End-to-End Integration of Laser Ablation, ICP–MS, and Data Reduction: A World First!

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Introduction

Data reduction of LA–ICP–MS data sets has been realised previously via loosely coupled systems supplied by a range of different vendors. While this approach provides considerable flexibility, that same flexibility can result in propagation of mistakes due to the onerous requirements of the workflow, such as manual editing of data files and duplication of set-up in multiple software packages. In addition, the limitations of this approach have resulted in some laboratories imposing unnecessary limitations on what they believe can be measured during a single analytical session.

To address this problem Norris Scientific has mapped out and implemented the first end-to-end workflow that allows users to set up, execute, and reduce data from any LA–ICP–MS session without the need to duplicate input or use spreadsheet software to edit any files. Multiple quantification routines can be easily mixed together, and the not-insignificant risk of mistakes due to mishandling is eliminated. All of these advantages allow the analyst to focus on more important aspects of LA–ICP–MS such as sampling, instrument tuning, and optimisation of ablation conditions.

While this workflow has been first implemented in *GeoStar* and *LADR*, with support for some ICP–MS instruments, it is hoped that other manufacturers will emulate this workflow to the benefit of the LA–ICP–MS community.

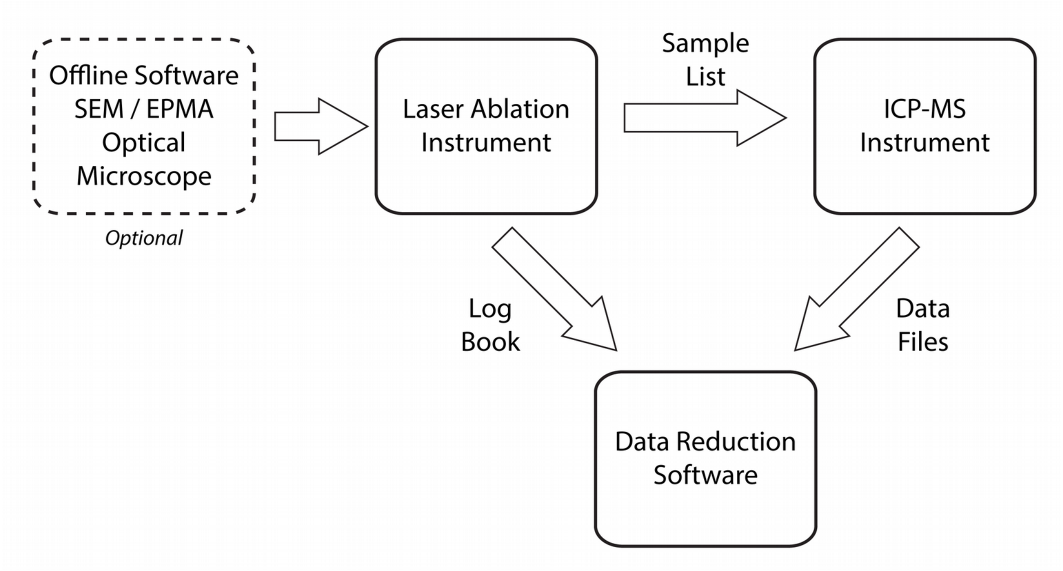


Figure 1. The new workflow enabled by *GeoStar* paired with *LADR* data reduction software.

Workflow Summary

Practically all LA–ICP–MS sessions are measured by sample-standard bracketing where primary standards are measured every 45–60 minutes to calibrate the ICP–MS response and assess instrument drift over time. Secondary standards can be used in a number of ways, as either a qualitative check that quantification can recover known values, or more quantitatively such as determining matrix correction factors (at different spot sizes) or measuring excess uncertainty. To assess uncertainty it is desirable to place secondary standards half way between calibration standards, where models of drift will be least constrained.

The new workflow (Figure 1) requires the laser ablation instrument to send a trigger signal for each ablation to the ICP–MS, which saves the time resolved signals from each ablation to a separate file. Starting with the laser ablation instrument software (*GeoStar* in this example), the sample list is defined and transferred over to the ICP–MS instrument via a sample list file. This transfer allows the ICP–MS software to easily show the sample names and laser conditions and also ensures the acquisition time for each sample matches between the two instruments.

