Development of a high speed, high efficiency LA-ICP-MS interface

This item was submitted to Loughborough University’s Institutional Repository by the/an author.

Additional Information:

- A Doctoral Thesis. Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University.

Metadata Record: [https://dspace.lboro.ac.uk/2134/12164](https://dspace.lboro.ac.uk/2134/12164)

Publisher: © David Neil Douglas

Please cite the published version.
This item was submitted to Loughborough University as a PhD thesis by the author and is made available in the Institutional Repository (https://dspace.lboro.ac.uk/) under the following Creative Commons Licence conditions.

CC BY-NC-ND 2.5

You are free:

- to copy, distribute, display, and perform the work

Under the following conditions:

**Attribution.** You must attribute the work in the manner specified by the author or licensor.

**Noncommercial.** You may not use this work for commercial purposes.

**No Derivative Works.** You may not alter, transform, or build upon this work.

- For any reuse or distribution, you must make clear to others the licence terms of this work.
- Any of these conditions can be waived if you get permission from the copyright holder.

Your fair use and other rights are in no way affected by the above.

This is a human-readable summary of the [Legal Code (the full license)](http://creativecommons.org/licenses/by-nc-nd/2.5/).

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/
Development of a High-Speed, High-Efficiency, LA-ICP-MS Interface

By

David Neil Douglas

Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

December 2012

Research supervisors Professor Barry L. Sharp and Doctor Helen J. Reid

© David Neil Douglas 2012
“The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' but 'Hmm...That's funny...” – Isaac Asimov
Abstract

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) is now a well established analytical technique used to sample solid materials and determine their elemental composition. Two areas that are becoming increasingly important, and for which LA-ICP-MS is a key tool, are bio-imaging and the analysis of micro-particulates. However, current instrumental designs limit the practicality of the technique for these applications.

This study investigates the development of a high speed, high efficiency LA-ICP-MS interface through modelling of the flow dynamics of a newly designed laser ablation cell and experimental investigation of single laser pulse response. Through this work the Sniffer-Dual Concentric Injector interface was realised. This interface reduced particle residence times within the laser cell and transport tubing. The interface was also used to investigate turbulence related aerosol dispersion within the ICP and potential designs to overcome this. The resulting design yields an interface with improved sensitivity and reduced aerosol dispersion such that a lower limit of detection is achieved, important when considering the mass of analyte in a single cell or micro-particulate, compared to existing designs. Thus the interface can be used to improve image spatial resolution as the ablation spot size, and thus pixel information, can be reduced; and also reduces total analysis time.

The calibration technique Laser Ablation of a Sample In Liquid (LASIL) was also investigated as a means of calibration for solid samples. The investigation lead to the development of LASIL in a droplet, a technique that can be used to calibrate solid samples when a matrix matched standard is unavailable. The mechanism of the technique resulted in an improved laser-energy sample coupling efficiency and a reduction in the liquid to ablated mass ratio, thus decreasing sampling time. As the technique captures the ablated particulate in solution, post chemistry techniques can be used to remove analyte interferences.
Acknowledgements

I thank my supervisors Professor Barry L. Sharp and Doctor Helen J. Reid for their constant support, guidance and patience. You have fuelled my passion for science and inspired me to be all I can be.

I would like to thank the DIAMOND consortium for sponsoring the PhD.

The person I thank most is my beautiful and dear partner, Gemma Louise Webber. Without you this journey would have been unbearable. I thank you for putting up with all my moaning and for lifting me out of those low moments.

I would like to thank my mother Angela Douglas, father Robert Douglas, brother Mark Douglas and stepfather Shane Thomas for your constant praise and enthusiasm. I thank my grandfather David William James Matthews for being my inspiration.

A huge thank you to all the support staff at Loughborough University for their support and for making life that little bit easier. A special thanks to Dave Wilson, Trevor Brown, Stuart Pinkney, Andy Kowalski and Mark Weller.

I would like to extend my thanks and gratitude to Doctor James Reynolds who was always busy, but never said no to helping.

A very special thanks to the Analytical research group, for moments that will always be cherished and never forgotten: Pareen Patel and Aref Zayed friendships that will never fade; Dhinesh Asogan and Claire Camp for their support and in helping me to grow; and thanks to Sarah Taylor, Grant Craig, Amy Managh, Tharwat Abduljabbar, Meng Wang and Tamer Shoeib.

My thanks to Gordon Watson-Broughton and Tim Rutherford, my secondary school chemistry teachers, who set me upon the path I now follow. I thank Dr Michael Foulkes and Dr Andy Fisher. Without you this journey would never have begun.

I also thank the shepherd Kaldi for discovering coffee, without which this PhD would never have succeeded.
CONTENTS

ABSTRACT .............................................................................................................................. 1-3

ACKNOWLEDGEMENTS ..................................................................................................... 1-4

CONTENTS TABLE ............................................................................................................... 1-2

LIST OF ABBREVIATIONS ................................................................................................. 1-6

LIST OF TABLES ................................................................................................................... 1-7

LIST OF FIGURES .............................................................................................................. 1-10

CHAPTER 1 INTRODUCTION – CURRENT LASER ABLATION AND ICP-MS TECHNOLOGY ..................................................................................................................... 1-15

1.1 INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (ICP-MS) ................... 1-16

1.1.1 Figures of Merit ...................................................................................................... 1-17

1.1.1.1 Limit of Detection for Fast Data Acquisition ......................................................... 1-17

1.1.2 The ICP – Formation and Ion Generation ............................................................ 1-18

1.1.2.1 Torch Design ............................................................................................................ 1-20

1.1.2.2 Sample Introduction ................................................................................................ 1-21

1.1.3 Mass Spectrometers ............................................................................................... 1-23

1.1.3.1 Vacuum interface .................................................................................................... 1-23

1.1.3.2 Quadrupole Mass Spectrometers........................................................................... 1-24

1.1.3.3 Time of Flight Mass Spectrometer ........................................................................ 1-24

1.1.3.4 Double-Focusing Sector Field Mass Spectrometer ............................................. 1-25

1.1.3.4.1 Element XR Scanning Modes .......................................................................... 1-27

1.1.3.5 Ion Detection ........................................................................................................... 1-27

1.1.3.6 Data Acquisition ...................................................................................................... 1-28

1.2 LASER ABLATION ..................................................................................................... 1-30

1.2.1 Laser Generation ................................................................................................... 1-30

1.2.2 Laser Ablation process ........................................................................................... 1-33

1.2.2.1 Elemental Fractionation ....................................................................................... 1-35

1.2.2.2 Calibration .............................................................................................................. 1-36

1.2.2.2.1 Matrix Matching ............................................................................................... 1-36

1.2.2.2.2 Dual Sample-Standard Calibration ................................................................... 1-37

1.2.2.2.3 Laser Ablation of a Sample In Liquid (LASIL) .................................................. 1-37

1.2.3 Laser Ablation Cell Design .................................................................................... 1-39

1.2.3.1 Single Cell Designs ............................................................................................... 1-39

1.2.3.1.1 The Zircon Cell ............................................................................................... 1-39

1.2.3.1.2 The Rotary Cylindrical Cell .......................................................................... 1-39
The Ablation Cell with less than 100 ms Washout Time .......................... 1-39
The Cyclonic Flux Cell........................................................................... 1-40
Cell Within Cell Designs....................................................................... 1-40
The HelEx/Laurin Cell .......................................................................... 1-40
The Volume-Optional and Low-Memory (VOLM) Cell.......................... 1-41
The Laminar Flow Reactor (LFR) Cell .................................................. 1-41
In-Torch Ablation.................................................................................. 1-41
Limitations of cell designs.................................................................... 1-42
AIMS ........................................................................................................ 1-43
OBJECTIVES .......................................................................................... 1-43
CHAPTER 2 FLOW SIMULATION OF A HIGH-SPEED, HIGH-EFFICIENCY, LA-ICP-MS INTERFACE ................................................................. 2-45
INTRODUCTION ..................................................................................... 2-45
Software................................................................................................... 2-46
DUAL CONCENTRIC INJECTOR (DCI) ...................................................... 2-47
Design Brief ............................................................................................ 2-47
The DCI Design ...................................................................................... 2-48
THE SNIFFER CELL ............................................................................... 2-53
Design Brief ............................................................................................ 2-53
Cell Design ............................................................................................. 2-53
The Inner ‘Sniffer’ Cell .......................................................................... 2-54
The Outer Cell ......................................................................................... 2-54
Total Transport Volume ......................................................................... 2-58
Modelled Gas Flow for the Modified UP213 Cell Lid ............................. 2-59
The Model ................................................................................................ 2-60
200 µm Gap Distance Between Sniffer and Sample Surface .................. 2-63
200µm Sniffer-Sample Gap - Gas Flow Trajectories and Velocity ...... 2-65
200µm Sniffer-Sample Gap – Particle Trajectories and Residence Times 2-70
50 µm Gap Distance Between Sniffer and Sample Surface .................. 2-78
50 µm Sniffer-Sample gap – Particle Trajectories and Residence Time 2-79
The Enterprise Cell ................................................................................ 2-84
CONCLUSIONS ..................................................................................... 2-85
FURTHER WORK ................................................................................... 2-87
CHAPTER 3 EXPERIMENTAL EVALUATION OF A HIGH-SPEED, HIGH-EFFICIENCY, LA-ICP-MS INTERFACE ................................................................. 3-90
INTRODUCTION ..................................................................................... 3-90
Data Processing....................................................................................... 3-90
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES</td>
<td>Atomic Emission Spectrometry</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer Aided Design</td>
</tr>
<tr>
<td>DCI</td>
<td>Dual Concentric Injector</td>
</tr>
<tr>
<td>DCP</td>
<td>Direct Current Plasma</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionised</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma-Mass Spectrometry</td>
</tr>
<tr>
<td>ID</td>
<td>Internal Diameter</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>LA</td>
<td>Laser Ablation</td>
</tr>
<tr>
<td>LA-ICP-MS</td>
<td>Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry</td>
</tr>
<tr>
<td>LASIL</td>
<td>Laser Ablation of a Sample In Liquid</td>
</tr>
<tr>
<td>LFR</td>
<td>Laminar Flow Reactor</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit Of Detection</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>NPT</td>
<td>National Pipe Thread</td>
</tr>
<tr>
<td>OD</td>
<td>Outer Diameter</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>QMS</td>
<td>Quadrupole Mass Spectrometer</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SEM</td>
<td>Secondary Electron Multiplier</td>
</tr>
<tr>
<td>SFMS</td>
<td>Sector Field Mass Spectrometer</td>
</tr>
<tr>
<td>SHIP</td>
<td>Static High Sensitivity ICP Torch</td>
</tr>
<tr>
<td>SRM</td>
<td>Standard Reference Material</td>
</tr>
<tr>
<td>TOFMS</td>
<td>Time Of Flight Mass Spectrometer</td>
</tr>
<tr>
<td>TRA</td>
<td>Time Resolved Analysis</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-Violet</td>
</tr>
<tr>
<td>VOLM</td>
<td>Volume Optional and Low Memory cell</td>
</tr>
</tbody>
</table>
List of Tables

