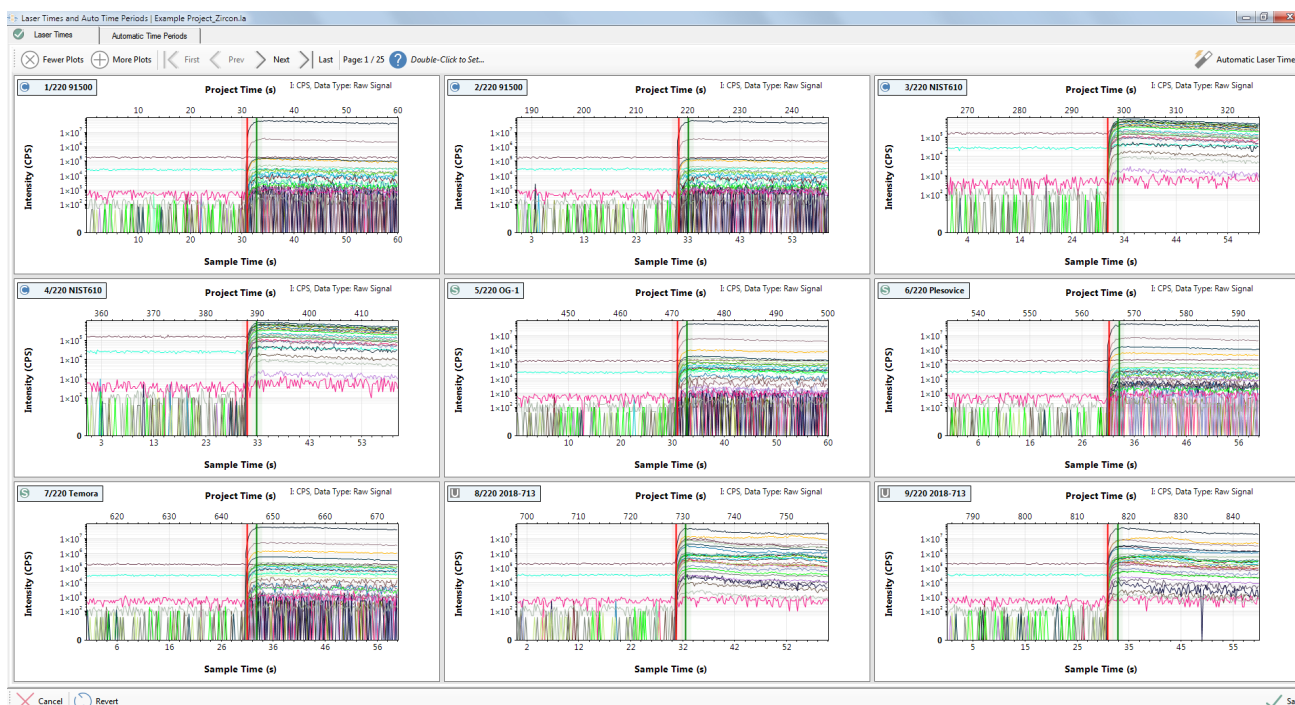
Figure 46 Laser times tab of the laser times and auto time periods window.

To improve ease of inspection, the laser times are assessed for completeness and the anomalous and missing entries are shown automatically in a table (Figure 47). Clicking an entry in the table will jump the charts to show the problematic sample as the first chart on the page. Clicking the "Next to Check" button will advance the selection to the next sample.

When an issue arises with automatic laser time generation:

1. The user can double-click on the graph of the problematic sample and manually input laser times. This is only recommended if there are a small number of analyses that could not be assigned start times.

2. If there are many errors, it is recommended that users adjust the laser times options.
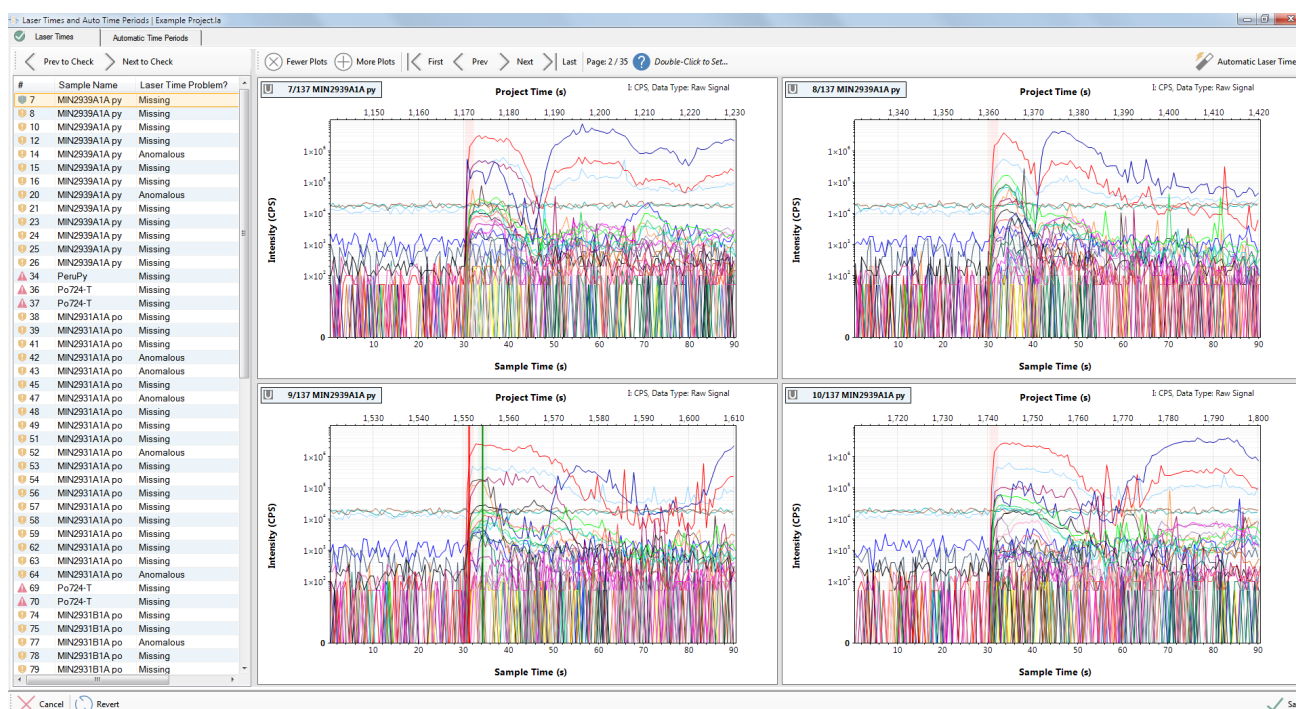
Figure 47: Laser Time window for a project with many problematic time values. The shaded regions show the median relative time period (± a standard deviation value) for all laser times in the project. In a situation like this where many laser times have been missed it will be best to adjust the settings.

What to do About Missing Ablations?

Sometimes a sample will not be ablated. In general, you should upgrade, or repair, your hardware so this does not occur. However, it is known to happen and can be handled by LADR in a number of ways:

- Depending on the QS, laser times within a project are either compulsory or options. If any element or ratio in any QS is set to use down-hole correction then laser times are compulsory.

- If laser times are optional and there is no ablation on a sample, and thus no sensible location to put the laser time, then the sample can be ignored. In this case the sample will not receive any time periods if automatic time periods are used. However, it can help with housekeeping to mark the sample with a dummy laser time in the position it would have been expected to fall. The automatic time period will then be a measurement of the gas blank and the results will show as "below detection".

- If laser times are compulsory, and the missing ablation is an unknown, then it will not be possible to create a useful analysis entry on that sample as it will not be possible to apply down-hole correction. The results will show errors.

- If laser times are compulsory, and the missing ablation is marked as a calibration standard, and the user manually creates a time period on the sample, then this creates a big problem as the down-hole models (for all calibration standards) will fail to generate due to the missing laser time period. **In this case, if a sample is missing an ablation, and it was a calibration standard, it is best to remove the corresponding entry from the logbook table.**

Laser Times – Options

The laser times options can be modified from the Tools → Edit options → Project tab.

The current version of the software uses the prefix "`LaserTimes.001.`" for all of these options, which for clarity, is replaced by an ellipsis(…) in the text below.

Laser Times – Detection Method

- "…`DetectionMethod`" – Select a routine to determine the laser start time. Routines assume each sample starts with a gas blank period prior to ablation. There are three options available, but only one ("AdvancedSumThreshold") is available for use in the current version. Other options will be added in future LADR versions if required.

Laser Times – Clean Up

It is necessary to skip sweeps at the beginning and end of the signal to remove the possibility of incorrect laser time detection.

- "…`SkipSweepsAtEnd`" – Exclude this many sweeps from the end of the sample. Use to avoid washout time if included in the analysis.

- "…`SkipSweepsAtStart`" – Exclude this many sweeps from the start of the sample. Use to avoid a known unwanted signal, such as pre-ablation, at the start of the sample.

Laser Times – Aerosol Arrival Time Location

To define the laser start time LADR creates a histogram of the total counts and finds the time period defining the saddle between the gas blank and signal peaks. The following options are available to control this routine.

- **"…SumSignalFilter_SignalChangeFactor"** – When summing data, to include mass data the signal variation (observed / theoretical) must vary by more than this factor. This factor is used to remove masses which do not change by the factor. This is useful to remove gas interferences which may dominate the gas blank signal (e.g. Argide interferences)

- **"…MinimumBinThreshold"** – When pruning the signal histogram, trim bins with fewer than this fraction of sweeps. This is to avoid regions not containing a gas blank or sample signal.

- **"…SignalHistogramNumBins"** – Sets the number of bins to use on the signal histogram. If set to 0 then the number of bins will be computed using "AutoSignalHistogramNumBinsFactor".

- **"…AutoSignalHistogramNumBinsFactor"** – Used to compute the number of bins to use on the signal histogram: Num Bins = [Num Sweeps in Sample] / [AutoSignalHistogramNumBinsFactor].

- **"…AutoSignalHistogramNumBinsMinLimit"** – When computing the number of bins with "AutoSignalHistogramNumBinsFactor" this sets the lower limit to the number computed.

- **"…MinimumSaddleThreshold"** – When assessing the signal histogram, consider bins with fewer than this fraction of sweeps to be in the "saddle" made by the rise time.

Laser Times – Stable Signal Location

Use these settings to control the location of the stable signal in relation to the signal start time. If using a fixed rise time then the time value must be set (default 3s). Also, when a fixed rise time is used, moving the aerosol arrival time on the chart will cause the stable signal time to move automatically – however, the stable signal time can be moved independently if required.

- **"…UseFixedRiseTime"** – If true apply a fixed rise time ("FixedRiseTime") to find start of stable signal. If false, use the algorithm value to find the stable signal time.

- **"…FixedRiseTime"** – If "UseFixedRiseTime" is true, use this time (in seconds) from the aerosol arrival time for the stable signal time.

Laser Times – Display Options

The laser signal start and stable signal times are shown by lines with surrounding highlighted fields which are this percentage away from the median.

- **"…ExpectedTimeWindow"** – All laser times should fall within +/- this value relative to the median relative laser time. The value is hardware and system specific. Set it to the smallest value that encompasses the normal laser time variability that you observe on your system.

Automatic Time Periods

Once laser times are defined the automatic time period page can be used.

The automatic time period algorithm uses the laser times to place a gas blank time period prior to the aerosol arrival time, and an analysis time period after the stable signal time. The routine can be used to allocate automatic time periods to only gas blanks, or only analysis intervals, or to both (default).
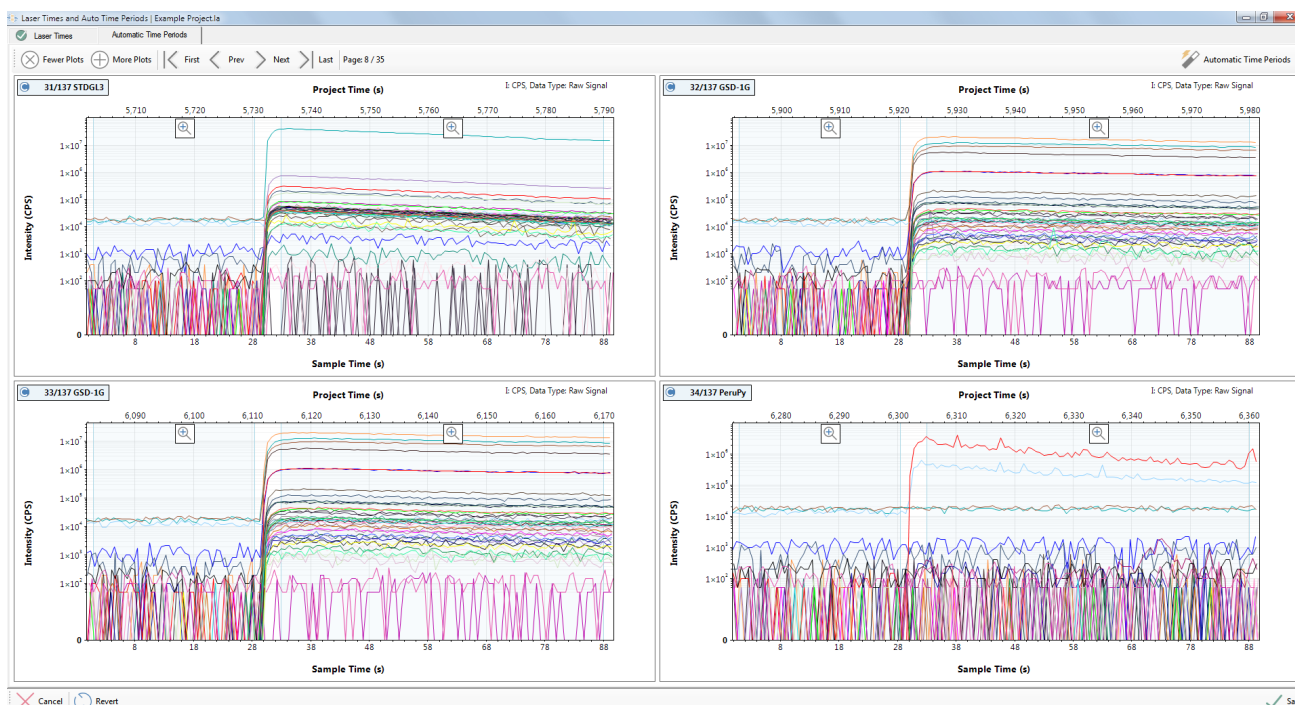
Figure 48 Automatic time periods tab of the laser times and auto time periods window.

Automatic Time Periods Options

The automatic time periods options can be modified from the Tools → Edit options → Project tab.

There are two overall ways to configure the automatic time period selection, either "fixed duration", or "rest of sample".

Note: Different options can be set for the gas blank and the analysis intervals separately: they do not have to be the same.

For clarity, since all of the automatic time periods start with "`AutoTimePeriods.001.`" this prefix has been replaced with an ellipsis (…) in the text below.

An example of fixed duration intervals is shown in Figure 49. To use fixed duration intervals set "`…GasBlankTimeMethod`" to "Fixed" and set "`…AnalysisTimeMethod`" to "Fixed". The intervals are set by:

- **A:** Fixed duration gas blank; set "`…FixedGasBlankTime`" to the required duration in seconds. If the laser time is too close to the start of the sample (not show) then the interval will be truncated to fit.

- **B:** Fixed duration analysis; set **"…FixedAnalysisTime"** to the required duration in seconds. If the stable signal time is too close to the end of the sample (not show) then the interval will be truncated to fit.
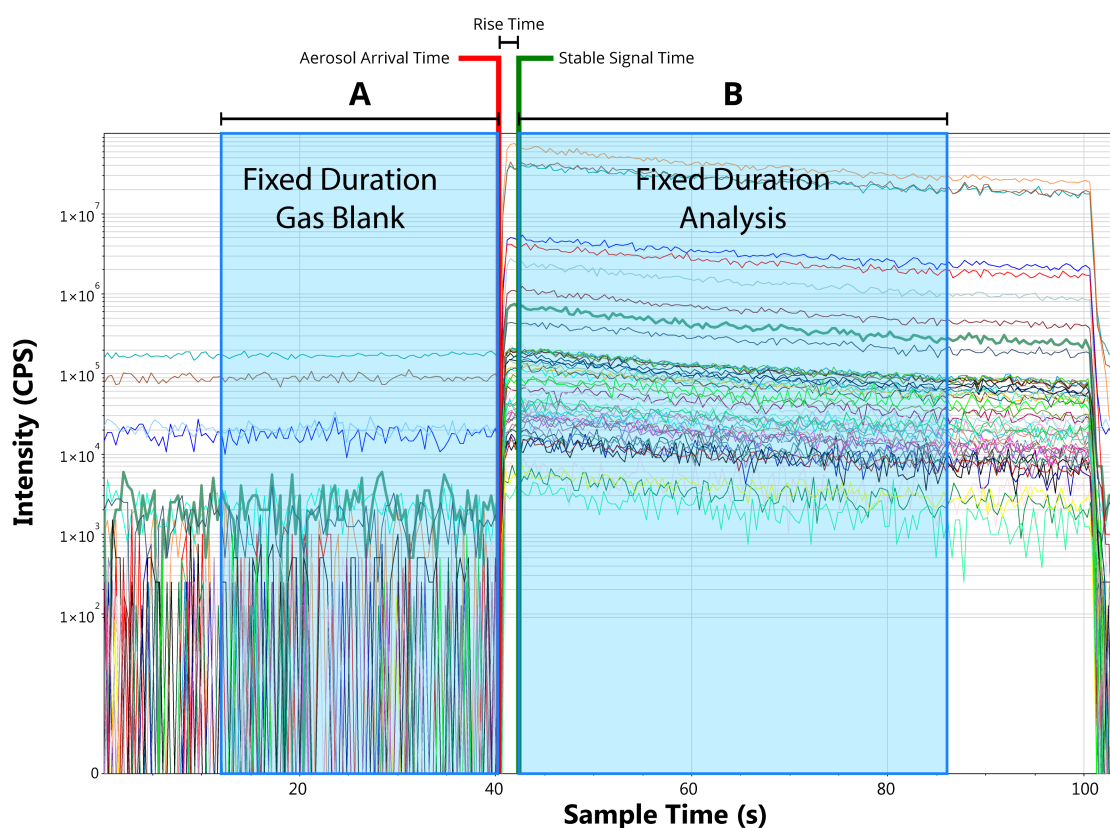
Figure 49: Automatic time periods using fixed times for gas blank and the analysis intervals. See text for a description of the lettered intervals.

An example of "rest of sample" style intervals is shown in Figure 50. To use this style of time period allocation, set **"…GasBlankTimeMethod"** to "LaserMinusOffset", and set **"…AnalysisTimeMethod"** to "SampleMinusOffset". The intervals are set by:

- **C:** Laser minus offset gas blank; the interval is chosen automatically.

- **D:** Set by **"…GasBlankLaserMinusOffset"**. Can be zero.

- **E:** Sample minus offset analysis; the interval is chosen automatically.

- **F:** Set by **"…AnalysisSampleMinusOffset"**. Can be zero.
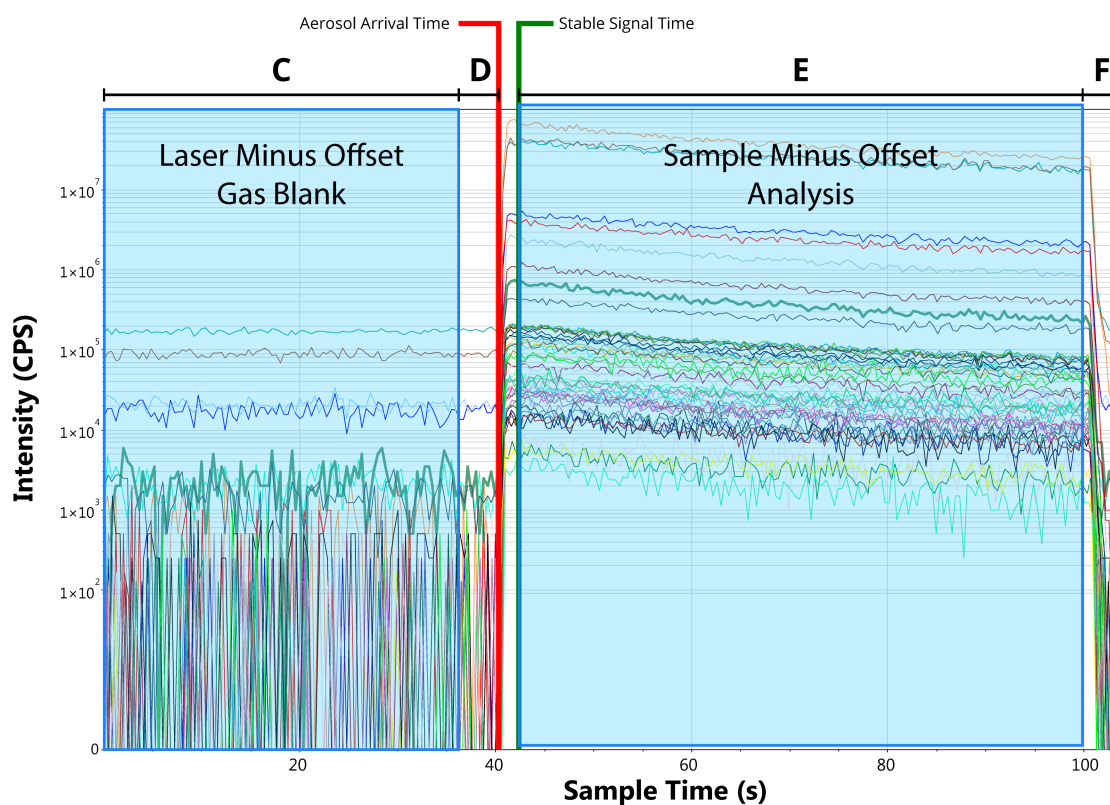
Figure 50: Automatic time periods using "rest of sample" style timing. See text for a description of the lettered intervals.

When using the "rest of sample" style options, there is an additional setting that prevents the intervals from being excessively small. The option **"…MinimumInterval"** sets the minimum allowed duration (in seconds) of any one analysis or gas blank time period.

Note: There is a third option for sample analysis times. Setting **"…AnalysisTimeMethod"** *to "RestOfSample" is the same as using "SampleMinusOffset" and setting "**…AnalysisSampleMinusOffset"** to zero.*

All of the options for automatic time periods are described in more detail in the following section.

Gas Blank Time Periods

These options control the creation of automatic time periods for the gas blank region of a signal. See Figures 49 and 50.

- **"…GasBlankTimeMethod"** – How to determine the start and end time of an automatic gas blank time period. Two options are "Fixed" and "LaserMinusOffset".

- **"…FixedGasBlankTime"** – Only used when **"…GasBlankTimeMethod"** is set to "Fixed". This option sets the duration in seconds of the gas blank interval.

- **"GasBlankLaserMinusOffset"** – Only used when **"…GasBlankTimeMethod"** is set to "LaserMinusOffset". The start of the interval is the start of the sample, and the end is the aerosol arrival time minus this duration in seconds.

Analysis Time Periods

These options control the creation of automatic time periods for the analysis log entries. See Figures 49 and 50. Regardless of the way they are created, all analysis time periods start at the stable signal time.

- **"…AnalysisTimeMethod"** – How to determine the end point of an automatic analysis time period. Start time is the start of the stable signal from the laser times. The three options available are "Fixed", "RestOfSample", and "SampleMinusOffset".

- **"…FixedAnalysisTime"** – Duration in seconds of the "Fixed" analysis time.

- **"…AnalysisSampleMinusOffset"** – When creating analysis time periods using "SampleMinusOffset" this is the offset from the end of the sample. This could be used to ensure signal washout is never included in the signal, but also to avoid the end of the ablation where down-hole fractionation may be more extreme.

Analysis Log

Choosing Analysis Intervals

The analysis log window is where the analysis intervals can be selected for samples in the project. These fields may be already selected if the "Automatic Time Periods" were generated previously.

- If the time periods have been selected than the user needs to check each analysis by examining each mass spectra. This process will ensure that changes in phase due to inclusions or mineral mixtures are not present as these will generally cause erroneous results.

- If the time periods have not been selected, then the user will need to select the analysis on the main chart to create a shaded region. This then causes the analysis to show up on the list on the left. Right-click on the one analysis containing a selected time period and choose "Copy time period to all samples in project". This time period will then be given to each analysis and each can be individually modified by hovering the mouse and dragging the edges of the shaded region.

Note: The analysis log chart functions are described in the "Data Chart" chapter on Page 46.

Multiple time periods can be created on the same laser signal by two methods:

1. To create two independently quantified signal selections on the same unknown, select two shaded regions. An additional entry will appear in the information table containing the same file name and metadata. These are now two separately quantified regions of the same analysis. This can be useful if there is compositional zoning present in the material, for example.

2. If multiple signal regions on the time-resolved chart should be quantified together, select the "Multi Integration" button at the top of the analysis log table. The user can then select a second region which will be combined with the first. This can be done multiple times. This option is useful to choose clean intervals on either side of an unwanted inclusion, for example.

Note: To remove a shaded region on the time resolved signal, select the red circle in the middle of the shaded region.
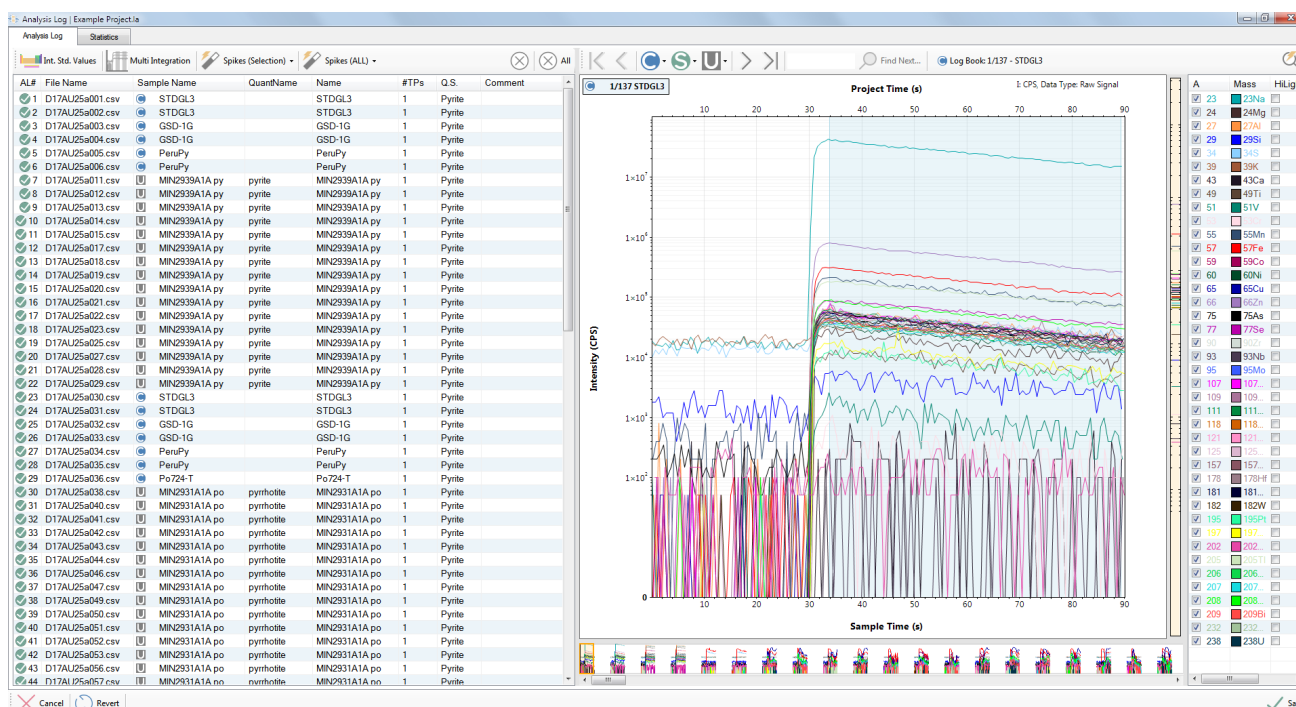
Figure 51 Analysis log window showing the sample chart and sample information table.

Analysis Log table

Information available in the analysis log chart can be controlled by right-clicking on the chart heading and selecting/deselecting the required columns (Figure 52). Columns available are:

- AL# – Analysis log number.

- File name – Name of the imported data file selected during the first step of the data reduction workflow.

- Sample name – If a sample name was designated in the imported logbook file this will be listed here. If no sample name was included the file name will be duplicated here.

- Quant name – The name of the QS chosen for this sample as shown in an imported logbook file.

- Name – Sample name is duplicated here. This field can be modified by double left-clicking on a name. It may be useful to modify this field when multiple sections of a single laser analysis are quantified independently.

- #TP's – The number of time periods is a number representing the number of segments of signal in one sample quantified together.

- Start (s) – Within analysis sample start time of chosen signal interval. This field can be modified and will automatically update the selected sample signal on the chart.

- End (s) – Within analysis end time of chosen signal interval. This field can be modified and will automatically update on selected sample on the signal chart.

- Time (s) – Total time for the section(s) of signal selected.

- Absolute start – Project absolute start time of choose signal.

- Absolute end – Project absolute end time of chosen signal.

- QS – QS from the quantification setup window used for each analysis. Standards can be used in multiple QSs and are therefore blank in this form. This column can be edited, and any QS available in the project can be selected.