Num.	Comment	S...	Time	Rep...	Energy	Type	Quant Name
1.	NIST610	30µm	1.2m	10Hz	4J.cm^{-2}	Primary	
2.	NIST610	30µm	1.2m	10Hz	4J.cm^{-2}	Primary	
3.	GSD	30µm	1.2m	10Hz	3.5J.cm^{-2}	Secondary	
4.	GSD	24µm	1.2m	10Hz	3.5J.cm^{-2}	Secondary	
5.	Sample1_GrainA	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
6.	Sample1_GrainA	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
7.	Sample1_GrainB	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
8.	Sample1_GrainB	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
9.	Sample1_GrainC	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
10.	Sample1_GrainC	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
11.	Sample2_GrainA	30µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
12.	Sample2_GrainA	30µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
13.	Sample2_GrainB	24µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
14.	Sample2_GrainB	24µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
15.	Sample2_GrainC	30µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
16.	Sample2_GrainC	30µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
17.	GSD	30µm	1.2m	10Hz	3.5J.cm^{-2}	Secondary	
18.	GSD	24µm	1.2m	10Hz	3.5J.cm^{-2}	Secondary	
19.	NIST610	30µm	1.2m	10Hz	4J.cm^{-2}	Primary	
20.	NIST610	30µm	1.2m	10Hz	4J.cm^{-2}	Primary	
21.	Sample3_GrainA	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
22.	Sample3_GrainA	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
23.	Sample3_GrainA	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
24.	Sample3_GrainA	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
25.	Sample3_GrainA	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
26.	Sample3_GrainA	30µm	1.2m	10Hz	3.5J.cm^{-2}	Sample	BasalticGlass
27.	Sample4_GrainB	24µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
28.	Sample4_GrainB	24µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
29.	Sample4_GrainB	24µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
30.	Sample4_GrainB	24µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
31.	Sample4_GrainB	24µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
32.	Sample4_GrainB	24µm	1.2m	10Hz	4J.cm^{-2}	Sample	Silicate
33.	GSD	30µm	1.2m	10Hz	3.5J.cm^{-2}	Secondary	
34.	GSD	24µm	1.2m	10Hz	3.5J.cm^{-2}	Secondary	
35.	NIST610	30µm	1.2m	10Hz	4J.cm^{-2}	Primary	
36.	NIST610	30µm	1.2m	10Hz	4J.cm^{-2}	Primary	

Figure 2. The sequence from *GeoStar* where the sample type and quant name can be defined.

After the sequence has been ablated, the data reduction software needs information from both instruments. The laser ablation software provides the sample type, quant name, and the laser parameters via the log book file, while the measured values come from the ICP–MS software via the data files.

Now that the data reduction software has all of the information about the sequence, the actual data reduction can be automated as much as possible, and the chance of transcription errors between the systems is greatly reduced.

Laser Ablation Instrument: Defining the Sequence

The laser ablation instrument is the natural location to set up the ablation sequence. Here the user has the best opportunity to clearly identify each sample and to place each ablation in the correct location. The laser ablation software offers tools to control the geometry of the sequence as well as to adjust lighting parameters: improving the chance of identifying the sample and material type correctly. This is also where the laser conditions are defined. Of course mistakes can still happen, and where possible the user should be assisted by additional information such as BSE[1] and CL[2] images or X-Ray maps.

As well as defining the sequence, the the laser ablation software needs to provide controls to set both the sample type (calibration standard, secondary standard, unknown, etc...) and the name of the quantification routine that will be used to quantify the ablation.

1 *Back scattered electron* imaging, typically collected on a scanning electron microscope (SEM).

2 *Cathodoluminesence* imaging, collected on an SEM or a dedicated instrument.

An example sequence set up in the laser ablation software *GeoStar* is shown in Figure 2. The columns "Type" and "Quant Name" show the type of ablation and the name of the quantification routine used for data reduction purposes. This example differentiates between quantification of a "basaltic glass" and a general purpose "silicate" routine (a fanciful example), but other sequences could use either a single quantification routine, or many, as dictated by the application.