TABLE 1 – PC HARDWARE CONFIGURATION ................................................................. 2-59
TABLE 2 – Flow simulation mesh refining criteria, physical features and thermodynamic conditions ......................................................................................... 2-62
TABLE 3 – Final mesh computation for 200 µm Sniffer gap distance ............... 2-63
TABLE 4 – Particle residence time and average velocity from particle injection within the viewing area for 200 µm gap ................................................................. 2-72
TABLE 5 – Particle residence time and average velocity from particle injection outside the Sniffer for 200 µm gap ................................................................. 2-76
TABLE 6 – Final mesh computation for 50 µm Sniffer gap distance ................. 2-78
TABLE 7 – Particle residence time and average velocity from particle injection within the viewing area for 50 µm gap ................................................................. 2-81
TABLE 8 – Particle residence time and average velocity from particle injection outside the Sniffer for 50 µm gap ................................................................. 2-82
TABLE 9 – Instrument operating parameters for initial Sniffer-DCI test using multiple tubes to transport particulate ................................................................. 3-96
TABLE 10 – Typical peak characteristics from the Sniffer-DCI interface (alpha outer cell) at varied sample gas flow rates .......................................................... 3-97
TABLE 11 – The percentage relative standard deviation associated with the average peak area and maximum for the Sniffer-DCI interface at 0.130 Lmin⁻¹ at varied DCI extensions ................................................................. 3-102
TABLE 12 – Peak characteristics for the Sniffer-DCI interface (alpha cell) for a 0.130 Lmin⁻¹ flow rate at varied DCI extensions ................................................ 3-102
TABLE 13 – Laser and ICP-MS operating parameters to investigate the use of a single transport tube ................................................................. 3-106
TABLE 14 – Peak characteristics for the Sniffer-DCI interface at a 2 mm extension and sample flow rate of 0.120 Lmin⁻¹ using a single continuous transport tube. Signal has been attenuated using medium resolution .................................. 3-107
TABLE 15 – Laser and ICP-MS operating parameters to investigate data acquisition method development ................................................................. 3-111
TABLE 16 – Peak characteristics obtained from the raw channels per mass peak transient signal method from the average profile at -10 and 2 mm DCI extension, 0.120 Lmin⁻¹, 100 µs time resolution ................................................................. 3-112
TABLE 17 – Peak characteristics obtained from the raw channels per mass peak transient signal method from the average profile at 2 mm DCI extension, 0.120 Lmin⁻¹, 200 and 500 µs time resolution ................................................................. 3-117
Table 18 – Peak characteristics obtained from the averaged channels per peak transient signal method from the average profile at 2 mm DCI extension, 0.120 Lmin⁻¹ ................................................................. 3-119

Table 19 – Laser and ICP-MS operating parameters used to investigate the peak profiles from the Enterprise cell ........................................................................................................ 3-122

Table 20 – The percentage relative standard deviation associated with the average peak area and peak maximum for the using the Enterprise cell at 0.050 and 0.100 Lmin⁻¹ at varied DCI extensions ........................................................................ 3-128

Table 21 – Peak profile characteristics for varied DCI extensions using the
Enterprise outer cell at a flow rate of 0.050 Lmin⁻¹ ........................................................... 3-128

Table 22 – Peak profile characteristics for varied DCI extensions using the
Enterprise outer cell at a flow rate of 0.100 Lmin⁻¹ ........................................................... 3-129

Table 23 – Laser ablation parameters and sampling regime for comparison of the DCI with the standard injector .......................................................................................... 3-133

Table 24 – Change in back pressure from the Zircon Cell when altering the sample gas flow rate using the two injector types ................................................................. 3-134

Table 25 – The average signal noise for the DCI and the standard injector at 0.025 Lmin⁻¹ helium flow rate ........................................................................................................... 3-136

Table 26 – The average signal to noise for the standard injector at various flow rates ................................................................................................................................. 3-138

Table 27 – Details of laser parameters ................................................................................. 4-149

Table 28 - Details of ICP-MS operating parameters and sample introduction system ................................................................................................................................. 4-160

Table 29 - R-squared values for calibration graphs used to quantify LASIL solutions ................................................................................................................................. 4-164

Table 30 – Certified concentrations of analytes within NIST 611 ........................................ 4-165

Table 31 - Measured elemental composition of NIST 611 expressed as element-to-uranium concentration ratio (500 µL D.I. water). The average ratio to uranium within a replicate and the associated %RSD are also presented calculated from elements of similar concentration to uranium in the solid. Elements in grey were not used to calculate the average ratio because they have significantly different concentrations in NIST 611 ................................................................................................................................. 4-167

Table 32 - Measured elemental composition of NIST 611 expressed as element-to-uranium concentration ratio (500 µL post acidified). The average ratio to uranium within a replicate and the associated RSD are also presented calculated from elements of similar concentration to uranium in the solid. Elements in grey were not used to calculate the average ratio because they have different concentrations in NIST 611 ................................................................................................................................. 4-168
| Table 33 – A comparison of the percentage RSD for signal intensities of post-acidified and non-acidified samples | 4-169 |
List of Figures

FIGURE 1 – SCHEMATIC DRAWING OF AN ICP TORCH BASED ON THE FASSEL DESIGN .......... 1-18
FIGURE 2 – SCHEMATIC DRAWING OF THE STATIC HIGH SENSITIVITY ICP (SHIP) TORCH AS
reported by Klostermeier et al 18 ................................................................................................................. 1-20
FIGURE 3 – SCHEMATIC DRAWING OF THE CONE INTERFACE BETWEEN AN ICP AND MASS
SPECTROMETER .................................................................................................................................................. 1-23
FIGURE 4 – SCHEMATIC DRAWING OF THE DATA ACQUISITION TERMINOLOGY USED THROUGHOUT
THIS THESIS. THE FIRST PEAK IS REPRESENTATIVE OF 100% MASS WINDOW WHILST THE
SECOND IS REPRESENTATIVE OF A 5% MASS WINDOW ..................................................................................... 1-29
FIGURE 5, SCHEMATIC DRAWING OF STIMULATED EMISSION WITHIN A LASER CAVITY ........... 1-31
FIGURE 6, A DIAGRAM SHOWING THE PATHWAY OF ABSORPTION AND EMISSION OF ENERGY FROM
A PHOTON ON A TWO, THREE AND FOUR ENERGY LEVEL SYSTEM ................................................................. 1-32
FIGURE 7 – RENDERED CAD IMAGE OF THE DCI WITH TORCH AND PARTIAL LOAD COIL FOR
CLARITY ................................................................................................................................................................. 2-47
FIGURE 8 - SCHEMATIC DRAWING OF THE DCI, INCLUDING ICP TORCH AND LOAD COIL FOR
CLARITY, A) A SECTIONED SIDE-ON VIEW AND B) A VIEW DOWN THE INJECTOR LOOKING
FROM THE LOAD COIL TOWARDS THE T-PIECE ................................................................................................. 2-50
FIGURE 9 – SCHEMATIC DRAWING OF THE DCI EXTENDING PAST THE SHEATH TUBE.
DIMENSIONS OF THE DISTANCE BETWEEN THE SHEATH AND AUXILIARY TUBE AND THE LOAD
COIL ARE GIVEN IN MM ......................................................................................................................................... 2-51
FIGURE 10 – RENDERED CAD IMAGE OF THE SNIFFER CELL, PARTIALLY TRANSPARENT FOR
CLARITY, FLOATING ABOVE A GLASS SAMPLE .................................................................................................. 2-53
FIGURE 11 – A) SCHEMATIC DRAWING OF THE SNIFFER CELL (THE INNER CELL) AND B) AN
ISOMETRIC REPRESENTATION OF THE SNIFFER CELL, PARTIALLY TRANSPARENT FOR
CLARITY ................................................................................................................................................................. 2-54
FIGURE 12 – A CUT SCHEMATIC DRAWING OF THE SNIFFER CELL HOUSED IN A MODIFIED UP213
CELL LID, THE ALPHA OUTER CELL .................................................................................................................. 2-56
FIGURE 13 - REPRODUCED SCHEMATIC DRAWING OF THE ENTERPRISE CELL, THE NEW OUTER
CELL FOR THE SNIFFER 70 ..................................................................................................................................... 2-57
FIGURE 14 – 3-DIMENSIONAL CAD IMAGE OF THE SNIFFER AND MODIFIED UP213 CELL LID, THE
MODEL IS SEMITRANSPARENT AND THE OPTICAL WINDOW CLAMP REMOVED FOR CLARITY. 2-61
FIGURE 15 – TWO CUT PLOTS SHOWING THE 2-DIMENSIONAL COMPUTED MESH FOR THE OUTER
CELL AND SNIFFER CELL AT A 200 µM GAP DISTANCE. A) THE Y-PLANE AND C) IN THE Z-
PLANE, BOTH PLOTS HAVE ARE ACCOMPANIED WITH MAGNIFIED POP-OUTS CENTRED
AROUND THE SNIFFER FOR CLARITY .................................................................................................................. 2-64
Figure 16 – Gas flow trajectories colour scale truncated from 0 to 0.1 m/s, A) viewed in the Y-plane with a magnified view of the Sniffer and B) an isometric cut-view with outer cell removed for clarity .................................................. 2-65

Figure 17 – Gas flow trajectories that contact the bottom of the Sniffer, truncated colour scale from 0 to 1 m/s, sectioned model and angled view in the Z-plane .................................................................................................................................................. 2-66

Figure 18 – Gas flow trajectories that contact the walls of the laser port, truncated colour scale from 0 to 1 m/s, sectioned model and viewed in the Z-plane .................................................................................................................................................. 2-67

Figure 19 – Gas flow trajectories that contact the micro-chamber walls, truncated colour scale from 0 to 1 m/s, model semi-transparent and viewed in the Y-plane .................................................................................................................................................. 2-68

Figure 20 – Gas velocity cut plots in A) colour scale 0-20 m/s, B) 0-1 m/s cross-section both in the Z-plane, velocity contour arrows included and C) in the Y-plane colour scale 0-2 m/s .................................................................................................................................................. 2-69

Figure 21 – Injection point position by number within the viewing area .......... 2-70

Figure 22 – Particle injection into fluid flow within the micro-chamber for a 200 μm gap distance, A), Y-plane, 0-0.4 m/s, B) Y-plane, 0-20 m/s and C) Z-plane, 0-0.4 m/s .................................................................................................................................................. 2-71

Figure 23 – Diagram of the possible eddy regions at the point where the DCI inlet meets the Sniffer outlet .................................................................................................................................................. 2-74

Figure 24 – Particle injection outside the Sniffer for a 200 μm gap: A) injection point position by number outside the sniffer in the Y-plane and B) angled Z-plane, both colour scales 0-1.0 m/s .................................................................................................................................................. 2-75

Figure 25 – Particle injection outside of the Sniffer for a 200 μm gap .......... 2-77

Figure 26 – Gas velocity cut plots in A) truncated colour scale 0-20 m/s cross-section in the Z-plane, velocity contour arrows included and C) in the Y-plane truncated colour scale 0-2 m/s .................................................................................................................................................. 2-78

Figure 27 – Particle injection into fluid flow within the micro-chamber at a gap distance of 50 μm, A), Y-plane, 0-1.0 m/s and B) Z-plane, 0-20 m/s ................. 2-80

Figure 28 – Flow trajectories for the Sniffer off-axis relative to the gas inlet A) in the Y-plane, B) isometric and C) a particle study viewed in the Z-plane, black arrows indicate the particulate path ................................................................. 2-83

Figure 29 – A) Schematic drawing of a new directed flow-Sniffer cell design (the inner cell) and B) an isometric representation of the Sniffer cell, partially transparent for clarity, where the sample gas is directly fed into the micro-chamber .................................................................................................................................................. 2-88

Figure 30 – A) Schematic drawing of a new closed Sniffer cell design (the inner cell) and B) an isometric representation of the Sniffer cell, partially
TRANSPARENT FOR CLARITY, WHERE SAMPLE GAS IS FED DIRECTLY INTO THE MICRO-
CHAMBER ........................................................................................................................... 2-89