- Comment – Sample specific notes can be made during signal interval selection. These comments will be exported with the final results.
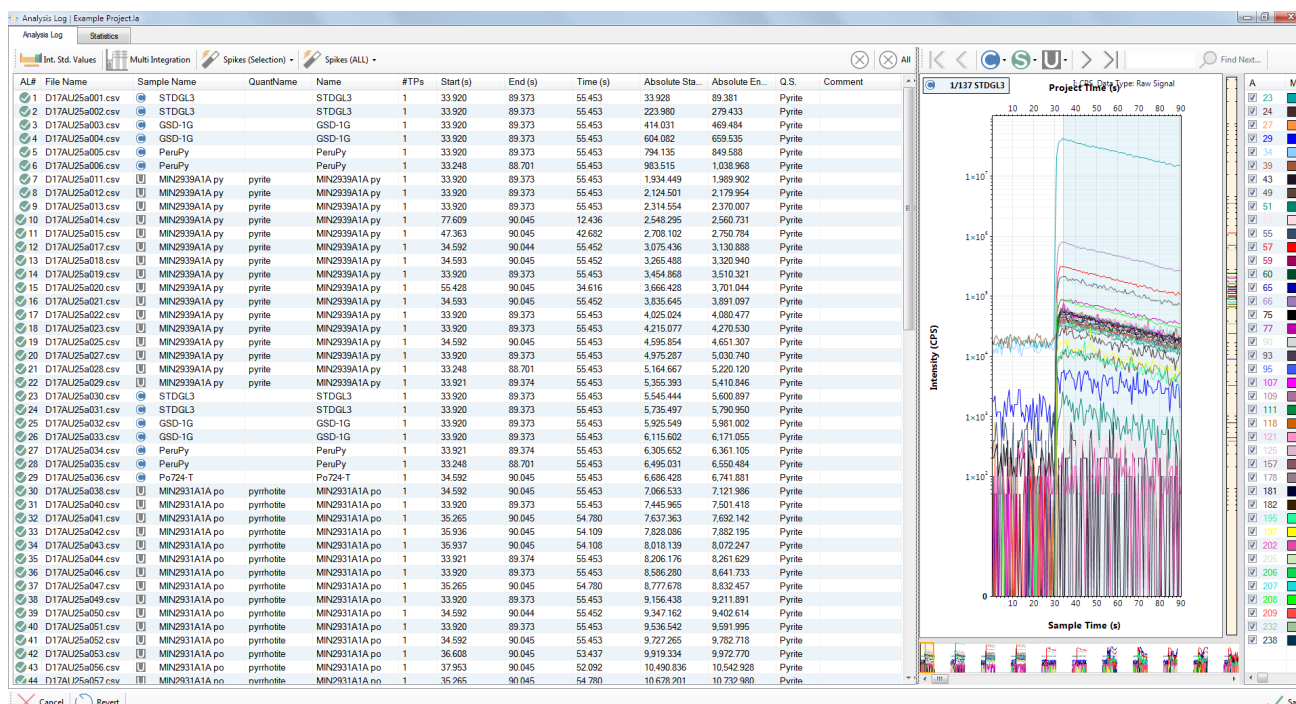

Figure 52 Analysis log table containing an example set of data.

The Analysis Log Table context menu can be opened by right-clicking anywhere on the table. The menu items are:

- Copy Time Period to All Samples in Project – Apply the selected time period to all samples in the project using time relative to the start of each sample.

- Fill Down to Selected Rows – Apply the selected properties from the top item in the selection to all others.

- Show on Chart – If a single entry is selected the chart will be zoomed to show the containing sample. If multiple entries are selected then the chart will be zoomed to show from the first to the last selected entry.

- Import From File – Only available when the Analysis Log is empty, the Analysis Log table can be filled using information from a CSV data file. The file format is described in the "Appendix C – Analysis Log Import File Format" section.

- Export To File – Only available when the Analysis Log contains at least one entry, the Analysis Log can be exported to a CSV data file. The export and import features can help when processing split stream data sets, allowing the Analysis Log to be copied from one project to another.

Spike Removal

Signal spikes can be produced during laser ablation ICP–MS when particles are, for example, randomly liberated in the interface tubing and dominate the signal during a small number of sweeps. Spikes should be removed if the user is confident that the source of spikes is not derived from the sample.

There are two options for spike removal:

1. Spikes (Selection) – Spike removal on only selected samples

2. Spikes (All) – Remove spikes from all samples in the project.

For either spike removal option there are three levels of spike removal available and the ability to undo the spike removal tool.

Three levels of spike removal are:

1. Remove ICP–MS sampling anomalies (Level 1) – This filtering level will only detect extreme spikes. These are spikes that could be introduced by the measuring circuitry of the ICP–MS detector. This is generally a safe level to filter for all data files, but in most cases it will be insufficient to remove all spikes.

2. Remove significant isolated spikes (level 2) – This filtering level is designed to detect spikes that are caused by particles entering the ICP that are not from the sample. It is possible to identify these spikes because they are statistically different to the signal surrounding them, and thus are unlikely to originate from the sample. One of the key requirements is that they are transient, and only exist for 1 sweep (assuming sweeps are 200 – 600 ms long) of the mass spec, which is consistent with small particles dislodged from the tubing.

Note: The main objective of level 2 filtering is to avoid removing anything that could be coming from the sample, such as micro-inclusions.

Note: Level 2 is the most useful spike removal default for most users on most samples.

3. Remove all statistically identified (Level 3) – This is a more aggressive filter that relaxes the single sweep requirement of level 2. This makes it more useful if the mass spec is being run atypically at very short sweep times. But in general, it means the filtering is more aggressive at the risk of removing sample micro-inclusions from the signal.

Note: If samples contain abundant micro-inclusions (sulfides, for example) then this filtering level should not be used as the resulting values will under-estimate the true composition.

Note: In relatively "clean" silicate signals the user may not notice any difference between level 2 and level 3, but this is because there aren't any level 3 spikes present in the signals.

Spike removal options

Spike removal options can be modified in the "Edit Options" menu. Since in the current version all spike removal options are prefixed by "`SpikeRemoval.001.`" this has been replaced by an ellipsis (...) in the text below.

Spike removal operating mode

- **"…`Signal.EnabledMode`"** – Operating mode for spike removal on signals. Option here are auto-enforced, auto with undo, disabled, and manual. If the auto spike removal function is chosen then the level of spike removal will need to be defined in the **"…`Signal.ProcessingLevel`"** option. If this option is disabled then spike removal tool buttons will be greyed-out. The manual spike removal option allows the user to apply a spike removal to different samples and at different levels.

- **"…`Signal.ProcessingLevel`"** – The level of spike removal including ICP–MS Sampling Anomalies / Significant Isolated Spikes / All Statistically Identified can be chosen here when an auto-enforced spike removal mode is chosen from the **"…`Signal.EnabledMode`"**.

- **"…`Signal.DetectDoubleSpikes`"** – Spike widths can vary dependent upon the spike abundance. If enabled then spikes up to 2 sweeps wide are accepted. If enabled spikes can only be 1 sweep wide.

Spike removal settings for ICP–MS Sampling Anomalies

- **"…`Level1.Signal.MinSignalError`"** – Minimum error on counting statistics for the setup in %.

Spike removal settings for "Significant Isolated Spikes"

- **"…`Level2.Signal.WidthOfSignalToCheckNoiseAroundSpike`"** – How many sweeps to assess for signal noise around the spike.

- **"…`Level2.Signal.NoiseThresholdLeftRightModifier`"** – Coefficient applied to the allowed noise on the signal left and right of the spike (resultant noise is then scaled by the height of the spike relative to the spike factor).

- **"…`Level2.Signal.SignalSlopeSpikeFactorModifier`"** – Slope on the signal around the spike to eliminate a spiky-end inclusion.

- **"…`Level2.Signal.SpikeFactorModifier`"** – Coefficient applied to the spike factor to assess the signal intensity around the spike.

- `"…Level2.Signal.SpikeHeightThreshold”` – Height of spike when you do not worry about signal variability around the spike.

- `"…Level2.Signal.SpikeFactorCoeff_X0”` – Coefficient for the spike factor curve, constant term (error_offset).

- `"…Level2.Signal.MinSignalError”` – Minimum error on counting statistics for the setup in %.

Spike removal settings for all "Statistically Identified Spikes"

- `"…Level3.Signal.SpikeFactorCoeff_X0”` – Coefficient for the spike factor curve, constant term (error_offset).

- `"…Level3.Signal.MinSignalError”` – Minimum error on counting statistics for the setup in %.

Note: It is possible to undo spike removal by simply choosing a different level of spike removal.

Internal Standard Concentration Values

Click the "Int. Stds. Values" icon, top-left, on the analysis log form.

The internal standard element will be the chosen element to ratio with every other mass in the project. This mass is designated during the QS setup (page 83).

- If "normalisation with internal standard" was selected in the QS then the "total" column will be available and will contain the total wt.% defined in the QS.

- If "use internal standard" was chosen in the QS then the element (e.g. 43Ca) will be available to be populated with element concentrations. These concentrations can also be identified in the imported logbook, in which case this form should be populated with that information.

The calibration and secondary standards identified in the logbook will always use the internal standard concentration, automatically populated from the RM concentration information.

Several options for internal standards and total concentrations may appear if the project contains multiple QSs using different settings.

The "complete" column will contain either a red x or a green check to indicate whether the input value is appropriate, or something is still missing and needs to be fixed.

Note: *The QS cannot be changed in this window. The QS used for each sample needs to be set in the main "Analysis Log" window.*

To edit the table:

- Double click cells to edit.

- Choose the units using the drop-down in the top left.

- Click and drag on cells (similar to Excel) to select, and use the right click menu to fill down.

- Values can be copied and pasted from spreadsheet software like Excel.

- Click "Save" to save your values and close the form.

- Click "Save" on the analysis log form to save all changes (including internal standard values) and close the form.

Figure 53 Internal standard element window. The element chosen in the QS setup is shown and concentrations for unknown samples can be entered.

View Analysis Statistics

The statistics tab of the analysis window allows the user to view the statistics for the selected section of signal for each analysis. The top portion of the window contains all the calculated statistics for the entire project, and the selected line (e.g. mean) will display that statistic for each element in each sample in the lower portion of the window.

Use of this table is recommended as a convenient way to extract aggregated values from the raw data in the project. To extract the values from the program, use the standard Windows selection controls (or CTRL+A to select all) to make a selection, and then CTRL+C to copy the selected rows to the clipboard. The data can be pasted directly into a spreadsheet program such as Excel.

The available statistics of the signal in counts are:

- **Mean** – The sum of all data divided by the number of data points. The central tendency of a data set.

- **Standard deviation** – The degree of variability measured by the square root of the total sample variance.

- **RSD (%)** – Relative standard deviation is the amount of sample variation in proportion to the mean. (standard deviation/mean x 100%)

- **Error in mean** – The standard error calculated as the standard deviation divided by the square root of the number of values.

- **Relative error in mean (%)** – The relative standard error calculated as the error in mean over the mean times 100%.

- **Number of data points** – The number of sample sweeps for a given mass.

- **Maximum value** – Maximum number of counts on a particular mass.

- **Minimum value** – Minimum number of counts on a particular mass.

Figure 54 Analysis log statistics including the mean, standard deviation, % RSD, relative error of mean value, number of data points, maximum value, and minimum value for each element in each sample.

Interferences

Note: *This section of the software has not yet been enabled for general use.*

Note: *Interference correction is available via the QS, see "QS Settings – Interferences" on Page 103.*

Gas Blanks

Introduction

The gas blank consists of helium and argon gases flowing in to the ICP–MS without any ablation taking place. This is also referred to as a "background", but "gas blank" is the preferred term within LADR. The gas blank is a combination of contamination, gas based polyatomic species (e.g. $^{40}Ar + {}^{16}O = {}^{56}ArO = 56AMU$) and electronic noise from the detector. This gas blank signal must be removed from the sample signal derived from the ablation.

LADR applies a best fit curve to all sample gas blank measurements to produce a time integrated gas blank correction which is applied to all sample signals. The gas blank window is used to define/correct the gas blank signal location and define a best fit curve to define the change in gas blank signal throughout the analytical session. One advantage of this gas blank curve through all of the data is that it combines statistics on the gas blanks for all analyses in a project to provide a more representative estimate of the gas blank. This is significant for masses with low gas blanks and short counting times.

Note: Typically the gas blank for an analysis is measured prior to the ablation and LADR is designed around this concept. However, LADR can support arbitrary data collection protocols if the gas blank and ablation signals are chosen manually.

In LADR, the gas blank definition comes after the analysis intervals have been defined. This serves a critical purpose, as knowing the approximate intensity values for the analysis intervals allows the user to make an informed decision about the quality of the gas blank model fitting. The intensity from the analysis intervals are shown on the gas blank plot as coloured dots.

While the automatic routine for setting up the gas blank models works for most projects, in some cases there will always exist the requirement for judicious inspection and customisation of the models. LADR provides sufficient flexibility to do so, at the expense of the analyst's time spent setting up the project.

Interface

The gas blank window features three tabs, with a left-to-right workflow. Start with "Time Intervals" and finish with "Gas Blank Models".

For convenience, if the time intervals have already been set (for example, by the "Automatic Time Periods" routine) then the window will jump to the "Gas Blank Models" tab when it opens.

Time Intervals

The gas blank region of each sample must be defined be either:

1. Defining the gas blank signal location during the generation of automatic time periods (page 116). If the gas blank time periods were previously defined it is necessary to check them in this window.

2. Create time periods by manually clicking on dragging on the chart to create a defined gas blank region.

Note: If using a more flexible gas blank measurement protocol, flick through the "Time Intervals" tab of the "Gas Blanks" section and click and drag to create time periods on each gas blank.

Note: If all samples were measured using the same protocol, right click on the first time period that was created, then choose "Copy Time period to all Samples" to duplicate the time period.

It is advised that the user should use the controls above the chart to flick through the samples to ensure the time-periods are appropriates for all samples.

Information available in the time intervals tab table:

- LB# – Logbook number (usually corresponds to the gas blank interval number if there is one gas blank per analysis).

- Sample – Sample name as defined in the log book.

- Start (s) – Within sample start time of chosen gas blank interval. This field can be modified and will automatically update on the selected sample signal chart.

- End (s) – Within sample end time of chosen gas blank interval. This field can be modified and will automatically update on the selected sample signal chart.

- Duration – Total time for the selection gas blank.

- Global start – Project absolute start time of chose signal.

- Global end– Project absolute end time of chosen signal.
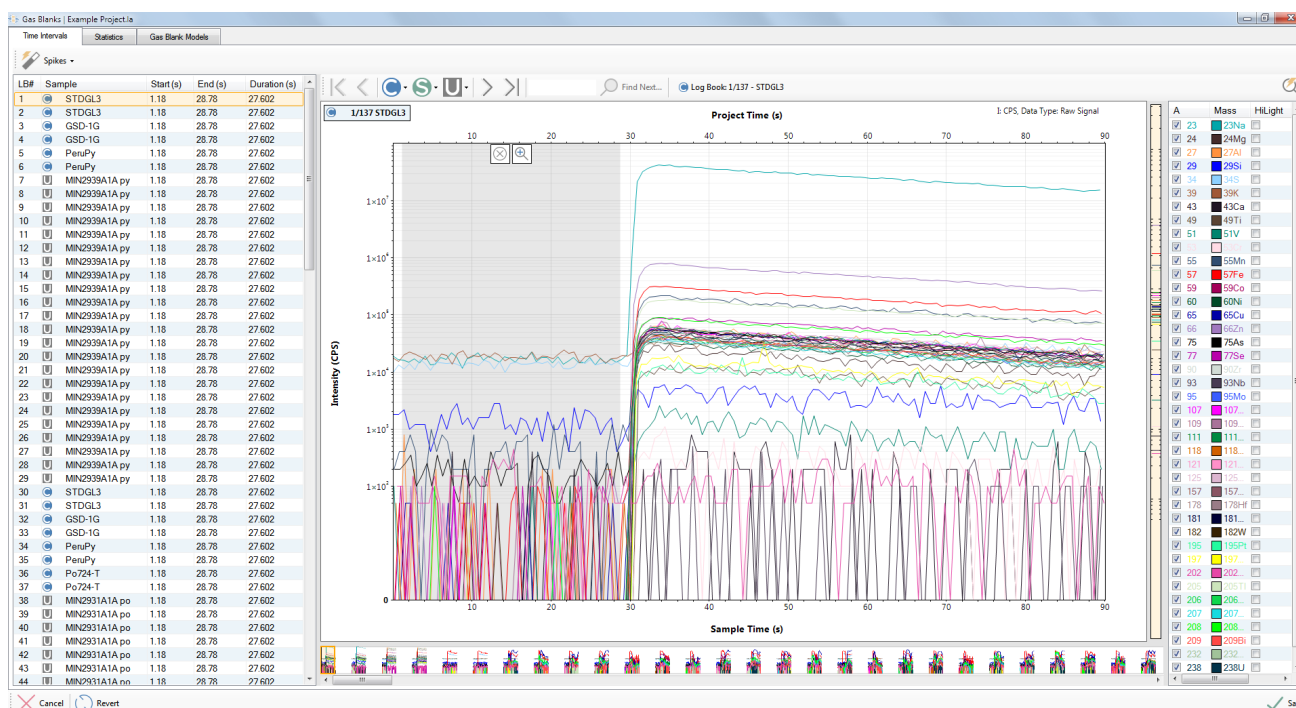
Figure 55 Gas blank time intervals window.

Spike Removal

Signal spikes in the gas blank signal can be removed using the spike removal tool in the gas blanks window. Spikes can be reviewed before and after spike removal in the tools → review spikes window.

Since all of the spike removal options are prefixed by **"SpikeRemoval.001."** it has been replaced by an ellipsis (…) in the following text.

There are two main options to remove spikes from the gas blank signal:

1. Go to the Edit options window → project options and choose to apply a gas blank spike removal to all samples automatically (use the **"…GasBlank.EnabledMode"** and **"…GasBlank.ProcessingLevel"** options). If these changes are made to the profile option, then all future projects will have an automated spike removal in the gas blank.

2. Apply a gas blank spike removal manually, by selecting the spike removal button in the time intervals window. It will be necessary to choose the level of spike removal.

Note: *For a discussion of the three spike removal levels see the section on spike removal in the analysis log, Page 124.*

Spike Removal Options – General

- "…`GasBlank.EnabledMode`" – Operating mode for spike removal on gas blanks. Options here are auto-enforced, auto with undo, disabled, and manual. If the auto spike removal function is chosen then the level of spike removal will need to be defined in the "…`Signal.ProcessingLevel`" option. If this option is disabled then spike removal tool buttons will be greyed-out. The manual spike removal option allows the user to apply a spike removal to different samples and at different levels.

- "…`GasBlank.ProcessingLevel`" – The level of spike removal including ICP–MS Sampling Anomalies / Significant Isolated Spikes / All Statistically Identified can be chosen here when an auto-enforced spike removal mode is chosen from the "…`GasBlank.EnabledMode`".

- "…`GasBlank.DetectDoubleSpikes`" – If enabled then spikes up to 2 sweeps wide are accepted. If enabled spikes can only be 1 sweep wide.

Spike Removal Options – Significant Isolated Spikes

- "…`Level2.GasBlank.WidthOfSignalToCheckNoiseAroundSpike`" – How many sweeps to assess for signal noise around the spike

- "…`Level2.GasBlank.NoiseThresholdLeftRightModifier`" – Coefficient applied to the allowed noise on the signal left and right of the spike (resultant noise is then scaled by the height of the spike relative to the spike factor)

- "…`Level2.GasBlank.SignalSlopeSpikeFactorModifier`" – Slope on the signal around the spike to eliminate a spiky-end inclusion.

- "…`Level2.GasBlank.SpikeFactorModifier`" – Coefficient applied to the spike factor to assess the signal intensity around the spike

- "…`Level2.GasBlank.SpikeHeightThreshold`" – Height of spike when you do not worry about signal variability around the spike

- "…`Level2.GasBlank.SpikeFactorCoeff_X0`" – Coefficient for the spike factor curve, constant term (error_offset)

- "…`Level2.GasBlank.MinSystemError`" – Minimum error on counting statistics for the setup in %.

Spike Removal Options – All Statistically Identified

- "…`Level3.GasBlank.MinSystemError`" – Minimum error on counting statistics for the setup in %.

- "…`Level3.GasBlank.SpikeFactorCoeff_X0`" – Coefficient for the spike factor curve, constant term (error_offset)

Statistics

Gas blank statistics are calculated using the regions selected on the "Time intervals" tab.

Use of this table is recommended as a convenient way to extract aggregated values from the raw data in the project. To extract the values from the program, use the standard Windows selection controls (or CTRL+A to select all) to make a selection, and then CTRL+C to copy the selected rows to the clipboard. The data can be pasted directly into a spreadsheet program such as Excel.

The available values are:

- Number of data points – Number of sweeps per sample times the number of samples.

- Mean – The sum of all data divided by the number of data points. The central tendency of a data set.

- Standard deviation – The degree of variability measured by the square root of the total sample variance.

- **Standard error** – The standard error calculated as the standard deviation divided by the square root of the number of values.

- **RSD (%)** – Relative standard deviation is the amount of sample variation in proportion to the mean. (standard deviation/mean x 100).

- **Sum** – The total counts or CPS for a mass for a sample.

- **Maximum value** – Maximum number of counts on a particular mass.

- **Minimum value** – Minimum number of counts on a particular mass.

Note: Each of the statistics are listed for both counts and CPS.

Note: The "advanced" statistic values are only applicable to single-shot analysis where each sample contains measurements of a single laser shot. This is typically only performed using a time-of-flight MS.

Figure 56 Gas blank statistics which can be copied to an external program for further processing.

Gas Blank Models

Click on the "Gas Blank Models" tab in the "Gas Blanks" window. The opening view shows you the average gas blank value for each mass across the entire project.

Click the "Automatic Defaults (All Masses)" button to generate all of the default gas blank curves. This process assesses the observed variability for each mass over the project and chooses the most appropriate function to fit the gas blank. There are limitations to this process, so it is necessary for the user to inspect and possibly modify the automatic selections.

The boxes shown on the plot represent the mean and variance of the intervals. The variance can be changed to suit the user, and the value currently shown is indicated at the top-right of the chart.

Inclusion of any interval can be toggled for a specific mass by clicking on it. Once an interval is deselected it will stay that way until the "auto gas blanks" is chosen for the mass, and the option to select all intervals is set to true (the default). In general, if spikes are present it is better (less work, better statistics on the gas blank) to remove the spikes than to deselect the time intervals, however deselection has the primary advantage of being mass-specific. Furthermore, if there exist gross artefacts in the gas blank, or an incorrect time period selection, then these should be corrected via the "Time Periods" rather than deselecting the intervals for all of the masses.
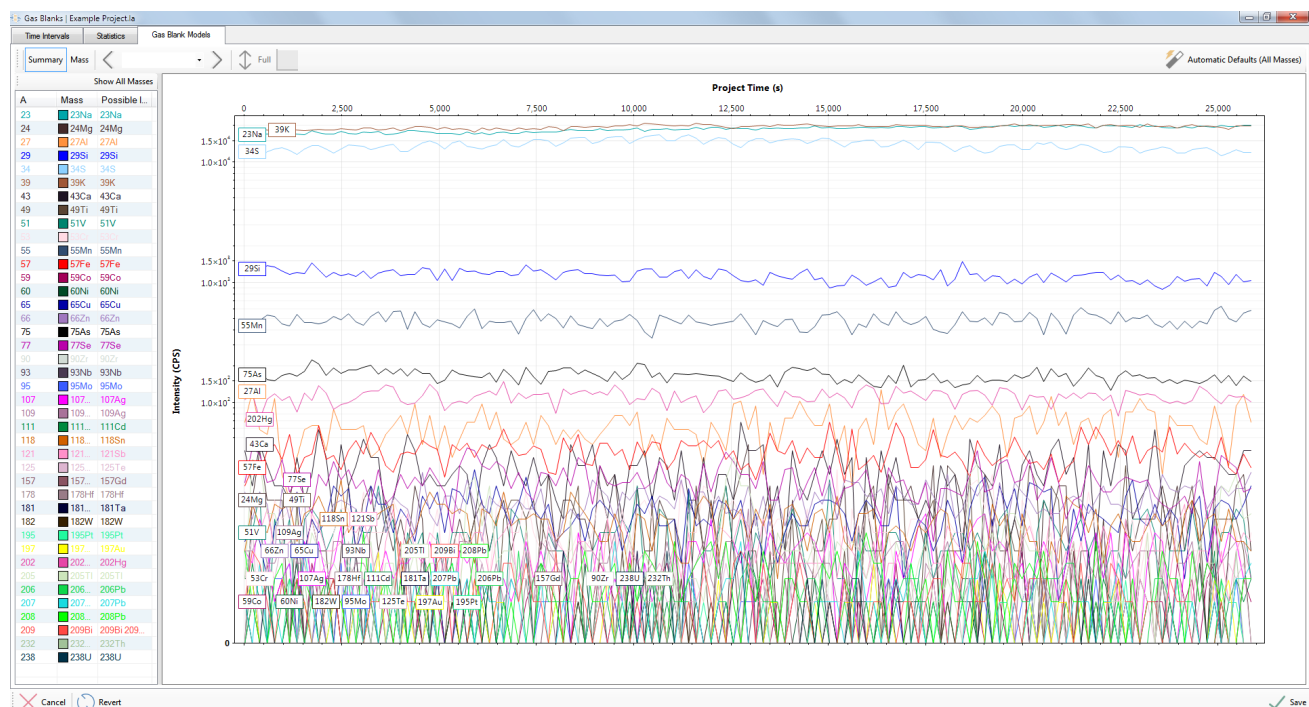
Figure 57 "Gas Blank Models" tab showing the mean value of each gas blank time period for every mass over the entire project.
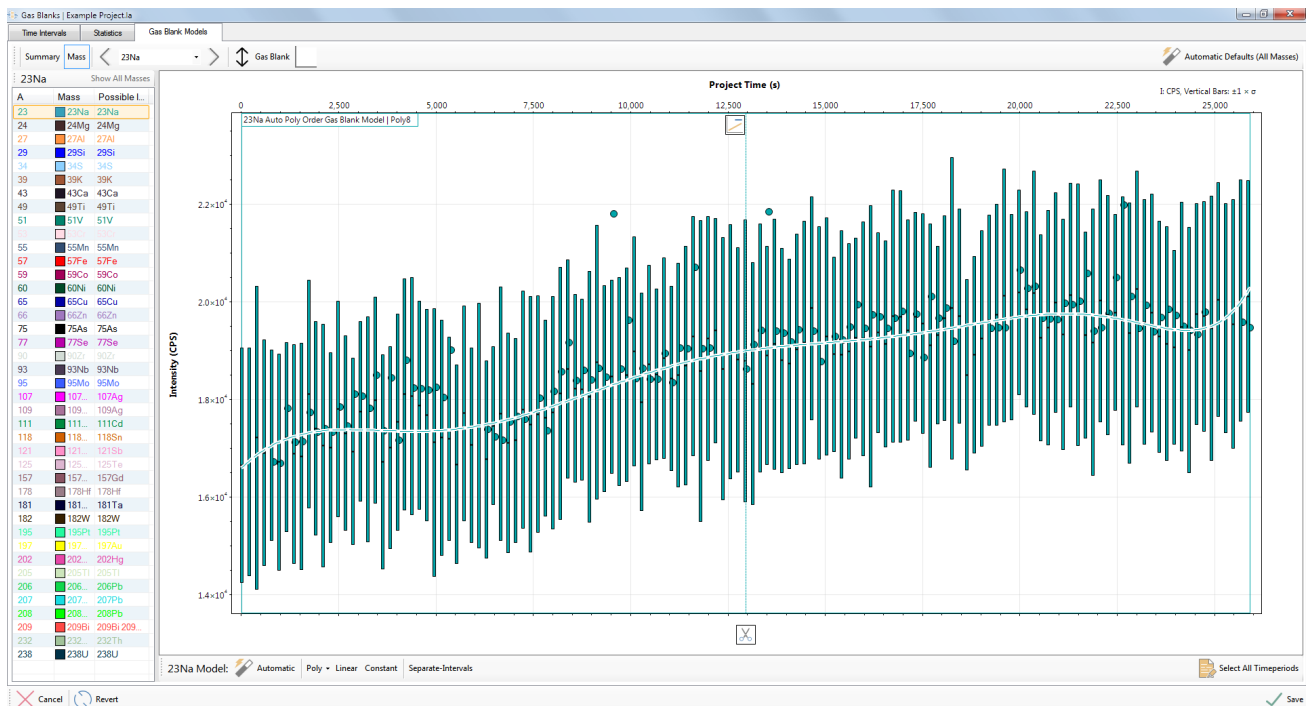
Figure 58: "Gas Blank Models" tab showing the selected model for a single mass (Na25).

Options for controlling the automatic gas blank routine are:

- "Quant.GasBlankFittingStyle" - Should gas blank curves be fitted on means or sweeps.

- "Profile.Quant.DefaultGasBlankModels.ReselectAllTimePeriodsOnSingleMassAuto" – False == De-selected time periods remain de-selected when the background is auto generated.

- "Profile.Quant.DefaultGasBlankModels.Variance" – What kind of variance is used for assessing misfits and curve fitting suitability?

- "Profile.Quant.DefaultGasBlankModels.WiggleEnvelope_VarianceMultiplier" – Multiplier to variance when assessing curve fitting suitability.

