

Laser Ablation Techniques for the Analysis of Key Radionuclides in Nuclear Decommissioning: Work package 2.3.1.1

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Introduction

Laser Ablation (LA) is a solid sampling technique that operates by delivering a focused laser beam onto a solid surface, irradiating the sample and causing material to be vaporised and ejected. It allows for direct sampling with no or little sample preparation. Coupling to an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) allows for solid sampling and isotopic detection in a very short period of time. It has been used in the analysis of soils, graphite and concrete¹. The aim of this project is to develop novel LA sampling techniques for the analysis of decommissioning samples; Matrix Assisted Laser Ablation (MALA) and Laser Ablation In Fluid (LAIF).

MALA

Adding a binder which absorbs strongly at the wavelength of the incoming laser beam to the matrix of interest has been shown to increase the ablation efficiency². For a laser operating at 213 nm vanillic acid (the binder) can be used as its λ_{max} at 217 nm has a molar absorptivity of 22,900 L Mol⁻¹ cm⁻¹. The aim of the experiment is to develop a suitable sample preparation technique for sludge analysis by LA-ICP-MS.

LAIF

LAIF is the ablation of a submerged sample. The advantages are the ejected particulate is collected in aqueous or acidic solution allowing for an easier calibration strategy than compared to conventional LA in helium and an increase in safety with respect to containment of alpha and beta particles. It is also the dissolution and dilution enabling a reduction in waste solvent.

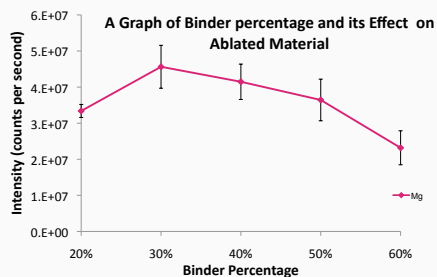
MALA Experimentation

- Sludge Simulant: 5% Lake Sediment Reference Material(LKSD-4, Canada) and 95% Mg(OH)₂ (≤100 nm particle size, Sigma Aldrich).
- Sample Disk: Vanillic acid (99% Alpha Aesar) as shown in Table 1. KBr press at 10 tons for 5 minutes.
- The disks were ablated and analysed on-line by ICP-MS, conditions given in Table 2.

Table 1 – Ratio of Simulant to Binder

Sludge Simulant (%)	Vanillic acid (%)
80	20
70	30
60	40
50	50
40	60

MALA Results and Discussion



The highest ablation yield occurred at 30 % binder ratio. The confidence limits shown indicate a large error in the sampling, this is partly due to the laser beam being rastered across the surface of the disk (showing a true heterogeneous matrix). This was evident as the particles of the LKSD-4 were visible as dark spots.

Instrumentation

Table 2- Laser and ICP-MS conditions

MALA	Experiment	LAIF
UP213 Laser (NewWave)		
213	Wavelength (nm)	213
20	Frequency (Hz)	10
55	Spot size (µm)	110
8	Fluence (J/cm ²)	5 and 10
4	Pulse duration (ns)	4
0.78	He Gas (L min ⁻¹)	-
Element 2 XR ICP-MS (Thermo)		
1300	RF power (W)	1250
14.26	Cool Gas (L min ⁻¹)	15.85
0.80	Aux Gas (L min ⁻¹)	0.80
0.856	Sample Gas (L min ⁻¹)	1.062

MALA Future work

- Develop the homogenisation step.
- Develop vanillic acid pot and investigate addition of binder to sample

LAIF Experimentation

- Custom cell shown in Figure 1: Incorporation of a split ring into the lid to hold the optical window
- NIST 611 glass ablated in degassed deionised water (18MΩ). Solution sonicated, collected and 2% nitric acid added.
- Solution analysed by ICP-MS, conditions given in Table 2.

References

1. J. S. Becker, C. Pickhardt & H. -J. Dietze International Journal of Mass Spectrometry, 2000, **202**, 283-297
2. C. O'Connor, M. R. Landon & B. L. Sharp, J. Anal. At. Spectrom., 2007, **22**, 227-234

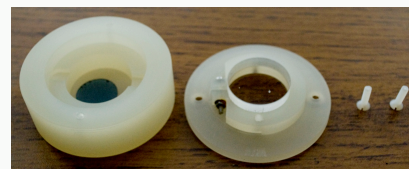
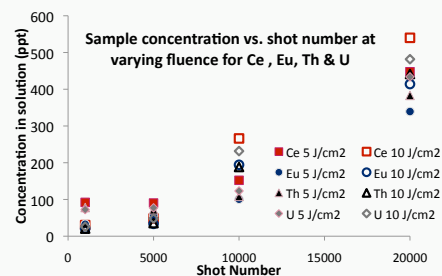


Figure 1 – Custom Cell for LAIF

LAIF Results and Discussion



An increase in shot number gave an increase in total ablation yield. The relationship, however, was not linear. During the ablation process cavitation occurs at the sample surface, the bubbles released from this can then pass through the path of the next incoming laser beam. This causes refraction and reflection, reducing the fluence delivered to the surface. Degassing the water reduced this effect. Self-focusing of the beam in water gives roughly one third the intended size in helium.

LAIF Future work

- Investigate schemes to reduce bubble release.
- Investigate different focal points on the sample.
- Investigate the size of particles released.

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