Figure 31 – Schematic drawing of the multiple transport tubing used in the initial
Sniffer-DCI configuration. [1] Sniffer outlet (0.5 mm I.D x 4 mm), [2] stainless
steel tubing (0.51 mm I.D x 80 mm), [3] PFA tubing (0.5 mm I.D. x 100 mm), [4]
borosilicate glass (0.5 mm I.D. x 200 mm), [5] custom Macor reducer (from 0.5 to
0.25 mm I.D. x 2 mm), [6] fused silica capillary (0.25 mm x 40 mm). Diagram is not to
scale ........................................................................................................................................3-94

Figure 32 – Peak profiles of $^{238}$U for the Sniffer-DCI interface (using the alpha
cell) at flow rates: A) 0.050, B) 0.075, C) 0.100 and D) 0.130 Lmin$^{-1}$. The x-axis has
been truncated to between 20 and 25 seconds to show the peaks profiles in
detail ...................................................................................................................................... 3-99

Figure 33 – Example peak profiles for the Sniffer-DCI interface (alpha cell) at a
0.130 Lmin$^{-1}$ flow rate and varied DCI extensions. Profiles have been offset by
0.3 seconds on the x-axis and by $2 \times 10^5$ counts s$^{-1}$ on the y-axis for clarity ...3-100

Figure 34 – A) average peak area and B) average peak maximum for the Sniffer-DCI
interface at a 0.130 Lmin$^{-1}$ flow rate for varied DCI extensions, errors bars are
given as 1 standard deviation ..............................................................................................3-101

Figure 35 – A typical peak profile from using a single continuous transport tube, 2
mm DCI extension and 0.120 Lmin$^{-1}$ sample gas flow rate. The peak was
generated by averaging 10 peaks about the peak maximum................................. 3-108

Figure 36 – Peak profiles for a -10mm extension at a 0.120 Lmin$^{-1}$ flow rate, obtained
using the raw channels per mass peak transient signal method A) five
individual pulses offset consecutively by 0.01 s on the x-axis and $1 \times 10^6$ counts s$^{-1}$ on the y-axis and B) the average peak profile from the 5 separate pulses3-113

Figure 37 – Peak profiles for a 2mm extension at a 0.120 Lmin$^{-1}$ flow rate, obtained
using the raw channels per mass peak transient signal method A) five
individual pulses offset consecutively by 0.05 s on the x-axis and $1 \times 10^6$ counts s$^{-1}$ on the y-axis and B) the average peak profile from the 4 separate pulses
(peak 1 excluded due to failing the Grubbs test based on peak maximum) .....3-114

Figure 38 – Peak profiles for A) 12mm and B) 16 mm extensions at a 0.120 Lmin$^{-1}$ flow
rate, obtained using the raw channels per mass peak transient signal method,
five individual pulses offset consecutively by 0.05 s on the x-axis and $1 \times 10^6$
counts s$^{-1}$ on the y-axis .................................................................................................3-116

Figure 39 – A) the average peak area and B) the average peak height from 5 separate
peaks at time per channel of 100, 200 and 500 µs. Errors are given as the
standard deviation of the mean .........................................................................................3-118

Figure 40 – Peak profiles for a 2mm extension at a 0.120 Lmin$^{-1}$ flow rate, obtained
using the averaged channels per peak transient signal method A) five
INDIVIDUAL PULSES OFFSET CONSECUTIVELY BY 0.05 S ON THE X-AXIS AND 2 X 10^4 COUNTS S\(^{-1}\) ON THE Y-AXIS AND B) THE AVERAGE PEAK PROFILE FROM THE 5 SEPARATE PULSES

**Figure 41** – Peak profiles for varied extension of the DCI, Enterprise cell configuration, at a flow rate of A) 0.050 and B) 0.100 L/min\(^{-1}\). Peaks have been successively offset by 0.05 seconds on the x-axis and 1 x 10^6 counts per second on the y-axis for clarity ................................................................. 3-120

**Figure 42** - The average peak maximum for the Enterprise configuration Sniffer-DCI interface at A) a 0.050 and B) a 0.100 L/min\(^{-1}\) flow rate for varied DCI extensions, errors bars are given as 95% confidence intervals. The dotted lines represent the end of the sheath gas tube at 0 mm, the first and second turn of the load coil at 5.3 and 9.3 mm respectively. .............................. 3-123

**Figure 43** – The average peak area for the Enterprise configuration Sniffer-DCI interface at A) a 0.050 and B) a 0.100 L/min\(^{-1}\) flow rate for varied DCI extensions, errors bars are given as 95% confidence intervals ........................................ 3-124

**Figure 44** – Schematic drawing of the Zircon cell ................................................................. 3-131

**Figure 45** – An example signal intensity for one line, with washout periods either side. Standard injector response in red and the DCI at a 4mm extension in blue (off-set by an order of magnitude for clarity) ................................................................. 3-135

**Figure 46** - A) average signal intensity and B) signal area, from analysis of NIST611 for different DCI positions and the standard injector at 0.025 L/min\(^{-1}\), errors given are 1 standard deviation for the four ablation tracks ............................................... 3-137

**Figure 47** - A) average signal intensity and B) signal area, from analysis of NIST 611 at different flow rates using the standard injector, errors given are 1 standard deviation for the four ablation tracks ............................................... 3-139

**Figure 48** - A) Exploded CAD image and B) schematic representation of the LASIL pot ................................................................. 4-151

**Figure 49** – NIST glass surface profiling images, tracks inverted for clarity: A) a track image from non-degassed D.I. water; B) a track image and C) a track profile from degassed water at a notional laser fluence of 14.9 J/cm\(^2\); (d) a track image and (e) a track profile from degassed D.I. water at a notional laser fluence of 31.6 J/cm\(^2\); (f) a track image and (g) a track profile from 4 x 10^4 mol/L solution of TBACl at a notional laser fluence of 46.5 J/cm\(^2\) .................................................. 4-156

**Figure 50** - A diagram of LASIL within a droplet showing ablation plume, micro cavity and resulting bubbles after micro cavity collapse. Note that the diagram shows multiple events that occur after each other and that sizes and angles are exaggerated for clarity ................................................................. 4-159

**Figure 51** - SEM analysis of filtered particulate from a D.I. water droplet LASIL experiment at a notional fluence of 30.1 J/cm\(^2\) (a) 10,000 times magnification
AND (B) 50,000 TIMES MAGNIFICATION; A NOTIONAL FLUENCE OF 10.9 J/cm² (C) 5,000 TIMES MAGNIFICATION AND (D) 50,000 TIMES MAGNIFICATION. .......................... 4-163

**Figure 52 - Bar charts showing the calculated concentrations versus the certified concentrations 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 six replicates 6 x 25 ml droplets at a notional fluence of 9.1 J/cm². ..................... 4-170**
Chapter 1 Introduction – Current Laser Ablation and ICP-MS Technology

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) is now a well established analytical technique used to sample solid materials and determine their elemental composition \(^1\)-\(^4\). The fundamental principles of LA-ICP-MS are well understood and the technique is used in many fields of research and industry, finding applications in geology, forensics and medicine. Two areas that are becoming increasingly important, and for which LA-ICP-MS is a key tool, are bio-imaging and the analysis of micro-particulates. However, current instrumental designs limit the practicality of the technique for these applications.

The response and washout time of current LA cells is slow; around 0.5 seconds for commercially available designs and tens to a few hundred milliseconds for research based cells. Faster response times and shorter washout times are desirable to reduce temporal aerosol dispersion. By decreasing the aerosol dispersion and maintaining the aerosol transport efficiency an increase in the signal to noise ratio is achieved, thus improving the limit of detection. This is essential for bio-imaging when one considers the analyte concentration within a single cell and the mass of analyte within a micro-particle. Improving the washout time of ablation cells is crucial to reducing the total analysis time. For example, if a cell has a washout time of 100 ms and a target image is of the size 10 mm x 10 mm; then at 10 \(\mu\)m resolution (the same order as a single biological cell) the total time taken to image the sample will be around 28 hours.

This introduction gives a brief background to the techniques used and discusses current LA-ICP-MS technology and its shortcomings. Calibration for LA-ICP-MS is also briefly discussed as a separate project was undertaken in which the technique, Laser Ablation of a Sample In Liquid (LASIL), was developed.
1.1 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

ICP-MS is an analytical technique where a sample is introduced into an inductively coupled plasma in which it is desolvated, atomised and ionised. The resulting ions are then extracted through a vacuum interface and separated according to their mass to charge ratio \((m/z)\) and finally detected.

The roots of mass spectrometry can be traced as far back as 1886, when Eugen Goldstein observed the deflection of positively charged particles or kanalstrahlen (translated as canal rays) from an anode through a perforated cathode. In 1899 Wilhelm Wien showed that these particles could be deflected and separated by electric and magnetic fields according to their mass to charge ratio. This work was improved by Joseph John Thomson, around 1912, by reducing the pressure of the apparatus and producing the first-clear mass spectrograph. Instrumental developments followed such as separation of the electric and magnetic fields, development of the ion path geometry and a scanning ability that allowed separation of a focused ion beam. Further advances came when dedicated ion generation sources were coupled to the scanning mass analyser \(^5\), the most influential of which for elemental detection was the Inductively Coupled Plasma (ICP).

The ICP was first described by Reed \(^6\) and used to grow single crystals. Its potential as a spectrometric ion source wasn’t realised until 1964, when Greenfield et al \(^7\) compared the ICP performance against a Direct Current Plasma (DCP) for atomic emission spectroscopy (AES, also denoted as Optical Emission Spectroscopy, OES). AES is an element specific technique where an ion or atom in an excited state, relaxes towards its ground state configuration (that of lowest energy). Many pathways exist by which the ion or atom can relax but the main mode of relaxation is via collisions with surrounding atoms and vibrational relaxation. The energy may also be released as a photon of light with energy, and thus wavelength, corresponding to the energy difference between the excited electron energy level and the electron relaxed energy level. As atoms have a unique and electron configuration the energy gap is elemental specific. The photon can be detected using many different types of detector and the intensity directly correlated to the analyte concentration.
In 1980 the ICP was coupled to a mass spectrometer by Houk et al. and used to analyse an aspirated solution. This new technique offered improved sensitivity and lower limit of detection (LOD) as well as improved isotopic information compared to AES.

1.1.1 Figures of Merit

The advantages of using ICP-MS are:

- A large linear dynamic range
- Detection of almost all the elements of the periodic table due to the high temperature plasma
- Low instrumental background and therefore improved limit of detection (LOD)
  - This is conventionally defined as given in Equation 1 where $X_{bl}$ is the mean of the blank (or background), and $\sigma_{bl}$ is the standard deviation of the blank.
- A good sensitivity
  - Defined as the signal response relative to the sample concentration, often expressed as counts s$^{-1}$/ppm
- The ability to obtain isotopic information

$$LOD = X_{bl} + 3\sigma_{bl} \quad \text{Equation 1}$$

1.1.1.1 Limit of Detection for Fast Data Acquisition

As sample data integration time becomes shorter so the distribution moves from that of Gaussian to Poisson as background signal within a given integration time falls below c.a. 70 counts. It has been suggested by Tanner and Günther that Equation 2 be used to determine the LOD for fast time resolution data, where B is the expected number of background counts. This equation accounts for the discrete nature of the Poisson distribution which otherwise would yield a LOD of 0 for zero counts.

$$LOD = 2.71 + 3.29\sqrt{B} \quad \text{Equation 2}$$
1.1.2 The ICP – Formation and Ion Generation

The plasma, an ionised gas that is overall neutral, of an ICP is commonly composed of argon gas. It is relatively abundant and therefore cheap and it can excite and ionise most of the periodic table due to its relatively high ionisation potential. The gas is passed through three concentric quartz tubes, commonly referred to as the ICP torch, the design and dimensions of which were described by Richard Wendt and Velmer Fassel in 1965. The most commonly used torch configuration, the Fassel torch, as described by Fassel in 1978 is shown in Figure 1. The shape and positioning of the load coil was changed from the torch described in 1965 and the design has largely remained unchanged.