- "Profile.Quant.DefaultGasBlankModels.PolyExtrapolationThreshold" – If extrapolating a poly curve for more than this % of total project time, use a constant curve for extrapolation instead.

- **"Profile.Quant.DefaultGasBlankModels.NumOutliersThresholdPercent"** – How many outliers (% total number) are needed to switch to individual interval gas blanks.

- **"Profile.Quant.DefaultGasBlankModels.OutlierVarianceMultiplier"** – Multiplier to variance when assessing interval misfit.

- **"Profile.Quant.DefaultGasBlankModels.CurveFit"** – What kind of curve to fit to calibrations by default. Other rules also apply.

There are several different sample view options available (see Table 8 for examples):

- Viewing all data together in a gas blank intensity curve window.

- Zoomed into the gas blank curve with bars equal to one RSD of the gas blank intensity.

- Gas Blanks curve and ±1 standard deviation (by default) bars with a horizontal mark showing the median.

- The entire laser signal can be activated and displayed with the average signal concentration circles.

- The gas blank signal can be split and modified on the chart.

Single continuous polynomial curve fitted to the entire project timeline. The vertical range is scaled to "Full" and the circles show the mean values of each analysis log entry.	
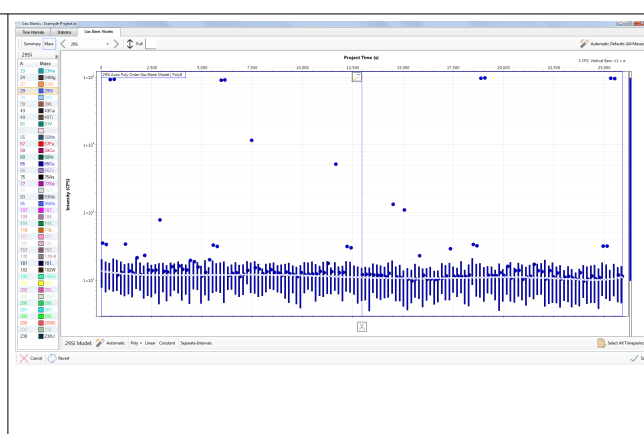
Single continuous polynomial curve fitted to the entire project timeline.

The vertical range is scaled to "Gas Blank" showing more detail to the variation in the gas blank over the project.
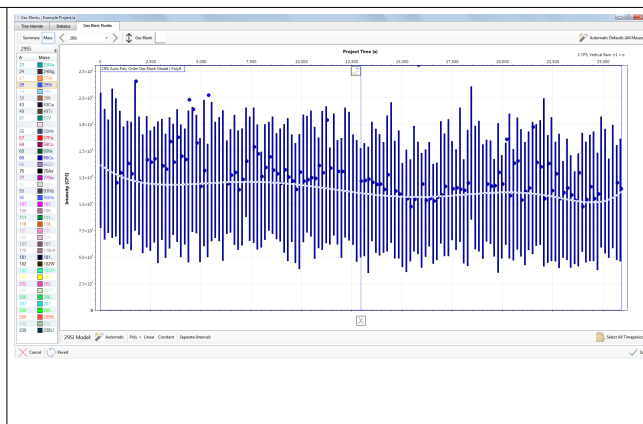
The "show signals" button can be clicked to show the signal intensity trace on the chart.

To see more detail, hold down the CTRL key while hovering the mouse over a region of interest.
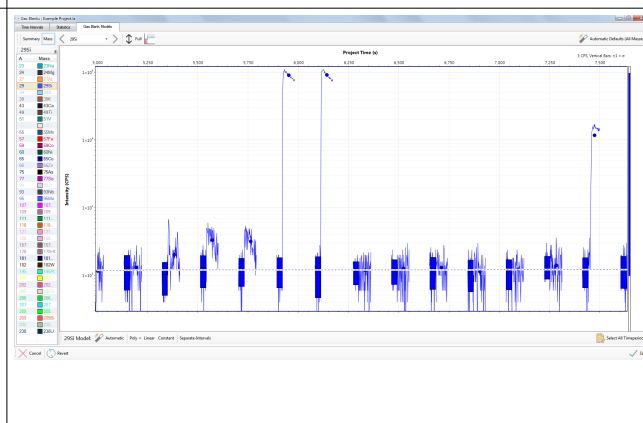
The continuous gas blank model can be split using the "cut" icon. The boundary can be dragged using the mouse. When the boundary is moved it jumps so as to always fall between samples.
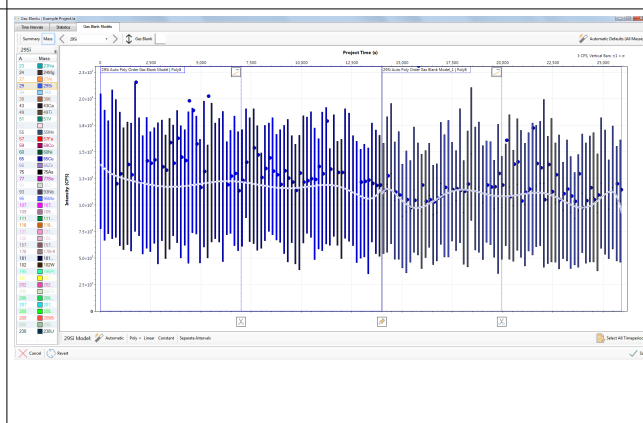
If it is not possible to fit sections of polynomial curves to the shape of the gas blank, then splitting to "Separate Intervals" will interpolate between successive gas blank time periods.

The reduced number of measurements in the gas blank models will result in a higher detection limit for the mass.
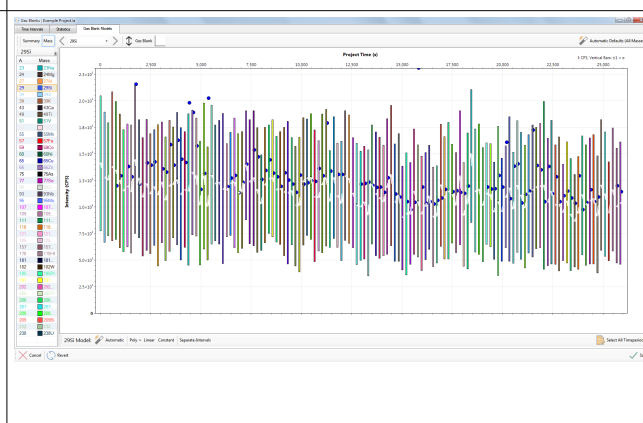
A complex example showing how different gas blank models can be used to model the behaviour over the entire project. Changes in gas blank intensity (such as shown at right) can be caused by memory effects or residual air trapped in the cell following a sample exchange.	

Table 8: Different ways to view and set up the gas blank models.
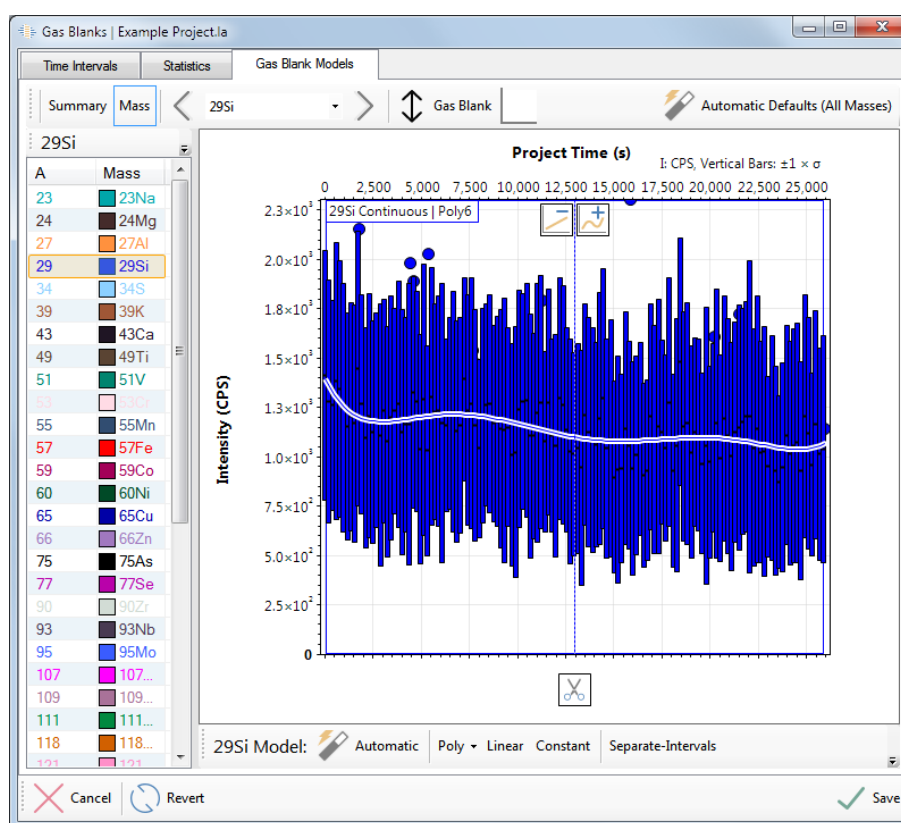
Figure 59 Gas blank tab displaying the gas blank of each sample in the current project for 29Si. The buttons for manually changing the gas blank function is clearly shown.

The user should view each gas blank curve for each mass in the project, by either using the arrows in the tool bar, or selecting each mass in the list.

Use the controls at the bottom to change the curve type for the entire project time period.

The different functions are:

- Automatic – Runs a data fit function to find the best function to fit the data.

- Poly – A 2nd to an 8th order polynomial can be manually applied to the data.

- Linear – A best fit linear curve is applied to the data.

- Constant – A best fit constant signal is applied to the data.

- Separate intervals – A separate gas blank is calculated for each sample.

Note: When the user selects "separate intervals" for a mass, it is no longer possible to deselect individual time periods since this would invalidate the gas blank model for that sample.

Use the "scissors" icon to split the curve, click and drag the boundary to move. A split may be necessary if the gas blank changes dramatically and a curve fit is not appropriate.

Use the polynomial order buttons at the top of each boundary to set the curve order for an existing segment. The current order is shown in the model label, at top-left of the model segment.

Split curves can be re-joined using the "merge" icon at the bottom of each boundary.

Note: Knowing when to adjust gas blank curves depends on the application, the instrument, and the user's attention span. The advantage of showing the ablation signal intensities (round markers) is to provide guidance on the impact of the gas blank subtraction on the results.

Note: Be wary of over fitting the gas blank signal, meaning there should not be any extra curves not supported by the gas blank signal.

Note: Use of the "separate intervals" option for a mass will use the gas blank intervals immediately before and after the ablation measurement. The allocation takes into account gas blank measurements consisting entirely of zeros (common with heavier masses on well-running instruments) and will allow the applicable models to run through those samples to the next sample that contains a non-zero data point: the zeros are, of course, included in the fit. The default behaviour of this routine is to interpolate the gas blank from sample to

sample, which works well for the common scenario where the gas blank is measured immediately prior to each ablation. However, in some cases the user may wish to use a constant gas blank model, which is effectively the average gas blank that runs for the rest of the sample. Using this style of modelling allows LADR to use the same style of gas blank fitting as other data reduction packages and facilitates comparative evaluation. The option in the profile to control this behaviour is called, and is set to "true" by default:
`"Profile.Quant.DefaultGasBlankModels.InterpolateBetweenIntervals".`

Calibrations

Introduction

Creating the calibration curves is the moment when all of the LADR project set up comes together. The software knows all of the information required to create a calibration curve for each mass (and ratio) for each quantification setup (QS) and set of unique laser parameters. The result is a dramatic simplification of what would otherwise be a tedious, and error prone, step in the workflow.

The "Time Intervals" tab is provided for completeness, since in practice most users will skip over this tab since the time periods were already allocated by either the "Automatic Time Periods" or the "Analysis Log" window.

The "Down-Hole" tab is only required when down-hole models are enabled on one of the QSs. The page shows the down-hole models to the user, and allows the user to customise them, for example, by excluding a measurement if necessary.

Note: The down-hole tab is very useful during method development, since after enabling down-hole correction for all masses on the QS this is where the user inspects the observed down-hole trend (if any) for each mass.

The "Calibration Models" tab is the primary page on this form. Here, the automatic routine takes the internal standard, and the calibration RM for each mass (and ratio) and determines the most appropriate fit for the measurements. When the QS specifies that quantification should be split based on laser parameters, a separate set of curves will be generated for each unique set of laser parameters on the calibration RM over the entire project.

In general, the automatic routine chooses the most appropriate set of models for the project, however as always, LADR provides the flexibility for the user to completely customise the models in the project if they so wish.

Note: A key advantage of the LADR software is that all calibration curves will be created for all QSs in the project, even if those QSs are not allocated to any unknowns. The calibration models will also be created even if the calibration will not result in a quantified result, for example, if the concentration in the RM is unknown. This feature allows the user to include curves for marker masses, making it trivial to monitor oxide levels (e.g. 238ThO) or

contaminants (e.g. Hg) throughout the project, which will ultimately never be quantified to a concentration in the results.

Interface

The calibrations window (Figure 60) features a number of tabs that should be worked through from left to right. When opened, the window will select the first incomplete tab. If all tabs are complete, then the window remembers the last viewed tab.

The left-to-right workflow is enforced by clearing down-stream pages. For example, editing the time periods on the "Time Intervals" tab will clear all down-hole and calibration models.

The status of each tab is shown in the tab by a status icon, and hovering the mouse over the icon will show a pop-up explaining the current problem.

Time Intervals

If the sample signal time intervals were not chosen during the automatic time periods selection (page 116) or during the analysis log step (page 121), then they need to be defined in the "Time Intervals" tab in order to progress through the data reduction process.

Note: Only calibration standards are shown on the "Time Intervals" tab page.
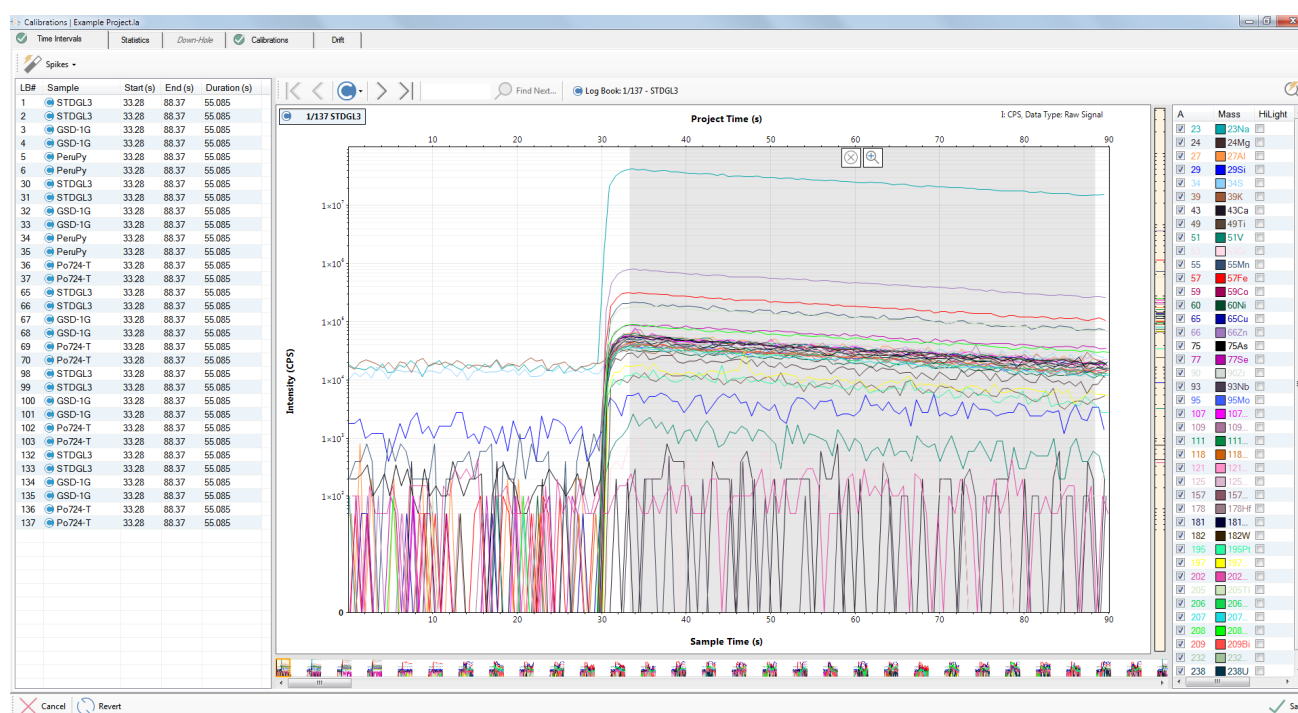
Figure 60 Time intervals tab of the calibrations window.

Spike Removal

The spike removal tool may already have been applied to the calibration standards:

1. If the RM time intervals were selected in the "Analysis Log" window, and a spike removal was selected for all samples (see page 124 for more information).

2. If the automatic spike removal tool has been activated (see options listed on page 125).

If spike removal for the standards has not been done previously, it can be done using the options available in the Calibrations → Time intervals window. These spike removal options are identical to the options and levels described in the analysis log window on page 124.

Note: A higher level of spike removal may be used for standards as it is assumed that the material has been independently verified to be homogenous.

Note: Running spike removal multiple times does not remove successively more spikes. The spike detection settings are fixed by the options for each processing level.

Statistics

Statistics are available for the calibration standards. These statistics can be copied to another program such as Excel for further analysis. For a list of statistics available please see the previous statistics available in the analysis log (page 129) and gas blanks (page 136).

Use of this table is recommended as a convenient way to extract aggregated values from the raw data in the project. To extract the values from the program, use the standard Windows selection controls (or CTRL+A to select all) to make a selection, and then CTRL+C to copy the selected rows to the clipboard. The data can be pasted directly into a spreadsheet program such as Excel.
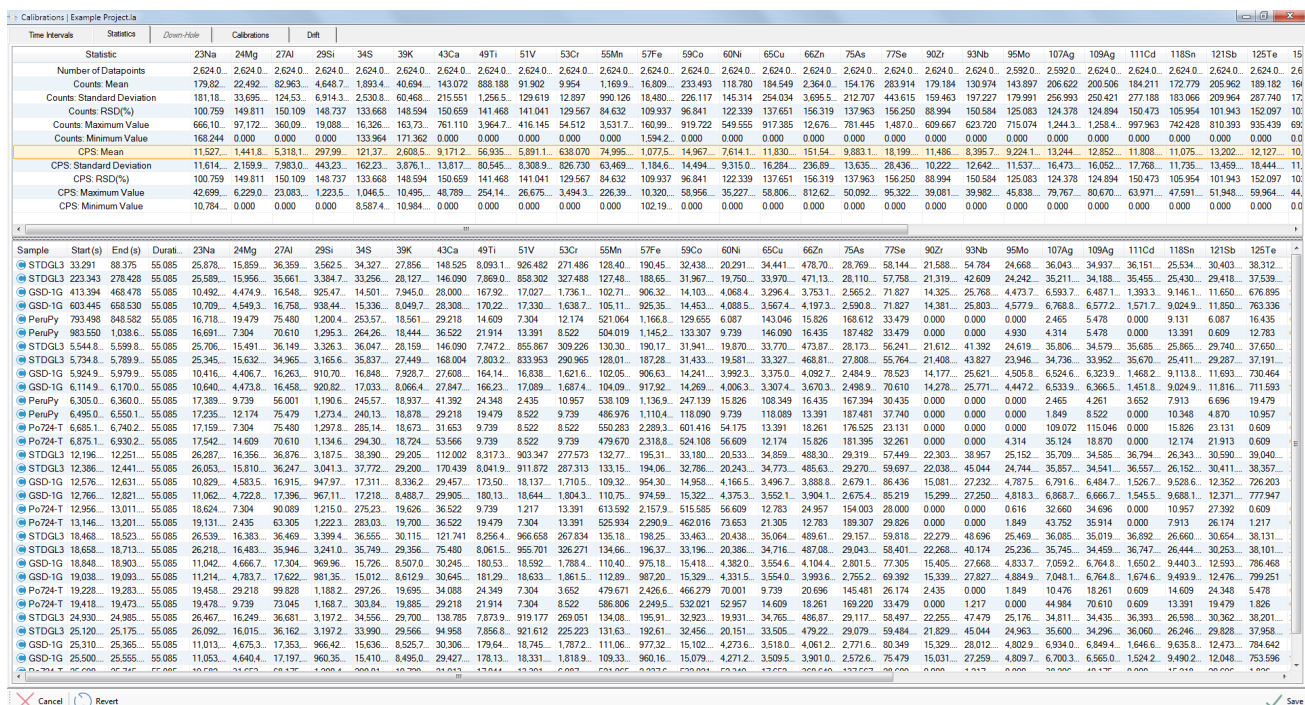
Figure 61 Summary statistics for the calibration standards.

Common Lead Removal

For projects that contain at least one QS with UPb and common lead removal enabled, the "Common Pb" tab is enabled on the calibrations form.

Here the user must click the "Remove Common Lead" button to apply the chosen removal method from all of the the UPb standard measurements present in the project.

The window shows a number of charts designed to illustrate the degree of common lead removal from the standard measurements. Each chart can be clicked to expand into separate charts, showing one for each measurement.

The charts show the corrected values as thin curves in solid colours. The shaded portions show the difference from the original signal, thus illustrating the amount of common lead that was removed. It should be noted that the 206/207 removal method can result in the **addition** of small amounts of common lead due to small fluctuations in the measured values. To remain physically meaningful it is important that the average amount of common lead removed over the entire interval is positive or zero.
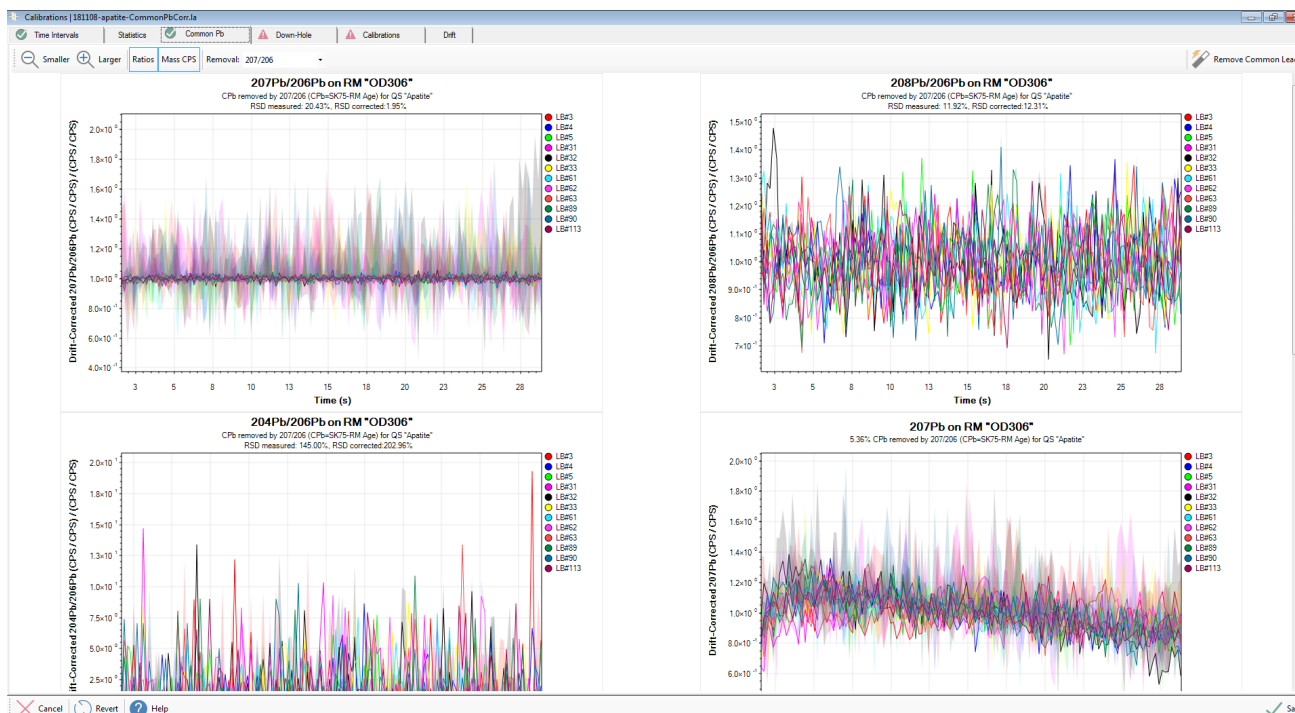
Figure 62: The common lead removal tab on the calibrations form shows visualisations of how much common lead was removed from the standards.

The charts show additional information to assist the analyst, such as the observed uncertainty of the ratios before and after common lead removal, and the amount of common lead removed as a percentage in CPS.

Note: *Common lead removal is specific to UPb and the QS for which it is enabled. It is possible to have multiple QSs in the project, some with and some without common lead removal, and the corrected values remain applicable to each individual QS.*

Once common lead has been removed, the corrected values are used for all subsequent calculations, including down hole correction models, and calibration curves. Quantified results on the reference material will also use common lead correct values.

Down-Hole Corrections

The purpose of down-hole corrections, the decision of whether to use a down-hole correction, and the modelled curve options were discussed in the QS section (Page 98). The down-hole tab in the calibrations tab allows the user to view the down-hole correction's effect on the data (Figure 63).

When the down-hole tab is first opened the user will have to generate the down-hole curves by selecting either "Generate for QS" or "Generate for all".

Note: The process of generating new down-hole curves will clear any previously generated calibration models.

If no down-hole correction is required because this option was not selected in a QS then the corresponding tab in the Calibrations → Down-hole window will say "No down-hole correction models because down-hole correction is disabled".

Note: The data source tab (traces, UPb dating, and quant ratios) will be greyed out if the current project is not calculating that data source. The tab will have a green check if a down-hole correction was not selected in the QS or a down-hole model has been applied. The tab will have a red "x" if the user needs to generate a down-hole correction model as defined in the QS.
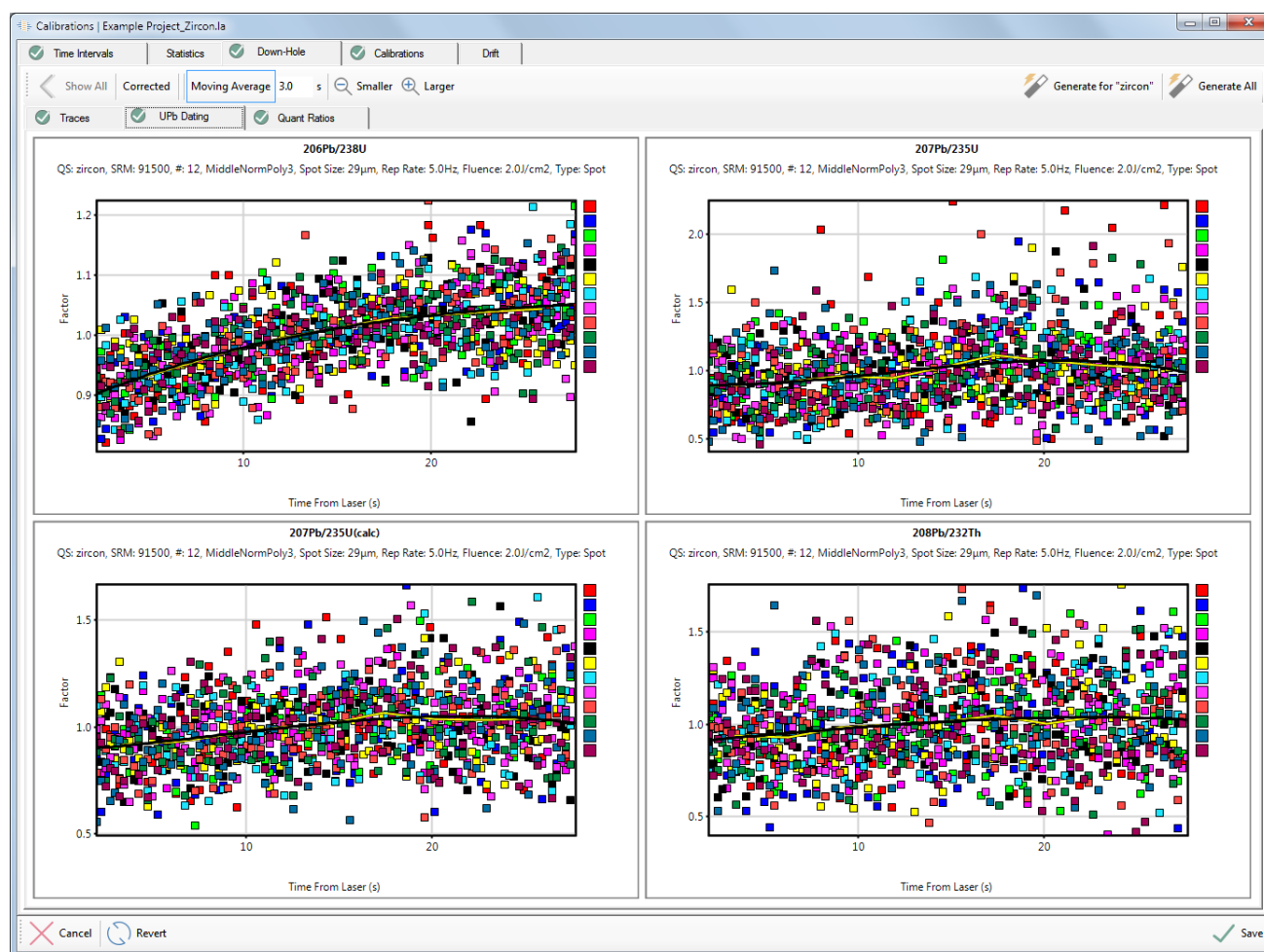
Figure 63 Down-hole correction tab showing the main viewing features and the three data sources of trace elements, UPb dating, and Quant ratios.

