

Comprehensive software for data reduction of LA-ICP-MS data sets

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Introduction

Since Longerich et al. published [1] their formula for LA-ICP-MS data reduction there has been considerable demand for practical software implementations [2]. Currently there are many software titles available (Iolite [3], Glitter [4], SILS [5], Lamtrace, UranOS [6], UPb Redux [7], LA Tools [8], UPb.Age [9] ...) as well as various scripts and spreadsheets used by laboratories *in-house*. Here we introduce a new software package LADR (pronounced "ladder") that provides a comprehensive software solution for data reduction of laser ablation ICP-MS data sets.

LADR is a standalone program, developed in .NET for Windows 7, 8, and 10, that is also compatible with Linux and OSX under Mono (full support to be supported in late 2019). The software is able to load data files from all makes and models of ICP-MS instruments, and is compatible with all laser ablation platforms.

As well as performing basic data reduction calculations, LADR can: identify and remove transient spikes; correct for interferences; model variations in background intensity; synchronise data with laser firing time; model and correct for down hole fractionation; model calibration drift; use secondary standards to correct for matrix effects; add unmeasured elements by stoichiometry; quantify to a total; support mixed quantification routines within a data set; and most important, apply a robust error propagation from all sources of uncertainty [10][11][12][13].

The software estimates the total uncertainty budget for the calculation, and reports uncertainty values for various applications, such as intra-run, intra-laboratory, or inter-laboratory comparison.

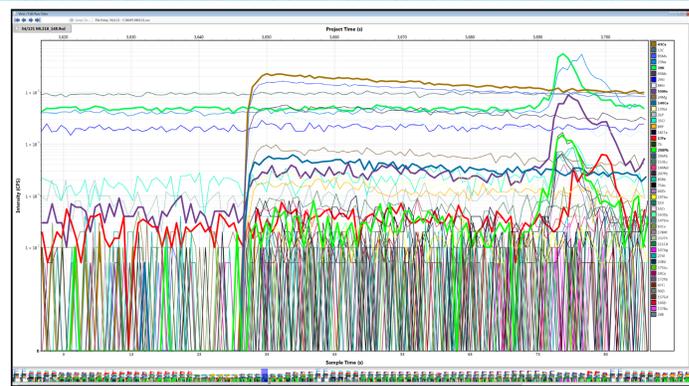


Figure 1. Data can be viewed using the charting tool in either counts or CPS on linear or log vertical scales. The colour and visibility of masses can be set individually, and here a small number of masses have been hi-lighted. The long plot at the bottom shows a longer segment of time from the project and can be used to control the chart. These data are from a carbonate mineral, and were collected on an Agilent 7900 ICP-MS coupled to an ASI RESOLUTION laser ablation instrument with S155 ablation cell.

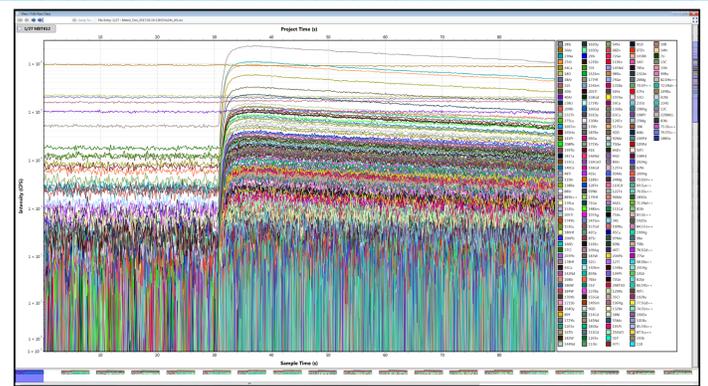


Figure 2. The charting tool is powerful enough to display many data, and here we show traces for 226 masses simultaneously. The legend has expanded automatically and demonstrates flexible mass identification, including doubly charged isotopes at half integer values, oxides, and "non elements" such as background at mass 220. These data are from the reference material NIST 612, and were collected on a TOFWerk TOF-ICP-MS coupled to an ASI RESOLUTION laser ablation instrument with S155 ablation cell.

