

## **Laser ablation of samples in liquid droplet (LASIL) – a sampling technique for the nuclear sector**

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### **ABSTRACT**

This paper describes the development of Laser Ablation of Samples In Liquid (LASIL) and its application for the nuclear sector. The analytical characteristics of LASIL are the ease of quantification, containment of radioactive particles emitted from radionuclides, the ease of generating suspended solids in solution from insoluble materials and the its control over dissolution and dilution to generate measurable samples. NIST 611 (trace elements in glass) was used as a surrogate for wastes encapsulated in borosilicate glass.

Establishment of laser ablation (LA) in a liquid droplet of 25 µl volume allowed the quantification of the trace elements in NIST 611 and investigation of the particle size generated from the ablation mechanism. Particle sizes were found to vary with laser energy. Higher energies produced larger particle size distribution with greater variation in shape; jagged particles of 1-2 µm from microjet impingement, spherical particles from vapour condensation and melt ejection, thin string-like particles from particle agglomeration. At lower energies the particle shape became spherical and formed agglomerates. At this small particle size (below 250 nm) by the action of Brownian motion a very slow settling rate occurred. Particles remained suspended in solution long enough to be introduced by traditional solution nebulisation into a spray chamber from which the aerosol was analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). By calibration against aqueous standards the concentration of elements in the solution and thus the particulate was determined. Internal standardisation for elements was then performed by calculating the concentration ratio of uranium in the solution to that in the original solid.

### **INTRODUCTION**

Laser Ablation (LA) is an established technique for the sampling, scribing or cutting of solid materials. When coupled to elemental detection, such as inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-optical emission spectroscopy (ICP-OES), it becomes a versatile analytical tool for the direct analysis of solids with the ability to map and depth profile elements with micrometer resolution. The principal difficulty is calibration because it is not possible to prepare matrix matched standards for all the potential sample types. For bulk analysis, a further problem arises from the difficulty of obtaining data that represents the whole sample. The sample must be ablated in a raster mode, or at multiple sampling points, to overcome sample heterogeneity.

This paper describes Laser Ablation of a Sample In Liquid (LASIL), a technique where the ablation mechanism occurs at a solid sample surface submerged in a liquid. A laser beam is delivered to the sample surface through a liquid medium

transparent to the laser wavelength. The energy couples with the sample and an ablation plume/plasma is formed; expanding into the liquid<sup>1</sup>. In front of the expanding ablation plume, energy is released as a shock wave which in gaseous media dissipates energy into the surrounding environment<sup>2</sup>. In LASIL, vaporisation of the liquid surrounding the ablation plume leads to the formation of a micro-cavity that surrounds the ablation site. This has the advantage of reflecting energy back onto the ablation site, which generates a more efficient ablation coupling as energy transfer to the surrounding environment is reduced. Containment in the micro-cavity results in a smaller ablation plume and an increase in the pressure and temperature of the plasma<sup>2-3</sup> which is normally a magnitude higher than that experienced in a gaseous atmosphere<sup>4</sup>. The expansion of the micro-cavity occurs faster than that of the ablation plume and as a result the diameter of the micro-cavity can become much larger than the plume diameter<sup>3,5</sup>.