The calibration standards are shown for the relevant data source (traces, UPb dating, and quant ratios) in the same way. The data is divided into groups using the designated laser conditions in the "Group quantification by laser parameters" section of the down-hole tab of the QS window (Page 98). Each box point on the chart corresponds to a single ICP–MS sweep, and the colour corresponds to a single standard analysis. The x-axis is the time from the start of the laser aerosol arrival defined in the Laser Times section (see page 111), while the Y axis ("Factor" on Figure 63) is the change in the element ratio (e.g. 206Pb/238U) relative to the average of a single analysis.

Graph display options for the down-hole correction include:

- Show all – This option is selected to show all standards on one graph for a set of laser conditions.

- Corrected – Show the corrected data, making the down-hole curve equal to 1 throughout the analysis. (Figure 64).

- Moving average – Generates a moving average line (in yellow). The average is calculated using sweeps contained in a set length of time.

- Smaller-Larger – The size of individual graphs can be increased and decreased which changes the number of graphs visible at the same time.
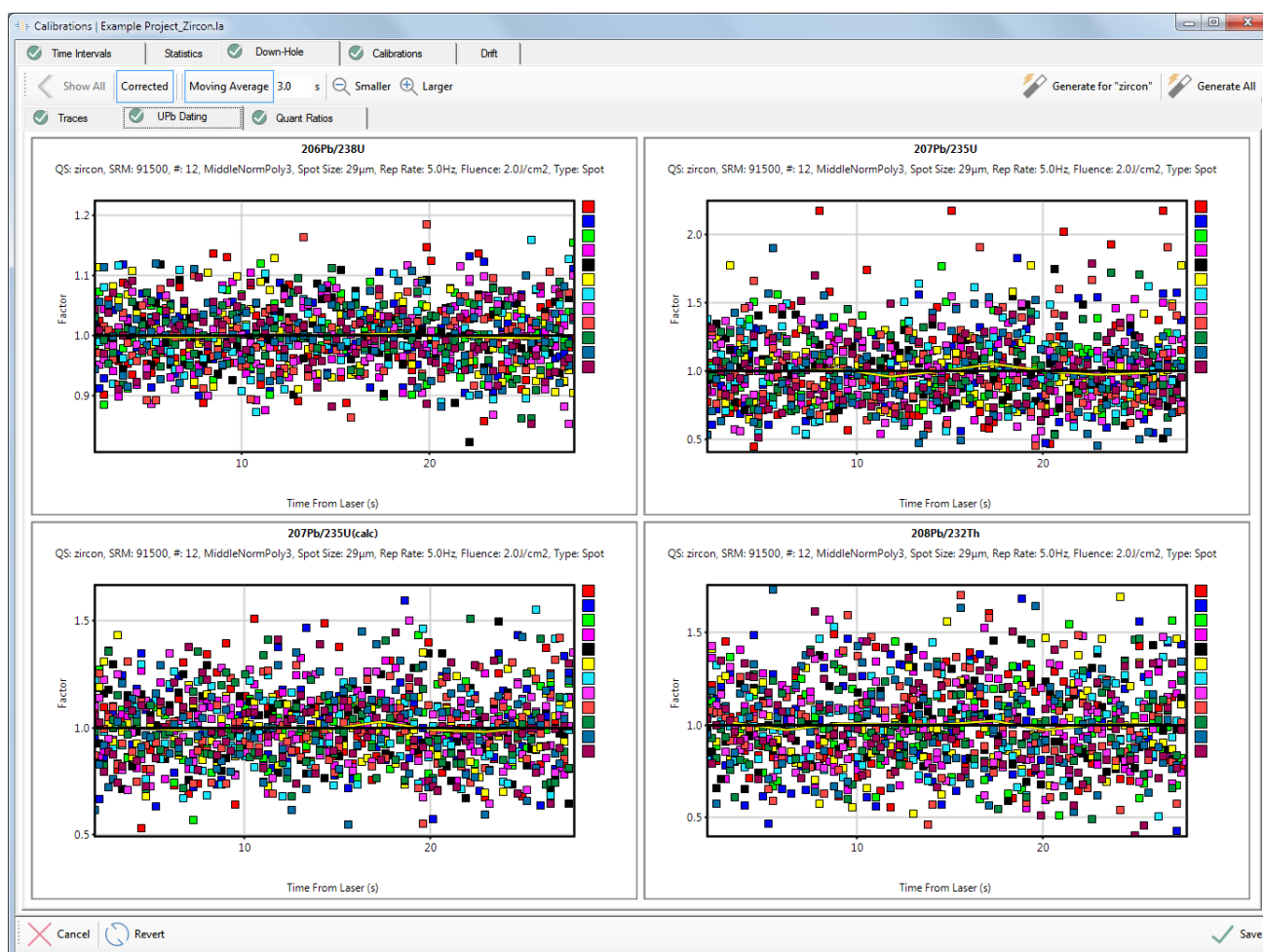
Figure 64 Corrected UPb data for the down-hole fractionation effects.

By default, a single down-hole curve correction is applied to all unknowns using all of the calibration standards for a given set of laser conditions, however this assumes no change in the shape of the down-hole curve. To investigate the possibility of the down-hole fractionation changing shape throughout an analysis session, right-click a single down-hole graph to generate several time-dependent graphs for a single ratio (e.g. 206Pb/238U) at a set of laser conditions (Figure 65). Multiple calibration standards are shown in each graph and would ideally represent sets of standards run between unknowns. Each graph represents different standard sets throughout the analysis session.

A single down-hole curve is calculated with all calibration standards, and shown on these graphs by a black solid line. The down-hole curve can be calculated for each set of standards by selecting the "Interpolate" button. This is useful if there are significant changes in the down-hole curve shape from the beginning to the end of the analytical session.
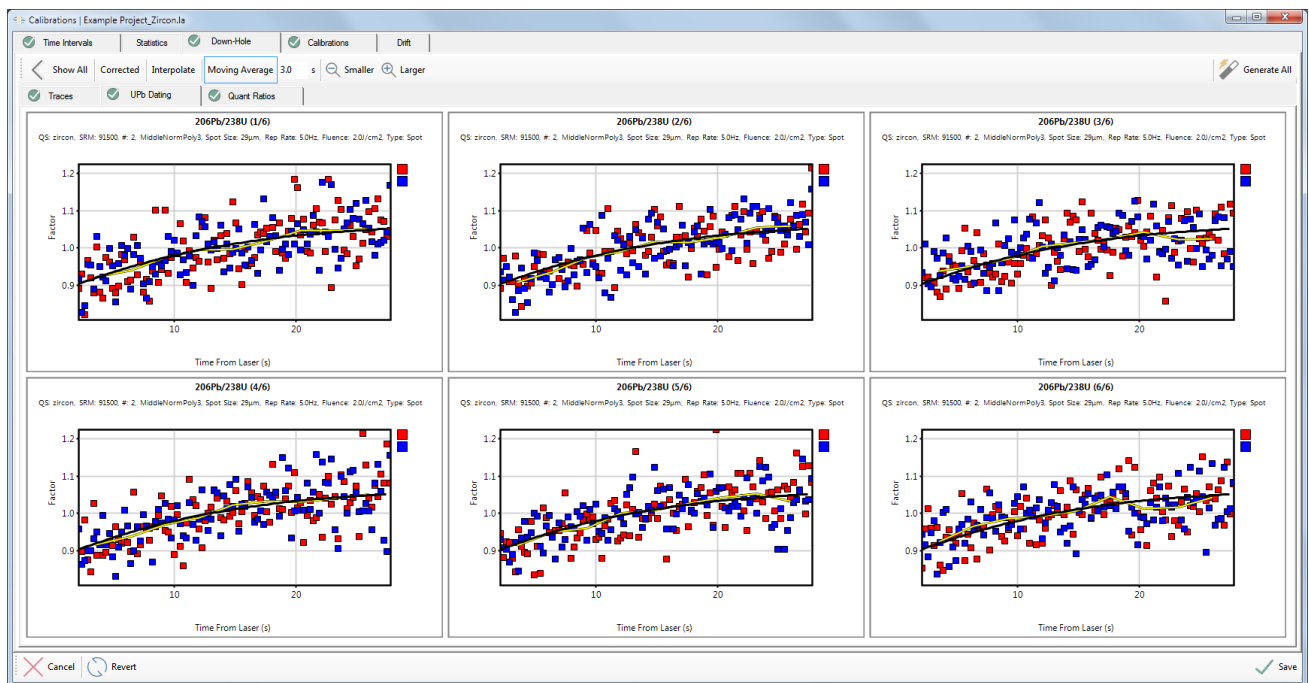
Figure 65 Calibrations window, down-hole fractionation curves for a standard showing down-hole fitting for 6 groups over the analysis session.
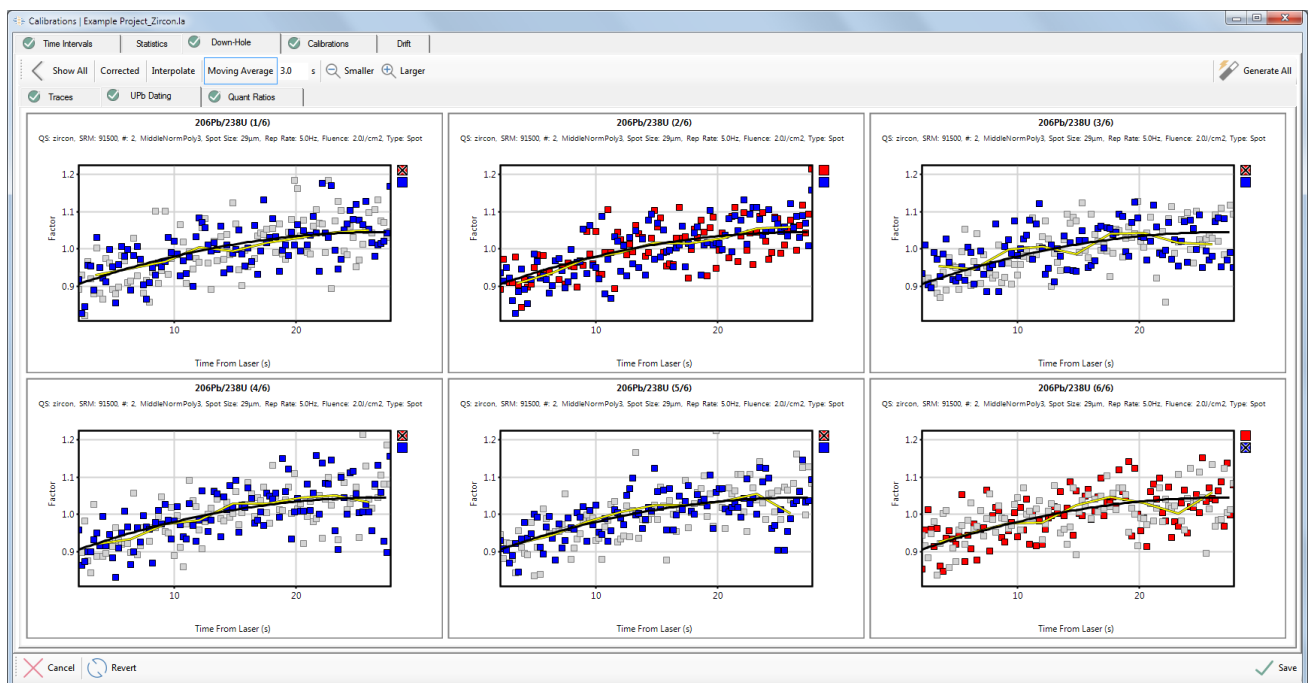
Figure 66: Down-hole models showing manual deselection of individual standard measurements.

Calibration Models

A calibration curve relates relative intensities of a mass in an unknown to a known concentration in a RM. This signal intensity is normalized to an internal standard element and plotted with time during the project. This allows the user to account for signal intensity variations which may occur during the length of a project.

When the calibrations page is first opened it will say "No calibration curves". The calibration curves need to be generated by selecting the "Automatic Defaults (All QSs, All Types)" button.

*Note: If a calibration standard time period or down-hole curve is changed then the calibration functions will need to be re-generated.*

Note: The calibrations for traces, UPb dating, and Quant ratios each need to be generated and inspected.

Note: Each QS will have its own calibrations and will need to be inspected independently.

In the text below, most of the option names begin with `"Profile.Quant.DefaultCalibrationModels."` which for clarity has been replaced by an ellipsis(…). Options for the generation of automatic intervals are:

- `"Quant.CalibrationUncertaintyCalculation"` – How to assess uncertainty of calibration curves?

- `"Quant.CalibrationFittingStyle"` – How should calibration curves be fitted?

- `"…WiggleEnvelope_VarianceMultiplier"` – Multiplier to variance when assessing curve fitting suitability.

- `"…Variance"` – What kind of variance is used for assessing misfits and curve fitting suitability?

- `"…ReselectAllTimePeriodsOnSingleMassAuto"` – False == De-selected time periods remain de-selected.

- `"…PolyExtrapolationThreshold"` – If extrapolating a poly curve for more than this % of total project time, use a constant curve for extrapolation instead.

- "…OutlierVarianceMultiplier" – Multiplier to variance when assessing interval misfit.

- "…NumOutliersThresholdPercent" – How many outliers (% of total number of groups) are needed to switch to individual intervals.

- "…CurveFit" – What kind of curve to fit to calibrations by default. Please note that other rules also apply.

Calibration Models – Trace Elements

Trace element calibrations are created for each QS based on the quantification setup step of data reduction (see "Trace Elements Scheme" on Page 84 for more information).

The calibration summary window allows the user to view every mass relative to the internal standard element in the project for comparison purposes.
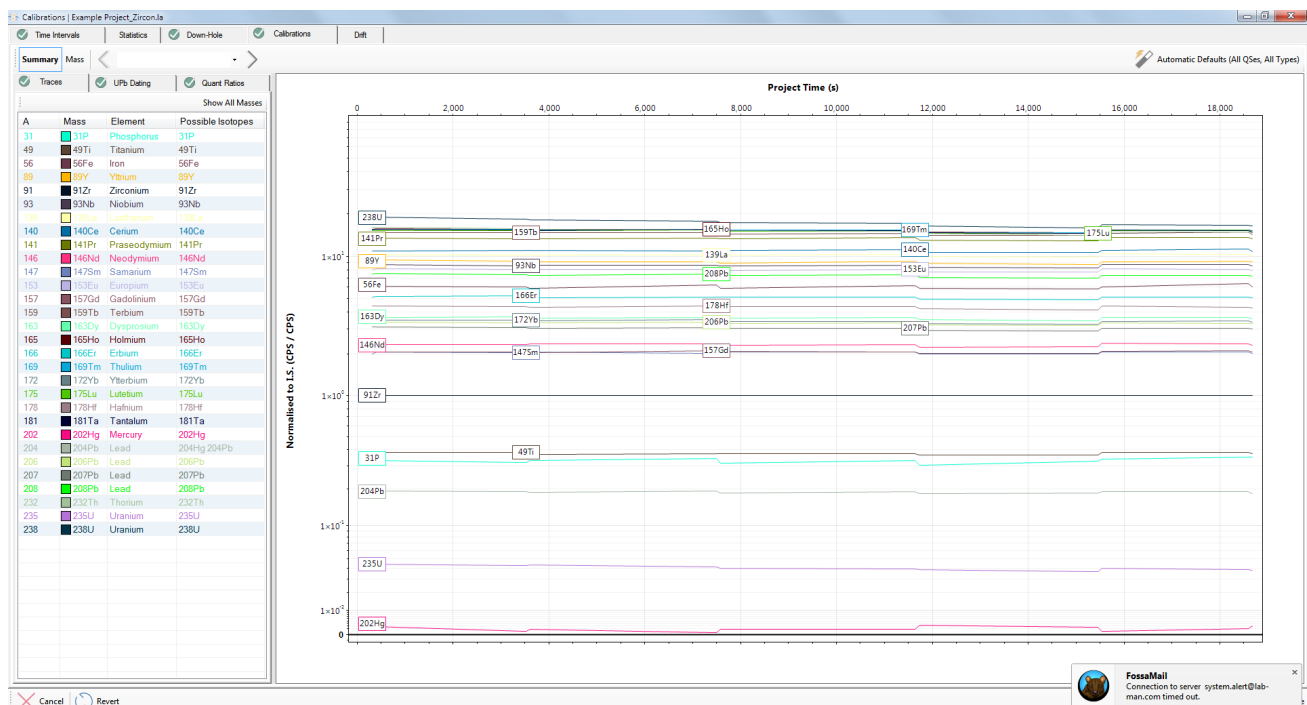

Figure 67 Calibrations tab displaying all masses present in the project. Details about the generated calibrations for each mass are shown and visualization of the calibration curve with time is displayed.

Each mass in the project can be viewed separately by selecting the "mass" button (Figure 68) to show the "drift", or the time dependent change in the mass (i.e. 24Mg) to internal standard element ratio in the RM for the whole project. ICP–MS instruments can change sensitivity over an analytical session and this change in sensitivity is not the same for all masses. Since there is typically one internal standard element (often of light mass), if there is a change in the relative sensitivities of the light to heavy masses in the ICP–MS, a "drift" correction needs to be applied. This highlights the importance of analysing RMs regularly in a project so that any "drift" in the ICP–MS can be accurately estimated. Review each mass in each QS in the project to check the automatic "drift" fitting equations created by LADR.

Note: Vertical bars show ±1 standard deviation by default, which can be changed in the program options. The current value shown by the vertical bars is labelled at the top-right of the chart.

Note: The large vertical shaded regions highlight the groups of calibration standards.

Note: The pink shading shows the envelope that the algorithm uses for choosing the best polynomial order for the fit. The size of this envelope can be changed using the options.

Note: LADR uses an algorithm to estimate the best fit function to the drift in a set of RM analyses when the "Automatic Defaults" button is clicked.

If the user identifies a mismatch in the automatic "drift" curve and the real distribution of the data, the user can manually select the drift curve function.

Options available for a manual line-fit to the drift in the calibration standards are:

- Make all trace elements in "QS" the same – Set all trace elements in this QS to the same function of the drift line-fit.

- Automatic – Apply the LADR automatic default drift curve to the selected mass.

- Constant – Apply a constant line-fit to the drift in the calibration standards.

- Linear – Apply a linear line-fit to the drift in the calibration standards.

- Poly – Apply a 2nd to 8th order polynomial calibration fit to the drift in the calibration standards.

- Separate intervals – Create separate calibration drift lines for different time intervals in the project.

- Select all time periods – Selected all standards in project (if standards have been de-selected).

Use the "scissors" icon to split the drift curve, click and drag the boundary to move. A split may be necessary if the calibration standards change dramatically and a curve fit is not appropriate. Split curves can be re-joined using the "merge" icon at the bottom of each boundary.

If a standard is significantly different from all other calibration standards analysed, the user should:

1. Check the time interval for that standard (in calibrations → time intervals) to ensure that the signal does not include gas blank signal or go beyond the end of the laser signal.

2. Look for potential large spikes which may be affecting the average signal and remove any spikes present.

3. If steps 1 or 2 do not resolve any anomalous standard values, users may left-click on the standard on the graph in Figure 68 to remove that standard from the generation of a calibration drift curve.

Note: Ensure the calibration drift curves do not "overfit" meaning there are any extra curves not supported by the number of RMs analysed.

Note: An underlying assumption with the drift curves is that the RM analysed is homogeneous for the mass of interest and the internal standard element. If there is heterogeneity in the RM, the drift curves will not accurately reflect the sensitivity change of the ICP–MS.
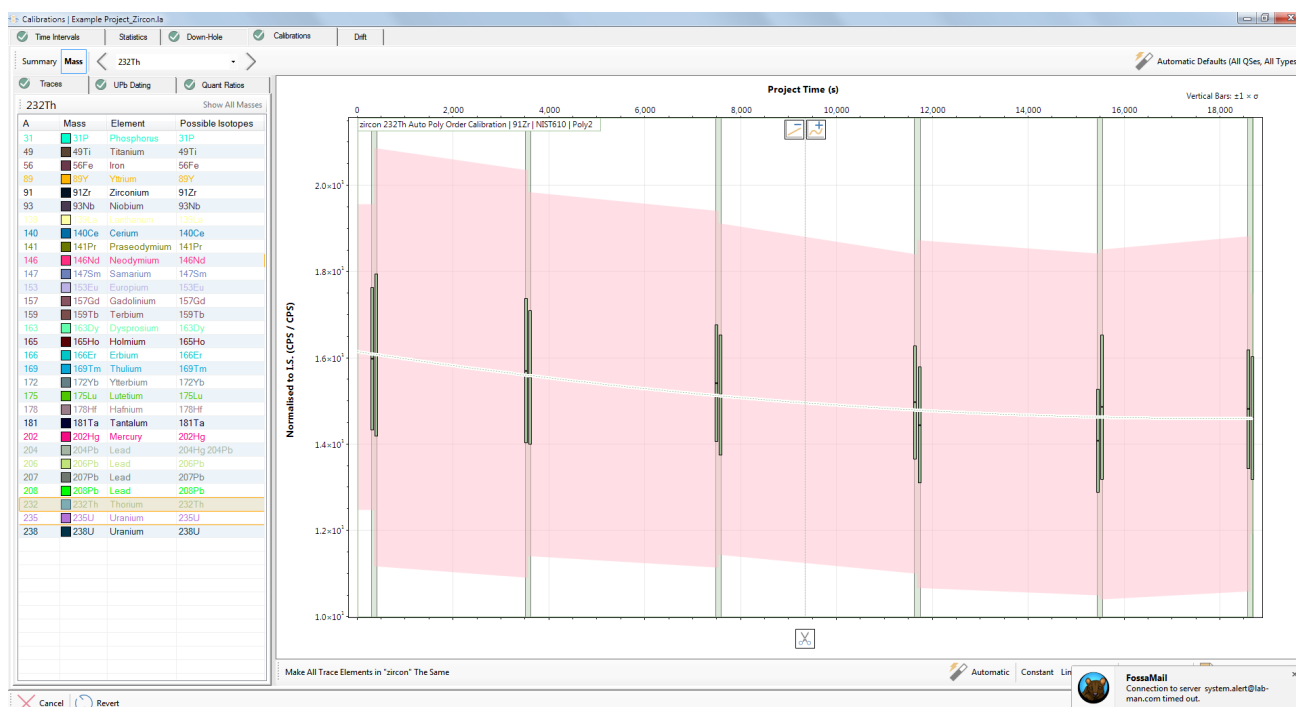
Figure 68 Calibration curve displayed for a single mass (232Th/91Zr on NIST610).

Calibration Models – UPb Dating

Note: *The previous section on trace elements contains some general guidance on using the interface that also applies to UPb dating.*

If the "Automatic Defaults" button was selected in the traces tab then there will be calibration drift lines already generated for the UPb tab of the calibrations window. If this button has not been selected, please do this now to generate calibration drift lines for the UPb ratios.

Each ratio defined in the UPb section of the QS setup will be calibrated for each set of laser conditions as defined in the QS setup. These different calibrations are listed in a table as in Figure 69, including all the selected laser conditions.

As with the trace elements calibration models, it is necessary to run through all the UPb automatically generated calibration models and adjust the function fit manually, where necessary (Figure 70).

Figure 69 UPb calibration summary in the calibrations window.
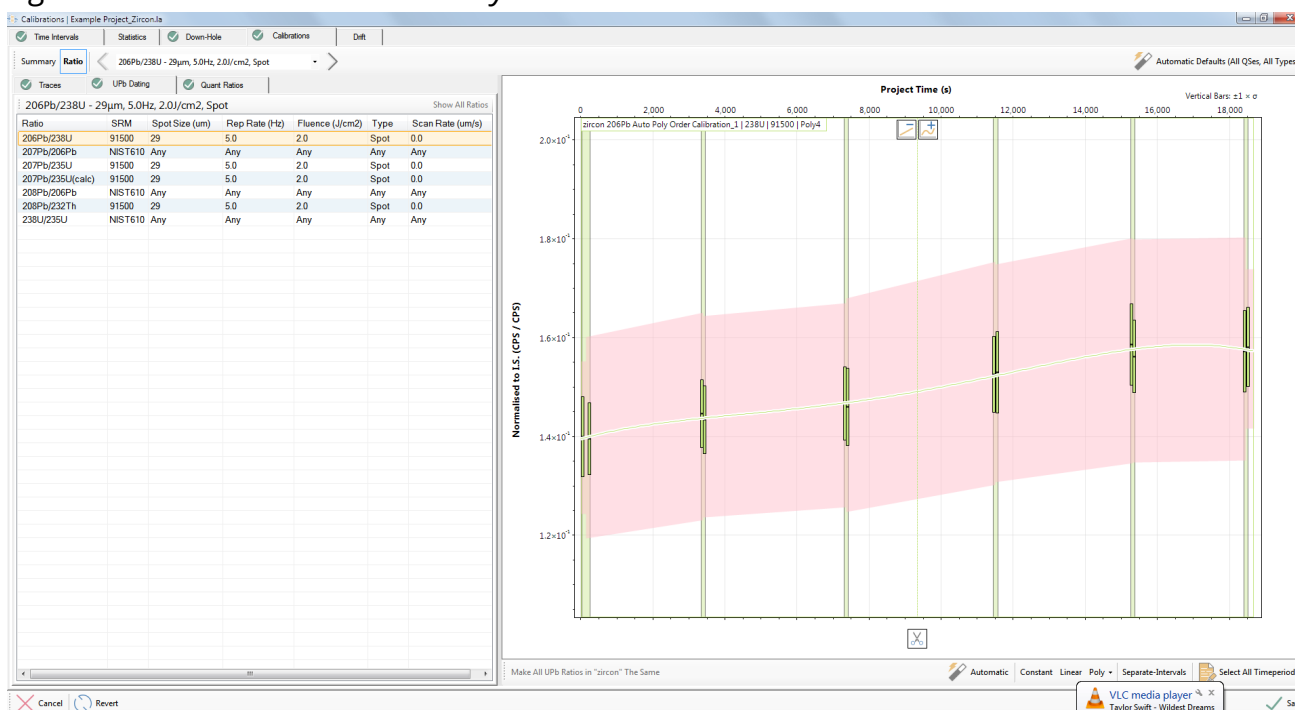
Figure 70 Single ratio calibrations in the UPb calibrations window.

Calibration Models – Quantified Ratios

Note: *The previous sections on trace elements and UPb dating contains some general guidance on using the interface that also applies to quantified ratios.*

Calibration models of quantified ratios, selected in the QS setup, are generated in a similar way to the UPb dating tab. Calibration lines are created for each set of laser conditions as defined in the QS setup (see page 102 for more information).

Drift

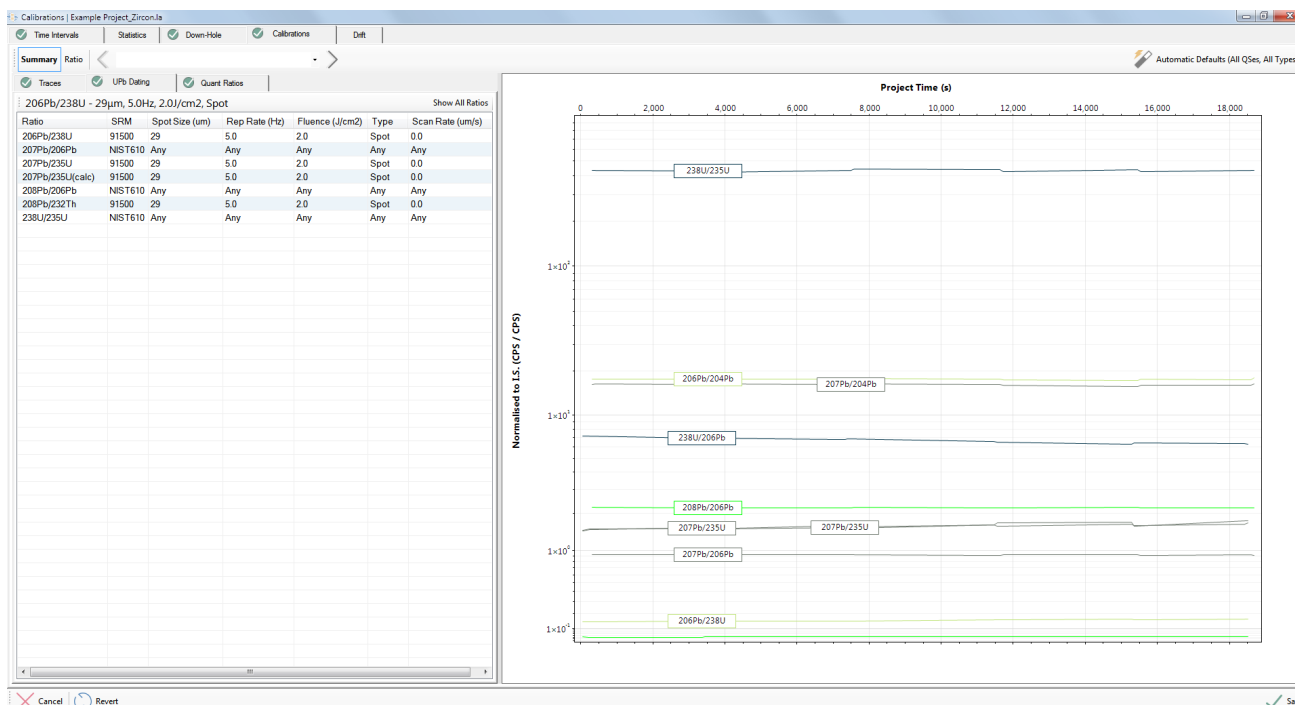To view the amount of instrument drift as a quantitative number, the "Drift" tab is available

The drift tab in the calibrations window allows the user to view and asses the degree of drift present during an analytical session. This may be useful if the user is attempting to target sources of analytical error, look for RM heterogeneity or potential instrument maintenance issues. If the degree of drift is high (30-40%) then the user may want to investigate the source. If there is a substantial degree of element drift, this may cause higher errors as the applied drift function may not accurately characterize the drift in the unknowns between blocks of RMs.