![Schematic drawing of an ICP torch based on the Fassel design](image)

**Figure 1 – Schematic drawing of an ICP torch based on the Fassel design**

The gas in the outer tube, referred to as the cool gas, is introduced such that it flows tangentially along the torch, typically at a flow rate of 15-20 Lmin$^{-1}$. This improves the cooling of the outer torch tube and ensures the plasma remains central and concentric. The gas within the second concentric tube is commonly referred to as the plasma gas (or the auxiliary gas) and ensures the plasma does not contact the injector; flow rates are typically 0.5-1.2 Lmin$^{-1}$. The gas within the inner concentric tube, the sample gas, creates a central sample channel through the plasma, referred to as ‘punch’ through, and is used to introduce the sample aerosol into the plasma.
To establish the plasma the gas is seeded with electrons, commonly introduced by a Tesla spark, which are accelerated by a magnetic field, induced by the radio frequency (R.F., high frequency, typically 27 MHz) energy coupled from a surrounding copper coil. The accelerated electrons ionise the argon gas; as long as the R.F. field is present the resulting electrons and ions will continue to collide with enough energy to sustain the plasma by thermal ionisation, charge transfer, electron impact and Penning ionisation pathways as shown in Equation 3, Equation 4, Equation 5 and Equation 6 respectively. Where X and A represent a atom/ion of the plasma gas or analyte.

\[
X + A \rightarrow X + A^+ + e^-
\]  \hspace{1cm} \text{Equation 3}

\[
X^+ + A \rightarrow X + A^+
\]  \hspace{1cm} \text{Equation 4}

\[
e(\text{fast}) + A \rightarrow A^+ + 2e^- (\text{slow})
\]  \hspace{1cm} \text{Equation 5}

\[
X^M + A \rightarrow X + A^+ + e^-
\]  \hspace{1cm} \text{Equation 6}

Typical powers used to sustain the plasma are 0.6-1.4 kW. This creates a flow of electrons, ions, metastable and neutral species. Radiative recombination of the argon ions with electrons leads to excited argon atoms and the emission of high energy photons.

The tangential flow of the cool gas destabilises the base of the plasma such that the sample gas introduced from the inner concentric tube, the injector, can punch through the plasma. This allows a sample aerosol to be passed through the centre of the plasma. On passing through the plasma the sample becomes desolvated, atomised and ionised. The sample is finally introduced into the mass spectrometer using a vacuum interface.

Desolvation and atomisation occur primarily by thermal pathways. Coupling of the R.F. energy is strongest in the outer regions of the plasma. Energy is transferred to the central channel via conduction and convection of the energy between ions and excited atoms and by radiative transfer from the emitted photons released as a result of argon radiative recombination. This results in a temperature within the central channel of plasma of between 6000 and 10000 K; enough energy to evaporate solvent and decompose solid particulate and molecules. The resulting atoms can then be ionised, the efficiency of which is controlled by plasma conditions such as sample gas flow and RF power, and the atom ionisation
potential. Thermal ionisation is the dominant pathways by which the resulting atoms are ionised, however other ionisation pathways exist as described for the ionisation of the plasma gas.

1.1.2.1 Torch Design

The Fassel torch is common place in most commercial ICPs and the design has varied little since its introduction in 1978 [11]. The majority of torch developments have been the miniaturisation of the torch dimensions to reduce gas consumption and aerosol dilution by plasma gases [12–15], or reduction of plasma gas consumption by improving the cooling efficiency of the torch [16,17].

1.1.2.1.1 The Static High sensitivity IcP (SHIP) Torch

A new torch design was recently described by Klostermeier et al [18], the Static High sensitivity IcP (SHIP) torch, the geometry of which is significantly different from that of the Fassel design, see Figure 2. Similarly the torch consists of an injector tube through which the sample aerosol is transported to the plasma. However, a single argon gas flow, the auxiliary plasma gas, is fed tangentially into the torch and flows into a bulb shaped expansion zone, note the absence of a cool gas within the torch. This zone is surrounded by the load coil and is where the plasma is formed. The expansion zone then tapers into a chimney outlet. The torch is cooled externally by a separate flow of air.

![Figure 2 – Schematic drawing of the Static High sensitivity IcP (SHIP) torch as reported by Klostermeier et al [18]](image)

The SHIP torch has a much lower total argon gas consumption of 0.6 L\(\text{min}^{-1}\) compared to c.a. 18 L\(\text{min}^{-1}\) consumed by the Fassel torch, it can also operate at a
much lower RF power. Initially the signal stability, sensitivity and LOD of the SHIP torch were worse than the conventional Fassel torch \(^{18}\), however further improvements of the geometry lead to comparable figures of merit for AES \(^{19}\). Further characterisation of the SHIP torch has been performed for its use in AES applications \(^{20-22}\). Modification of the SHIP torch geometry facilitated its coupling to a mass spectrometer \(^{23}\), however initial investigations showed no real improvement in using this torch over the Fassel design. For elements that form stable oxides the signal stability and sensitivity were much lower due to the low RF power used.

1.1.2.2 Sample Introduction

Interfaces for solid, liquid and gaseous sample introduction into an ICP have been developed and modified to suit various applications. The most common sample introduction system for liquid samples is the nebuliser and spray chamber. The nebuliser uses a high-velocity gas (normally a flow rate of 0.5-1.0 Lmin\(^{-1}\) argon) to aspirate a solution at a flow rate of 0.00005-0.001 Lmin\(^{-1}\). The resulting mist is filtered using a spray chamber such that droplets of large diameter (typically >5 \(\mu\)m) are separated and transported to waste. Droplets of a smaller diameter are carried to the ICP.

Solid sample introduction into the ICP has taken many forms, however the technique with growing interest and applications is that of laser ablation. The technique is used to generate an aerosol containing nanometer and micrometer sized particulate that represent the solid sample. This technique is discussed in more detail later in this chapter.

Sample introduction into the torch has seen significant development with many nebuliser-spray chamber designs and combinations for various liquid introduction applications \(^{24,25}\). Solid sample introduction by laser ablation has also seen the development of different laser ablation cells, optimised for specific applications and sample types, discussed further in section 1.2.3

1.1.2.2.1 Integration of the Torch and Sample Introduction System

Incorporation of the sample introduction system into the torch minimises sample loss and increases analyte transport efficiency. For liquid sample introduction the Direct Injection Nebuliser (DIN) was developed by replacing the aerosol injector in
the conventional torch with an extended nebuliser that aspirates the solution directly into the plasma. The design minimises dead volumes, important for separation techniques where dead volumes create band broadening and possible cross contamination regions. Although having analyte transport efficiency to the plasma of 100%, the large droplet size and droplet velocity distributions limit the sensitivity and limit of detection of the technique. Large droplets with a high velocity are not fully processed by the ICP resulting in a reduction in the number of potential ions is produced. This problem was addressed by the development of the Direct Injection High Efficiency Nebuliser (DIHEN). This configuration incorporated the High Efficiency Nebuliser (HEN), a nebuliser design with reduced critical dimensions, at the injector tip to reduce the mean droplet diameter and size distribution. Other developments of the DIHEN have included making the component demountable enabling easy exchange of the components when damaged; increasing the internal diameter of the injector to reduce clogging and incorporating a recessed capillary in the nebuliser tip, the Vulkan DIN. Integration of the nebuliser at the base of the torch has been developed by Todoli and Mermet as the Torch Integrated Sample Introduction System (TISIS). This design places a standard nebuliser at the base of the conventional injector.

Little work has been reported of integrating the ICP torch and a solid-sample introduction system. Tanner and Günther reported the development of an In-Torch laser ablation system. The design modified the Fassel torch to accommodate a solid sample suspended from the injector, 2 mm extended from the injector tip and 10 mm retracted behind the second concentric tube, the auxiliary gas tube. A laser beam was then focused through the torch and upon the sample surface, allowing ablated particulate to be carried through the plasma. This design and its figures of merit have been discussed further in section 1.2.3.
1.1.3 Mass Spectrometers

1.1.3.1 Vacuum interface

Sample ion introduction from an ICP source to a mass spectrometer is complicated due to their respective operating at atmospheric and reduced pressure. The first reported ICP-MS design\(^8\) used a cone with a small orifice placed between the mass spectrometer and the ICP. Within the mass spectrometer two separate chambers were used where the pressure was sequentially reduced. This was later improved by placing two cones, the sampler and skimmer cone, between the ICP and mass spectrometer, see Figure 3.

![Figure 3 – Schematic drawing of the cone interface between an ICP and mass spectrometer](image)

The plasma flows from a region of atmospheric pressure to a region of reduced pressure (0.2 kPa) through the sample cone orifice, typically 1.0 mm diameter. On passing into a region of lower pressure the plasma expands and results in an increase in the velocity. The plasma exceeds the speed of sound resulting in the formation of a supersonic free jet, shown in Figure 3 as the zone of silence. The region where the plasma begins to slow is the mach disk. The orifice of the skimmer cone, typically 0.8 mm in diameter, is placed in front of the mach disk and samples the plasma. Behind the sample cone the pressure is further reduced to \(1 \times 10^{-5}\) kPa. The configuration of the cone interface has been described extensively by Campargue\(^{38}\) and the physical processes involved have been discussed by Niu and Houk\(^{39}\).
From here ions are focused and accelerated in the mass analyser housing and separated based on their $m/z$ ratio. There are three commonly available mass analysers used for elemental analysis: the quadrupole (QMS), the time of flight (TOF) mass spectrometer and the double-focusing magnetic sector field (SFMS).

1.1.3.2 Quadrupole Mass Spectrometers

The Quadrupole Mass Spectrometer (QMS) is one of the simplest and cheapest instruments used to separate ions relative to their $m/z$. It is constructed such that four stainless steel (or molybdenum) rods are arranged in a square. These rods are typically 15-20 cm in length and 1 cm in diameter. Opposing rods are paired electrically; an RF voltage is applied to the first pair and the second pair with an RF voltage $180^\circ$ out of phase. Parallel rods are supplied with a superimposed positive or negative DC current. Ions travelling through the poles will begin to oscillate due to the RF and DC fields. The amplitude of the oscillation increases along the length of the poles until ions either exit the poles or collide and become neutralised. The path the ions take are dependent on their $m/z$. By varying the DC and RF fields ions can selectively be transported to the end of the rods.

This mass filter has a low resolution compared to the SFMS. However due to a short transit time and the ability to quickly vary the RF and DC fields the scanning speed across a mass spectrum (5-256 amu) with a quadrupole is much faster than a SFMS.

