

Optimization of internal standards in LA-ICPMS analysis of geologic samples using lithium borate fused glass

Conrey, Richard M.¹; Bailey, David G.¹; Singer, Jared W.²; Wagoner, Lauren¹; Parfitt, Benjamin³; Hay, John³; Keh, Oliver³

1- Geosciences Dept., Hamilton College, 198 College Hill Rd, Clinton, NY USA 13323

2- Corman Center for Mass Spectrometry, Earth & Environmental Sciences, Rensselaer Polytechnic Institute, 110 Eighth Street, Troy, NY USA 12180

3- Computer Science Dept., Hamilton College, 198 College Hill Rd, Clinton, NY USA 13323



1. Introduction

LA ICP-MS analysis of geologic materials typically employs an internal standard (IS) element of known concentration in the unknown sample and a single calibration material. Concentration data for other elements are calculated using the Longerich et al (1996) equation, shown here for calculation of La concentration using Ca as an internal standard (CAL = calibration material, UNK = sample).

$$La_{ppm}^{UNK} = La_{cps}^{UNK} \times \left[\frac{\left(\frac{La_{ppm}^{CAL}}{La_{cps}^{CAL}} \right) \times \left(\frac{Ca_{cps}^{CAL}}{Ca_{ppm}^{CAL}} \right)}{\left(\frac{Ca_{cps}^{UNK}}{Ca_{ppm}^{UNK}} \right)} \right]$$

The Longerich equation is more simply written using sensitivity terms, where

$$Sensitivity = S = \frac{cps}{ppm}$$

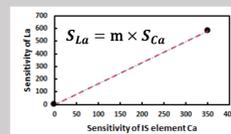
Using sensitivities, the equation is:

$$La_{ppm}^{UNK} = \left[\frac{La_{cps}^{UNK}}{S_{Ca}^{UNK}} \right] \times \left[\frac{S_{Ca}^{CAL}}{Ca_{ppm}^{CAL}} \right] \text{ or } \frac{La_{cps}^{UNK}}{La_{cps}^{UNK}} \times S_{Ca}^{UNK} = \left[\frac{S_{Ca}^{CAL}}{S_{Ca}^{UNK}} \right]$$

The first term in the latter expression is simply the inverse of the La sensitivity in the unknown, thus the Longerich equation is equivalent to the statement that the ratios of Ca to La sensitivities in the unknowns and the calibration material are equal.

The Longerich equation is, therefore, based upon the assumption that sensitivities scale linearly, which underlies the common usage of a single point internal standard calibration (e.g. with NIST 610).

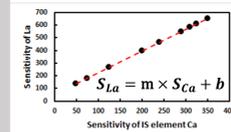
Single point sensitivity calibrations assume linearity and a zero intercept, as illustrated at right.



A multiple calibration standard strategy tests the assumption of linearity. If the intercept is found to be non-zero the basic assumption underlying the Longerich equation needs modification. Regressed linear equations such as:

$$S_{La}^{CAL} = m \times S_{Ca}^{CAL} + b$$

establish the calibration parameters, the slope and non-zero intercept of the sensitivity correlation. As a check (see section 4) on the validity of the calibration, the concentrations of the reference materials (RMs) can be calculated from the predicted sensitivity with the expression at right.



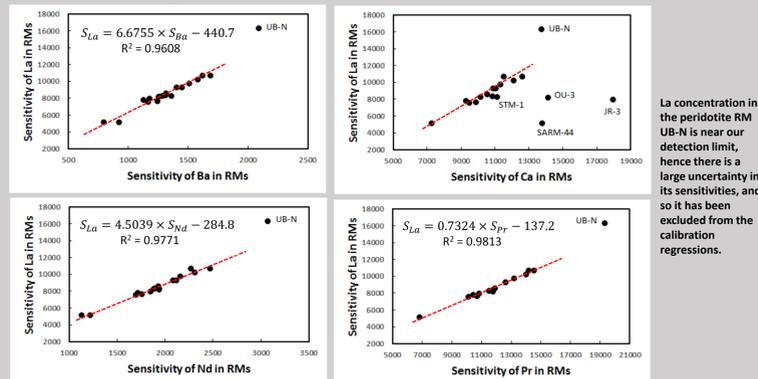
Once the calibration parameters are known, the concentrations in the unknowns can be calculated in similar manner.

$$La_{ppm}^{UNK} = m \times S_{Ca}^{UNK} + b$$

$$La_{ppm}^{UNK} = \left[\frac{La_{cps}^{UNK}}{S_{La}^{UNK}} \right]$$

2. Do sensitivities scale linearly? Not always.

We use 18 diverse, well characterized RMs to establish linear relationships between element sensitivities. We find that small non-zero intercepts are common, slight violations of the basic assumption of the Longerich equation. Examples of linear relationships with La sensitivities are shown below; as would be expected, the sensitivities of other LREEs are similar to the sensitivity of La. Ca sensitivity is a poor choice of IS for samples with low Ca concentrations.