The numbers in the table for Figure 71 are the change in the mass to internal standard element ratio in an RM for the last block of RMs analysed in the project normalized to the first block of RMs analysed in the project. A value of 1 on the graph implies no drift. The internal standard element is 1 by definition. The graph in Figure 71 show the same data but graphically in %.

This drift value is calculated by the equation:

$$\frac{Value\,at\,the\,end\,of\,the\,calibration\,curve}{Value\,at\,the\,beginning\,of\,the\,calibration\,curve} * 100$$
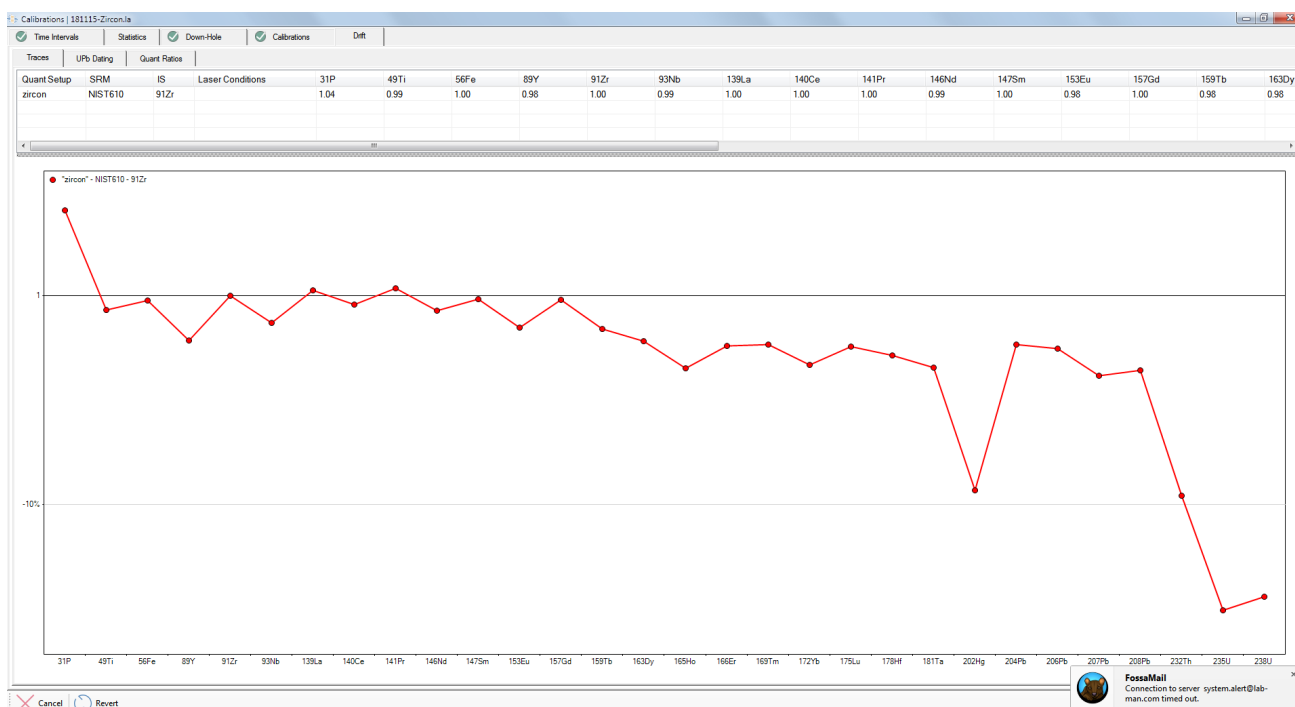
Figure 71 Drift tab in the calibration window. Displays the percent drift for each element during an analytical session.

Note: *The amount of drift is typically mass dependent and if a light mass (e.g. 43Ca) is used as the internal standard element, then the amount of drift typically increases with mass.*

Note: *The trace element drift chart is usually the most informative as it shows drift values for all masses.*

Analysis Log Review

Introduction

Once the previous workflow stage, "Calibrations", has been completed, LADR will enable the "Compute" button.

The "Analysis Log Review" window is optional, but provides the user with a final opportunity to adjust the analysis intervals. It is positioned at the end of the workflow because once the calibration and down-hole models have been generated it is possible to show down-hole and drift corrected ratios, which can greatly assist with selection of analysis intervals. This is put to particular use by the UPb dating tab, which shows fully corrected ratios plotted on a range of concordia diagrams.

The user is able to perform all of the same tasks as the "Analysis Log" window, except time periods on calibration standards cannot be edited.

Interface

The analysis log review main window consists of the analysis log table down the left-hand side, and a range of charts designed for editing analysis intervals.
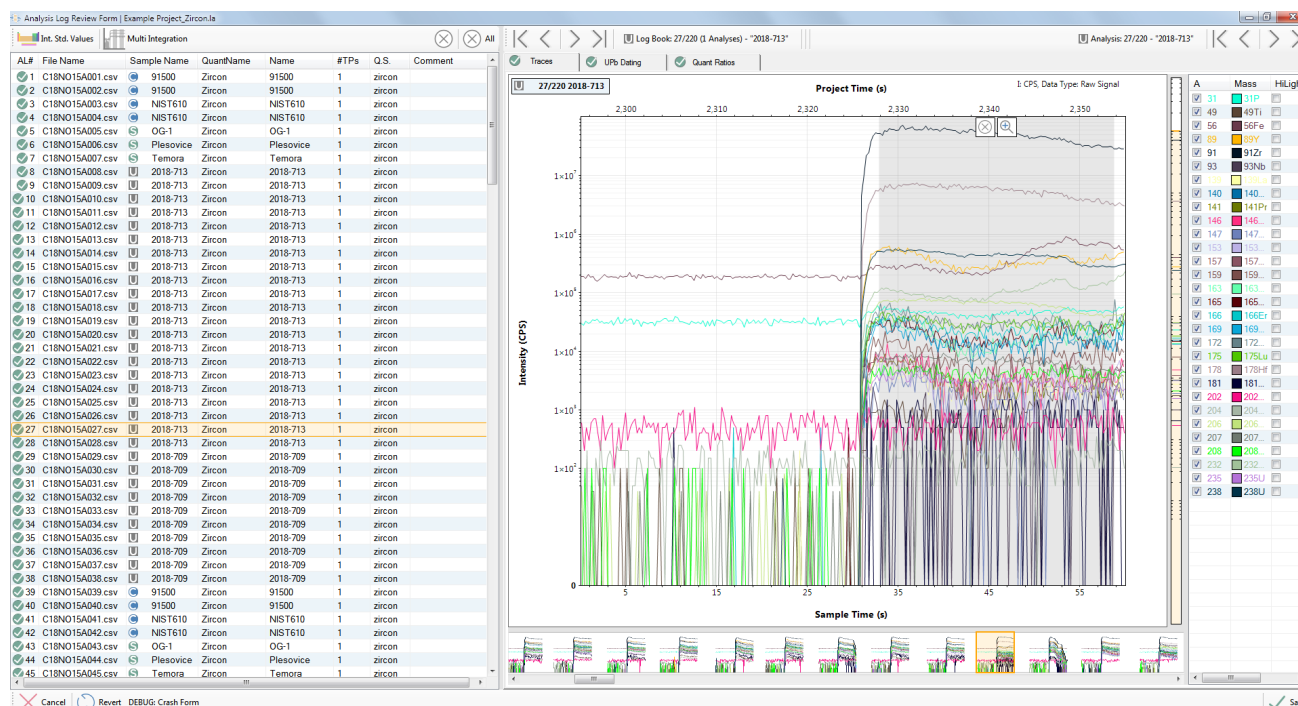
Figure 72: The analysis log review main window, showing the trace elements tab.
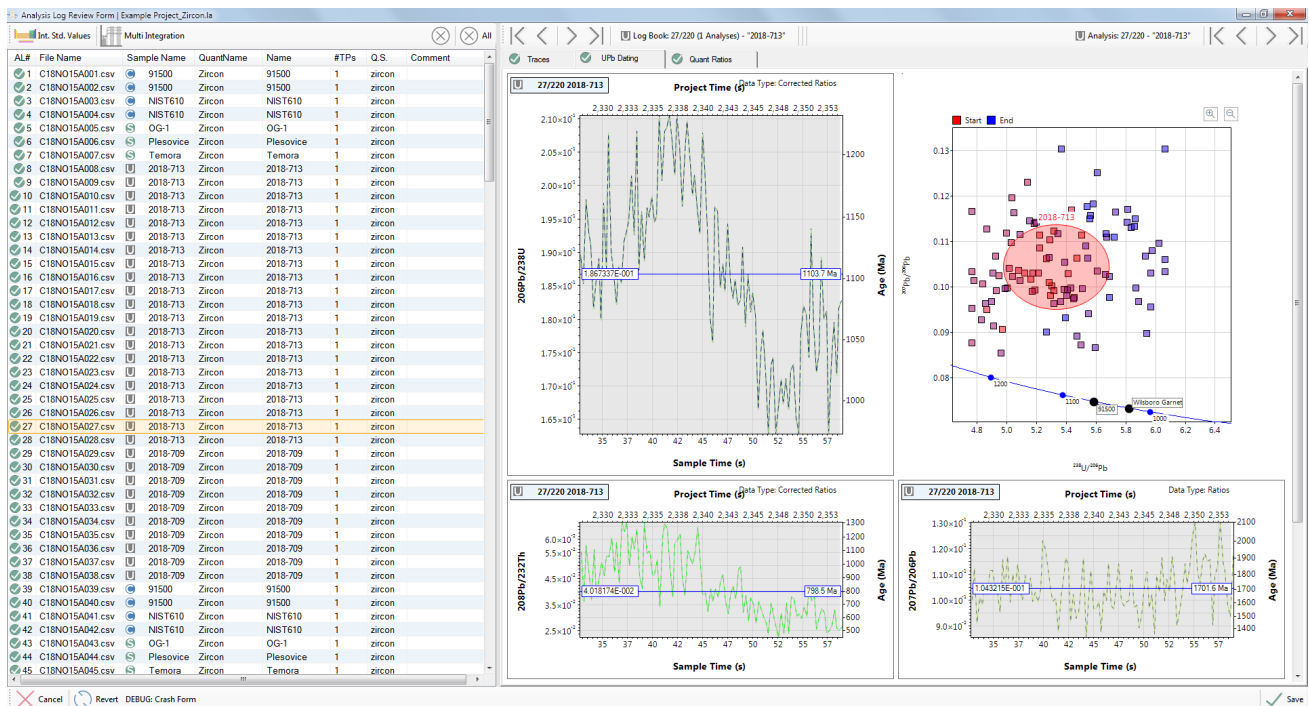
Figure 73: The analysis log review main window, showing the UPb dating tab. The concordia plot can be changed to one of either: "206/238 vs 207/235", or "208/232 vs 207/235", or "207/206 vs 238/206".
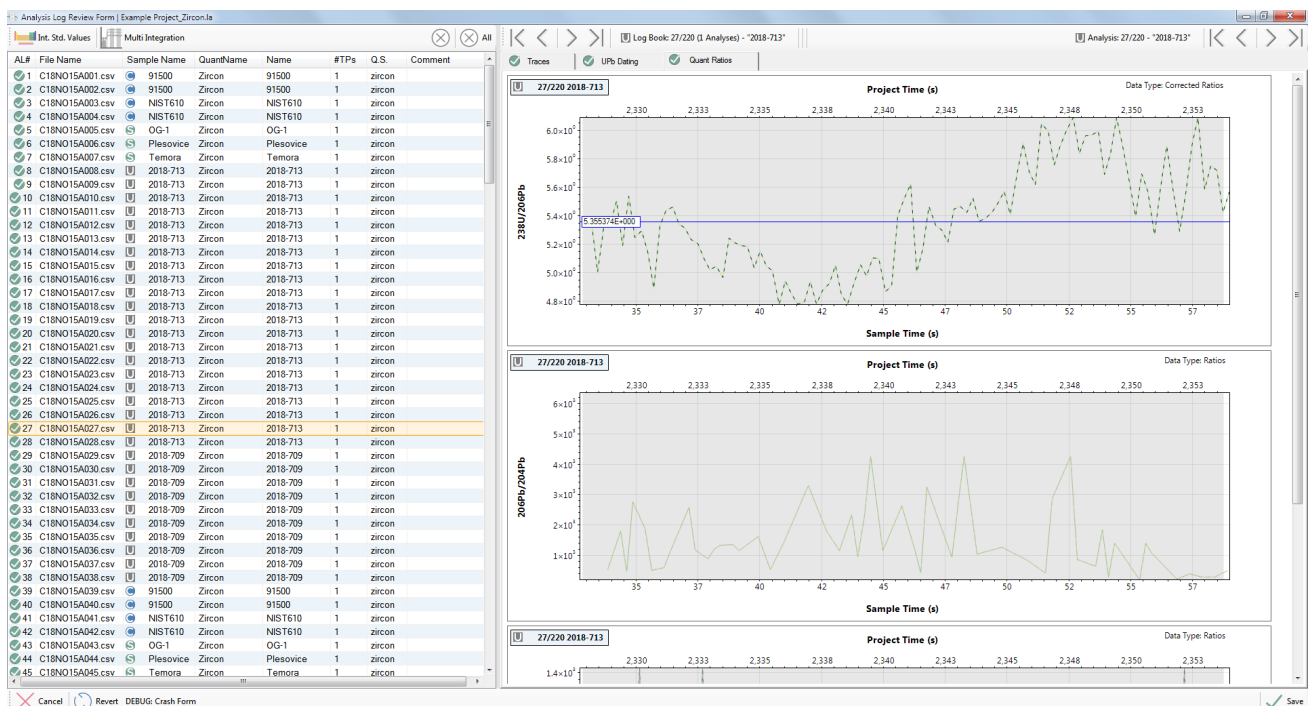
Figure 74: The analysis log review main window, showing quantified ratio plots.

Trace Elements

The "Traces" tab is very similar to the "Analysis Log" window, and allows the user to edit or create analysis log entries.

The internal standard values can be examined or modified in the "Analysis Log Review Form" using the internal standard values form. This form has been discussed in the analysis log section on page 127.

Note: This is an optional window if users are only performing trace element analysis and do not wish to review the selected time intervals of signal for each sample.

Note: Users are unable to modify the calibration standard time intervals on this window.

To view the signals in a more convenient form, right click on the chart and choose "View"→"GB Sub and IS Norm and Cleaned Up From QS..." to show masses gas blank subtracted and normalised to the internal standard.
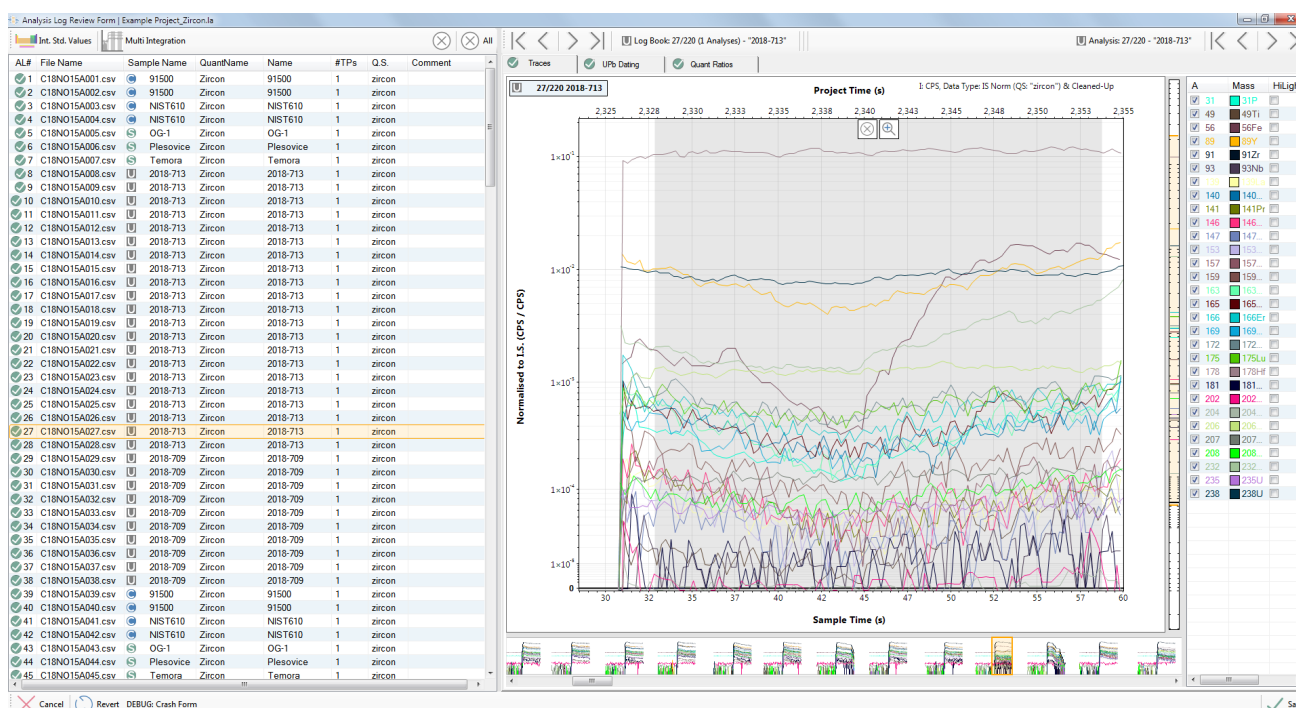
Figure 75: The trace elements chart showing gas blank subtracted signals normalised to the internal standard. To activate this view, right click the chart and choose "GB Sub and IS Norm and Cleaned Up From QS...".

UPb Dating

If UPb dating was selected in the QS, then the "Analysis Log Review Form" window becomes a mandatory step for data reduction.

Select the UPb tab to show several time-resolved isotopic ratio plots (Figure 73). Toggle between the "Traces" tab and the "UPb dating" tab to better visualise how inclusions or zoning in trace elements are affecting the UPb isotopes.

The three plots displaying isotopic ratios with sample time have a fixed X-axis equivalent to the time generated in the "Laser Times" window.
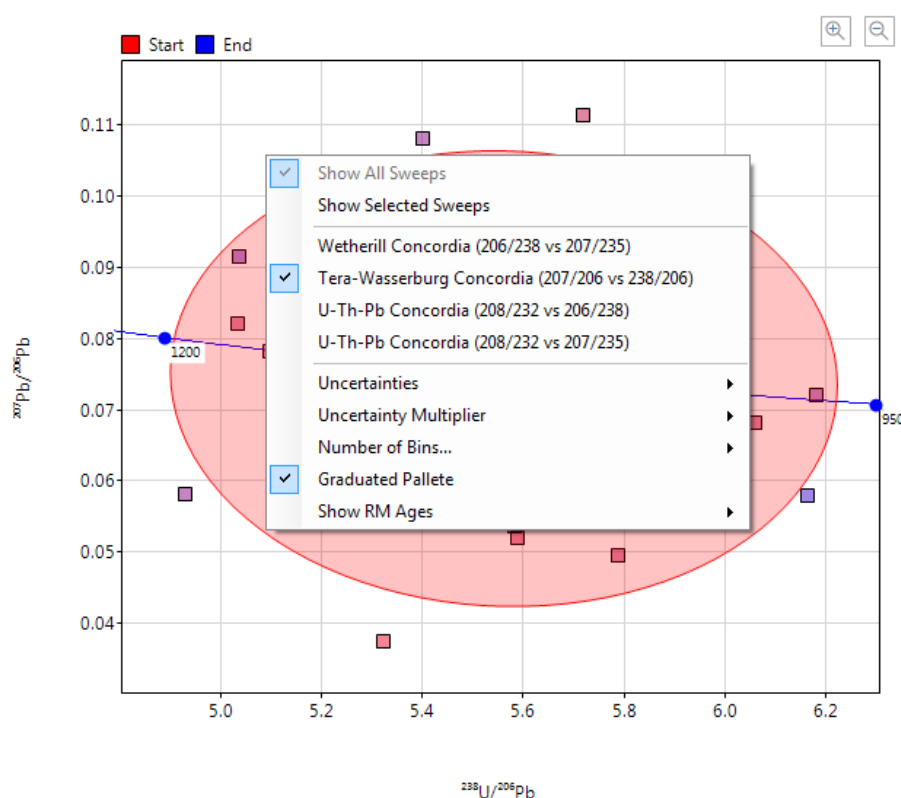
Figure 76 Option for the Concordia diagram in the UPb tab of the Analysis Log Review form.

By default the concordia plot shows the location of every sweep in the selected sample time interval. This plot can be customised by right-clicking and selecting from the options (Figure 76). Plot options will be remembered by the program.

These options are:

- Show All Sweeps – Show all sweep information for the entire sample signal displayed.

- Show Selected Sweeps – Show only sweeps that have been highlighted (selected) in the time resolved windows (grey-shaded region).

- Concordia_206_238_vs_207_235 – Change the type of Concordia diagram displayed to a 206Pb/238U versus 207Pb/235U Wetherill Concordia plot.

- Concordia_207_206_vs_238_206 – Change the type of Concordia diagram displayed to a 207Pb/206Pb versus 238U/206Pb Tera-Wasserburg Concordia plot.

- Concordia_208_232_vs_206_238 – Compare the Th and U ages via this 208Pb/232Th versus 206Pb/238U plot.

- Concordia_208_232_vs_207_235 – Compare the Th and U ages via this 208Pb/232Th versus 207Pb/235U plot.

- Uncertainties – Show as either crosses or ellipses. Use the "Cross" marker to identify the mean with uncorrelated uncertainties in X and Y, while use the "Ellipse" to see correlated uncertainty ellipses.

- Uncertainty Multiplier – Show either 1, 2, or 3 standard deviations.

- Number of Bins – Divide the displayed data in a certain number of bins which will each be displayed as an ellipse. Users can choose between 1, 2, 3, 5, and 10 bins.

- Graduated Palette – When no bins are displayed, a graduated palette can be turned on and off. The gradations are in reference to the beginning to end of the sample signal and are for better visualization of changes in the UPb isotopic system through the analysis.

- Show RM Ages – RMs containing UPb age information and defined in the profile can be displayed or removed from the Concordia diagram.

Note: The correlated error ellipses shown in red on the Concordia plots are based on the calculation of a Pearson Correlation Coefficient computed from the ratios for each sweep in the interval.

These plot can be zoomed in by holding ALT, click, and drag to create a zoom in box. Zooming in is also possible by holding Ctrl while the mouse cursor is over a desired region to zoom into.

Time periods can be modified in the UPb section by:

- Deleting the highlighted region using the icon at the top of the time periods.

- Use the multi-integration tool to select multiple sections of signal and treat as one.

- Select multiple sections of signal and treat as multiple samples.

- Click and drag a new time period to create a new analysis log entry.

Any changes on the selected time period in the UPb dating tab will automatically be reflected on the concordia diagram. These changes will be reflected in the chosen sample intervals in both the traces and quant ratios tabs if these were activated in the QS setup.

Note: You are unable to edit time periods on the standards.

Selection of time intervals for UPb age calculations needs to be done in accordance with an understanding of the literature and current geochronology community practices. In general, things to be considered on these plots are Pb loss, different age domains (inherited cores), metamict zones, etc. This is an expansive topic that goes rapidly beyond the scope of this document. If this is new to you, we recommend talking to an expert well established in the field and following their advice in the first instance.

Quantified Ratios

The quant ratios portion of the Analysis Log Review Form displays the defined ratios in the QS setup window (Figure 74). These ratio plots are down-hole, drift, and mass-bias corrected so the true isotopic variations within a single analysis can be assessed and the integration intervals changed according to user objectives.

These plot can be zoomed in by holding ALT, click, and drag to create a zoom in box. Zooming in is also possible by holding Ctrl while the mouse cursor is over a desired region to zoom into.

Note: *You are unable to edit time periods on the standards.*

Compute

Once all stages of the project have been completed the compute button will become available. If there is any reason the project cannot be computed, hover the mouse over the disabled compute button to see a pop-up tooltip explaining the problem.

Click the "compute" button to start the calculation. The calculation can be cancelled, and the results that were computed prior to cancellation viewed in the "Results" window.

Errors

In general the calculation will finish without reporting any errors. However, the calculation proceeds with a "best effort" approach, and will make every attempt to keep going even if many errors do occur.

Note: The most common error is forgetting to assign a QS to the analysis log entries, followed closely by forgetting to enter an internal standard concentration for each analysis log entry (when required to by the QS).

When the calculation encounters errors, these are (as much as possible) collated into a condensed message:
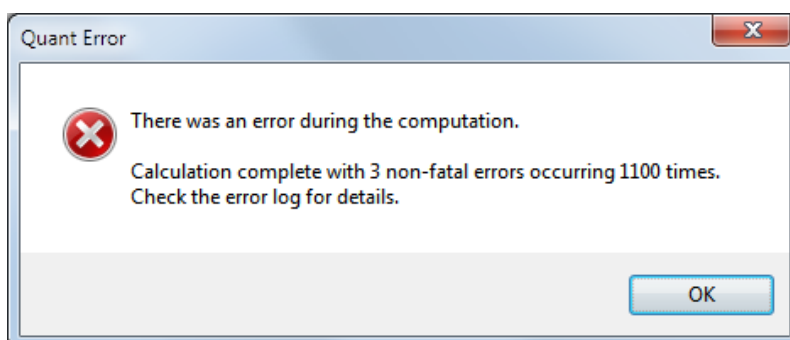
Figure 77: Example of an error message shown after the calculation is complete.

More information about the specific error messages can be found in the "Action Log".

Performance

The main calculation in LADR is CPU bound, runs multithreaded, and scales well with the number of CPU cores on the system.

Results

Once the main calculation is complete (even partially, in case it was aborted) then the results window becomes available and displays all of the results for the project.

Now that the workflow has been completed, the user is able to access all of the windows in any order. Certain actions will reset downstream stages, for example editing gas blank models will reset the calibration models. Other actions do not, for example going to the "Manage Reference Materials" window and editing a concentration in a reference material will not reset the project, however the user will need to press the compute button to ensure the change propagates through to the results.

Note: At the time of writing, no actions will automatically recompute results. While we have been diligent with the implementation, it is possible that some actions will not trigger the results to be cleared, when they logically should. If this happens, please report such transgressions to LADR support (ladr@norsci.com) and always press the compute button after making any changes.

Figure 78 The results window.

To view raw statistics for data that contributed to a calculated result, right-click on any cell in the results table and select "Inspect Statistics".

To view all of the intermediate values that contributed to a calculated result, right-click on any cell in the results table and select "Inspect Calculation".

The tool bar shown at the top of the results window contains several options for controlling the display.

The View Menu is found in the top-left and contains options for controlling the appearance of the Results form (see Figure 79).
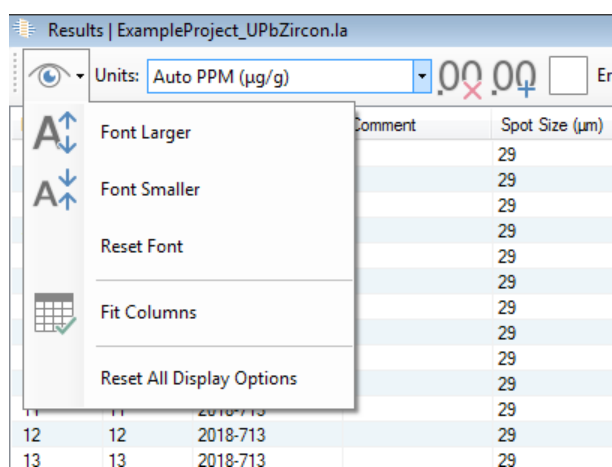
Figure 79: The Result View Menu.

The text size can be modified in the Results window table by using the controls in the View Menu for increasing and decreasing text respectively (Figure 79). The chosen text size will be remembered by the program.

The units section of the top bar allows the user to select the units displayed in the table. Concentration data in the table can be listed as weight percent, PPM (µg / g), weight percent compound (e.g oxide, but the exact compound depends on the QS stoichiometry settings, see "QS Settings – Trace Elements – Element Stoichiometry"), and PPM compound. The "Auto PPM" option is intended to improve readability of the results and will show values in weight percent for concentrations greater than 1 weight percent and PPM for concentrations below. To differentiate between the displayed units, the text "^{wt}%" will be shown as a superscript next to those values in weight percent.

The number of decimal point displayed in the table can be adjusted using the decimal points buttons in the tool bar.