**Table 1** Instrumental parameters used in the investigation

<b>Laser Ablation System</b>	
Type	Solid State Nd:YAG, UP-213
Wavelength	213 nm
Pulse duration	4 ns
Repetition rate	20 Hz
Sampling strategy	Line scan
Laser energy; Spot diameter	100 µm aperture imaged, actual image at sample surface:
	Calibration samples, laser energy 0.084 mJ; 34.3 µm spot diameter
	Particle size studies, laser energy 0.255 mJ and 0.092 mJ; 32.9 µm spot diameter
Solid sample	NIST SRM 611 Trace Elements in Glass
Translation rate	2 µms <sup>-1</sup>
Sampling medium	Deionised water (18 MΩ) 25 µl
<b>ICP-MS</b>	
Type	Thermo Scientific, Element 2 XR Magnetic sector field ICP-MS
Cool gas flow	15.5 L min <sup>-1</sup>
Auxiliary gas flow	0.80 L min <sup>-1</sup>
Sample gas flow	0.904 L min <sup>-1</sup>
Sampling time	Low resolution 0.01 for <sup>28</sup> Si and 0.02 for all other elements Medium resolution 0.025 for all elements
Plasma RF power	1250 W
Isotopes monitored	Low resolution <sup>28</sup> Si, <sup>139</sup> La, <sup>140</sup> Ce, <sup>153</sup> Eu, <sup>232</sup> Th, <sup>238</sup> U Medium resolution <sup>44</sup> Ca, <sup>59</sup> Co, <sup>88</sup> Sr, <sup>133</sup> Cs,
Acquisition mode	Peak hopping
Detector mode	Triple (secondary electron multiplier, counting and Faraday cup)
Sample introduction	Self aspirating PFA-ST nebuliser with a 0.25mm I.D. exchangeable capillary delivering a 100 µl min <sup>-1</sup> uptake (Elemental Scientific Inc., Omaha, USA). Twinnabar cyclonic spray chamber, volume 20 ml (Glass Expansion, Melbourne, Australia).

It has been reported <sup>3</sup> that after the initial expansion of this micro-cavity the plasma cools and the result is a vapour bubble <sup>1</sup>. If the cavitation bubble forms close to a solid surface it does not form a spherical shape but elongates perpendicular to the solid surface, the radius of this

bubble increases with increasing laser energy <sup>6</sup>. The bubble can continue expanding until a maximum is reached after which it begins to distort, shrink and finally collapse due to the decay in interior pressure from plasma cooling; at this point micro-jets form <sup>1</sup>.

The time taken for the collapse is increased due to the elongation relative to the solid surface <sup>6</sup>. Very little work has been performed on particle formation of the ablated material but it has been postulated that particle formation occurs during the cooling period of the ablation plasma through condensation of the vapour <sup>7</sup>.

The formation of micro-jets adds a mechanical mechanism for removal of material <sup>1, 3, 6</sup>, inhibits particle agglomeration and also clears the ablation site for the next incoming laser beam <sup>8</sup>. Mechanical stress can lead to fracture or hydrodynamic removal of particles from a melt zone <sup>4, 9</sup>. Thermal convection and bubble induced liquid motion also aid in the removal of particulate from the ablation site <sup>3</sup> when nano-second pulse lengths and repetition rates below 1kHz are used. After collapse of the micro-cavity smaller bubbles become evident. These are created by diffusion of dissolved gases in the liquid into the expanding micro-cavity <sup>5</sup>. The rising bubbles can hinder ablation due to laser refraction or reflection and cause the laser beam to deviate from the intended ablation track.

The overall process of energy coupling, plume formation, shock wave formation, micro-cavity (vapour bubble) generation and micro-jet formation are relatively fast such that the next laser beam-sample coupling is not inhibited, e.g. by plasma shielding <sup>10</sup>. After cavity collapse the particulate is ejected into the solution. If this particulate is below 250 nm in diameter it forms a solid suspension due to Brownian motion with a very slow settling rate due to a Stoke's law terminal settling velocity of  $3.06 \times 10^{-8} \text{ ms}^{-1}$  (in pure water) <sup>11</sup>.

Provided that the particulate is <150 nm <sup>12</sup> (ensuring complete atomisation and ionisation) the resulting solution can be collected and analysed by ICP-MS against aqueous standards to determine the concentration of the element in solution. Using an internal standard, or by measuring the volume of the ablated material, a concentration for the original solid can be determined. Alternatively, post ablation chemical processing, e.g. addition of acid, can be used to dissolve the nano-scale particulate.

## EXPERIMENTAL

### Instrumentation

A commercially available UP-213 laser ablation system (ESI, New Wave Research Division, Huntingdon, Cambridgeshire, UK) operating in the

deep UV (213 nm) was used to ablate the sample. An Element 2 XR SF-ICP-MS (Thermo Scientific, Bremen, Germany) was used to analyse the samples. Operating conditions are given in Table 1 where the laser parameters given are for quantification in a droplet or particle size experimentation.