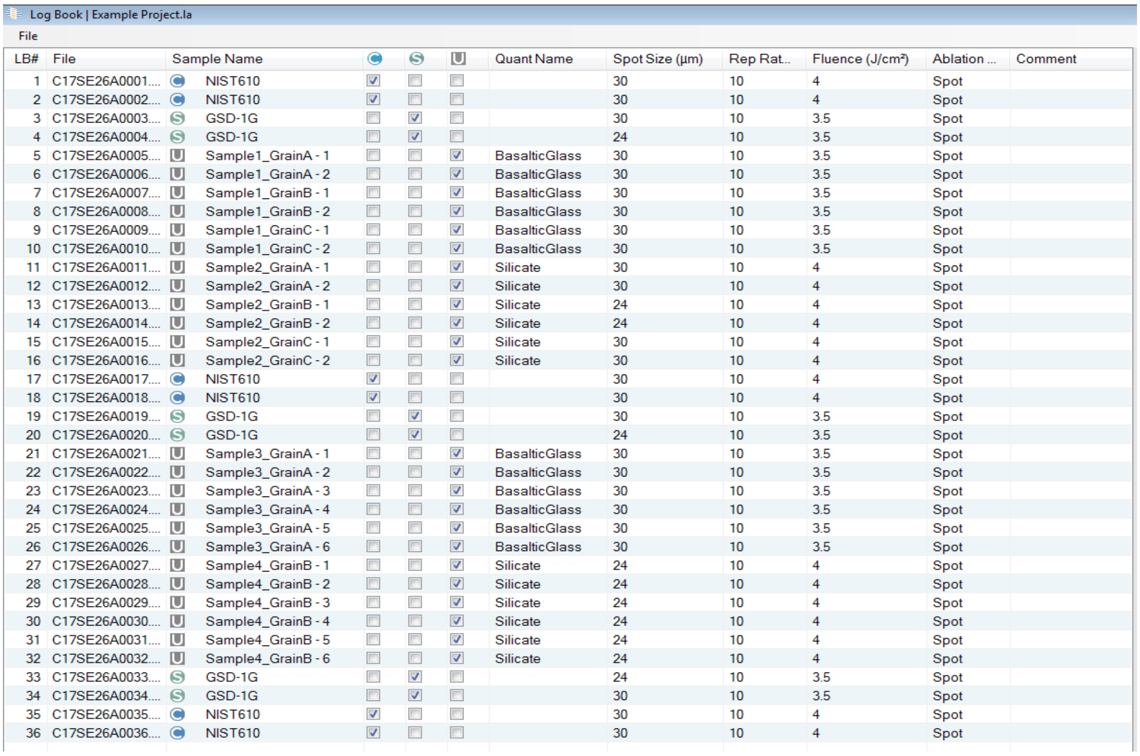
The laser ablation software directly exports two files: one is the "Universal Log Book" file for use by data reduction software (such as *LADR*). This contains all of the entries in the sequence, including the sample name ("Comment" in Figure 2), laser conditions, and the quant name and sample type. The second file is the ICP–MS import file. This file is saved in the specific format specified by the ICP–MS manufacturer's control software. Currently *GeoStar* can export files for use by Agilent *Mass Hunter*, Analytik Jena *ASpect MS*, and Thermo *Qtegra* software. Additional formats will be added to *GeoStar* on request.

ICP–MS: Setting Up The Run Table

The ICP–MS software is the best location for operating, tuning, and configuring the ICP–MS, but requires duplicated effort to set-up for samples defined on the laser. To simplify set-up and minimise mistakes, the run table should be imported into the ICP–MS software using a file created by the laser ablation software specifically for this purpose.

While the details vary between software packages, all ICP–MS software allows the user to import a run table from an external file. The file exported from the laser ablation software is selected, the run table is set-up automatically, and now shows additional metadata such as the sample name and laser ablation parameters.

In practice, different ICP–MS software packages handle sample names in different ways. The *Mass Hunter* software from Agilent allows the user to specify the file name and the sample