1.1.3.3 Time of Flight Mass Spectrometer

The Time Of Flight Mass Spectrometer (TOFMS) separates ions based on their kinetic energy. Ions are delivered into a flight tube in packets as a pulsed ion beam. The ion packet is accelerated such that all ions achieve an equal kinetic energy, $E_k$. As the velocity, $V$, of an ion is a function of its $E_k$ and mass, $m$, then ions of different $m$ but equal $E_k$ will achieve different $V$, see Equation 7.

$$KE = \frac{mv^2}{2} \quad \text{Equation 7}$$
As ions travel along the flight tube of distance $L$, with a characteristic $V$, then the relationship of their transit time, $T$, to their m/z, see Equation 8, can be used to separate and detect elements of different mass.

\[
\frac{m}{z} = \frac{2VT^2}{L^2} 
\]  
\textbf{Equation 8}

This technique offers many advantages over QMS and SFMS. All masses can be monitored pseudo-simultaneously and the instrument can theoretically output data at a time resolution of 30 µs. Thus the noise from transient-plasma effects is reduced and data can be acquired at a much faster time resolution, important for separation or imaging techniques (such as laser ablation).

\subsection*{1.1.3.4 Double-Focusing Sector Field Mass Spectrometer}

As previously discussed a magnetic field can be used to separate ions of different mass and charge. The configuration of Sector Field Mass Spectrometer (SFMS) discussed here is that of the commercially available Element XR ICP-MS (Thermo Scientific, Bremen, DE), a reverse Nier-Johnson geometry (employing a magnet mass filter prior to an electrostatic sector).

Ions are extracted from the interface region and are accelerated by a series of focusing lenses such that the initial circular (as a result of the ICP and cone orifice geometry) ion beam becomes rectangular. Ions pass through a slit and enter the magnetic sector; the slit can be used to control the mass resolution of the instrument by changing the width of the slit and thus the ion beam dispersion. Three slits are present in the Element XR configuration, an entrance slit, an intermediate slit and an exit slit. The sector generates a magnetic field perpendicular to the ion beam but parallel to the slit (curving away from the initial ion beam direction). The ions deviate from their initial path, following a curved trajectory. The magnetic sector is dispersive relative to ion energy and mass (its momentum), such that ions of differing $m/z$ ratio will separate spatially and follow different angles of curvature. By keeping the radius of the magnetic sector constant and varying the field strength, ions of differing $m/z$ can be focused onto an intermediate slit stopping the transmission of ions of higher or lower $m/z$. The
relationship of the magnetic field strength, $B$, curvature, $R$, and the initial ion velocity, $V_0$, to the mass to charge ratio is given in Equation 9

$$\frac{m}{z} = \frac{B^2 R^2_m}{2V_0}$$

Equation 9

As the curvature of the ion path is also influenced by the initial ion velocity, as such varying the accelerating voltage can also be used to focus particular $m/z$.

However, ions of the same mass can differ in kinetic energy, as a result of formation position within the plasma etc., and will be deviated with a different curvature. This leads to peak broadening and a loss in resolution. Thus a second focusing sector is used, the electrostatic sector. This component is dispersive with respect to ion energy not mass. Two curved plates, either side of the ion beam are held at opposing voltages such that ions are again deviated into a curved path. The ion beam then passes through the exit slit and into the detection housing, so that the electrostatic sector acts as an energy filter.

The combination of these two discriminators where the energy dispersion of the magnetic and electrostatic sectors are equal in magnitude but opposite in direction will result in focusing of both ion energies and angles but dispersive with respect to mass.

As previously discussed by placing slits in the path of the ion beam the resolution of the instrument can be controlled. Resolution is defined as the ability of the instrument to separate one mass peak from another. For sector field instruments this is defined as separation of two ions at 5% peak height, $\Delta m$, and resolution, $r$, is given as shown in Equation 10.

$$r = \frac{m}{\Delta m}$$

Equation 10

For the Element XR resolutions of 300 (low), 3000 (medium) and 10,000 (high) are achieved by varying the slit width of the entrance and exit slits. The disadvantage of a higher resolution is that as the ion beam becomes smaller the number of transmitted ions is reduced, thus reducing the sensitivity. At low resolution the mass peak shapes are trapezoidal (flat topped) and at medium and high resolution become Gaussian.
1.1.3.4.1 Element XR Scanning Modes
The Element XR has three modes of data acquisition. The B-scan, where the electric field is held constant and the magnetic field is varied to scan across \( m/z \). This is a slower mass scanning option due to the relatively long time taken to alter the magnetic field. However, this method is suitable for full mass range scanning and does not suffer from mass related intensity differences.

The E-scan mode sets the magnet to a fixed magnetic field value and alters the accelerating voltage and electric field. This mode of operation only allows a 30% mass range to be covered and so the magnetic is jumped to different magnetic field values once the 30% mass range has been exceeded so that the entire mass range may be covered. This method is much faster than the B-scan method as changing the accelerating voltage and the electric field is quite quick.

A SyncScan mode is also available in which the magnetic and electric field are varied to filter particular \( m/z \). This mode is akin to peak hoping in quadrupole mass analysers and generates a single point per mass. The scanning speed of this method is between the B-scan and E-scan methods.

1.1.3.5 Ion Detection
The Element XR houses two types of detector, a Faraday cup and a Secondary Electron Multiplier (SEM) composed of discrete dynodes.

The Faraday cup consists of a metal plate connected to ground via a resistor, surrounded by a cage. Ions entering the detector strike the metal plate. Neutralisation of the ions generates a current flow within the system which is measured as a potential change. The current is directly proportional to the number of ions. The surrounding cage neutralises secondary emissions. The working range of the Faraday cup in the Element XR is \( 1 \times 10^7 \) to \( 1.5 \times 10^7 \) counts per second, equating to a lowest working ion current of \( 1.6 \times 10^{-12} \). It has been reported that the Faraday cup can measure currents as small as \( 1 \times 10^{-16} \).
Before entering the SEM the ion beam is directed towards a conversion dynode where upon impact an electron is ejected, ensuring the detector response is linear across the mass range. The SEM is composed of a series of 18 discrete dynodes coated in a metal oxide. When an electron hits the first dynode surface one or more electrons is released. The dynodes are successively connected with resistors to create a voltage gradient and due to their orientation the ejected electrons zigzag down the detector dynodes resulting in an exponential cascade of electrons and thus amplification of $10^7$-$10^8$ of the initial ion signal. The resulting signal is normally 100 mV and 10 ns in duration. This duration is commonly referred to as the detector dead time and during this period the detector is inactive such that any ion entering during this time will not be detected. Amplification using all of the dynodes is referred to as the counting mode of the detector, and can detect from 0 to $5 \times 10^6$ counts per second.

An analogue mode is also available when using the SEM detector. This mode uses only a few of the dynodes to amplify the signal, achieving a gain of $10^3$-$10^4$ and a working range of $5 \times 10^6$ to $1 \times 10^7$ counts per second.

\subsection*{1.1.3.6 Data Acquisition}

Different instrument manufacturers use different terminology to describe data acquisition parameters therefore the terminology used within this thesis has been clarified below, described for E-scanning mode only. A typical peak profile and scanning parameters are detailed in Figure 4.

- The magnet mass is the related to the magnetic field strength applied during an E-scan. This value typically corresponds to a mass lower than the intended analyte mass.
- The settling time is the time designated to allow the magnet field to stabilise.
- The accurate isotope mass is the isotope mass as defined by IUPAC. This is defined as the centroid of the analyte mass peak, and the mass around which the accelerating voltage and electric field will be changed to scan the peak.
- The mass window is a percentage of the peak width over which the E-scan takes place. This can be set to 100\% to scan the entire peak, but is normally set from 5 to 20\% when low resolution is used such that the flat top of the mass peak is scanned.
The search window is a percentage of the peak width over which the centroid of the peak is determined. This value is typically 120%, and is used to search for mass peaks that may have shifted from the calibrated $m/z$. Shifts can occur due to temperature variation of the magnet and as a result of magnet hysteresis effects.

The number of channels defines the number of points to measure along the mass peak. The number of channels is affected by the mass window, so that for a 50% mass window and 20 channels, only 10 points will be measured across that 50% of the mass peak.

The sampling time is defined as the time spent measuring each channel.

The dwell time is the time taken to measure the entire peak and is a function of number of channels and the sampling time. If there are 10 channels each with a sample time of 0.001 s then the dwell time will be 0.010 s.

A pass is defined as a single successive measurement of all the analyte peaks, where the magnet settles a particular magnet mass, jumps to other masses according to the mass range being measured and returns to the initial magnet mass to scan the mass range again. If the mass range falls only within the scan range of the electrostatic analyser then a pass is defined as one scan of the mass range (from lowest to highest mass).

**Figure 4** – Schematic drawing of the data acquisition terminology used throughout this thesis. The first peak is representative of 100% mass window whilst the second is representative of a 5% mass window.
1.2 Laser Ablation

Light Amplification by Stimulated Emission of Radiation (LASER) was first described in 1960 by Maiman, coined as the ruby laser. The amplification process was further improved by the introduction of Q-switching by McClung and Hellwarth, leading to the term giant pulse formation in which the laser output was a series of pulses with much higher peak power. This technique utilises a variable attenuator to generate a population inversion within the laser gain medium. The switch inhibits reintroduction of emitted light from the gain medium back into itself, until such time that the medium becomes saturated (maximum population inversion). At which time the switch is altered to allow light to re-enter the gain medium and facilitate in stimulated emission, which results in the production of a short pulse of intense light.

It wasn’t until 1985 when Gray first reported the use of laser ablation as a means of sampling solid materials for on-line introduction into ICP-MS.

1.2.1 Laser Generation

A laser pulse is generated by the absorption of a photon of light with energy equivalent to the discrete energy levels of the molecular or atomic laser generating medium. This excites an electron from a ground state energy level to that of an excited level. A small percentage of this absorption can be followed by spontaneous emission of a photon with frequency equal to transition of the excited electron to a lower energy level. If photons of the same energy are present in the environment of the excited species this increases the probability of emission from the excited species and promotes emission in the same direction of passing photons. This is denoted as stimulated emission. This amplifies the amount of emissions taking place and thus increases the irradiance of the beam. In a solid-state laser system once a stimulated emission has been achieved further stimulation is not required as the emission from the other molecules in the system act as the stimulant. The initial irradiance of this, however, is very small so that the photons must be reflected back into the system. This is known as the resonating and pumping process of a laser as shown in Figure 5.
Figure 5, Schematic drawing of stimulated emission within a laser cavity

For a continuous and steady beam a population inversion is required between the two levels at which emission occurs. For emission from a two energy level system, as shown in Figure 6, the population of electrons will be greater in $E_1$ than $E_2$. A population inversion is not created as the decay rate is quicker than the pumping rate such that a pulse of energy is generated by the cascading of electrons from $E_2$ to $E_1$, governed by the decay kinetics. An inversion is difficult to generate in a three level energy system. However, in a four level system the energy level $E_4$ rapidly decays to the energy level $E_1$ whilst the population at energy level $E_3$ is maintained for longer period of time. Thus a population inversion is created and a continuous laser occurs.
Figure 6. A diagram showing the pathway of absorption and emission of energy from a photon on a two, three and four energy level system.

There are numerous laser mediums: solid-state transition metal ion lasers, semiconductor lasers, atomic and ionic gas lasers, molecular gas lasers, dye lasers and free-electron lasers. Each medium has advantages over the others and it is often a case of selecting medium based on the desired wavelength output, laser stability and running costs.
The most common lasing mediums used for ablation are solid-state transition metal ions with a four level system as the mode of emission, with neodymium ions in a yttrium aluminium garnet crystal (Nd:YAG) being the most popular. Further discussion will relate to this medium as this is the material used in the commercially available UP213 (ESI, NewWave Research Division, Huntingdon, UK).