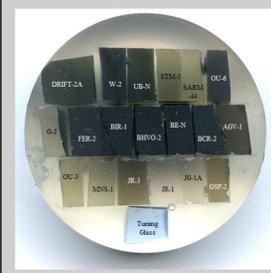
La concentration in the peridotite RM UB-N is near our detection limit, hence there is a large uncertainty in its sensitivities, and so it has been excluded from the calibration regressions.

3. The HAL LA-ICPMS recipe

- calculate background and drift corrected averaged intensities for all RMs and unknowns (see methods)
- calculate sensitivities for 18 RMs with known concentrations
- regress the RM sensitivities to determine the optimal IS elements and their regression parameters – but restrict choice of IS elements to those accurately determined by WDXRF
- for unknowns, calculate sensitivities for elements with previously determined WDXRF concentrations
- using the same (restricted) optimal set of IS elements as for the RMs, calculate the analyte sensitivities using the calibration parameters and then calculate the concentrations
- recalculate sensitivities for all analyte elements in the unknowns using the above calculated analyte concentrations
- choose optimal IS elements again now with no restriction
- recalculate concentrations in the unknowns using the new IS choices

4. How well does this recover RM values?

Multiple IS elements are employed for each analyte element, and a weighted mean sensitivity is calculated based upon the standard errors of the linear calibrations (better linear fits weighted more highly). For example, La concentrations for all 18 RMs calculated from a weighted mean sensitivity model using Ba, Sr, Ce, and Nd as IS elements closely match the given RM concentrations.

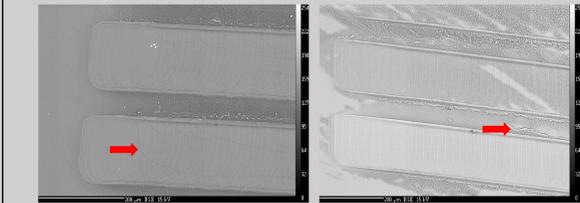


HAL calibration #3 puck with 18 RMs, drift 2A, and ICPMS tuning glass

	HAL model	Accepted	%rsd
AGV-1	38.52	38.19	0.87
BCK-2	25.29	25.08	0.83
BE-N	82.97	82.55	0.51
BHVO-2	15.30	15.20	0.64
BIR-1	0.65	0.63	3.81
FER-2	17.47	17.40	0.43
G-2	89.05	88.40	0.74
GSP-2	185.39	186.00	0.33
JG-1A	21.95	21.13	3.86
JR-1	25.64	24.95	2.76
JR-3	177.76	179.00	0.69
MNS-1	159.25	162.60	2.06
OU-3	92.42	94.64	2.35
OU-6	32.75	33.20	1.34
SARM-44	104.18	110.90	6.06
STM-1	146.61	151.10	2.97
UB-N	0.37	0.32	16.15
W-2	10.76	10.63	1.22

5. Method description

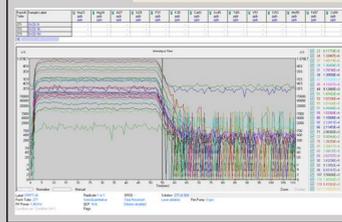
Samples and standards are ablated using a Photon Machines Analyte 193 (G1) ablation station (UV excimer laser, 193nm, with laminar flow frame cell). The laser spot size is 150µm² and 7 Hz rep rate. The stage scans ~1000µm, at 100µm/sec, taking 5 passes (50 sec total per ablation). The first pass (~10 sec) is cropped to remove surface contamination. The laser beam power is maximized to facilitate ablation of highly transparent samples. Transparent low-absorbing samples have lower yield, produce less molten ejecta, and also show a fine crack pattern (presumably thermal stress cracks in high Si glasses). High-absorbing samples (high-Fe) have a higher ablation yield, more molten ejecta, and more fine aerosol. Fluence of ~10J/cm² is excessive for some of these glass compositions but facilitates good ablation on a wide range of compositions.



