A Low Flow Desolvating Nebulizer System as a Tool for Calibration in LA-ICP-MS

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Introduction

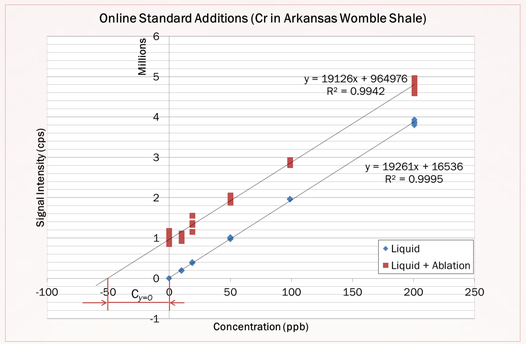
Calibration for laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a continuing challenge to analysts. Precise matrix matching is usually required to ensure ablation characteristics and subsequent plasma dynamics are consistent between calibrants and samples.

The online addition of liquid standards to ablated aerosol streams has been shown to eliminate the need for precise matrix matched standards and still provide good calibration.[1–9] In this method, a dried aerosol of liquid standards is mixed with the ablated aerosol to prior to the ICP-MS to provide a 'standard additions' type experiment:

The Aridus II™ Desolvating Nebulizer System is a specialized sample introduction accessory for ICP-MS. The Aridus II™ can enhance analyte sensitivity up to 10+ times and can greatly reduce solvent based interferences such as oxides and hydrides. By drying the aerosol through the Aridus II™, the liquid standard aerosol matches the laser aerosol and has similar performance in the plasma. An added benefit of the Aridus II™ is a nitrogen addition valve, which means N_2 can be added easily to stabilize the plasma and enhance sensitivity.

Theory

A calibration line is generated for both the standard aerosol response and the mixed standard aerosol – ablated material. Assuming that fractionation can be minimized an internal standard can be used to correct for mass flux differences.



The concentration of the analyte can then be determined according to the following:

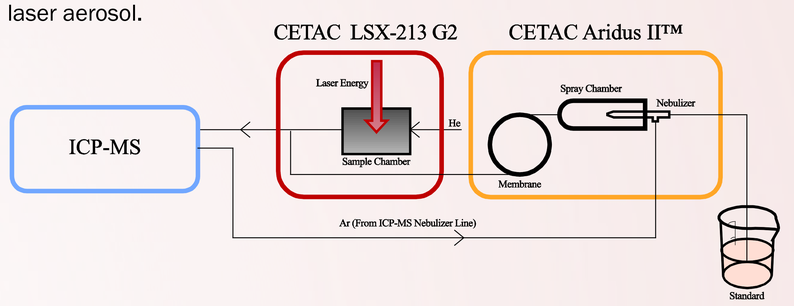
$$C_{Analyte} = -R_m \times R_{Sens} \times C_{y=0}$$

Where R_m is the mass flux ratio between the standards and the sample calculated from the internal standard response curves, R_{Sens} is the ratio of the sensitivity calculated from the ratio of the slopes and $C_{y=0}$ is the concentration calculated from the standard addition method. Since the mass flux of the nebulizer tends to be much higher than the laser itself, the concentration range of the liquid standards is much lower than that expected in the solid sample, generally in the ppb range to calibrate for solid concentrations in the ppm range.

Experimental

A sample of Arkansas Womble Shale was micronized using a Retsch MM-200 Mixer Mill (Retsch Inc., Newtown, PA, USA) and pressed into a 31 mm disc using a disc press under 10 tons of pressure for 15 minutes.

A set of multi-element standards were made up in the concentration range of 10 – 200 ppb for online additions (SCP Science, Baie D'Urfe, QC, Canada). These were aspirated using a 50 µl/min C-flow nebulizer (CETAC Technologies, Omaha, NE, USA) through the Aridus II™ desolvating nebulizer. The output of the Aridus II™ was connected to the carrier-gas inlet of a LSX-213 G2 Laser Ablation System (CETAC Technologies. Omaha, NE, USA) so that it was tee'd in to the laser aerosol.



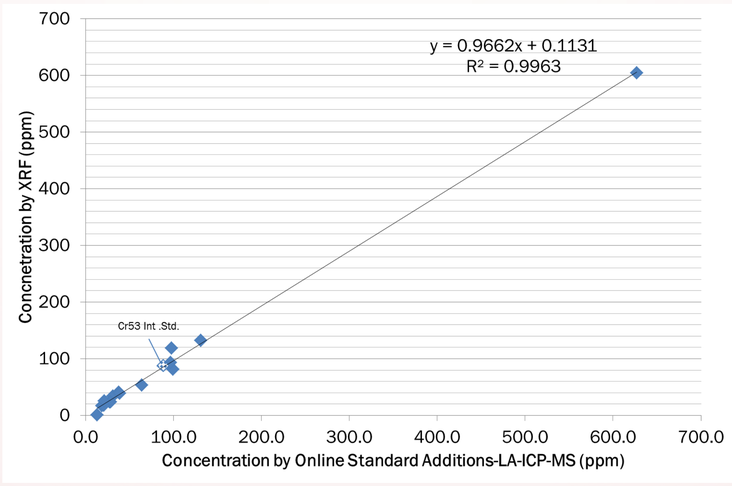
To obtain the liquid only signal, the ICP-MS was triggered and the laser shutter remained closed for 30 seconds. The shutter was then opened and a line scan (at 10 µm sec^{-1}) was ablated for a further 30 seconds.

The Arkansas Womble Shale was run six times at each liquid standard concentration to build the online calibration lines. XRF data calibrated against USGS SGR-1b Green River Shale reference material was used for internal standardization to estimate the mass flux ratio into the plasma.

Results

Using Cr-53 as an internal standard, the concentrations for a range of elements present in Arkansas Womble Shale are summarized below. Comparing the values against XRF data (shown right), those elements of a similar concentration to the internal standard element show good agreement.

Element	Concentration by XRF (ppm)	Concentration by OLA-LA-ICP-MS (ppm)	Recovery
K39	23600	22710.8	96%
Ti47	3460	3809.7	110%
V51	81	99.2	122%
*Cr53	88	88.0	-
Mn55	132	131.0	99%
Co59	17	18.4	108%
Ni60	34	30.9	91%
Cu63	24	27.4	114%
Cu65	24	28.5	119%
Zn66	93	96.4	104%
Ga69	26	106.9	411%
As75	1.2	13.1	1092%
Rb85	202	222.3	110%
Sr88	41	37.5	92%
Y89	39	38.6	99%
Zr90	119	97.9	82%
Ba137	604	627.2	104%
Ce140	53	63.9	120%
Pb208	18	20.8	115%
Th232	25	21.3	85%



Conclusions

When quantifying a solid material and a suitable solid reference is not present, online standard additions can be a viable alternative when the sample is homogeneous.

Care must be taken when optimizing ablation parameters, however, to avoid fractionation effects that will reduce the accuracy of the technique.

Acknowledgements

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