This medium has a fundamental output wavelength of 1064 nm and can be shortened by optical frequency doubling (532 nm), tripling (355 nm), quadrupling (266 nm) and quintupling (213 nm). It can be operated at a medium (10 - 20 Hz) or high (1 – 5 kHz) repetition rate.

Shorter wavelengths are now common place for laser ablation, compared to longer ones used historically. Wavelengths in the ultra violet (UV) region have been deemed the best choice for ablation as the shorter wavelength can be focused into a smaller spot size (allowing for better spatial resolution) and many solid samples will absorb UV light, even without the presence of a chromophore. The shorter wavelength corresponds to a higher energy photon; with increased absorption efficiency more energy is delivered into the ablating volume. This reduces the effects of lower order thermal processes that lead to fractionation. Fractionation is defined here as process which results in a non-stoichiometric representation of the solid in the sub sample (the ablation plume). Fractionation effects are briefly discussed later in the chapter.

1.2.2 Laser Ablation process

The sample is placed within a closed cell, such that atmosphere is excluded and a dedicated gas flow can be used to transport sampled material. Laser ablation is a process where a laser beam is focused upon the sample surface. The laser energy is absorbed by the sample and begins a rapid phase transition and heating of the volume localised around the point of laser focus. The ablation mechanism process described here is for nanosecond laser pulse duration, material ejection from femto and picosecond pulse durations are dominated by photochemical pathways. Nanosecond pulse duration is dominated by thermal mechanisms. Wavelength and laser energy also affect the dominance of particular pathways.
Photons couple to the electronic and vibrational modes of the target sample. The electronic coupling leads to an increase in the excitation of the electrons, efficient electron-electron coupling, and a rapid increase in the electron temperature resulting in heating of the sample lattice. This eventually causes a vaporisation of the sample material. However, for nanosecond pulse widths this process has a minor contribution to total material ejected. As mentioned thermal process contribute to a large ejection of the sample material \(^{44,45}\). A large increase in temperature causes the localised sample region to melt, forming a liquid layer. From this layer evaporation of the target material occurs. Material can also escape from the liquid layer by melt ejection (fragmentation), where pressure changes and recoil pressures induce a splashing effect and liberation of sample material. If the laser energy is high enough phase explosion occurs, such that vaporised material within the liquid layer forces the ejection of large melt regions, a sputtering effect \(^{43}\), increasing the particle size distribution.

As soon as material is ejected from the sample surface it begins to expand away from the sample as an ablation plume. The expanding vapour plume interacts with the surrounding gas, resulting in a shock front. This retards plume expansion and results in an increase in ejected material density at the shock front \(^{44}\). However, due to the nanosecond laser pulse width the laser beam interacts with the expanding plume, increasing the temperature and thus promoting expansion. This laser-plume interaction increases the ionisation of ejected atoms, causes multiphoton absorption and inverse bremsstrahlung interactions, resulting in the formation of a plasma \(^{46}\).

After a period of expansion the plasma begins to cool and particulate begins to form by nucleation and condensation pathways. The particle size distribution of the resulting particle plume changes with respect to distance from the sample surface. Modelling of laser plume expansion and particle formation reported by Bogaerts and Chen \(^{47}\), described that when nanosecond pulse widths were used the vapour fraction of the expanding plume formed particles 1-10 nm in diameter in the middle of the plume and 0.1-2 nm diameter at the shock front. The particle density was much lower in the middle of the plume compared to that at the outer edges. Larger particles sizes within the plume are as a result of the melt ejection processes. These particles tend to be found close to the sample surface and are typically less than 1 µm.
1.2.2.1 Elemental Fractionation

Fractionation is defined as a process that results in the sub-sample (ablation plume) having a different elemental stoichiometry than that of the original sample. Three sources of fractionation have been surmised by Horn and Blackenburg.\textsuperscript{48}

Laser induced fractionation is a preferential evaporation of volatile elements occurs. This results in an ablation plume enriched in volatile elements. The laser pulse duration has been reported to be the main cause of this process. It has been reported that laser ablation with femtosecond pulse width does not yield preferential evaporation conditions. The Pb/U ratio has been used to investigate this process due to the significant difference in boiling point of the two elements. The difference in true ratio of Pb/U to that measured has been shown to increase when ablating down-hole.

Particle size related fractionation is a process in which elements are distributed in different ratios across different particle sizes \textit{i.e.} elements are enriched in different particle size fractions. Particle transport efficiency is not linear across the particle size distribution. As such, elements enriched in particle sizes with high transport efficiency will be artificially higher than those in particles with poorer transport efficiency. The processing efficiency of the ICP \textit{i.e.} the efficiency percentage of atomisation, also results in artificial enrichment, as elements enriched in smaller particles will be closer to complete atomisation than those in larger particles. The Th/U ratio is commonly used to investigate this process as the two elements are similar in mass and have similar first ionisation potentials. This effect has been investigated for ablation of NIST SRM 610 glass standard by Guillong and Günther.\textsuperscript{49} It was reported that during the first few seconds of down-hole ablation the ratio differed significantly from the true ratio. During the first few seconds of down-hole ablation the particle size distribution is quite large, reducing as the hole depth increases. After a particular hole depth the particle size distribution is much smaller and has a much smaller mean particle diameter. A fractionation index has been developed that normalises the analyte signal intensity to that of the calcium signal intensity. Calcium was chosen as laser ablation is an important tool for geochronology and calcium is present in most rock types at a known concentration, thus making it a good normalisation element. This process is opposite to that described for laser induced preferential evaporation.
The final fractionation process is that of laser induced isotopic fractionation. This effect is a combination of the sample matrix and that of a changing particle size distribution. As the total ablated mass reaching the ICP is very small, small differences in the mass loading will result in significant variation in plasma conditions. As such plasma temperature fluctuates as does the total number of ions entering the mass analyser, as the number of total ions varies so does the space charge effect. This effect is the electrostatic repulsion of ions of the same charge. Lighter mass isotopes are affected more by this and as such by varying the mass load the isotope ratio of the same element will vary with time.

1.2.2.2 Calibration
Many different calibration techniques have been developed for quantifying element concentrations by laser ablation sample introduction. Calibration can be difficult due differences between the sample and standard matrix. Different matrices will vary in their response to the energy of the focused laser beam. For example, some matrices will be more absorbing whilst other more reflecting; this will result in a different amount of energy being absorbed and thus a different mass of material being ejected. The overall signal response will therefore vary for these matrices.

1.2.2.2.1 Matrix Matching
Matrix matching yields the best results as a calibration technique. This method involves using a standard of the same matrix composition as the sample and contains the analyte of interest at a known concentration. The signal response is thus directly comparable between the standard and sample. By matrix matching the sampling mechanisms will remain constant between standard and sample. True matrix matching can be difficult in that sample matrices are unknown or too complex or dangerous to replicate in the laboratory.

Semi-quantitative analysis can be performed by using a standard of similar matrix to the sample. An instrument analyte response is generated by monitoring an internal standard response in both standard and sample and ratioing the analyte response to that. This reduces the error caused by differing ejected mass. However, as the standard becomes more unlike the sample the accuracy of the calibration becomes worse. A similar approach can be taken by directly ablating liquids. The
liquid has a known concentration of analyte and by using different types of
cromophore can be adjusted to achieve similar absorption to the sample.

1.2.2.2 Dual Sample-Standard Calibration

Similar to wet-analysis calibration, standard additions can be used to calibrate
laser aerosols and is referred to as dual sample-standard calibration. The
calibration curve of the liquid aerosol is plotted along with the curve of the liquid
aerosol and laser aerosol combined. Using the formula in Equation 11 the
ccentration of the analyte in the solid can be determined, where $C$ is
ccentration, $X$ is the sensitivity and $M$ is the mass flow rate. Superscript letters
denote $S$ as the solid, $L$ as the liquid and $S+L$ as the solid and liquid; subscript
letters denote $I$ as the internal standard and $A$ as the analyte.

$$
C_A^S = - \frac{M_A^L}{M_A^S} \cdot \frac{X_A^L}{X_A^{S+L}} \cdot C_A^{L+S} \quad \text{Equation 11}
$$

The sensitivity ratio in the component can be measured directly from the slope of
the two calibration graphs, and the point at which the liquid-and laser aerosol
crosses the x-axis (the concentration of liquid and solid) can be determined by
extrapolation of the curve. The mass flow rate ratio can be determined by
measuring the response of an internal standard with respect to both calibration
lines.

This calibration technique requires that the slopes of the calibration curves be
parallel to account for potential differences in matrix effects. An internal standard
within the sample is also required to calculate the mass flow ratio; however this
isn’t always practically achievable and elemental fractionation must not occur
between the internal standard and the analyte.

1.2.2.2.3 Laser Ablation of a Sample In Liquid (LASIL)

LASIL is a technique where laser induced ablation occurs at a solid-liquid
interface, where the sample is submerged or a liquid droplet is placed on the
sample surface. The ejected particulate is collected in solution, which is aspirated
by conventional nebulisation and the signal response monitored. A series of
aqueous calibration standards are then used to determine the concentration of
analyte in solution. By measuring the total ablated mass directly or using an
internal standard the concentration of analyte in the original solid can be
calculated. The mechanism and technique is described further in the LASIL chapter.

This technique was originally developed by Belkov et al.\textsuperscript{50} and ICP-AES used to analyse the samples. The recoveries and subsequently calculated analyte concentrations differed significantly from the true analyte concentration. The technique was further improved by Muravitskaya et al.\textsuperscript{51}.

The technique utilises a large pot in which to house the sample, subsequently the volume of liquid required to immerse the sample is large and necessitates a long sampling time to generate a significant concentration of analyte in solution. The technique also requires the presence of an internal standard within the sample to calculate the mass of material liberated from the sample; fractionation must not occur between internal standard and analyte. Alternatively the remaining track or pit left on the sample can be measured directly, however this increase the total analysis time and necessitates extra instrumentation.
1.2.3 Laser Ablation Cell Design

1.2.3.1 Single Cell Designs

Historically laser ablation cells have been constructed such that the sample sits inside the cell, being completely encompassed by the cell and excluded from atmosphere. These cell designs rely on efficient gas flow dynamics throughout the entire cell volume to carry particulate from ablation site to the cell outlet. However, due to single gas inlets and outlets the transport efficiency of the cell varies spatially, such that particle residence times can vary considerably when the sample is ablated at different positions within the cell. Due to the large volume of the cell aerosol dispersion is large and sample dilution significant.

1.2.3.1.1 The Zircon Cell

The Zircon cell was developed by Horstwood et al.\textsuperscript{52} following the work of Bleiner and Günther\textsuperscript{53}. The cell volume is c.a. 3 cm\textsuperscript{3} and has a washout time to 10% peak maximum of 0.8 s for a repetition rate of 10 Hz, the cell is described in detail in Chapter 3.

1.2.3.1.2 The Rotary Cylindrical Cell

The rotary cylindrical cell described by Feldman et al.\textsuperscript{54} was designed to image protein spots on membranes. The cell was designed such that the membrane was placed upon a cylinder within the laser cell. A PTFE insert was then used to minimise the remaining sample volume, leaving a laser viewing gap along the axis of the gas inlet. The cylinder could be freely rotated so that ‘new sample area’ could be brought scrolled into the gap, allowing full imaging of the membrane with a total working volume of 11.3 cm\textsuperscript{3}. However, to ensure free rotation of the cylinder a gap between the PTFE block and it was designed. This resulted in an extra cell volume of 12 cm\textsuperscript{3}, defined as the cell dead volume. The cell washout time was reported as < 1 s and an overall reproducible peak area of 8%.