#### Calculating the fluence at the sample surface

Due to the increase in refractive index when using a liquid medium, compared to a gaseous one, the ablated spot diameter was smaller than the nominal value as the objective had to be moved further from the target to bring the sample into focus. The fluence was calculated from the laser energy reading from the laser system and by measuring the diameter of the ablated track. This is reported as a notional fluence as energy will have been lost through absorption by species in the water and through scattering when interacting or passing through different surfaces.

#### Reagents

All reagents were supplied by Sigma-Aldrich unless otherwise stated. Deionised water was prepared by use of a commercial Millipore water purification system (Millipore, Watford, UK).

#### Preparation of sample

NIST 611 (National Institute of Standards and Technology, Maryland, U.S.A.) was chosen due to its high concentrations of analytes (nominal 500 mg/kg) and its common use as a calibration standard for laser ablation. For the droplet experiment the sample was sonicated in 2% performed v/v nitric acid (Suprapure, Romil) prior to ablation as it had been observed that the NIST glass had an associated surface contamination probably induced by re-grinding. This was performed with silicon carbide grit paper P1200 (particle size roughly 15  $\mu\text{m}$ ) followed by P2500 (particle size roughly 6  $\mu\text{m}$ ) followed by diamond paste (particle size roughly 6  $\mu\text{m}$ ). The sample was prepared by washing with acetone followed by D.I. water for the large cell experiment.

#### Quantification in a liquid droplet

The custom cell was used as a sample platform for the NIST glass and a 25  $\mu\text{l}$  droplet of deionised water was placed onto the sample surface by means of a pipette. LASIL was performed at a laser power of 0.084 mJ and a spot size of 34.3  $\mu\text{m}$ ; notional fluence of 9.1  $\text{J}/\text{cm}^2$  for 6, 1mm length tracks. Non-degassed D.I. water was used as ablating off centre to the droplet ensured minimised bubble-laser interaction as bubbles collected at the top of the droplet. The solution was collected by means of a pipette and transferred to a 15 ml centrifuge tube where it was diluted to 500  $\mu\text{l}$ . Post ablation chemistry samples were also prepared in the same manner, but using nitric acid (Ultrapure, Romil) as the diluent to give a final acid concentration 2% v/v. Six replicates and four

method blanks for each solution condition were prepared.

#### Preparation of calibration standards

Calibration standards were prepared by serial dilution of multi-element solution standards (Claritas PPT for ICP-AES and ICP-MS, Spex Certiprep, Middlesex, UK). Standards were diluted with 2% v/v nitric acid (Ultrapure, Romil, Cambridge, UK).

The limit of detection was calculated using the calibration curve, given in Equation 1.

$$y_{\min} = b + 3s_E \quad (1)$$

Where  $y_{\min}$  is the lowest detectable signal,  $b$  is the intercept (corresponding to the blank signal) and  $S_E$  is the standard error of the slope of the calibration curve.

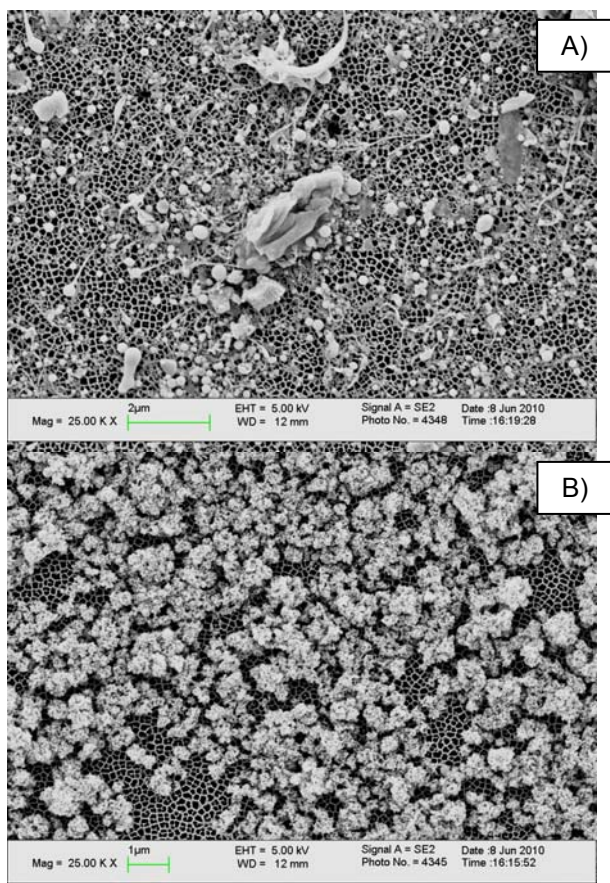
#### Preparation of samples for particle collection