Backscatter electron images of Low- and High-absorbing samples (left and right, respectively). Note stress cracks (arrow) in the low absorbing sample. For high absorbing samples note the accumulation of ejecta (arrow) on successive ablation lines.

6. Method description – continued

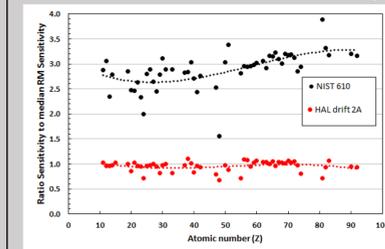
Aerosol is carried from the laser cell toward the Varian 820 ICPMS by He carrier gas, mixing with Ar make-up gas in a mixing volume (20ml) just before the torch. Argon plasma is run under “hot” plasma conditions with no collision mode. The ICPMS is run in peak-hopping, time-resolved mode for 54 major and trace analytes (in blue). Dwell times are ~10ms per mass. Detector is run in medium attenuation mode for major elements and none/auto attenuation for traces. Gas blank is also acquired between samples for background subtraction.



Typical time resolved data shown for HAL drift glass 2A (see below). 4-5 tracks are ablated during a run for each sample and RM.

7. In-house glass drift monitor

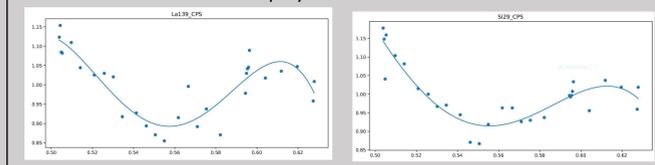
The most commonly used drift monitor, NIST 610, is a trace element doped soda-lime glass that ablates far more readily than do 2:1 Li-tet glasses. The sensitivity of NIST 610 compared with the median RM sensitivity is not constant across a wide range in atomic number. An in-house drift monitor made of 2:1 Li-tet glass has similar sensitivities at all atomic numbers to the median sensitivity of the 18 calibration RMs.



The sensitivity of NIST610 is far greater for all elements than the median sensitivity of the 18 calibration RMs. The HAL 2A drift monitor gives more uniform signal and ablates similarly to the RM and sample glasses for all atomic numbers.

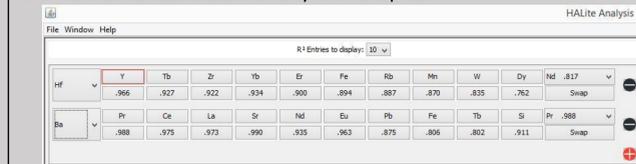
8. HALite – new code for LA-ICPMS

Older LA-ICPMS code (e.g., lolite) is based upon use of a single internal standard element. Our new code was written to calculate weighted means for multiple internal standards. The core of the code is a responsive architecture, which connects with all calculated values and updates them when any value is changed elsewhere in the code. HALite takes background corrected intensities from lolite (as .csv files) and fits high order polynomials to the drift monitor for each element. The 4th order polynomials shown are the default.

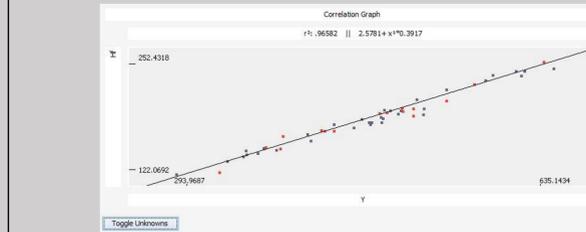


8. HALite – new code continued

The 4-5 drift corrected track intensities per sample or RM are averaged. Sensitivities for the RMs are calculated for each element using their known concentrations (chiefly from Jochum et al 2015 and GeoREM). For the unknowns, sensitivities are calculated where possible using previously determined WDXRF concentrations. The first panel in HALite displays up to the ten elements whose sensitivities best correlate (with R² shown) with the sensitivity of the chosen analyte for the RMs. A swap feature allows any element to be substituted for any of the top ten.



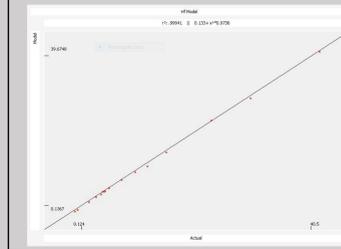
The second HALite panel graphically displays the correlation between element sensitivities (red for RMs and black for unknowns). The correlation coefficient and the equation of the regressed calibration line are displayed. Unknowns can be toggled on or off and any individual point can be selected and removed from the linear fit.