1.2.3.1.3 The Ablation Cell with less than 100 ms Washout Time

The cell design reported by Gurevich and Hergenröder\textsuperscript{55} minimised turbulent flow throughout the cell by adjusting the position of the gas inlet relative to the gas outlet and ablation position. A washout time of less than 100 ms to 10% peak maximum was reported when using a femtosecond laser pulse duration. However, when nanosecond laser pulse duration was used the washout time was reported as
30-40 ms to 37% peak maximum. Several large satellites were reported to have occurred in the transient data after the initial peak, increasing washout between 300 and 500 ms. These large satellites were due to the increased particle size distribution when using nanosecond pulse width, highlighting possible particle size temporal separation due to turbulent effects downstream of the cell, such as the mixing point of sample gas and makeup gas.

1.2.3.1.4 The Cyclonic Flux Cell
The cyclonic flux cell, reported by Monticelli et al.\textsuperscript{56}, is of a closed cylindrical shape of c.a. 21 cm\textsuperscript{3} volume. The gas inlet is placed tangentially to the cell wall whilst the gas outlet is placed in the centre of the cell, on-axis to the inlet. The gas flows into the cell contacts the wall on its cycle and then begins to spiral inwards towards the outlet. This spiralling does not lead to any turbulent flow within the cell. Cell washout time was reported to be 30 ms to 10% peak height. The transport efficiency was shown to be consistent throughout the cell, however the peak maximum and width showed spatial variation. As the sampling position was moved further from the outlet so the peak height reduced and the peak width increased.

All single cell designs discussed report connecting the cell to the ICP torch using tubing of conventional diameter (3.18 mm I.D.) and length typically 1-3 meters. Argon was mixed with the sample aerosol between laser cell outlet and ICP torch inlet to improve plasma stability, as helium was used as a sample gas within the cells.

1.2.3.2 Cell Within Cell Designs
Cell within cell designs are now being developed due to the significant variation in transport efficiency and variable aerosol dispersion relative to sampling position of single cell designs.

1.2.3.2.1 The HelEx/Laurin Cell
The HelEx cell was first used in 1998 by Eggins et al.\textsuperscript{57}, but was not described until 2005\textsuperscript{58}. The cell within cell design used a 2.5 cm\textsuperscript{3} inner cell to achieve a washout
time of 0.5 s. In 2009 the HelEx cell was described as the Laurin cell by Müller et al.\textsuperscript{59} The cell consisted of a funnel shaped inner cell of 1-2 cm\textsuperscript{3} volume, housed within a square outer cell of 380 cm\textsuperscript{3}. Th gas inlet was placed at the bottom of the cell. The sample gas then flowed into the funnel through openings in the top and bottom, entraining the ablation plume.

1.2.3.2.2 The Volume-Optional and Low-Memory (VOLM) Cell

The cell described by Liu \textit{et al.}\textsuperscript{60} used an existing cylindrical cell, 40 cm\textsuperscript{3} volume, as the outer cell and placed a cylindrical cell of much smaller volume 0.4 cm\textsuperscript{3} upon the sample surface, becoming the inner cell. A washout time of 0.45 s to 10% peak height was reported with 3.5-12.3 improvement in sensitivity compared to the outer cell operating as a single cell.

1.2.3.2.3 The Laminar Flow Reactor (LFR) Cell

A cell was designed and the flow dynamics within it investigated by computer simulation by Autrique \textit{et al.}\textsuperscript{61}. The cell was designed such that a tube, contained within a larger cell, surrounded the ablation site. The cell was later constructed and a LFR component added to reduce turbulent mixing of the sample aerosol with the argon makeup gas.\textsuperscript{62} The washout time of the cell was reported as 45 ms to 10% peak height and a half width of a single pulse peak of 16 ms.

The advantage of using a cell within cell design is that the critical gas flow, the flow local to the ablation site, has a consistent transport efficiency as the sample is moved rather than the sampling position.

1.2.3.3 In-Torch Ablation

Aerosol dispersion as a result of cell volume, transport volume and length or mixing induced turbulence is minimised by placing the ablation cell as close as possible to the plasma. This was realised by the development of in-torch ablation by Tanner and Günther\textsuperscript{37,63,64}. Samples were suspended from a recessed injector and the sample gas passed across the surface. The laser beam was focused through the torch onto the sample surface and the resulting ablation plume was free to expand into the plasma. When the in-torch ablation configuration was investigated using a ICP-QMS peaks from single shot laser ablation were said to be baseline
resolved with a 4 ms FWHM\textsuperscript{37}. Peak height and area were reported to vary with a 21% and 16% RSD respectively. The torch was then coupled to a ICP-TOFMS and the main bulk of the signal was reported to occur within the first 1-2 ms of the peak width, whilst the rest of the aerosol increased the total peak width to 30 ms\textsuperscript{63}. The peak area was reported to by 5.3% RSD between pulses, an improvement attributed to improved time resolution. However, this technique is slightly impractical as the torch needs to be removed to change sample, is limited in the sample size that can be analysed and shows spatially dependant transport efficiencies.

### 1.2.3.4 Limitations of cell designs

Current cell designs limit the practicality of laser ablation for bio-imaging and micro-particulate analysis. Single cell designs result in spatially dependant transport efficiencies due to non-uniform flow dynamics throughout the cell volume. This leads to a range of particle washout time’s dependant on where in the cell ablation occurred. This design limitation is impractical when imaging tissue sections as generation of pixelled information requires each laser ablation event to be resolved from the event before and after it. If the washout time varies then the laser repetition rate must also vary to match the washout time, otherwise pixel information will overlap and distort the image and impair resolution.

Using cell in cell designs offers consistent flow dynamics, as the critical flow is localised around the ablation site. However cell within cell designs have yet to reach aerosol dispersion characteristics similar to that reported for in-torch ablation. All cell designs rely on connective tubing to the ICP torch that leads to aerosol dilution, turbulent mixing effects and do not address turbulence within the plasma.
1.3 Aims

The aim of this project is to design and test a new LA-ICP-MS interface that will reduce the peak width of single laser ablation events and increase overall transport efficiency from the sampling area to the ICP-MS cone interface. The interface will be designed from a holistic view point, rather than treating the sample introduction as three separate areas: ablation cell, transport tubing and ICP torch. Designing a system that achieves these aims will significantly decrease analysis time (compared to current interfaces), increase sensitivity, improve the signal to noise ratio and ultimately improve the LOD.

Another aim of the project is to investigate a laser ablation calibration strategy that could be used for samples of a complex or unknown matrix by which existing strategies are impractical. The strategy will need to minimise waste volumes compared to those generated by conventional dissolution and dilution sample preparation. It also needs to contain the laser generated aerosol in a medium such that it lowers the risk compared to conventional laser techniques where the aerosol is transported from sampling sight to an instrument as an aerosol.

1.4 Objectives

The aim to design a new LA-ICP-MS interface will be achieved by:

- Designing a cell within cell system that effectively contains and captures the laser generated aerosol, minimises dilution of the laser generated particulate by reducing the volume of sample gas used and reduces turbulence from sampling point to injection of particulate in the ICP.
- The ablation cell will be integrated with the aerosol transport tubing and ICP torch to achieve a holistic approach rather than the current interchangeable systems. However, the design must be such that the new ICP torch and aerosol transport can be implemented with existing laser ablation cells.
- CFD modelling will be used to investigate the flow patterns within designed laser ablation cells. This can then be used to identify design features that result in gas flow trajectories that lead to efficient particle capture and transport. This significantly reduces the development costs compared to testing concepts through experimental trial and error.
• Experimental investigation of the LA-ICP-MS interface will then be conducted for resolved single pulse laser ablation events.

The aim to investigate a new LA-ICP-MS calibration strategy will be achieved by:

• Investigating the feasibility of using an existing calibration strategy, where the laser ablation mechanism occurs at a solid-liquid interface, such that the resulting laser plume is effectively captured within a surrounding solution.

• Improving this calibration strategy by minimising the volume of liquid used, thus minimising analysis time and potential loss of material.

• The technique will then be evaluated using one of the NIST glass standard reference materials to determine its applicability to sample types found in nuclear decommissioning whilst also allowing for comparison with existing techniques.
Chapter 2  Flow Simulation of a High-Speed, High-Efficiency, LA-ICP-MS Interface

2.1 Introduction

An LA-ICP-MS interface was developed to overcome limitations imposed by current designs, outlined in the introduction, by: decreasing cell washout time, minimising aerosol dilution and optimising analyte transport efficiency through both the ablation cell and the ICP. As discussed in the thesis introduction, existing LA-ICP-MS interface-design is focused primarily on improving the ablation cell to maximise transport efficiencies and thus minimise particle residence time within the cell. However, whilst recent research has achieved a reduction in residence time, the approach has ignored downstream effects (those after the ablation cell):

- The large transport tube volume (tube diameter and path length) from ablation cell to ICP torch causes temporal broadening of the ablation plume resulting in aerosol dilution
- Mixing of the helium sample gas with an argon make-up gas, to retain plasma stability through the central channel, results in a lower plasma temperature compared to pure helium, reducing thus particle processing efficiency
- The turbulent mixing of sample aerosol and carrier gas in the transport tubing causes further aerosol dilution and temporal distortion at the mixing point
- Recirculation of the aerosol in the ICP, notably at the base of the plasma, results in further temporal broadening and aerosol diffusion into the surrounding plasma gases

Although the transport tubing length and volume have been reported to have a small effect on the aerosol dispersion and density, the ablation cell volume having the most significant effect. This is true only when the ablation volume far exceeds that of the transport tubing volume; as ablation cells become more efficient, with respect to residence times, this volume becomes more critical.
Only recently has progress been made into improving sample aerosol and make-up gas mixing, by development of a laminar mixing component in the transport tubing in conjunction with a new cell design. Less development has been undertaken in improving the transport efficiency of aerosols generated by laser ablation through an ICP torch; most work has focused on external cooling of the torch, lowering total gas consumption by modifying gas flow and reducing the ICP torch size, or integration of the sample introduction system into the base of the torch for liquid aerosols on reducing total gas consumption or improving the flow of gas that makes up the plasma.

However, all developments so far have focused on improving one component at a time i.e. only the ICP torch or ablation cell. This approach improves the transport efficiency of each component as an individual variable. The new LA-ICP-MS interface described here, takes the approach that the ablation cell, transport tubing and ICP torch can all be better designed considering them as a whole; an integrated system to maximise transport efficiency.

2.1.1 Software

Solidworks (Educational Edition 2011-2012, 2011 SP5.0, NT CADCAM, Worcestershire, UK), 3-dimensional CAD software, was used to design, assemble and produce schematic drawings of components. The integrated rendering tool was used to generate photo-like representations of the assemblies.

The Flow Simulation (2011, 5.0. Build: 1747) tool-package in the Solidworks software was used to model the fluid flow through the Sniffer cell in a modified UP213 cell lid (see section 2.3 for description details). The flow simulation software is primarily used in engineering applications and as such cannot include conditions such as pressures induced by laser ablation plume formation or the incorporation of plasma conditions for the Dual Concentric Injector (DCI). Modelling was undertaken to verify that the design concept was operationally practical before committing to expensive fabrication, to give an estimate of particle residence times and in trouble shooting should the interface not deliver the expected outcome.
2.2 Dual Concentric Injector (DCI)

Figure 7 - Rendered CAD image of the DCI with torch and partial load coil for clarity

2.2.1 Design Brief
The DCI torch was designed such that it:

- Is compatible with use on an Element XR ICP-MS (Thermo Scientific, Bremen, DE), but can operate on other commercially available ICP-MS systems by modification of one component.
- Forms a plasma and sample channel in the same way as a standard ICP torch, thus producing a stable plasma.
- Minimises sample transport and gas volume.
- Allows one sample transport gas to be used, negating the need to mix/add any other gas to the sample aerosol.
- Extends the point at which the aerosol is injected into the plasma past the noisy/recirculating base of the plasma.
- Keeps the aerosol on-axis, relative to the orifice of the sample cone.
Enables pure He transport environment of the aerosol through the plasma, providing better particle processing capability compared to a helium-argon mix, see section 2.2.2 for details.