Samples were prepared as above, for LASIL in a liquid droplet. The cell was then placed in an AtmosBag, two handed, size M, closure type, zipper-lock (Sigma-Aldrich) to avoid adventitious contamination from atmospheric particles. The bag was purged of air with nitrogen. The solution was collected by means of pipette and filtered through an Anodisc filter membrane (200 nm pore size, Whatman). This procedure was performed using a spot size of 32.8  $\mu\text{m}$  for 0.255 mJ; notional fluence of 30.1  $\text{J}/\text{cm}^2$  and 0.092 mJ; notional fluence of 10.9  $\text{J}/\text{cm}^2$ . The lower energy was chosen for subsequent work due to the homogenous particle size and shape produced. No post ablation chemistry samples were prepared.

## RESULTS AND DISCUSSION

#### Particle size

The images from the SEM analysis are shown in Figure 1. At the higher fluence of 30.1  $\text{J}/\text{cm}^2$  the particle size distribution was wide with significant variability in particle shapes. Three distinct particle shapes were evident: spherical particles in the nanometer range from condensates and those in the micrometer range from ejection of melt; long thin string-like structures associated with nano-material agglomeration<sup>13</sup>; and large jagged particles associated with the mechanical removal of material by micro-jet impact on the sample surface with sizes in the 1-2  $\mu\text{m}$  in size. Because these samples are subsequently nebulised for introduction into the ICP additional particle size selectivity is introduced at that stage.



**Figure 1** SEM analysis at 25,000 magnification of particles collected on an Anodisc filter membrane from 25  $\mu$ L droplet LASIL solutions at the fluence of A) 30.1 J/cm<sup>2</sup> and B) 10.9 J/cm<sup>2</sup>

At the lower fluence of 10.9 J/cm<sup>2</sup> the particle size was much smaller and more homogenous. Particles were less than 200 nm in size but formed larger agglomerates, possibly through the ablation process or drying during filtration.

### Analysis of NIST 611 by LASIL

From the standard solutions, calibration graphs were generated and from these the concentrations of analytes in solution calculated. The ratio of uranium concentration in solution to uranium concentration in the solid was calculated and applied as an internal standard to calculate the concentration of analytes in the original solid (assuming the ablation process did not give rise to fractionation).

The errors given for the certified concentrations are standard deviations ( $1\sigma$ ) for the measurements except for strontium, thorium and uranium where they represent 95% confidence intervals. The uncertainties for the LASIL calculated values are 95% confidence intervals based on t-statistics and the standard error of the mean.

### Quantification using the droplet

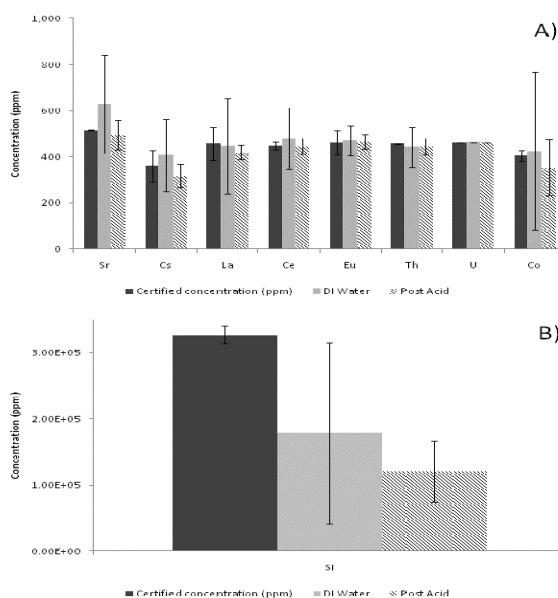
The problems encountered using the cell led to the concept of a non-cell solution hence ablation in isolated droplets.