Values reported in the Results Table are not always taken from the raw data. For example, when viewing calibration or gas blank values, the values shown is the average modelled values over the interval. If you wish to access aggregated raw data from the data in the project, use the statistics tables in the Gas Blanks (see "Gas Blank Statistics"), Calibrations (see "Calibration Statistics"), or Analysis Log (see "View Analysis Statistics") windows. The values shown in the tables can also be copied and pasted into a spreadsheet program for further processing.

Uncertainty Levels

Data uncertainty can be viewed in the table using the checked box. The degree of uncertainty can vary from 1 to 5 sigma using the drop-down menu. The source of uncertainty can be defined as:

- Signal Precision – The standard error of the gas blank subtracted and interference corrected signal. When the interval contains invalid ratios (typically due to negative or zero values on the denominator) or the standard deviation is zero (e.g. the internal standard divided by itself) then the standard error is replaced by the theoretical uncertainty from Poisson counting statistics.

- Quantification Precision – Adds the observed precision on the calibration standards.

- Within-Run Analytical Precision – Adds the uncertainty from the misfit of the calibration model.

- Full Within-Lab Analytical Precision – Adds the uncertainty associated with the heterogeneity of analyte element and internal standard element in the calibration standard.

- Full Within-Lab Analytical Precision with Secondary Standard Correction – This uncertainty is similar to the "Full Within-Lab Analytical Precision", but also includes the SS uncertainties. The secondary standard error is the variation of the secondary standard correction factor over the length of the analytical session.

- Full Analytical Uncertainty Without Secondary Standard Correction – Adds uncertainties associated with the known values of the internal standard and

analyte mass (or the ratio) in the calibration standard. **This value includes all known sources of uncertainty.**

- Full Analytical Uncertainty With Secondary Standard Correction – Same as above, but includes uncertainties associated with the SS correction as in "Full Within-Lab Analytical Precision with Secondary Standard Correction". **This value includes all known sources of uncertainty.**

Note: The uncertainty of the UPb age calculation is controlled by the option "Profile.Results.UPbDating.AgeUncertaintyCalc" When computing age from ratios, the uncertainty can be calculated as the relative error of the age range. The "Relative Error" option propagates the percent uncertainty from the ratios, while "Compute Age Range" computes an age range (often asymmetric).

The display drop-down menu allows the user to view many different sources of information for each element in each sample. Final results and associated uncertainties can be displayed as well as many intermediate calculation steps from the initial CPS to final PPM.

- Filtered Result – The final analysis results with below detection limit data removed and replaced with a "<" and the calculated detection limit for that individual analysis.

- Results – The concentration of the mass in the given sample based upon the calibration lines, internal standard elements, gas blank subtraction, and any other correction applied to the data.

- Uncertainty (relative percent) – The desired source and level (sigma) of uncertainly as defined in LADR before results were exported. Uncertainty is presented as the uncertainty (PPM) of a mass / the concentration of the mass * 100%.

- Uncertainty (Absolute) – The desired source and level (sigma) of uncertainly as defined in LADR before results were exported. This is the absolute uncertainty in PPM.

- Detection Limit – The detection limit is calculated using the standard deviation of the gas blank (σ), the sensitivity to the mass (S), and the number of time slices investigated in the analysis and gas blank (n_a and n_b respectively). The equation

from Longerich et al., 1996 is:

$$DetectionLimit = \frac{3\sigma}{S}\sqrt{\frac{1}{n_b} + \frac{1}{n_a}}$$

- Known Value – The standard values defined in the project standard list. See page 37 for more information on adding and modifying standards in the profile and project.

- Result Normalized to Known Value – The ratio of the calculated value and the known value for the samples defined as standards in the project.

- Secondary Standard Correction Factor – A correction factor applied to the project unknowns, generated by examining the difference in the secondary standards from the expected value. The equation is:

$$correcteddata = uncorected \frac{data * SSknownvalue}{averageSSresult}$$

- Uncorrected Result – The results without the secondary standard correction applied. The default is the ratio of the means.

- Normalizing Mass – The mass chosen to be the internal standard element.

- Normalizing Mass Concentration – The concentration defined by the user for the knowns or produced from the list of reference materials in the project of the internal standard element.

- Uncorrected Result (Sweeps) – Each sweep is reduced to a concentration and the average taken.

- Uncorrected Result (Ratio of Means) – Results not corrected to the secondary standard. The ratio of the mean analyte concentration to the mean internal standard concentration in the chosen signal interval.

- Uncorrected Result (Mean Ratio) – Results not corrected to the secondary standard. The mean ratio of the analyte concentration to the internal standard concentration in the chosen signal interval.

- Mass Signal – The average analyte counts for instrument readouts in the chosen signal interval.

- Mass Gas Blank signal – The average modelled analyte counts in the chosen gas blank interval based on the gas blank function chosen.

- Mass Gas Blank-Subtracted Signal (Counts) – The signal with a gas blank subtraction in counts.

- Mass Gas Blank-Subtracted Signal (CPS) – The signal with a gas blank subtraction in CPS.

- Normalizing Mass Signal – The average modelled internal standard element counts over the chosen signal interval.

- Normalizing Mass Gas Blank Signal – The average internal standard element counts in the chosen gas blank interval.

- Normalizing Mass Gas Blank-Subtracted Signal – The internal standard signal with a gas blank subtraction in counts.

- Mass / Normalizing Mass Ratio (Mean Ratio) – The mean of the analyte counts over the internal standard counts in the chosen signal interval.

- Mass / Normalizing Mass Ratio (Ratio of the Means) – The ratio of the mean analyte counts to the mean internal standard counts in the chosen signal interval.

- Calibration Curve Value – This is the calibration curve with time correction, showing the instrument sensitivity drift during a project.

- Calibration Yield Value – This is the CPS/PPM conversion factor created by the calibration standard values.

- Down-Hole Correction Factor (Ratio of Averages) –

- Mass Compound (for Compound View) – Displays the defined mass compound chosen for each mass (e.g. SiO_2) in the project QS. If no mass compound was chosen, it defaults to elemental mass (e.g. Si).

- Average Time (s) – The project time in seconds that is in the middle of the chosen signal interval for a sample.

There are two ways to export results into either .CSV or .XLSX format. The currently displayed data in the form can be exported into a single file, or a combined data file can be created which contains multiple tabs (.XLSX only) with different sets of information for each samples (e.g. results and uncertainty).

The default combined file exported tables are:

- Filtered Concentration (PPM) – The final analysis results as in the "Concentrations" tab, with the exception that data that fall bellow the detection limit

- Concentration (PPM) – The concentration of the mass in the given sample based upon the calibration lines, internal standard elements, gas blank subtraction, and any other correction applied to the data.

- Uncorrected Concentration (PPM) – This tab displays the results of the data without a secondary standard correction. If a secondary standard correction was not applied then the results in this tab would be identical to the results in the "Concentration" tab.

- Uncertainty (Percent) – The desired source and level (sigma) of uncertainly as defined in LADR before results were exported. Uncertainty is presented as the uncertainty (PPM) of a mass / the concentration of the mass * 100%.

- Uncertainty (PPM) – The desired source and level (sigma) of uncertainly as defined in LADR before results were exported. This is the absolute uncertainty in PPM.

- Detection Limit (PPM) – The detection limit for each mass as calculated in the equation above.

- GBSub (CPS) – Gas blank subtracted count rates in the signal for each mass, and for each sample.

- Gas Blank (CPS) – The average gas blank count rates in CPS.

- Compound – The compound associated with each mass as defined in the QS. If no compound was defined then the elemental mass is shown.

- Filtered Concentration (Wt Pc Compound) – The filtered concentration is similar to above, however the units are now weight percent compound (e.g. Wt. % oxide). The compound used for each element is shown in the "Compound" tab.

- Concentration (Wt Pc Compound) – Similar to the results in the "concentration" tab, however the units are now weight percent compound (e.g. Wt. % oxide). The compound used for each element is shown in the "Compound" tab.

- Information – The information tab displayed addition information about the data file including the software version used, the date of file creation, the location of the saved profile and project used, the number of data files, and the source and sigma level for the exported uncertainty.

Note: Any saved file will contain the maximum available precision, while the number of decimal points shown in the "Results" window will be ignored.

Note: The confidence level (sigma), and uncertainty source of any exported data will reflect the options chosen in the "Results" window.

The three types of results that can be shown in the table (trace elements, UPb age dating, and quantified ratios) can be independently viewed and exported using the tick boxes at the top right for each option (Figure 78).

Inspect Statistics

Right clicking any cell in the results table and clicking "Inspect Statistics" will display the form shown in Figure 80.

Note: The inspect statistics window will be shown top-most to other forms. This allows the window to be resized and positioned alongside any number of inspection windows to facilitate comparison between results.
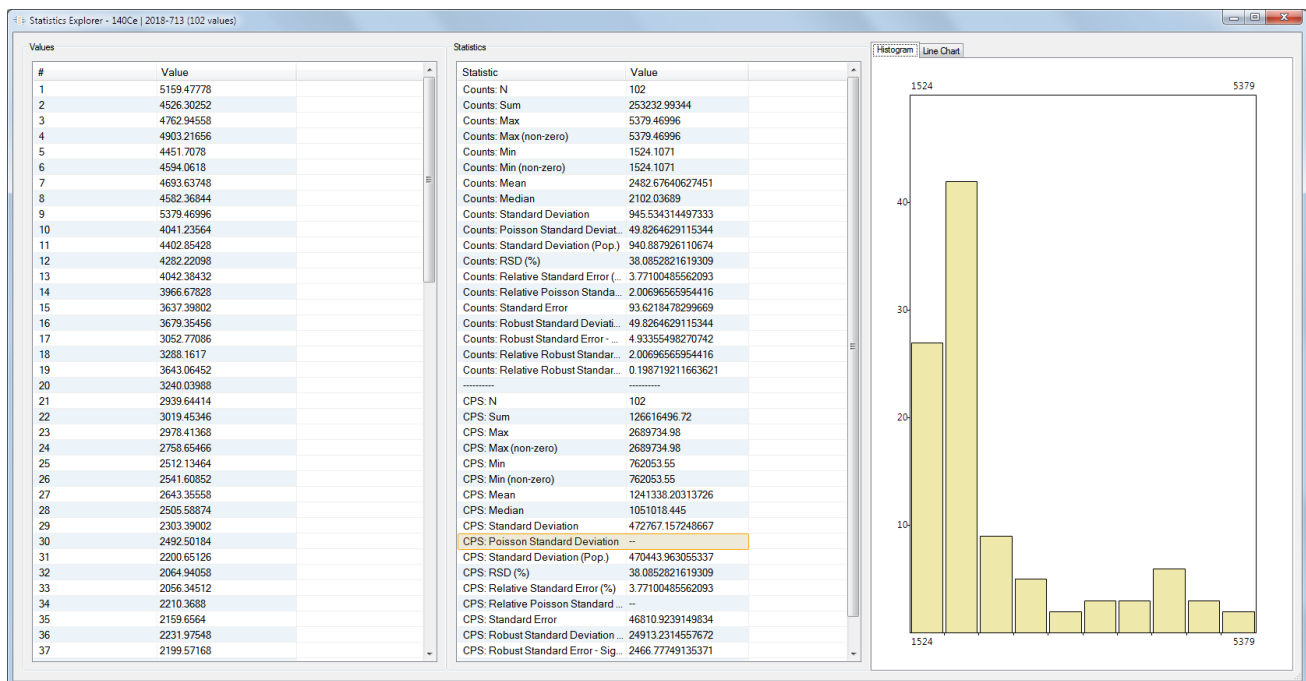
Figure 80: The "Inspect Statistics" window.

Inspect Calculations

Right clicking any cell in the results table and clicking "Inspect Calculation" will display the form shown in Figure 80.

Note: The inspect calculation window will be shown top-most to other forms. This allows the window to be resized and positioned alongside any number of inspection windows to facilitate comparison between results.

The uncertainty tree can be shown/hidden using the button on the toolbar to the top-right of the window. The tree shows all uncertainty components that have propagated to the final uncertainty.

- The tree represents the relative associations between different parts of the uncertainty calculation. When relative uncertainties are combined the order is irrelevant to the result[14].

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14 Given $U = \sqrt{U_1^2 + U_2^2}$ then:

$$U = \sqrt{U_a^2 + U_b^2} = \sqrt{\left(\sqrt{U_{a1}^2 + U_{a2}^2}\right)^2 + \left(\sqrt{U_{b1}^2 + U_{b2}^2}\right)^2} = \sqrt{U_{a1}^2 + U_{a2}^2 + U_{b1}^2 + U_{b2}^2}$$

- The square nodes represent the "uncertainty levels" reported by LADR. They are coloured consistently for all uncertainty trees.

- The round nodes show other sources of uncertainty.

- Those nodes marked in red indicate zero values. In theory, all uncertainty values should be entered and contribute something, even if vanishingly small, to the total uncertainty.

- Right-click the chart to control the appearance. Mouse over nodes, or the list, and click to expand/collapse the tree.
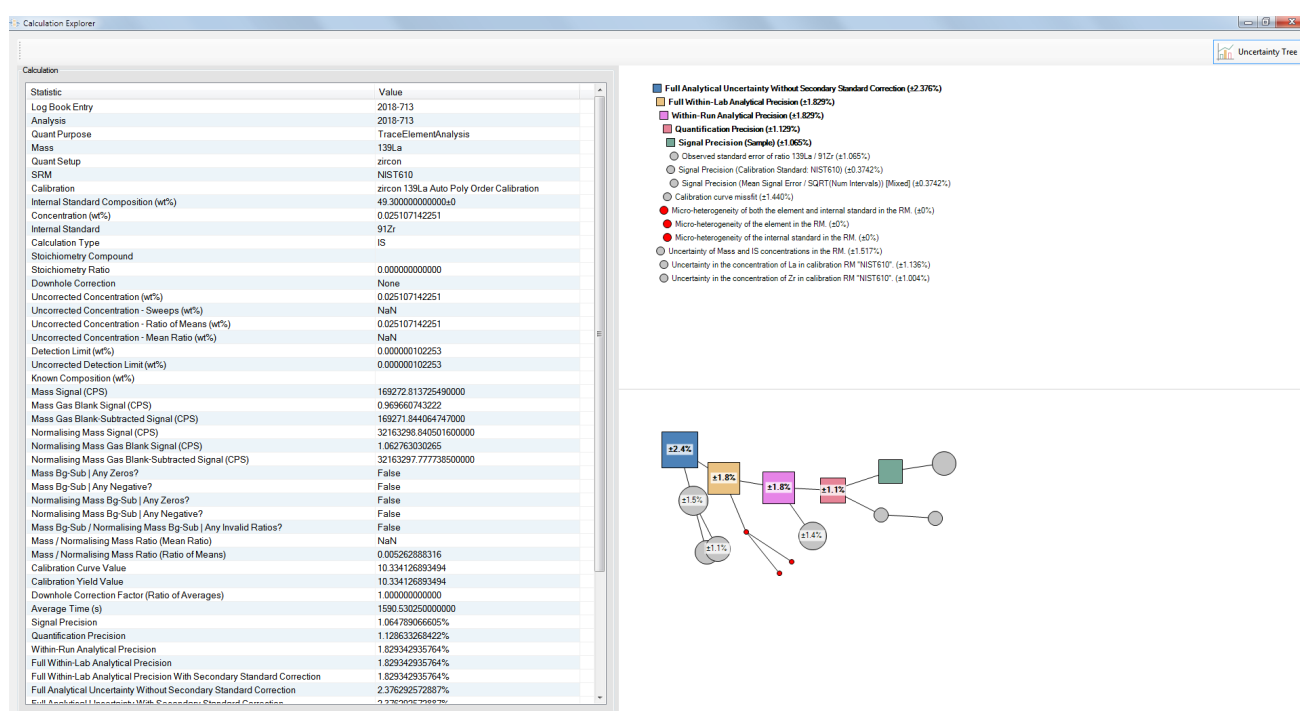
Manage Quantification Setups

Introduction

This window allows for management of quantification setups (QSs) in both the profile and the project.

Note: QSs can only be created and edited in the project. They are copied to the profile for storage and reuse by subsequent projects. If you wish to edit a QS in the profile, load a compatible project, or data file(s), copy the QS to the project, edit, and copy back to the profile. This behaviour is not to be confused with the "Manage Reference Materials" window which uses a different logic.

Interface

The QS manager can be accessed vie the profile menu on LADR. This window allows the user to transfer QSs between the project and profile, copy, delete, or edit a profile. This window provides many functions which are typically performed in the data workflow stages (see Quantification setup, page 83).

Note: When a QS is transferred from the profile to the project a symbol at the left of the name defines that QSs compatibility with the project.

Figure 81 QS manager window visible in the profile menu.

Manage Timing Templates

Introduction

The timing templates (TTs) can be held in the profile and reused in subsequent projects. This feature is really only of use when working with mass spectrometers that do not report the complete timing information in the output files.

Interface

Timing templates can be moved from the profile to the project and from the project to the profile. TTs can be edited, copied, or deleted in both the profile or project window. For more information on how to modify a TT see page 56.

Filter Data

Introduction

This feature will be documented in a future version of this manual.
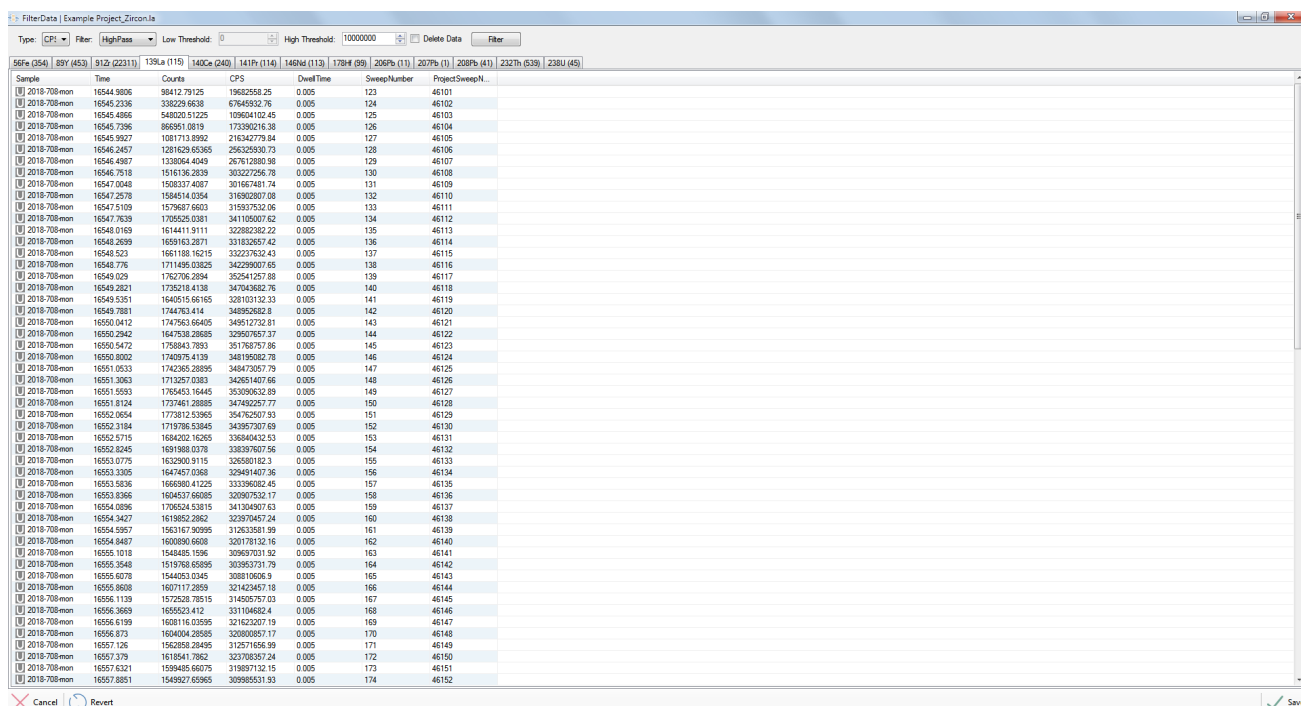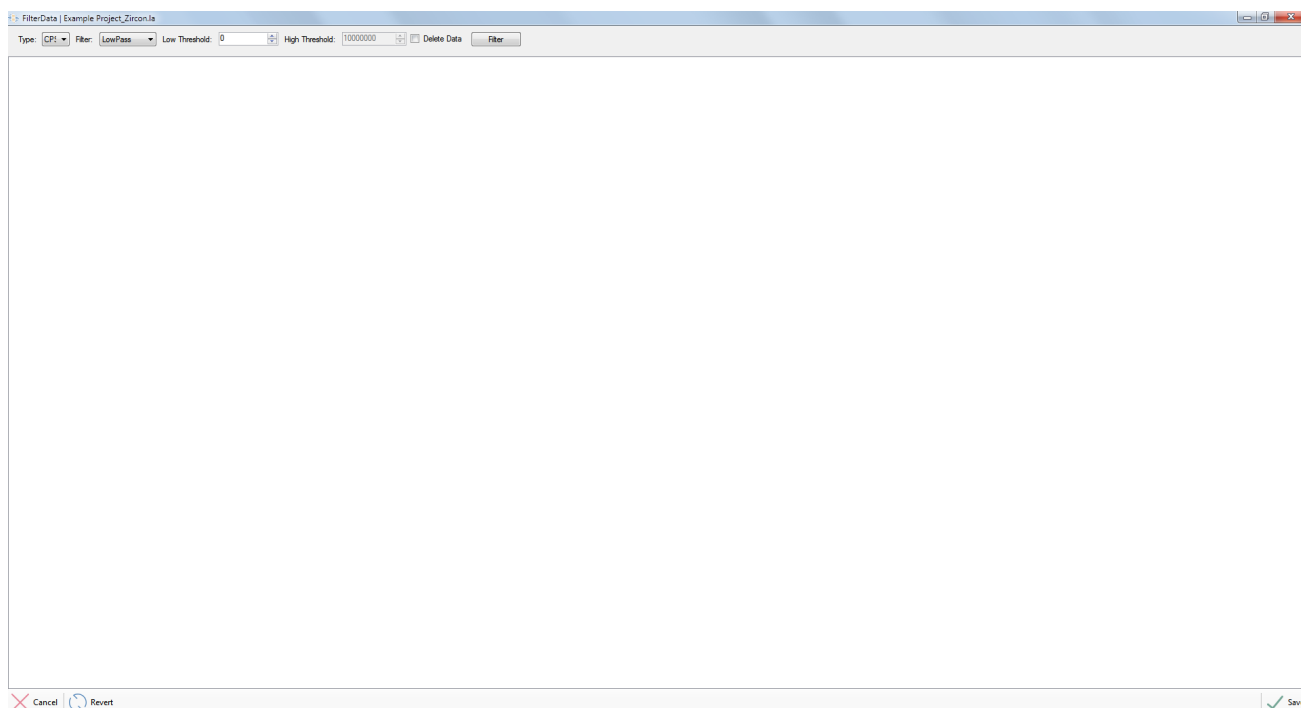
Review Spikes

Introduction

Spikes are removed from the signal by an automated algorithm that assesses the noise in the signal.

This form allows the user to review all of the spikes that were removed, and to manual undo the removal if they feel the spike is a feature of the sample.

Ideally, the spike removal options will be tuned to ensure that no manual review of spikes is required.

Interface

Signal spikes are removed during the data reduction workflow (see "Analysis Log", page 121). The spike review form allows the user to view the spike distribution sorted by sample, or by element.

To sort the menu in the spike removal form left-click on the column heading.

Individual spikes, specific samples, or specific elements can be viewed by selecting a single line or a group.

The laser time-resolved graph setting can be modified as discussed in the "Data Chart" chapter on page 46.

Note: Individual or groups of spikes can be removed or undone by right-clicking and selecting one of the options. The "undone?" column is true when a spike is still present, and false when a spike has been successfully removed.
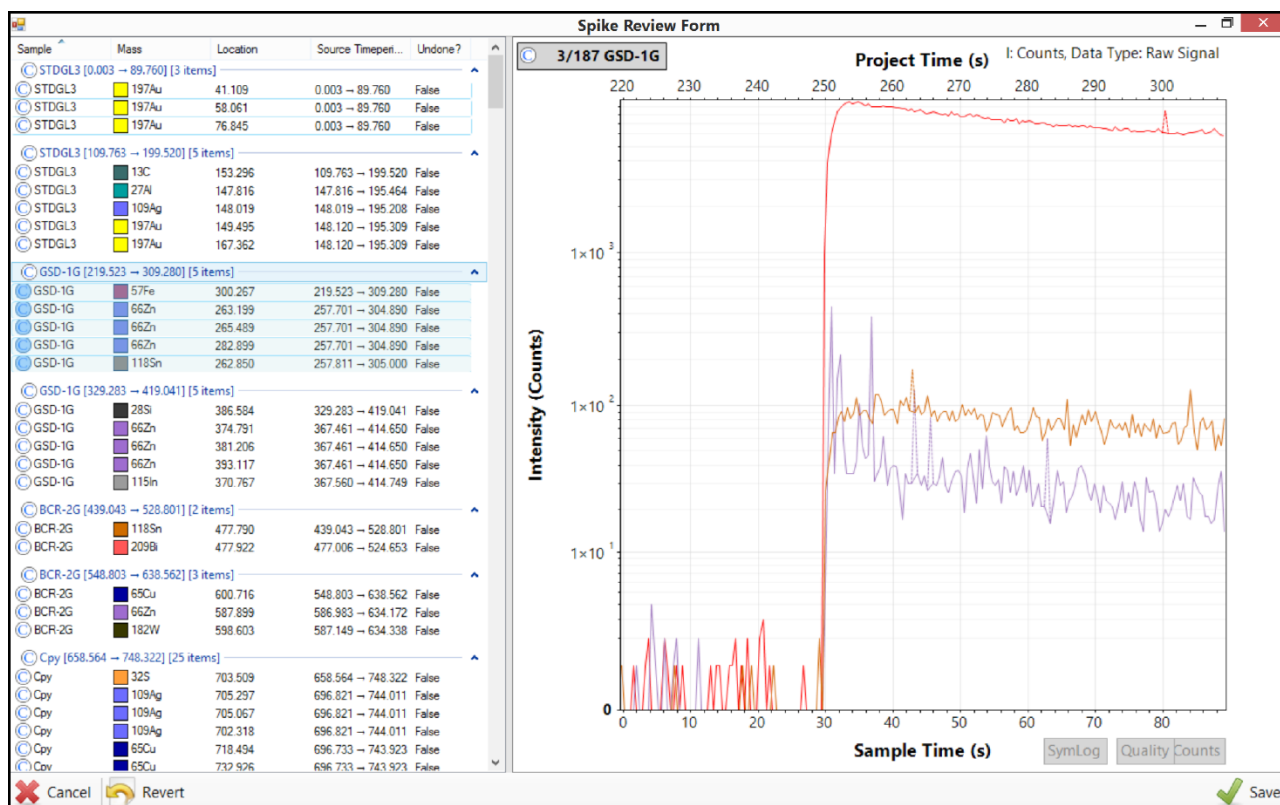
Figure 82 Spike removal form available in the tools menu.

Manage Profile

The "Manage Profile" window can be launched using the "Profile" menu on the main LADR window, and is shown in Figure 83.

The first section allows the profile to be locked using a password. When the profile is locked then users are unable to edit Reference Materials, Quantification Setups, Timing Templates, or Options. This feature is recommended for established users who wish to distribute a well-configured profile to inexperienced or untrusted users. In this way, data reduced using the locked profile are guaranteed to conform to all of the restrictions imposed by the locked profile.

Note: If the profile locking feature is of interest, and you have a more complicated use case please contact us for more information. There is a "Managed Mode" that provides even greater administrative control over how users reduce data with LADR.
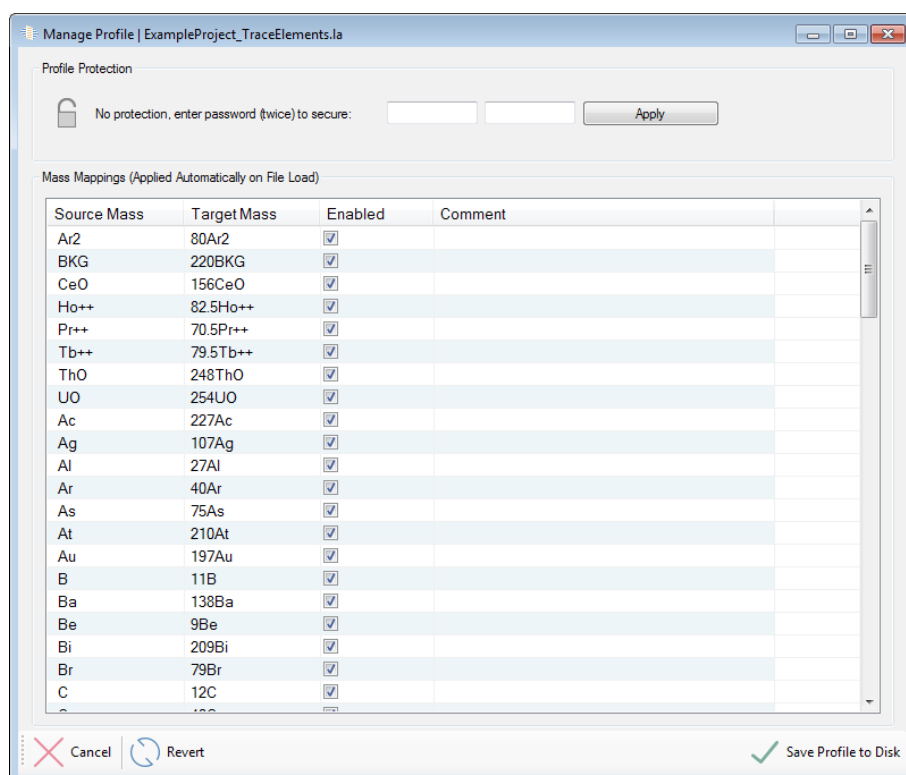
Figure 83: The "Manage Profile" window.