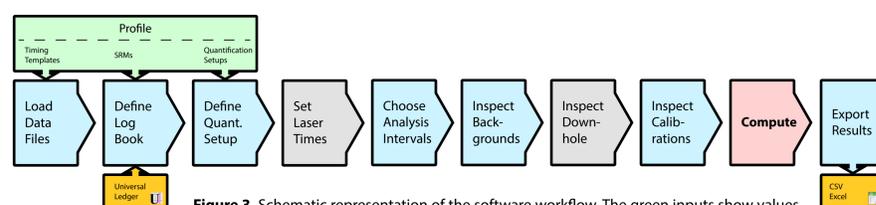


Figure 3. Schematic representation of the software workflow. The green inputs show values that were saved previously to the user's *Profile*, which saves considerable time on subsequent *Projects*. The log book input from "universal ledger" allows for automation of *Project* setup.

Workflow

To improve usability a strict workflow is enforced by the software, with each stage requiring validation before the user can proceed. The user can go backwards, but doing so will invalidate downstream components. Progress through the workflow is aided by a verbose notification system. The entire *Project* (including all SRMs and original data files) can be saved to disk and resumed at any stage. The *Profile* stores elements that can be re-used between *Projects*, allowing rapid processing of subsequent *Projects* with the same mineral types.



Background Modelling

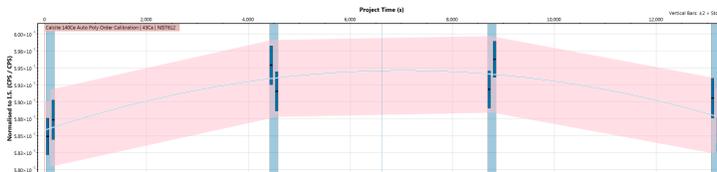
Contribution from the background ("gas blank") must be removed prior to quantification. Typical protocols measure the background immediately prior to each ablation, however, LADR is flexible enough to accommodate any arrangement of background and ablation intervals. Backgrounds are modelled as either continuous or separate curves, displayed graphically (Figure 4.) so the user can make appropriate decisions about the quality of fit.

Figure 4 (left). Mean background values for each mass are plotted separately across the entire project. Vertical bars show ± 3 standard error. The upper plot shows background readings for 63Cu which are modelled by using a continuous polynomial curve. The lower plot shows 56Fe, which due to non-continuous variability is modelled using separate polynomial curves over short intervals.

Figure 5 (below). Mean calibration values for a single mass are plotted across the entire project. The values shown are the background-subtracted ratios of the mass to the internal standard measured on the reference material. The reference material was measured in duplicate, and these have been grouped together for the purpose of fitting the continuous calibration curve. Vertical bars show ± 2 standard error.

Calibration Drift Correction

Calibration values are computed as background-subtracted values normalised to the internal standard for each mass as measured on the calibration reference material. The software creates the calibration curves automatically based on the configuration of the QS(s) in the Project. Drift in the calibration values is fitted with either continuous curves (Figure 5.) or separate regions as for backgrounds.



Spike Removal

Spikes are a frequent occurrence in LA-ICP-MS analysis and must be removed prior to quantification. Failure to identify and remove spikes will result in erroneous results.

LADR offers three levels of filtering (demonstrated in Figure 6.) that all work by comparing the spike intensity with the shape of the signal around the spike. Input from the operator is required when choosing the correct filtering level, as over filtering may result in removal of micro-inclusions from the measurement.