The lower HALite panel displays the weighted mean model for each RM and unknown. The example below shows a Hf model using Y, Zr, and Dy sensitivities. The standard deviation and weighted mean of the Hf sensitivities for each RM or sample are shown, as well as the calculated concentrations. For the RMs the given values are displayed, for the unknowns the XRF values (if available) are shown, or the calculated values from a first model which has been reiterated.

	Y	Zr	Dy	Std Dev	WM	Model	Actual
AGV-1	170	169	170	1	170	5.163	5.086
BCK-2	198	191	194	3	195	5.081	4.972
BE-N	223	218	211	6	220	5.878	5.720
BHVO-2	213	212	210	2	212	4.366	4.470
BR-1	202	201	179	13	200	.552	.582

The final HALite panel, a graph of model concentrations vs. given, is used to aid in internal standard selection.



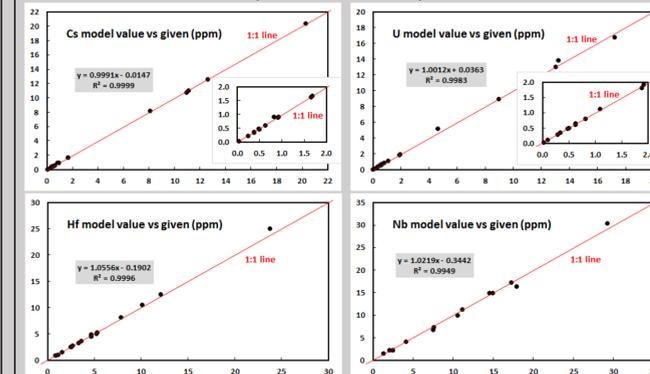
Due to the responsiveness of HALite, the effect of addition of another IS element can be gauged by whether it improves the linear fit, intercept, and/or slope of the calculated model concentrations for the 18 RMs. (Only if signal strength is very low for an analyte, and background correction skews the net intensities, the calculated OLS linear fit of the RMs - or, better, a WLS fit - can be used for additional correction to the unknowns.)

References

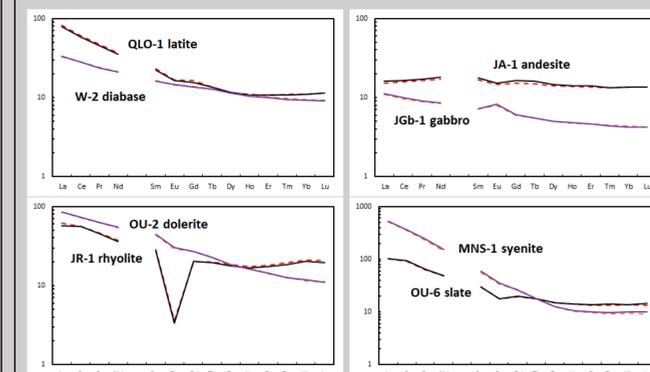
http://georem.mpch-mainz.gwdg.de/
Jochum et al 2015 Geostandards and GeoAnalytical Research, v 40, p 333-350
Longerich et al 1996 JAAS, v 11, p 899-904

9. Validation

The method was validated with 17 RMs, 11 of which are not included in the calibration RM set. Validation RM concentrations were calculated in the same manner as unknowns, that is, WDXRF data was used to calculate weighted mean sensitivities. The initial models yielded concentration data for the full set of REEs and many other trace elements not analyzed with WDXRF, or with much lower uncertainty than the latter. Hence, a second (reiteration) model was calculated using the initial model concentrations; reiteration greatly expands the choice of internal standard elements and improves the accuracy of the final data.



Concentrations of all REEs (less Pm) of eight of the RMs run as unknowns (model data solid lines) are compared with given values (dashed lines) in these CH-normalized plots below.



10. HAL LA-ICPMS approach vs. solution ICPMS

ADVANTAGES:

- Sample preparation is relatively safe and simple.
- All data (XRF and ICPMS) are obtained on a single relatively large and homogeneous sample aliquot, which minimizes nugget effects.
- Relatively low cost.
- Precision and accuracy of data are comparable for most elements.

DISADVANTAGES:

- Requires high quality WDXRF (or other method) data on all samples.
- Requires a custom in-house drift monitor and a standard disk with 15-20 RMs for calibration.
- Requires averaging of intensity data from multiple (4-5) laser tracks on all samples and standards.
- Data processing is time consuming, even with HALite software.

Improvements to HALite are a work in progress: incorporation of analytical uncertainties in intensities and WDXRF concentrations will speed the data processing and result in better data, and knowledge of the overall accuracy and precision of the method.