Mass Mappings

Mass Mappings are a powerful feature that allow mass values loaded from data files to be mapped to different values. The most common application is to accommodate

instrument configuration limitations, or as a workaround for known issues with mass spectrometer data files.

The default mappings serve as an example of how the system works, and also handles common mappings from elements to the most commonly measured isotopes. In every case, the default mappings should be inspected carefully. If in doubt, select all of the mappings and right-click and choose "Delete", or "Set to…" → "Disabled".

The individual Mass Mappings can be enabled/disabled directly by using the checkboxes.

Most manipulation is achieved via the right-click menu shown in Figure 84. The menu items are:

- Add Mapping – Show a window for entering a source and target mass. The input formats are basic mass and element symbol. Support for more complex formats will be added in the future. Please note that if adding a mapping and the source mass is already defined, then the target mass will be automatically updated to the new value.

- Edit Mapping – Shows a window that allows the target mass to be edited.

- Set to… – Expands a sub menu that allows the entire selection to be set to "Enabled" or "Disabled" in one action.

- Delete Mapping – Will delete the selected mappings from the list. To easily delete all mappings use the keyboard shortcut CTRL+A before choosing this menu item.

- Reset to Defaults – Will restore the default mappings.
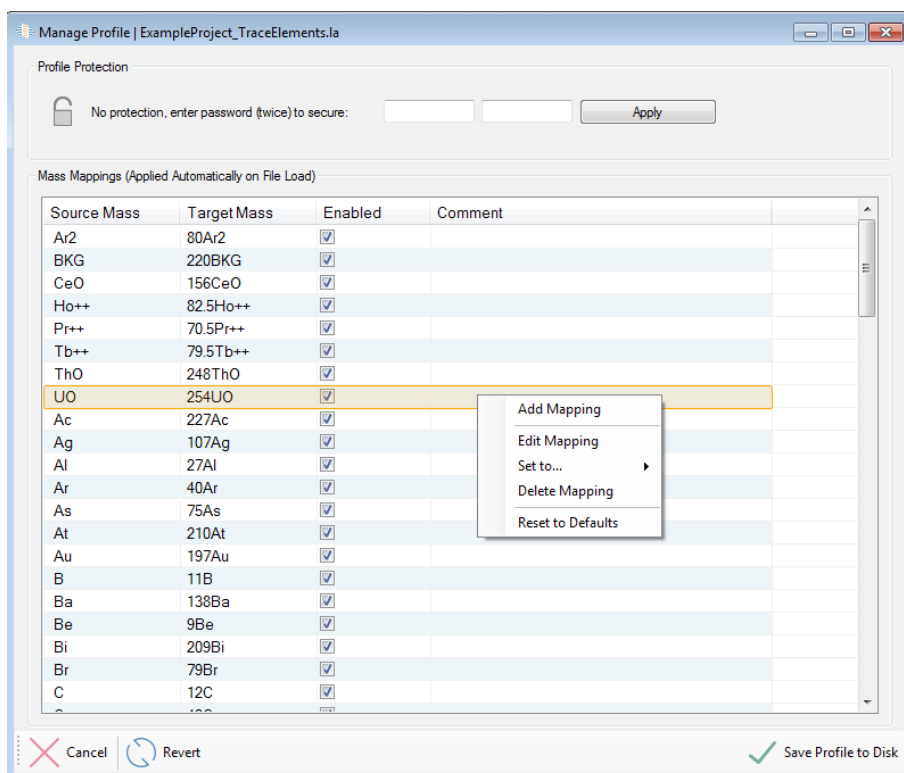
Figure 84: The "Mass Mappings" right-click menu.

Note: *During data loading any source masses present in this list will be mapped to the target masses. If this is not the desired behaviour be sure to disable or delete the unwanted mappings prior to loading data.*

Note: *When data are loaded with incomplete masses and the user is prompted to enter additional information (e.g. choose a mass or an element) then the mapping is added to the Mass Mappings list for future use.*

Program Settings

Introduction

The program settings expose options specific to the program.

There are not very many since the philosophy of LADR is that most processing options reside in the profile.

Interface

Program settings allows the user to create a password protection, to set the program to either expert or managed mode, and to set the default colours for each measured mass.

Note: There is an option which controls the ability to lock projects: "Profile.Management.LockProjects".

Figure 85: The program settings window.

Appendix A – Options

Each option contains additional information available in the "program options" menu.

- Status is enabled when the option is active in LADR and disabled when the function related to the option is unavailable.

- Behaviour – The behaviour of the option refers to the location the option values are taken from when used in a project.

    o Program – LADR specific options that pertain to program functionality.

    o Profile – Profile options are only visible in the Tools → Edit options → Profile tab. These options generally pertain to quantification of signal and gas blank and file loading options.

    o Profile is Default – These options are in both the profile and project tabs of the Tools → Edit options window. These options are copied from the profile to the project during project creation. Changes must be made in the project tab to take effect in the current project, changes in the profile are used when a new project is created.

    o Profile Is Module Default – These options are copied from the profile to the QS when a QS is created. Each QS has independent options values that must be edited in the QS → General tab to take effect in the current project.

Note: The default profile options values can be loaded to the profile or QS list of options at any time. The profile options values can also be reloaded to the LADR default values.

- Name – Indicates the region(s) of data reduction where the option is applicable. This field is searchable in the "program options" window.

- Type – Either Boolean for true-false statements, String when several text options are available, Double is for numeric values with a double precision (64 bit), and integer for numbers without a decimal point.

- Value – May be numeric, select from a drop-down menu, or true-false dependent upon the data type.

- Guidance – If data is numeric, the suggested range of values is listed. If the value is selected from a drop-down menu then the options are presented.

- Notes – Short description of the option function.

Options – Program

Option	Type	Default	Guidance	Notes
Program.ShowFullProfilePathInFormTitles	Boolean	FALSE		When set to true the full path of the current Profile is shown in form titles. If false, just the filename is shown.
Program.ShowFullProjectPathInFormTitles	Boolean	FALSE		When set to true the full path of the current Project is shown in form titles. If false, just the filename is shown.
Program.LogProgramErrorsToServer	Boolean	TRUE		Enables program errors to be logged directly to the Norris Scientific development server.
Program.LogProgramErrorsToDisk	Boolean	TRUE		Enables program errors to be logged to disk.
Program.MultiThreadedCalc	Boolean	TRUE		Enables multi-threaded calculations.

Options – Profile

Option	Type	Default	Guidance	Notes
Profile.Quant.DefaultGasBlankModels.MissfitThresholdSignalDistanceMultiplier	Double	0.05	0.0001 - 1	Missfit threshold is distance to signal intervals multiplied by this value. If larger, switch to separate gas blank models.
Quant.ComputeAnalysisInCounts	Boolean	TRUE		False == Compute in CPS
Profile.Results.UPbDating.AgeUncertaintyCalc	String	RelativeError	{ RelativeError | ComputeAgeRange }	When computing age from ratios, how to compute the error? "RelativeError" propagates the % error from the ratios, while "ComputeAgeRange" computes an age range (often assymetric).
FlatSignal.001.Enabled	Boolean	TRUE		

Option	Type	Default	Guidance	Notes
`FlatSignal.001.DEBUG_Rejoin Intervals`	Boolean	TRUE		
`FlatSignal.001.DEBUG_Analys isDurationCheck`	Boolean	TRUE		
`FlatSignal.001.DEBUG_SlopeC heck_TotalAnalysis`	Boolean	TRUE		
`FlatSignal.001.DEBUG_SlopeC heck_Interval`	Boolean	TRUE		
`FlatSignal.001.DEBUG_SlopeC heck_Window`	Boolean	TRUE		
`FlatSignal.001.InternalStan dardChangeThreshold`	Double	1.5		How much change is accepted in the counts of the internal standard mass.
`FlatSignal.001.WindowSlopeT hreshold`	Double	1.4	0.01 - 10	How much slope to accept in normalised values over all timeperiods for new analysis entry.
`FlatSignal.001.SimilarityTh resholdForJoiningTimePeriod s`	Double	2	0.01 - 10	How similar should concentration be to add timeperiods to same analysis entry.
`FlatSignal.001.WindowSizeFo rRSD`	Integer	9	≥5	The number of surrounding datapoints to use for RSD evaluation at each data point. Odd numbers only, rounded down.
`FlatSignal.001.TheorErrMult iplierAdjustment`	Double	0	0 - 2	Adjusts the theoretical error multiplier, at count rates below the MinSignalError to make the theoretical error closer to Poisson at low count rates.
`FlatSignal.001.Psychometric Factor`	Double	1		Controls the acceptable variation of mid-range signals. Lowering the value increases the acceptable variation at these count rates.
`FlatSignal.001.FlatSignalTh reshold`	Double	5		A replacement for the theoretical error for signals which are above the level where it equals the minimum signal error.
`FlatSignal.001.TheorErrMult iplier`	Double	1	1 - 5	Multiplier to the theoretical error to be used for comparing with the calculated signal RSD

Option	Type	Default	Guidance	Notes
`FlatSignal.001.SignalCleanUpThreshold`	Double	2		This is a multiplier to the theoretical error to be used as a parameter to determine if the data point is to be considered for smoothing.
`FlatSignal.001.NumCleanUpPasses`	Integer	3	1 - 10	How many clean up passes to apply.
`FlatSignal.001.MinSignalError`	Double	1.5	0.1 - 10	Minimum error on counting statistics for the setup in %. Used as a cut-off for counting statistics at high counts. TYPICALLY SET TO BE THE SAME AS SPIKE REMOVAL VALUE!
`FlatSignal.001.MinimumInterval`	Double	5	1 - 1000	Minimum acceptable analysis interval. Entered in seconds.
`FlatSignal.001.TraceElements`	String	49,57,88		Comma separated list of masses to use for identification of flat signals. Should not be empty. All masses should be present in the project.
`DownHoleFract.001.CleanUpAfterNormalisation`	Boolean	TRUE		Whether to clean up the mass/IS ratio before fitting the model.
`DownHoleFract.001.CleanUpUPbAndQuantRatiosBeforeNormalisation`	Boolean	TRUE		Whether to clean up the mass and IS raw signals before normalisation. For UPb and quant ratios only. This option is always true for trace elements.
`SumToTotal.BelowDetectionLimitMultiplier`	Double	0.5	0 - 1	This is the multiplier when using "DetectionLimitMultiplier" option to compute a total.
`SumToTotal.BelowDetectionLimitHandling`	String	Exclude	{ Include | Exclude | DetectionLimitMultiplier }	When computing a total, how should concentrations below detection limit be handled?
`QSQuant.TraceElement.ComputeUIsotopesSeparately`	Boolean	TRUE		When computing U, should isotopes be computed separately? To use this, the RM must have the U isotopic composition defined, and the U isotopes 235 and 238 must be analysed in the Project.

Option	Type	Default	Guidance	Notes
`QSQuant.TraceElement.ComputePbIsotopesSeparately`	Boolean	FALSE		When computing Pb, should isotopes be computed separately? To use this, the RM must have the Pb isotopic composition defined, and the Pb isotopes 206, 207, and 208 must be analysed in the Project.
`QSQuant.MassFiltering.AdditionalMassBiasUncertainty`	Double	0	≥0	Added to the signal uncertainty when converting U235<=>U238 on unknown samples. Enter as relative percent.
`QSQuant.MassFiltering.DefaultRatioOfU238/U235`	Value	137.818±0.0225		Used when converting U235<=>U238. The default value provided is taken from: Hiess et al. 2012
`Profile.MassFiltering.001.U235U238DefaultU238ThresholdCPS`	Double	1000000	≥0	When creating new Quant Setups: use this U238 CPS threshold by default.
`Profile.MassFiltering.001.U235U238DefaultEnabled`	Boolean	FALSE		When creating new Quant Setups: should U238 mass filtering be enabled by default?
`QSQuant.CleanUp.CleanUpBeforeQuantification`	String	Disabled	{ Enabled | Disabled }	During quantification, should data be cleaned-up before quantification? Applies to UPb, and quantified ratios. Support for traces will be added in future versions.
`CleanUp.001.StdDevMultiplier`	Double	2	≥0	Applied to the theoretical standard deviation. Basic outlier rejection.
`CleanUp.001.RejectionThreshold`	Double	2	0 - 50	Remove this % from top and bottom of data. Basic outlier rejection.
`SpikeRemoval.001.Level3.Signal.SpikeFactorCoeff_X0`	Double	1.1	1 - 1.6	Coefficient for the spike factor curve, constant term (error_offset)
`SpikeRemoval.001.Level3.Signal.MinSignalError`	Double	2.5	0.1 - 10	Minimum error on counting statistics for the setup in %. TYPICALLY SET TO BE THE SAME FOR FLAT SIGNAL!
`SpikeRemoval.001.Level3.GasBlank.SpikeFactorCoeff_X0`	Double	1.2	1 - 1.6	Coefficient for the spike factor curve, constant term (error_offset)
`SpikeRemoval.001.Level3.GasBlank.MinSystemError`	Double	1.5	0.1 - 100	Minimum error on counting statistics for the setup in %. TYPICALLY SET TO BE THE SAME FOR FLAT SIGNAL!

Option	Type	Default	Guidance	Notes
SpikeRemoval.001.Level2.Signal.WidthOfSignalToCheckNoiseAroundSpike	Integer	3	≥0	How many sweeps to assess for signal noise around the spike
SpikeRemoval.001.Level2.Signal.NoiseThresholdLeftRightModifier	Double	3		Coefficient applied to the allowed noise on the signal left and right of the spike (resultant noise is then scaled by the height of the spike relative to the spike factor)
SpikeRemoval.001.Level2.Signal.SignalSlopeSpikeFactorModifier	Double	2.5		Slope on the signal around the spike to eliminate a spiky-end inclusion.
SpikeRemoval.001.Level2.Signal.SpikeFactorModifier	Double	0.8		Coefficient applied to the spike factor to assess the signal intensity around the spike
SpikeRemoval.001.Level2.Signal.SpikeHeightThreshold	Double	100	≥0	Height of spike when you do not worry about signal variability around the spike
SpikeRemoval.001.Level2.Signal.SpikeFactorCoeff_X0	Double	1.2	1 - 1.6	Coefficient for the spike factor curve, constant term (error_offset)
SpikeRemoval.001.Level2.Signal.MinSignalError	Double	5	0.1 - 10	Minimum error on counting statistics for the setup in %. TYPICALLY SET TO BE THE SAME FOR FLAT SIGNAL!
SpikeRemoval.001.Level2.GasBlank.WidthOfSignalToCheckNoiseAroundSpike	Integer	5	≥0	How many sweeps to assess for signal noise around the spike
SpikeRemoval.001.Level2.GasBlank.NoiseThresholdLeftRightModifier	Double	5		Coefficient applied to the allowed noise on the signal left and right of the spike (resultant noise is then scaled by the height of the spike relative to the spike factor)
SpikeRemoval.001.Level2.GasBlank.SignalSlopeSpikeFactorModifier	Double	1		Slope on the signal around the spike to eliminate a spiky-end inclusion.
SpikeRemoval.001.Level2.GasBlank.SpikeFactorModifier	Double	0.8		Coefficient applied to the spike factor to assess the signal intensity around the spike
SpikeRemoval.001.Level2.GasBlank.SpikeHeightThreshold	Double	100	≥0	Height of spike when you do not worry about signal variability around the spike
SpikeRemoval.001.Level2.GasBlank.SpikeFactorCoeff_X0	Double	1.2	1 - 1.6	Coefficient for the spike factor curve, constant term (error_offset)

Option	Type	Default	Guidance	Notes
`SpikeRemoval.001.Level2.GasBlank.MinSystemError`	Double	1.5	0.1 - 100	Minimum error on counting statistics for the setup in %. TYPICALLY SET TO BE THE SAME FOR FLAT SIGNAL!
`SpikeRemoval.001.Level1.Signal.MinSignalError`	Double	2.5	0.1 - 10	Minimum error on counting statistics for the setup in %. TYPICALLY SET TO BE THE SAME FOR FLAT SIGNAL!
`SpikeRemoval.001.GasBlank.ProcessingLevel`	String	Level2	{ Level1 | Level2 | Level3 }	ICP-MS Sampling Anomallies / Significant Isolated Spikes / All Statistically Identified
`SpikeRemoval.001.Signal.ProcessingLevel`	String	Level2	{ Level1 | Level2 | Level3 }	ICP-MS Sampling Anomallies / Significant Isolated Spikes / All Statistically Identified
`SpikeRemoval.001.GasBlank.DetectDoubleSpikes`	Boolean	TRUE		If enabled then spikes up to 2 sweeps wide are accepted. If enabled spikes can only be 1 sweep wide.
`SpikeRemoval.001.Signal.DetectDoubleSpikes`	Boolean	TRUE		If enabled then spikes up to 2 sweeps wide are accepted. If enabled spikes can only be 1 sweep wide.
`SpikeRemoval.001.GasBlank.EnabledMode`	String	Manual	{ Disabled | Manual | AutoWithUndo | AutoForced }	Operating mode for spike removal on gas blanks.
`SpikeRemoval.001.Signal.EnabledMode`	String	Manual	{ Disabled | Manual | AutoWithUndo | AutoForced }	Operating mode for spike removal on signals.
`Profile.LiveResults.Enabled`	Boolean	TRUE		When enabled the fully quantified results are shown in the Analysis Log Review form.
`Profile.Quant.DefaultGasBlankModels.PolyExtrapolationThreshold`	Double	5	0 - 100	If extrapolating a poly curve for more than this % of total project time, use a constant curve for extrapolation instead.
`Profile.Quant.DefaultGasBlankModels.OutlierVarianceMultiplier`	Double	1	0 - 10	Multiplier to variance when assessing interval missfit.
`Profile.Quant.DefaultGasBlankModels.WiggleEnvelope_VarianceMultiplier`	Double	2	0.01 - 100	Multiplier to variance when assessing curve fitting suitability.

Option	Type	Default	Guidance	Notes
`Profile.Quant.DefaultGasBlankModels.Variance`	String	StandardDeviation	{ StandardDeviation | StandardError }	What kind of variance is used for assessing missfits and curve fitting suitability?
`Profile.Quant.DefaultGasBlankModels.NumOutliersThresholdPercent`	Double	10	0.0001 - 100	How many outliers (% total number) are needed to switch to separate interval gas blank models?
`Profile.Quant.DefaultGasBlankModels.CurveFit`	String	Poly8	{ Constant | Linear | Poly2 | Poly3 | Poly4 | Poly5 | Poly6 | Poly7 | Poly8 }	What kind of curve to fit to calibrations by default. NB: Other rules also apply.
`Profile.Quant.DefaultGasBlankModels.ReselectAllTimePeriodsOnSingleMassAuto`	Boolean	TRUE		False == De-selected time periods remain de-selected.
`Profile.Quant.DefaultGasBlankModels.InterpolateBetweenIntervals`	Boolean	TRUE		When true, gas blank models are linear between adjacent intervals. When false, curves are constant and step between samples.
`Profile.Quant.DefaultCalibrationModels.PolyExtrapolationThreshold`	Double	5	0 - 100	If extrapolating a poly curve for more than this % of total project time, use a constant curve for extrapolation instead.
`Profile.Quant.DefaultCalibrationModels.OutlierVarianceMultiplier`	Double	1	0 - 10	Multiplier to variance when assessing interval missfit.
`Profile.Quant.DefaultCalibrationModels.WiggleEnvelope_VarianceMultiplier`	Double	2	0.01 - 100	Multiplier to variance when assessing curve fitting suitability.
`Profile.Quant.DefaultCalibrationModels.Variance`	String	StandardDeviation	{ StandardDeviation | StandardError }	What kind of variance is used for assessing missfits and curve fitting suitability?
`Profile.Quant.DefaultCalibrationModels.NumOutliersThresholdPercent`	Double	10	0.0001 - 100	How many outliers (% of total number of groups) are needed to switch to individual intervals.

Option	Type	Default	Guidance	Notes
`Profile.Quant.DefaultCalibrationModels.CurveFit`	String	Poly8	{ Constant | Linear | Poly2 | Poly3 | Poly4 | Poly5 | Poly6 | Poly7 | Poly8 }	What kind of curve to fit to calibrations by default. NB: Other rules also apply.
`Profile.Quant.DefaultCalibrationModels.ReselectAllTimePeriodsOnSingleMassAuto`	Boolean	TRUE		False == De-selected time periods remain de-selected.
`AutoTimePeriods.001.GasBlankLaserMinusOffset`	Double	5	≥0	When creating gas blank time periods using "LaserMinusOffset" this is the offset from the laser time.
`AutoTimePeriods.001.FixedGasBlankTime`	Double	20	≥0	Duration in seconds of the "Fixed" gas blank time.
`AutoTimePeriods.001.GasBlankTimeMethod`	String	LaserMinusOffset	{ Fixed | LaserMinusOffset }	How to determine the end point of an automatic gas blank time period. Start time is sample start.
`AutoTimePeriods.001.AnalysisSampleMinusOffset`	Double	5	≥0	When creating analysis time periods using "SampleMinusOffset" this is the offset from the end of the sample.
`AutoTimePeriods.001.FixedAnalysisTime`	Double	25	≥0	Duration in seconds of the "Fixed" analysis time.
`AutoTimePeriods.001.AnalysisTimeMethod`	String	Fixed	{ Fixed | RestOfSample | SampleMinusOffset }	How to determine the end point of an automatic analysis time period. Start time is laser start.
`AutoTimePeriods.001.MinimumInterval`	Double	5	≥0	The minimum allowed duration (in seconds) of any one analysis or gas blank time period.
`LaserTimes.001.ExpectedTimeWindow`	Double	1	0.001 - 100	All laser times should fall within +/- this value relative to the median relative laser time.
`LaserTimes.001.FixedRiseTime`	Double	3	≥0	If "UseFixedRiseTime" is true, use this time (in seconds) from the aersol arrival time for the stable signal time.

Option	Type	Default	Guidance	Notes
LaserTimes.001.UseFixedRiseTime	Boolean	TRUE		If true apply a fixed rise time ("FixedRiseTime") to find start of stable signal. If false, use the algorithm value to find the stable signal time.
LaserTimes.001.SumSignalFilter_SignalChangeFactor	Double	1	0 - 100	When summing data, to include mass data the signal variation (observed / theoretical) must vary by more than this factor.
LaserTimes.001.MinimumSaddleThreshold	Double	0.02	0 - 1	When assessing the signal histogram, consider bins with fewer than this fraction of sweeps to be in the "saddle" made by the rise time.
LaserTimes.001.MinimumBinThreshold	Double	0.01	0 - 1	When pruning the signal histogram, trim bins with fewer than this fraction of sweeps.
LaserTimes.001.AutoSignalHistogramNumBinsMinLimit	Integer	6	1 - 1000	When computing the number of bins with "AutoSignalHistogramNumBinsFactor" this sets the lower limit to the number computed.
LaserTimes.001.AutoSignalHistogramNumBinsFactor	Double	10	1 - 10000	Used to compute the number of bins to use on the signal histogram: Num Bins = [Num Sweeps In Sample] / [AutoSignalHistogramNumBinsFactor].
LaserTimes.001.SignalHistogramNumBins	Integer	0	0 - 1000	Sets the number of bins to use on the signal histogram. If set to 0 then the number of bins will be computed using "AutoSignalHistogramNumBinsFactor".
LaserTimes.001.SkipSweepsAtEnd	Integer	10	0 - 1000	Exclude this many sweeps from the end of the sample. Used to avoid changes caused by signal clean up routine.
LaserTimes.001.SkipSweepsAtStart	Integer	10	0 - 1000	Exclude this many sweeps from the start of the sample. Used to avoid changes caused by signal clean up routine.
LaserTimes.001.DetectionMethod	String	AdvancedSumThreshold	{ SimpleSumThreshold | PeakGasBlankRatio | AdvancedSumThreshold }	This routine determines the laser start time. It assumes each sample starts with a gas blank period prior to ablation.

Option	Type	Default	Guidance	Notes
`Quant.PairingStrategy`	String	InterpolateIS	{ SameProjectSweep | ClosestTime | ClosestDistance | InterpolateIS }	When normalising a single DataPoint, how to choose the denomenator DataPoint?
`Quant.AnalysisComputationStyle`	String	RatioOfMeans	{ Sweeps | MeanRatio | RatioOfMeans }	When quantifying, how to collate ratios over integration period? Should be same as Profile.Quant.CalibrationFittingStyle for correct results.
`Quant.CalibrationFittingStyle`	String	RatioOfMeans	{ Sweeps | MeanRatio | RatioOfMeans }	How should calibration curves be fitted?
`Quant.GasBlankNumReadingsCollation`	String	BracketingIntervals	{ BracketingIntervals | IntervalBehind | AllIntervals }	When computing the detection limit how should the value of N (number of readings in the gas blank) be computed?
`Quant.GasBlankFittingStyle`	String	Sweeps	{ Sweeps | Means }	How should gas blank models be fitted?
`Quant.CalibrationUncertaintyCalculation`	String	MeanMissfitTimeperiods	{ MeanMissfitTimeperiods | MeanMissfitSweeps }	How to assess uncertainty of calibration curves?
`Quant.DetectionLimitMultiplier`	Double	3	≥0	The multiplier used in the detection limit calculation.
`Quant.SecondaryCorrection.AveragingStyle`	String	AverageEachRMSeparately	{ AverageAllRMs | AverageEachRMSeparately }	When combining corrections from multiple secondary standards, how to average the correction factors? "AverageAllRMs" averages all RM concentrations; "AverageEachRMSeparately" averages each standard first, then averages the averages.
`Quant.ReportedUncertaintyMultiplier`	Integer	1	1 - 5	Report uncertainties using this multiple, e.g. 1 x SD, 2 x SD, etc...
`Results.Colouration.Level3.Colour`	String	#FF0000		The colour (in HEX notation) for level 3.
`Results.Colouration.Level3.Threshold`	Double	50	0 - 100	Level 3 threshold, in relative uncertainty at current level.

Option	Type	Default	Guidance	Notes
`Results.Colouration.Level2.Colour`	String	#FF3300		The colour (in HEX notation) for level 2.
`Results.Colouration.Level2.Threshold`	Double	25	0 - 100	Level 2 threshold, in relative uncertainty at current level.
`Results.Colouration.Level1.Colour`	String	#FFCC00		The colour (in HEX notation) for level 1.
`Results.Colouration.Level1.Threshold`	Double	10	0 - 100	Level 1 threshold, in relative uncertainty at the current level.
`Results.Colouration.Enabled`	Boolean	FALSE		Show colouration of the results table.
`Results.DisplayMeasuredStoichCompoundConcentration`	Boolean	FALSE		False == Do not show measured values in the results.
`Profile.Plotting.Legend.HideOffChartMasses`	Boolean	TRUE		When true, masses that are set to be visible but are not shown on the current plot (out of range, for example) are removed from the legend.
`Profile.Plotting.Legend.SortByFinalIntensity`	Boolean	TRUE		When true, the masses in the legend are shown in final intensity order, making it easier to identify them.
`Profile.UseBackwardFormatForIsotopes`	Boolean	FALSE		True == Ar40, False == 40Ar
`Profile.ShowSignalsInCounts`	Boolean	FALSE		False == Show in CPS
`Profile.FileLoading.Agilent_MassHunter.TimeStampFormat`	String	M/dd/yyyy h:mm:ss tt		The timestamp format string to use.
`Profile.FileLoading.Agilent_MassHunter.UseTimeStamps`	Boolean	FALSE		If true, then use the timestamps from the data files.
`Profile.FileLoading.ThermoFisher_iCAPQQtegra.TimeStampFormat`	String	MM/dd/yyyy hh:mm:ss tt		The timestamp format string to use.
`Profile.FileLoading.ThermoFisher_iCAPQQtegra.UseTimeStamps`	Boolean	FALSE		If true, then use the timestamps from the data files.

Option	Type	Default	Guidance	Notes
`Profile.FileLoading.ThermoFisher_XSeriesIIPlasmaLab2.TimeStampFormat`	String	M/dd/yyyy h:mm:ss tt		The timestamp format string to use.
`Profile.FileLoading.ThermoFisher_XSeriesIIPlasmaLab2.UseTimeStamps`	Boolean	TRUE		If true, then use the timestamps from the data files.
`Profile.FileLoading.ThermoFisher_XSeriesIIPlasmaLab2.DataType`	String	CPS	{ CPS | Counts }	What data type is present in Thermo X-Series II data files.
`Profile.FileLoading.TOFWERK_Tofware_v3.Triggering`	String	Internal (Continuous)	{ Internal (Continuous) | External (Single-Shot) }	How was TOF data acquisition triggered?
`Profile.FileLoading.TOFWERK_Tofware_v3.SweepTimePrecisionThreshold`	Double	0.1	0 - 100	When loading internal/continuous data, the average sweep time from the file must match the acquisition time to within this precent..
`Profile.FileLoading.TOFWERK_Tofware.AbridgeDataFiles`	Boolean	TRUE		Tofware data files contain additional sections that are not required. If this options is true then those extraneous sections are discarded.
`Profile.FileLoading.RejectNonUniqueMasses`	Boolean	FALSE		When true non-unique masses (e.g. Sn115 and In115) will be rejected during file loading.
`Profile.FileLoading.DefaultDataFileTimeGap`	Integer	100	≥0	For data files without absolute time information, this is the default time gap to insert between data files. Specified in whole seconds.