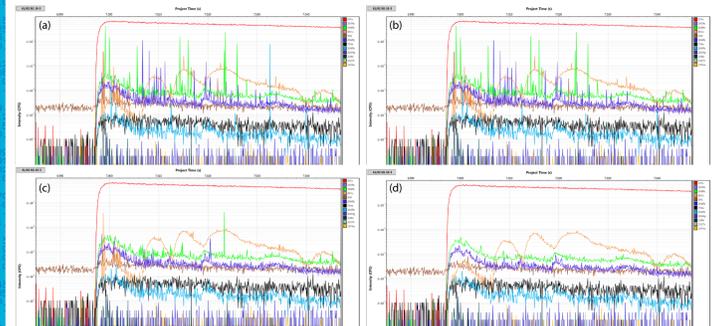
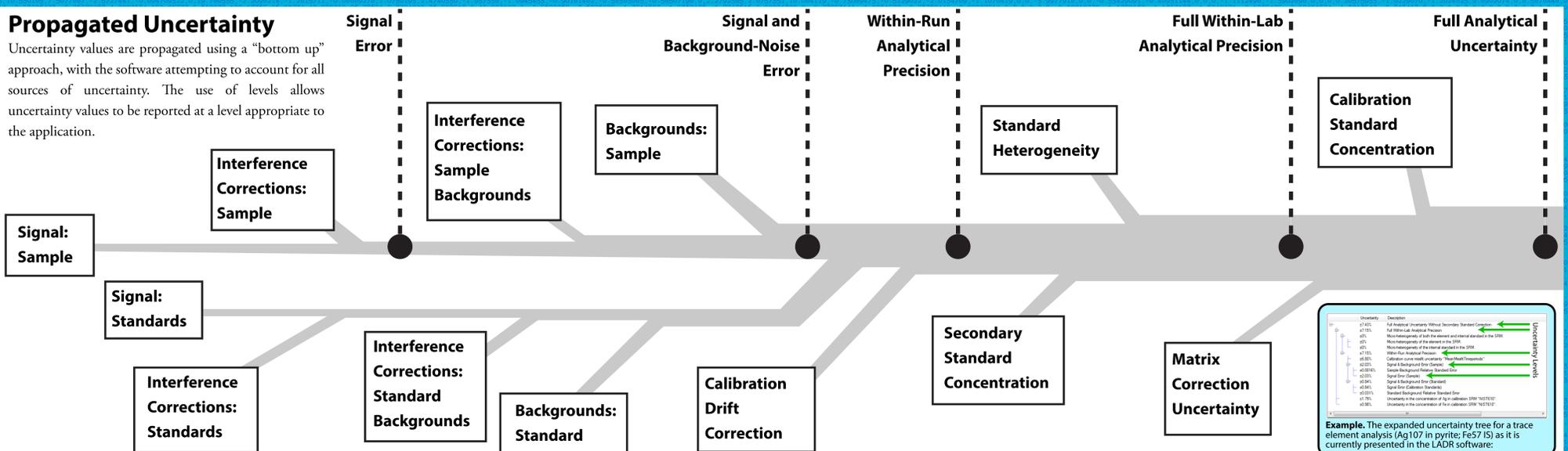


Figure 6. (a) Original data (pyrite). (b) Filtering level 1, ICP-MS detector anomalies. (c) Filtering level 2, isolated spikes, most recommended. (d) Filtering level 3, all spikes, may remove some micro-inclusions so must be applied judiciously.

Propagated Uncertainty

Uncertainty values are propagated using a "bottom up" approach, with the software attempting to account for all sources of uncertainty. The use of levels allows uncertainty values to be reported at a level appropriate to the application.



UPb Geochronology

LADR quantifies UPb ratios alongside trace elements, allowing ratios, ages and trace element concentrations to be computed simultaneously for every sample. Calibration of UPb ratios can be performed using different reference materials. If 235U is not measured then it can be computed using a specified ratio relative to 238U. If both 235U and 238U are measured, and the count rate of 238U exceeds a threshold (the upper limit of the pulse counting regime) then 238U counts are computed automatically from 235U counts. Downhole fractionation is corrected using curves observed on the reference materials. Once all calibration curves are generated, then data for each ablation can be inspected as fully corrected ratios (Figure 7.) shown in tandem with concordia plots. Intervals for analysis are selected using the mouse. Correction for common lead will be added soon.

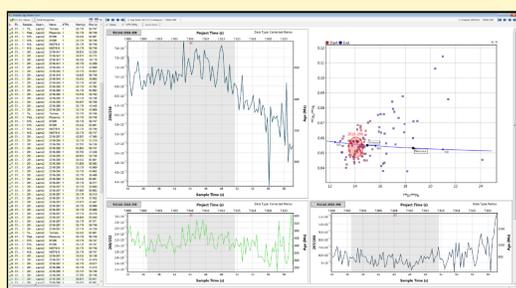


Figure 7. The charting tool is capable of plotting background-subtracted downhole-corrected mass ratios for the UPb system. Plots of ratios of interest can be shown alongside a range of concordia diagrams. These data from an anonymous zircon were collected on an Agilent 7900 ICP-MS coupled to an ASI RESOLUTION laser ablation instrument with S155 ablation cell.

Additional Features

In addition to the features described, LADR can also:

- Compute matrix correction factors using secondary reference materials.
- Correct for down-hole fractionation using observation of the down-hole trend on the standard.
- Support complex stoichiometry, including substitutions, e.g. As and Se for S.
- Download SRM compositions directly from the GeoRem database.
- Correct for arbitrary interference corrections, either isobaric or polyatomic.
- Show complete uncertainty budget for every quantified result.

Concluding Remarks

The LADR software described here has been used in-house at CODES (University of Tasmania, Australia) for over twelve months as a stable beta release.

This beta release can be downloaded from the author's website:

<http://norris.org.au/ladr/>

The software will be made commercially available in early 2019.