The graphs of calculated concentrations versus certified concentrations for the trace elements and main constituents in NIST 611 for D.I. water (with no additives) and post-acidified solutions are shown in Figure 2. The calculated values for six replicates are in excellent agreement with the certified values for all elements at both fluences. The calculated values were closer to the certified values, compared to the large cell quantification, as the loss of material was reduced yielding a solution that better represented the sample. Calcium was not monitored due to high blanks in the water used.

Post-acidification of samples again yielded smaller errors associated with the mean values due to reduced signal variability.

The uranium-thorium ratio for the six replicates was 1.04 for both the D.I. water and post-acidified solutions, in good agreement with the certified value.

The main constituent, silicon, was within the 95% confidence interval of the certified value, but with large variance. This could be attributed to silicon being favoured in the larger particles. In the post-acidified sample the concentration of silicon was lower than the certified value but the 95% confidence interval was much smaller. This is again due to the insolubility of silicon in acidic environments. The error is much smaller than that of D.I. water as the silicon that remained in solution or was better transported to the ICP was probably more uniform in particle size.



**Figure 2** Graphs showing the calculated concentration versus the certified concentration for LASIL in D.I. water and in D.I. water with post-acidification to give a final concentration of 2% nitric acid for, A) trace elements in NIST 611 and B) main constituents in NIST 611. Calibration was performed for a 25  $\mu$ L droplet of six replicates.

## CONCLUSION

NIST 611 has been ablated using the LASIL technique to form a suspended solid solution, which was then analysed by calibration against aqueous standards. Calculating the ratio of uranium concentration in the solution to that certified in the solid was used as an internal standard to calculate the concentration of the other elements in the original sample. The calculated concentrations were in good agreement with the certified values.

It has been shown that LASIL can be performed in a 25  $\mu\text{l}$  (or other size) droplet, giving accurate and precise quantification. Using droplet LASIL, no additives to the liquid medium were required and existing LA systems can be used with minimal or no modification. The technique is robust and easy to implement.

Where a larger sample is to be analysed and spatial averaging is required, a cell design might be preferred and, following the experience with droplet LASIL, it appears that a simple open pot without window immersion would be the preferred option.

The laser-bubble interaction can be circumnavigated in the droplet experiment by ablating off-centre to the droplet such that generated bubbles do not travel into the laser beam path.

LASIL has potential advantages over conventional LA when the containment of radioactive or highly toxic materials (such as those found in the nuclear sector) is favored and the generation of an aerosol would cause concern for safety. For example, the liquid would inhibit the emission of  $\alpha$  and  $\beta$  decay particles.

LASIL is an off-line sampling technique with a separate sample introduction step. As such samples can be analysed by many techniques that utilise liquid introduction or analysed by thermal ionisation mass spectrometry (TIMS) for accurate isotope ratio measurements.

Conventional acid digestion of materials often requires a large volume of solution (compared to LASIL) followed by multiple dilution steps to achieve a measurable concentration. In LASIL, dilution is controlled by the number of shots which can lead to a reduction in waste volumes, a significant factor in nuclear applications.

Finally, LASIL offers a potential solution to the problem of analysing materials that are insoluble or only soluble in solvents that are incompatible with the ICP. As previously described, the generation of particulate <250 nm in diameter creates a suspended solid which can be fully atomised and

ionised by the ICP allowing direct calibration with aqueous standards.

Following discussions with a NERC isotope geoscientist it has also been suggested that this technique could be used for the analysis of dust particles and the determination of the uranium isotope ratios for nuclear forensics.

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