Log Book | Example Project.la

File

LB#	File	Sample Name	C	S	U	Quant Name	Spot Size (µm)	Rep Rat...	Fluence (J/cm²)	Ablation ...	Comment
1	C17SE26A0001....	NIST610	✓				30	10	4	Spot	
2	C17SE26A0002....	NIST610	✓				30	10	4	Spot	
3	C17SE26A0003....	GSD-1G		✓			30	10	3.5	Spot	
4	C17SE26A0004....	GSD-1G		✓			24	10	3.5	Spot	
5	C17SE26A0005....	Sample1_GrainA - 1			✓	BasalticGlass	30	10	3.5	Spot	
6	C17SE26A0006....	Sample1_GrainA - 2			✓	BasalticGlass	30	10	3.5	Spot	
7	C17SE26A0007....	Sample1_GrainB - 1			✓	BasalticGlass	30	10	3.5	Spot	
8	C17SE26A0008....	Sample1_GrainB - 2			✓	BasalticGlass	30	10	3.5	Spot	
9	C17SE26A0009....	Sample1_GrainC - 1			✓	BasalticGlass	30	10	3.5	Spot	
10	C17SE26A0010....	Sample1_GrainC - 2			✓	BasalticGlass	30	10	3.5	Spot	
11	C17SE26A0011....	Sample2_GrainA - 1			✓	Silicate	30	10	4	Spot	
12	C17SE26A0012....	Sample2_GrainA - 2			✓	Silicate	30	10	4	Spot	
13	C17SE26A0013....	Sample2_GrainB - 1			✓	Silicate	24	10	4	Spot	
14	C17SE26A0014....	Sample2_GrainB - 2			✓	Silicate	24	10	4	Spot	
15	C17SE26A0015....	Sample2_GrainC - 1			✓	Silicate	30	10	4	Spot	
16	C17SE26A0016....	Sample2_GrainC - 2			✓	Silicate	30	10	4	Spot	
17	C17SE26A0017....	NIST610	✓				30	10	4	Spot	
18	C17SE26A0018....	NIST610	✓				30	10	4	Spot	
19	C17SE26A0019....	GSD-1G		✓			30	10	3.5	Spot	
20	C17SE26A0020....	GSD-1G		✓			24	10	3.5	Spot	
21	C17SE26A0021....	Sample3_GrainA - 1			✓	BasalticGlass	30	10	3.5	Spot	
22	C17SE26A0022....	Sample3_GrainA - 2			✓	BasalticGlass	30	10	3.5	Spot	
23	C17SE26A0023....	Sample3_GrainA - 3			✓	BasalticGlass	30	10	3.5	Spot	
24	C17SE26A0024....	Sample3_GrainA - 4			✓	BasalticGlass	30	10	3.5	Spot	
25	C17SE26A0025....	Sample3_GrainA - 5			✓	BasalticGlass	30	10	3.5	Spot	
26	C17SE26A0026....	Sample3_GrainA - 6			✓	BasalticGlass	30	10	3.5	Spot	
27	C17SE26A0027....	Sample4_GrainB - 1			✓	Silicate	24	10	4	Spot	
28	C17SE26A0028....	Sample4_GrainB - 2			✓	Silicate	24	10	4	Spot	
29	C17SE26A0029....	Sample4_GrainB - 3			✓	Silicate	24	10	4	Spot	
30	C17SE26A0030....	Sample4_GrainB - 4			✓	Silicate	24	10	4	Spot	
31	C17SE26A0031....	Sample4_GrainB - 5			✓	Silicate	24	10	4	Spot	
32	C17SE26A0032....	Sample4_GrainB - 6			✓	Silicate	24	10	4	Spot	
33	C17SE26A0033....	GSD-1G		✓			24	10	3.5	Spot	
34	C17SE26A0034....	GSD-1G		✓			30	10	3.5	Spot	
35	C17SE26A0035....	NIST610	✓				30	10	4	Spot	
36	C17SE26A0036....	NIST610	✓				30	10	4	Spot	

Figure 3. The log book in *LADR*, imported directly from *GeoStar* with no manual editing.

name separately. To maintain flexibility the *GeoStar* software can use a template for the file name, rather than the sample name. By specifying the file name in one place it ensures there is a perfect match between the Universal Log Book file and the ICP–MS data files. Using a template for the file name is optional, and if desired the sample names themselves can also be used as the data identifier/file name. While this can only work with *Mass Hunter* software if the sample names are all unique (made easier by the "Auto Numbering" feature in *GeoStar*), the *Qtegra* software saves run table entries to a "Lab Book" data file which has no uniqueness requirement.

While running the sequence it is extremely useful to have access to the additional meta data such as the sample name. This ensures the user can correctly monitor and assess the run as it progresses, as well as elegantly handle interruptions if they occur.

Once the sequence has been ablated the data files can be exported from the ICP–MS software in their preferred format, ready for data reduction.

Data Reduction Software: Pulling it all together

The data reduction software (in this example *LADR*) loads the Universal Log Book file as well as the data files from the ICP–MS. The log book defines the role of each ablation, and in combination with the laser conditions and the quantification routine, most of the data reduction set-up can be completed automatically (Figure 3).

In practice, the quant name specified during definition of the sequence in the laser software is a *first guess* based on the observed material exposed at the sample surface. Users are reminded that laser ablation is an inherently three dimensional analytical technique and that, especially in geological specimens, the material type can change substantially over a very short distance. As such, users are encouraged to review the measured signals for all ablations. Software such as *LADR* makes it trivial for the user to assign different quantification routines to different integration periods.

The workflow outlined in this document is fully supported by *GeoStar* v10.06, *LADR* v1.1.01, Agilent *Mass Hunter*, Analytic Jena *Aspect MS*, and Thermo *Qtegra*.

www.norsci.com/geostar/
www.norsci.com/ladr/

Support will be expanded to other software packages as instrument manufacturers and developers adopt this exciting new workflow.

Application Note NSAP19A1

LADR GeoStar

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