Option	Type	Default	Guidance	Notes
Profile.FileLoading.DefaultDataFileFormat	String	Last Choice	{ Last Choice | Agilent_ChemStation_v1 | Agilent_MassHunter_v1 | Agilent_MassHunterBatch_v1 | PerkinElmer_XLFile_v1 | PerkinElmer_REPFile_v1 | ThermoFisher_XSeriesII_PlasmaLab2_v1 | ThermoFisher_iCAPQ_Qtegra_v1 | ThermoFisher_ElementTXT_v1 | ThermoFisher_ElementFIN2_v1 | ThermoFisher_Neptune_v1 | AnalytikJena_CSVFile_v1 | AnalytikJena_PRNFile_v1 | TOFWERK_Tofware_v2 | TOFWERK_Tofware_v3 | NuInstruments_AttomTRA_v1 }	The default make and model to use for ICP data file selection.
Profile.LogBookMatchForRMs	String	Strict	{ Strict | Loose }	When loading log bok files how should the RM names be matched. "Strict" forces the full string in the logbook to match an alias of the RM. "Loose" allows the RM alias values to be sub-strings of the logbook entry.
Profile.AllowDataEditing	Boolean	TRUE		When true, the user is able to edit single sweep values on the data table.
Profile.Management.LockProjects	Boolean	FALSE		When true, ProfileIsDefault values in the project are locked to the profile defaults.

Options – Project

Option	Type	Default	Guidance	Notes
`Quant.ComputeAnalysisInCounts`	TRUE	Boolean	TRUE	
`FlatSignal.001.Enabled`	TRUE	Boolean	TRUE	
`SpikeRemoval.001.Level3.Signal.SpikeFactorCoeff_X0`	TRUE	Double	1.1	1 - 1.6
`SpikeRemoval.001.Level3.Signal.MinSignalError`	TRUE	Double	2.5	0.1 - 10
`SpikeRemoval.001.Level3.GasBlank.SpikeFactorCoeff_X0`	TRUE	Double	1.2	1 - 1.6
`SpikeRemoval.001.Level3.GasBlank.MinSystemError`	TRUE	Double	1.5	0.1 - 100
`SpikeRemoval.001.Level2.Signal.WidthOfSignalToCheckNoiseAroundSpike`	TRUE	Integer	3	≥0
`SpikeRemoval.001.Level2.Signal.NoiseThresholdLeftRightModifier`	TRUE	Double	3	
`SpikeRemoval.001.Level2.Signal.SignalSlopeSpikeFactorModifier`	TRUE	Double	2.5	
`SpikeRemoval.001.Level2.Signal.SpikeFactorModifier`	TRUE	Double	0.8	
`SpikeRemoval.001.Level2.Signal.SpikeHeightThreshold`	TRUE	Double	100	≥0
`SpikeRemoval.001.Level2.Signal.SpikeFactorCoeff_X0`	TRUE	Double	1.2	1 - 1.6
`SpikeRemoval.001.Level2.Signal.MinSignalError`	TRUE	Double	5	0.1 - 10
`SpikeRemoval.001.Level2.GasBlank.WidthOfSignalToCheckNoiseAroundSpike`	TRUE	Integer	5	≥0

Option	Type	Default	Guidance	Notes
SpikeRemoval.001.Level2.Gas Blank.NoiseThresholdLeftRig htModifier	TRUE	Double	5	
SpikeRemoval.001.Level2.Gas Blank.SignalSlopeSpikeFacto rModifier	TRUE	Double	1	
SpikeRemoval.001.Level2.Gas Blank.SpikeFactorModifier	TRUE	Double	0.8	
SpikeRemoval.001.Level2.Gas Blank.SpikeHeightThreshold	TRUE	Double	100	≥0
SpikeRemoval.001.Level2.Gas Blank.SpikeFactorCoeff_X0	TRUE	Double	1.2	1 - 1.6
SpikeRemoval.001.Level2.Gas Blank.MinSystemError	TRUE	Double	1.5	0.1 - 100
SpikeRemoval.001.Level1.Sig nal.MinSignalError	TRUE	Double	2.5	0.1 - 10
SpikeRemoval.001.GasBlank.P rocessingLevel	TRUE	String	Level2	{ Level1	Level2	Level3 }
SpikeRemoval.001.Signal.Pro cessingLevel	TRUE	String	Level2	{ Level1	Level2	Level3 }
SpikeRemoval.001.GasBlank.D etectDoubleSpikes	TRUE	Boolean	TRUE	
SpikeRemoval.001.Signal.Det ectDoubleSpikes	TRUE	Boolean	TRUE	
SpikeRemoval.001.GasBlank.E nabledMode	TRUE	String	Manual	{ Disabled	Manual	AutoWithUndo	AutoForced }
SpikeRemoval.001.Signal.Ena bledMode	TRUE	String	Manual	{ Disabled	Manual	AutoWithUndo	AutoForced }
AutoTimePeriods.001.GasBlan kLaserMinusOffset	TRUE	Double	5	≥0
AutoTimePeriods.001.FixedGa sBlankTime	TRUE	Double	20	≥0

Option	Type	Default	Guidance	Notes
`AutoTimePeriods.001.GasBlankTimeMethod`	TRUE	String	LaserMinusOffset	{ Fixed | LaserMinusOffset }
`AutoTimePeriods.001.AnalysisSampleMinusOffset`	TRUE	Double	1	≥0
`AutoTimePeriods.001.FixedAnalysisTime`	TRUE	Double	25	≥0
`AutoTimePeriods.001.AnalysisTimeMethod`	TRUE	String	SampleMinusOffset	{ Fixed | RestOfSample | SampleMinusOffset }
`AutoTimePeriods.001.MinimumInterval`	TRUE	Double	5	≥0
`LaserTimes.001.ExpectedTimeWindow`	TRUE	Double	1	0.001 - 100
`LaserTimes.001.FixedRiseTime`	TRUE	Double	1.9	≥0
`LaserTimes.001.UseFixedRiseTime`	TRUE	Boolean	TRUE	
`LaserTimes.001.SumSignalFilter_SignalChangeFactor`	TRUE	Double	1	0 - 100
`LaserTimes.001.MinimumSaddleThreshold`	TRUE	Double	0.02	0 - 1
`LaserTimes.001.MinimumBinThreshold`	TRUE	Double	0.01	0 - 1
`LaserTimes.001.AutoSignalHistogramNumBinsMinLimit`	TRUE	Integer	6	1 - 1000
`LaserTimes.001.AutoSignalHistogramNumBinsFactor`	TRUE	Double	10	1 - 10000
`LaserTimes.001.SignalHistogramNumBins`	TRUE	Integer	0	0 - 1000
`LaserTimes.001.SkipSweepsAtEnd`	TRUE	Integer	10	0 - 1000
`LaserTimes.001.SkipSweepsAtStart`	TRUE	Integer	10	0 - 1000

Option	Type	Default	Guidance	Notes
LaserTimes.001.DetectionMethod	TRUE	String	AdvancedSumThreshold	{ SimpleSumThreshold | PeakGasBlankRatio | AdvancedSumThreshold }
Quant.PairingStrategy	TRUE	String	InterpolateIS	{ SameProjectSweep | ClosestTime | ClosestDistance | InterpolateIS }
Quant.AnalysisComputationStyle	TRUE	String	RatioOfMeans	{ Sweeps | MeanRatio | RatioOfMeans }
Quant.CalibrationFittingStyle	TRUE	String	RatioOfMeans	{ Sweeps | MeanRatio | RatioOfMeans }
Quant.GasBlankNumReadingsCollation	TRUE	String	BracketingIntervals	{ BracketingIntervals | IntervalBehind | AllIntervals }
Quant.GasBlankFittingStyle	TRUE	String	Sweeps	{ Sweeps | Means }
Quant.CalibrationUncertaintyCalculation	TRUE	String	MeanMissfitTimeperiods	{ MeanMissfitTimeperiods | MeanMissfitSweeps }
Quant.DetectionLimitMultiplier	TRUE	Double	3	≥0
Quant.SecondaryCorrection.AveragingStyle	TRUE	String	AverageEachRMSeparately	{ AverageAllRMs | AverageEachRMSeparately }
Quant.ReportedUncertaintyMultiplier	TRUE	Integer	1	1 - 5

Options – Quantification Setup

Option	Type	Default	Guidance	Notes
CleanUp.001.RejectionThreshold	Double	2	0 - 50	Remove this % from top and bottom of data. Basic outlier rejection.
CleanUp.001.StdDevMultiplier	Double	3	≥0	Applied to the theoretical standard deviation. Basic outlier rejection.

Option	Type	Default	Guidance	Notes
`QSQuant.CleanUp.CleanUpBeforeQuantification`	String	Enabled	{ Enabled | Disabled }	During quantification, should data be cleaned-up before quantification? Applies to UPb, and quantified ratios. Support for traces will be added in future versions.
`QSQuant.MassFiltering.DefaultRatioOfU238/U235`	Value	137.818±0.0225		Used when converting U235<=>U238. The default value provided is taken from: Hiess et al. 2012
`QSQuant.MassFiltering.AdditionalMassBiasUncertainty`	Double	0	≥0	Added to the signal uncertainty when converting U235<=>U238 on unknown samples. Enter as relative percent.
`QSQuant.TraceElement.ComputePbIsotopesSeparately`	Boolean	TRUE		When computing Pb, should isotopes be computed separately? To use this, the RM must have the Pb isotopic composition defined, and the Pb isotopes 206, 207, and 208 must be analysed in the Project.
`QSQuant.TraceElement.ComputeUIsotopesSeparately`	Boolean	TRUE		When computing U, should isotopes be computed separately? To use this, the RM must have the U isotopic composition defined, and the U isotopes 235 and 238 must be analysed in the Project.
`SumToTotal.BelowDetectionLimitHandling`	String	Exclude	{ Include | Exclude | DetectionLimitMultiplier }	When computing a total, how should concentrations below detection limit be handled?
`SumToTotal.BelowDetectionLimitMultiplier`	Double	0.5	0 - 1	This is the multiplier when using "DetectionLimitMultiplier" option to compute a total.
`DownHoleFract.001.CleanUpUPbAndQuantRatiosBeforeNormalisation`	Boolean	TRUE		Whether to clean up the mass and IS raw signals before normalisation. For UPb and quant ratios only. This option is always true for trace elements.
`DownHoleFract.001.CleanUpAfterNormalisation`	Boolean	TRUE		Whether to clean up the mass/IS ratio before fitting the model.
`FlatSignal.001.TraceElements`	String	49,57,88		Comma separated list of masses to use for identification of flat signals. Should not be empty. All masses should be present in the project.

Option	Type	Default	Guidance	Notes
`FlatSignal.001.MinimumInterval`	Double	5	1 - 1000	Minimum acceptable analysis interval. Entered in seconds.
`FlatSignal.001.MinSignalError`	Double	1.5	0.1 - 10	Minimum error on counting statistics for the setup in %. Used as a cut-off for counting statistics at high counts. TYPICALLY SET TO BE THE SAME AS SPIKE REMOVAL VALUE!
`FlatSignal.001.NumCleanUpPasses`	Integer	3	1 - 10	How many clean up passes to apply.
`FlatSignal.001.SignalCleanUpThreshold`	Double	2		This is a multiplier to the theoretical error to be used as a parameter to determine if the data point is to be considered for smoothing.
`FlatSignal.001.TheorErrMultiplier`	Double	2	1 - 5	Multiplier to the theoretical error to be used for comparing with the calculated signal RSD
`FlatSignal.001.FlatSignalThreshold`	Double	5		A replacement for the theoretical error for signals which are above the level where it equals the minimum signal error.
`FlatSignal.001.PsychometricFactor`	Double	1		Controls the acceptable variation of mid-range signals. Lowering the value increases the acceptable variation at these count rates.
`FlatSignal.001.TheorErrMultiplierAdjustment`	Double	0	0 - 2	Adjusts the theoretical error multiplier, at count rates below the MinSignalError to make the theoretical error closer to Poisson at low count rates.
`FlatSignal.001.WindowSizeForRSD`	Integer	9	≥5	The number of surrounding datapoints to use for RSD evaluation at each data point. Odd numbers only, rounded down.
`FlatSignal.001.SimilarityThresholdForJoiningTimePeriods`	Double	2	0.01 - 10	How similar should concentration be to add timeperiods to same analysis entry.
`FlatSignal.001.WindowSlopeThreshold`	Double	1.4	0.01 - 10	How much slope to accept in normalised values over all timeperiods for new analysis entry.

Option	Type	Default	Guidance	Notes
FlatSignal.001.InternalStandardChangeThreshold	Double	1.5		How much change is accepted in the counts of the internal standard mass.
FlatSignal.001.DEBUG_SlopeCheck_Window	Boolean	TRUE		
FlatSignal.001.DEBUG_SlopeCheck_Interval	Boolean	TRUE		
FlatSignal.001.DEBUG_SlopeCheck_TotalAnalysis	Boolean	TRUE		
FlatSignal.001.DEBUG_AnalysisDurationCheck	Boolean	TRUE		
FlatSignal.001.DEBUG_RejoinIntervals	Boolean	TRUE		

Appendix B – Universal Log Book Format

Version

This is v1.6 of the format specification.

Summary and Introduction

The LADR data reduction program can process ICP-MS data collected in analytical measurements. These data are usually loaded as a multi-part file, or a collection of individual files. To date, no ICP-MS software outputs sufficient information to identify the structure of the analytical session, standards, samples, and meta-information such as laser parameters. The LADR software provides an interface and workflow for specifying all of this additional information by hand, however, to save time and reduce errors, a more convenient approach involves pairing data files to a ledger, or logbook file. The following document defines the format for this logbook file.

For brevity, this document does not describe in detail how the file is used within the LADR software.

It is hoped that the format defined here is not restrictive and will be able to handle expansion as additional features are added to the software package.

For users of the GeoStar laser ablation control software, it is possible to save the LADR Universal LogBook file directly from the software. Use the sequence menu above the sequence list, or consult the GeoStar software manual for more information.

Note: Throughout the definition double-angle brackets are used to identify field placeholders in the file (e.g. <<name>>) whereas double quotes are used to identify specific string values (e.g. ":::").

Basic file information

This file format is based on the CSV de facto standard RFC4180 but is not identical to it. The most notable difference is the presence of a header section. More information about the CSV file format can be found at https://en.wikipedia.org/wiki/Comma-separated_values.

The file is a UTF-8 encoded text file with or without a BOM. Byte Order Mark: The UTF-8 BOM is a sequence of bytes (EF BB BF) that allows the reader to identify a file as being

encoded in UTF-8. Normally, the BOM is used to signal the endianness of an encoding, but since endianness is irrelevant to UTF-8, the BOM is unnecessary. https://en.wikipedia.org/wiki/Byte_order_mark.

The file can have any file extension, which is ignored on loading, however *.csv or *.txt are recommended as by default LADR will filter files with these extensions.

It is also possible to load an Excel XLSX (or XLS) file that contains a data table in the first worksheet, that if saved as CSV, would produce a file compatible with this format. While loading Excel files in this way is possible, use of Excel files for this purpose is not recommended due to lack of control and the possibility of extraneous characters appearing due to the mysteries of Excel formatting.

The file loader will support all line endings from Windows, Linux and MacOS. This can be summarized by:

- Windows Line Endings: CR+LF ("\r\n", 0x0D0A)

- Linux Line Endings: LF ("\n", 0x0A)

- MacOS Line Endings: LF ("\n", 0x0A)

Empty lines at the end of the file are valid and will be truncated.

Basic structure

The file will have the basic overall structure:

- Header section: <<field name>><<delimiter>><<field value>> [Optional]

- Divider line ":::" [Optional, but must be specified if the header is present]

- Line of field names (column headers) separated by the delimiter.

- Then each subsequent line will represent each record and thus contain the field values separated by the delimiter.

Lines starting with a hash character ("#", 0x23) are interpreted as comments and are ignored completely.

The field names (columns) can be present in any order, but the field names must be spelt correctly. CamelCase is used to make them easier to read, but they are identified using a case-insensitive string comparison.

The delimiter for the file will be a comma character (",", 0x2C).

If a field name or value is to also include the delimiter then the field must be quoted with double quotes (""", 0x22).

If a quoted field value also contains a double quote character, then it must be escaped by using double-double quotes ("""", 0x22 0x22).

Spaces around delimiters will be stripped.

If a space is needed to be included, then the field value should be quoted, and the space included inside the quotes.

To make file editing easier, all trailing delimiters will be ignored. This will allow a user to open a file in a spreadsheet program (such as Excel, or LibreOffice) and view and manipulate the file. When this is viewed in a text editor, the header section will have delimiters appended to each record, and as stated, these will be stripped on file loading.

Logical structure

The header is used to represent information for the project or analytical session. This can include a project name, or the identifying information of the user who owns the data. The header is designed to be expandable, as well as optional.

The field names are simple strings and where possible, verbose names have been used to make them more memorable.

Each record represents a sample collected by the ICP-MS. This will either correlate to a single data file, or a single sample within a multi-sample data file.

Note: At the time of writing we envisage this format being extended to also identify sections of a continuous monolithic data file. This will involve adding two columns, "FileTimeStart" and "FileTimeEnd", which will call out the section of the file to use. For now this is not supported.

Header field names

The following header field names are supported.

"ProjectName"

This field can be used to specify the project name. It is not used in the project but is helpful for record keeping and workflow management.

"Date"

This is used to help identify the project. The unambiguous format (YYYY-MM-DD) is to be used.

"User"

This is used to help identify the project and the source of the data.

Header divider line

This line separates the header section from the column headers and records. If a header is present then it must be included. This line should hold three sequential colon characters (":::", 0x3A 0x3A 0x3A).

To make file manipulation easier, trailing delimiters will be stripped automatically. This will allow a user to open these files in a spreadsheet program and view them in a simple way.

If the header divider is omitted then the file is assumed to hold no header and the first valid line (skipping comment lines) of the file will be taken to be the field names line.

Field Names Line

The field names line marks the top of the table section of the file.

Compulsory Field Names

The logbook file must contain the following field names: "DataIdent", "Sample", "QuantName", "SampleType", and "AblationType".

In the detailed description to follow these are marked with an asterisk * character.

All Field Names

The following field names are supported.

"DataIdent"*

This field defines the data file filename, or the identifier for multi-part data files.

The log book file (being described here) defines the order of the samples in the project, and the order does not need to align with the order of segments in a multi-segment file, or the alphabetical (or other) sorting of the separate files in their folder.

At the time of writing there is no support for data files that do not support a text identifier. In such a situation the DataIdent field will contain an integer index to identify the segment.

"Sample"*

A user-specified name for this record. The name will be shown to the user by the software while working on the project.

"QuantName"*

A user-specified name which is matched to the QuantificationSetup name in the LADRlib software during data import into the software. This defines how the data reduction will take place. This is a critical part of built-in automation.

"SampleType"*

{ Primary | Secondary | Sample | Map | Background }

This is used by the software to identify the sample type for each entry in the log book. A valid log book must contain at least one sample of the type "primary".

It is possible to define combinations of sample types, where each one is separated by an underscore character "_".

"AblationType"*

{ Spot | Line | Map }

This is used to identify the type of ablation. The column should contain one of the three values shown, other values are ignored.

<<El>>

This field contains the known internal standard composition for the element identified by the element symbol <<El>>. To avoid any possible clashes between future field names and internal standard element symbols, all field names will be longer than three characters. The internal standard composition is to be specified in PPM (μg/g) and can be defined using one of three formats to provide support for different character sets in the application producing the file.

{ <<El>>"±" | <<El>>"σ" | <<El>>"~" }

This field contains the uncertainty on the internal standard composition identified by the element symbol El. To improve flexibility, there are three characters supported that can flag the column as holding the uncertainty. These are any one of ("±", 0xF1), ("σ", 0x3C3), or ("~", 0x7E). The default value the software assigns to this column is 0, if no values are provided in this column, or the column is not present.

"BeamSize"

This field holds the size of the ablation crater in μm.

The field value should contain only numbers, but if additional characters are included (e.g. "μm" suffix) then they will be stripped.

If the beam size is not uniform, then this field may contain the width and height separated by the "x" character.

If the beam size is unknown or undefined then either omit the column entirely, or use an empty string value "".

"BeamShape"

{ "Circle" | "Square" | "Triangle" | "Points" }

This identifies the shape of the beam, typically either circle or square. Identifiers for other shapes are supported, as listed above. The identifier "points" is used to indicate an arbitrary shape defined by a list of points, there is no support in this file for defining the shape further.

Note: The identifier "square" is used as a synonym for "rectangle".

If the beam shape is unknown or undefined then either omit the column entirely, or use an empty string value "".

"LaserFluence"

This field contains the on-sample laser fluence in J/cm2.

The field value should contain only numbers, but if additional characters are included (e.g. "J/cm2" or "J.cm-2" suffix) then they will be stripped.

If the laser fluence is unknown or undefined then either omit the column entirely, or use an empty string value "".

"LaserEnergy"

This field contains the laser source energy in mJ.

The field value should contain only numbers, but if additional characters are included (e.g. "mJ" suffix) then they will be stripped.

Note: This field is provided as a proxy for "Laser Fluence". When the laser fluence value is provided, this field is ignored.

If the laser energy is unknown or undefined then either omit the column entirely, or use an empty string value "".

"LaserFrequency"

This field contains the laser source repetition rate in Hz.

The field value should contain only numbers, but if additional characters are included (e.g. "Hz" suffix) then they will be stripped.

"ScanSpeed"

If the entry is a scan line, this field contains the scan speed in µm/s.

The field value should contain only numbers, but if additional characters are included (e.g. "µm/s" suffix) then they will be stripped.

"Geometry1X"

Note: All geometry field values should be defined using microns.

If the entry is a single point then this field contains the X coordinate for the point.

If the entry is a scan line then this field contains the X coordinate of the start location.

"Geometry1Y"

If the entry is a single point then this field contains the Y coordinate for the point.

If the entry is a scan line then this field contains the Y coordinate of the start location.

"Geometry1Z"

If the entry is a single point then this field contains the Z coordinate for the point.

If the entry is a scan line then this field contains the Z coordinate of the start location.

Note: Z coordinate values are optional, but may be used in future versions of the software for data processing.

"Geometry2X"

If the entry is a scan line then this field contains the X coordinate of the end location.

"Geometry2Y"

If the entry is a scan line then this field contains the Y coordinate of the end location.

"Geometry2Z"

If the entry is a scan line then this field contains the Z coordinate of the end location.

Note: Z coordinate values are optional, but may be used in future versions of the software for data processing.

"Geometry1"

This field is a convenient way to combine the three fields "Geometry1X", "Geometry1Y" , and "Geometry1Z" into a single field. The values are space separated and wrapped in square brackets, like so: "[12345.1 54321.0 123.5]". The Z coordinate is optional and can either be omitted and replaced with a placeholder value, e.g. "0".

"Geometry2"

As for "Geometry1" this field serves as a convenient way to combine the three fields "Geometry2X", "Geometry2Y" , and "Geometry2Z" into a single field.

"Comment"

A comment to describe the entry. This can contain any string, but should be quoted if there are commas present. The comment will propagate through the LADRlib software.

Meta-data fields

The file format can be extended to include fields of data associated with the record, but which are not used explicitly by the data reduction program. These field names can be chosen by the user and are identified by the suffix: "Meta_". The values of these fields are saved in the LADRlib project and can be shown to the user and exported alongside the results.

Sample file

Here is a very simple example of a three record logbook file:

```
ProjectName,Example Project

Date,2015-06-19

User,A. Norris

:::

DataIdent,Sample,QuantName,SampleType,AblationType,Si,Si±

DF0001.csv,NIST610,610Si,Primary,Spot,,

DF0002.csv,GlassA,610Si,Sample,Spot,34123,1200

DF0003.csv,NIST610,610Si,Primary,Spot,,
```

Appendix C – Analysis Log Import File Format

Version

This is v1.1 of the format specification.

Summary and Introduction

The following file specification can be used to import analysis log entries into LADR automatically. This allows for intervals to be synchronised with external events, or be defined using external software tools, as well as moved between projects, for example for split-stream work.

Basic File Information

This file format is based on the CSV de facto standard RFC4180. More information about the CSV file format can be found at https://en.wikipedia.org/wiki/Comma-separated_values.

The file is a UTF-8 encoded text file with or without a BOM. Byte Order Mark: The UTF-8 BOM is a sequence of bytes (EF BB BF) that allows the reader to identify a file as being encoded in UTF-8. Normally, the BOM is used to signal the endianness of an encoding, but since endianness is irrelevant to UTF-8, the BOM is unnecessary. https://en.wikipedia.org/wiki/Byte_order_mark.

The file can have any file extension, which is ignored on loading, however *.csv is recommended as by default LADR will filter files with this extensions.

The file loader will support all line endings from Windows, Linux and MacOS.

This can be summarized by:

- Windows Line Endings: CR+LF ("\r\n", 0x0D0A)

- Linux Line Endings: LF ("\n", 0x0A)

- MacOS Line Endings: LF ("\n", 0x0A)

Empty lines at the end of the file are valid and will be truncated.

Basic Structure

The field names (columns) can be present in any order, but the field names must be spelt correctly. CamelCase is used to make them easier to read, but they are identified using a case-insensitive string comparison.

The delimiter for the file will be a comma character (",", 0x2C).

If a field name or value is to also include the delimiter then the field must be quoted with double quotes (""", 0x22).

If a quoted field value also contains a double quote character, then it must be escaped by using double-double quotes (""""", 0x22 0x22).

Spaces around delimiters will be stripped.

If a space is needed to be included, then the field value should be quoted, and the space included inside the quotes.

Logical structure

The file contains a single block of columns and rows. The header row is compulsory. If any non-empty row fails to contain values for all three of the compulsory fields then the import will be aborted.

Compulsory Field Names

The following compulsory header field names must be present in the file.

"DataIdent"

The data ident is used by LADR to identify an ICP-MS measurement. For instruments that save data to separate filenames, such as Agilent systems, then the data ident is the filename of the measurement. For instruments that save multiple measurements to a single file, such as Thermo Qtegra systems, then the data ident is the sample name from the run table.

"Start"

The start time of the interval in seconds (to arbitrary precision) relative to the start of the data file identified by the DataIdent.

"End"

The end time of the interval in seconds (to arbitrary precision) relative to the start of the data file identified by the Data Ident.

Optional Field Names

The following optional header field names may be present in the file.

"AnalysisName"

The value to assign to the analysis log entry. This is typically the sample name, or other identifier for the analysis.

"QuantName"

The name of the quantification setup to use with this analysis. If the quant name is defined but the quantification setup is not present in the project then the import will be aborted.

"Comment"

A free form description to assign to the analysis log entry. It will be visible to the user in the analysis log and can be edited.

"Join"

When a "1" is present in this row, the compulsory field names ("DataIdent", "Start", and "End") will be used to define a time period, and this time period will be added as a multi-integration to the previous Analysis Log entry. Note that the time period cannot intersect any existing time period that is part of the analysis, or importing will be aborted. The first row in the table may not contain a "1" in this column.

Sample file

Here is a very simple example of a twenty-record Analysis Log import file:

```
DataIdent,Start,End,Join,QuantName,AnalysisName,Comment
D18MA02b001.csv,37.947736889,85.772282009,0,New QS,STDGL3,
D18MA02b002.csv,37.947736889,85.772282009,0,New QS,STDGL3,
D18MA02b003.csv,37.947736889,85.772282009,0,New QS,GSD-1G,
D18MA02b004.csv,37.947736889,85.772282009,0,New QS,GSD-1G,
D18MA02b005.csv,37.947736889,85.772282009,0,New QS,BCR-2G,
D18MA02b006.csv,37.947736889,85.772282009,0,New QS,BCR-2G,
D18MA02b007.csv,37.947736889,85.772282009,0,New QS,Cpy,
D18MA02b008.csv,37.947736889,85.772282009,0,New QS,Cpy,
```

```
D18MA02b009.csv,37.947736889,85.772282009,0,New QS,STDGL3 #24,
D18MA02b010.csv,37.947736889,85.772282009,0,New QS,STDGL3 #24,
D18MA02b011.csv,37.947736889,85.772282009,0,New QS,sample1 – 1,
D18MA02b012.csv,37.947736889,85.772282009,0,New QS,sample1 – 2,
D18MA02b013.csv,37.947736889,85.772282009,0,New QS,sample1 – 3,
D18MA02b014.csv,37.947736889,85.772282009,0,New QS,sample1 – 4,
D18MA02b015.csv,37.947736889,85.772282009,0,New QS,sample1 – 5,
D18MA02b016.csv,37.947736889,85.772282009,0,New QS,sample1 – 6,
D18MA02b017.csv,37.947736889,85.772282009,0,New QS,sample1 – 7,
D18MA02b018.csv,37.947736889,85.772282009,0,New QS,sample1 – 8,
D18MA02b019.csv,37.947736889,85.772282009,0,New QS,sample1 – 9,
D18MA02b020.csv,37.947736889,85.772282009,0,New QS,sample1 – 10,
```

Note: *This is the end of the document. Thank you for reading. Please send all corrections and comments to ladr@norsci.com.*