2.2.2 The DCI Design
The design here will be described in the context of coupling the DCI to a laser ablation cell (sample introduction in the form of an aerosol); a configuration for electrospray ionisation is being investigated.

As previously described in the introduction an ICP torch consists of three concentric tubes: the cool gas, auxiliary gas and sample-gas tubes. The inner most tube, the injector, is used to transport the sample aerosol to the plasma without prior mixing with plasma gases. The inner diameter of this tube can vary but is usually 3-4 mm at the base and tapered to between 0.8 and 2.0 mm at the tip (the point closest to the plasma).

The DCI, as shown in Figure 8, consists of four concentric tubes: the cool gas, auxiliary gas, sheath gas and sample gas (injector) tubes. The outer three tubes are from a commercially available semi-demountable torch (Glass Expansions, Melbourne, AU), with an exchangeable sheath-gas tube so that the tip diameter can be changed to between 0.8 and 2.0 mm. The injector is made from fused silica capillary and has an inner diameter much smaller than the conventional injector, typically 250 µm. This can be changed to suit application e.g. increasing the internal diameter to 500 µm to reduce back pressure within a laser ablation cell.
Sample transport tube - fused silica capillary
O.D. 360 µm, I.D. 250 µm, length typically 460 mm

Load coil
Cool gas tube
Auxiliary gas tube
Sheath gas tube
Custom PEEK injector adaptor
Cool gas
Auxiliary gas
Custom PEEK fittings
PFA T-piece
Macor centring component
3 mm OD, 0.5 mm ID borosilicate support
The injector is held concentric within the sheath-gas tube by a custom Macor® support (55% fluorophlogopite mica and 45% borosilicate glass, Ceramic Substrates and Components Ltd., Isle of Wight, UK). The component supports and holds the fused silica concentric to the outer injector. It is designed such that the sheath gas can pass to the plasma through 5 holes surrounding the central-smaller hole (injector support hole).

The injector is supported along the length of the torch by a borosilicate tube (0.5 mm I.D., 3 mm O.D., CM Scientific, Silsden, UK), which runs through a 1/8” NPT fitting and is secured by an o-ring. This seals the torch and allows the tube to slide back and forth, extending the injector past the sheath-gas tube (the injector tube in the standard torch) and into the base of the plasma or retracting it back in to it.

Figure 9 shows a schematic drawing of the injector tip protruding past the sheath-gas tube. Dimensions are given for the distances from the sheath-gas tube to the auxiliary tube and to the load coil (distances have been estimated from the setup used, but are typical of torch-load coil configurations). The 0 mm distance, parallel to the tip of the sheath gas tube, is used as a reference point for all DCI extensions and retractions. From this, the penetration depth of the injector relative to the base of the plasma can be inferred, assuming the plasma begins at the start of the first turn in the load coil. Extending the injector towards the plasma is favourable as recent modelling of an ICP has shown that there is a significant recirculation of the sample gas at the first turn in the load coil due to the formation of an eddy.
region\textsuperscript{66}. This is especially true when using argon at low flow rates and becomes more prevalent if the helium mole fraction is increased, at the same flow rate\textsuperscript{65}. The modelling performed was for a free standing ICP, at low injector gas flows (0.2-0.7 Lmin\textsuperscript{-1}). At higher flow rates a larger number of sample gas path lines passed straight through the plasma and thus reducing the eddy region, but not removing it completely.

![Figure 9 – Schematic drawing of the DCI extending past the sheath tube. Dimensions of the distance between the sheath and auxiliary tube and the load coil are given in mm.](image)

In a conventional torch significant mixing of the sample aerosol, with the auxiliary gas, occurs almost immediately after leaving the injector\textsuperscript{65,68}. The DCI allows the sample to be injected into the plasma past this turbulent mixing phase.

In early DCI designs, the fused silica capillary was 40 mm in length and was held in place by a custom Macor component. This component was glued to the end of the borosilicate tube that tapered the 0.5 mm I.D. down to the 0.25 \(\mu\)m I.D. of the fused silica. The borosilicate tubing was then connected to a conventional laser ablation cell or to the outlet of the Sniffer (see section 2.3 for description of this component). However, after initial experimentation is was quickly realised that a complete single transport tube would be more practical and efficient. So the injector was extended back to the ablation point so that it also became the transport tubing. Where this transport tubing meets the micro laser ablation cell outlet is denoted as the DCI inlet. The total injector length can be varied to suit the application but importantly it is a single transport tube without deviation, connectors or changes in internal diameter. This ensures the sample transport path is a straight tube with minimal curvature reducing turbulence and thus potential particle-wall interactions.
The injector in the standard torch is used as the sheath-gas tube in the DCI. The sheath gas is used to achieve punch through of the plasma (the point at which a sample-channel is established through the plasma) with argon used here as the sheath gas. By using this gas to maintain plasma stability and the sample channel, the gas flow from the laser cell can be much lower and does not require prior mixing with a make-up gas. This reduces any particle loss by gas-mixing related turbulence and dilution of the sample by a transport gas.

The use of pure helium as a transport environment of the aerosol through the plasma is advantageous as it shortens the coupling regions of the outer-boarders of the plasma such that the volume where power is coupled becomes smaller, resulting in a higher electron density in these regions for the same power and an increase in overall temperature. This along with the higher thermal conductivity of pure helium than compared with argon-helium mixture increases the temperature within the centre of the plasma and provides more efficient particle processing. Helium also increases the effective plasma length.

It is also important to note that although helium provides a better aerosol environment within the ICP, better plume capture and a faster transport velocity in tubing, it causes particle size related temporal broadening within the tubing due to a more complex flow structure. This is a potentially limiting factor when residence times within the system are short, as particle residence time within a cell decreases so the residence time within the transport tubing becomes critical. However, provided the transport distance is limited the effect is negligible.

The DCI has been developed for use with the Sniffer cell as described in the next section. However, due to its simplicity the injector can easily be configured to work with existing ablation cells as shown in section 3.4.
2.3 The Sniffer Cell

![Figure 10 – Rendered CAD image of the sniffer cell, partially transparent for clarity, floating above a glass sample](image)

2.3.1 Design brief
The Sniffer cell was designed such that it:

- Allows transport of particulate, efficiently, at low flow rates.
- Ensures localised capture of the ablation plume and minimises plume expansion.
- Accommodates sample sizes up to 25 mm by 25 mm.
- Keeps the cell outlet in the same physical space by moving the sample rather than the cell, ensuring consistent transport efficiency.
- Maintains a straight path for transport tubing (DCI fused silica) from cell to torch.
- Minimises potential eddy regions.

2.3.2 Cell Design
A cell within cell design was used to accommodate a large sample size whilst achieving capture of the ablation plume. This design localises the critical flows, those that most affect particle transport efficiency, to a small inner cell.
surrounding the ablation site whilst containing the sample in a larger outer cell; 
that excludes the atmosphere.

2.3.3 The Inner ‘Sniffer’ Cell

Figure 11 – A) Schematic drawing of the Sniffer cell (the inner cell) and B) 
an isometric representation of the Sniffer cell, partially transparent for 
clarity
The schematic drawing in Figure 11A shows the inner cell, described here after as the Sniffer cell, floating above a sample surface. The Sniffer is manufactured from one piece of Macor® (custom design, 55% fluorophlogopite mica and 45% borosilicate glass, Ceramic Substrates and Components Ltd., Isle of Wight, UK), measuring 10 mm x 3 mm x 3 mm with a 1.5 mm radius at one end. A 0.8 mm hole lies concentric to this radius, through which a laser beam is focused onto the sample surface. The top of this laser port has a radius of 0.25 mm to minimise gas turbulence. The area below this laser port is the ablation area and denoted here as the viewing area. The incorporation of an open laser port within the Sniffer, as shown later, provides a positive flow into the micro-chamber along the laser axis ensuring that gas flow does not become trapped and form eddies within the port, as would be the case if it were sealed with an optical window 62.

A 2 mm x 1 mm cut-out into the base extends 2.5 mm deep into the rounded end; ending in a 1.1 mm radius, forming a micro-chamber of c.a. 0.005 cm³, see Figure 11B. Ablation occurs within this micro-chamber, isolating it from the larger surrounding chamber (the outer cell) effectively capturing the particle plume. The two radii either end of the micro-chamber encourage equal flow to the ablation site, ensuring symmetrical transport efficiency within the ablation plume. By reducing the effective cell volume the flow-velocity within the micro-chamber is much higher than in the outer cell. Increasing the localised flow-velocity allows a much lower volume of gas to be used whilst maintaining fast cell washout, thus reducing aerosol dilution.

The outlet of the micro-chamber is a 0.5 mm hole with a 0.1 mm round, in which the DCI injector lies concentrically, at the edge of the micro-chamber, see Figure 11A. This feature means the Sniffer outlet and the DCI inlet can be 1.1 mm from the ablation site, minimising the transit time and distance of the particulate within the cell and reducing plume broadening. However, it proved difficult to fix the DCI inlet at this position and it often lay recessed in the Sniffer outlet such that it was between 2-5 mm from the ablation site.

The Macor component is supported by a stainless steel tube (0.5 mm I.D., 0.81 mm O.D., Coopers Needle Works Ltd., Birmingham, UK), such that it floats above the sample. This tubing also forms a support and fixing point for the fused silica capillary.
2.3.4 The Outer Cell

2.3.4.1 Modified UP213 Cell Lid

In the first design iteration, a UP213 standard cell lid was modified to house the sniffer, this is referred to as the alpha outer cell, see Figure 12.

Figure 12 – A cut schematic drawing of the Sniffer Cell housed in a modified UP213 cell lid, the alpha outer cell

A custom widow clamp supports (custom design, stainless steel, Ceramic Substrates and Components Ltd., Isle of Wight, UK) an optical window (fused silica, Ø25.0 mm, thickness 3.0 mm, AR coated both sides for anti reflection at 213nm 0° angle of incidence, CVI Melles Griot, Isle of Man, UK) and is sealed by o-rings. The Sniffer sits within a recess of the window clamp, fixed by a stainless steel tube, such that the laser port lies 3 mm off concentric relative to the optical window. The sniffer is 4 mm off-axis relative to the inlet due to constraints when modifying the lid.

The sample sits under the Sniffer in the recess of a sample tray (custom design, PTFE, Proto Labs Ltd., Shropshire, UK). The sample tray is supported by two stainless steel tubes that allow it to move towards or away from the gas inlet. The sample height can be varied to between 0 and 0.8 mm from the bottom of the Sniffer, by use of stainless steel spacer disks.

With the Sniffer, sample, sample tray and optical window in place the inner volume of the outer cell is c.a. 17 cm³.
The modified UP213 cell was used to evaluate DCI-Sniffer cell performance.

2.3.4.2 Enterprise Cell

As part of another PhD project, an improved outer cell has been designed by Amy J. Managh\textsuperscript{70}. This purpose built cell has also been used to evaluate DCI-Sniffer performance as each component was designed using the CAD software and thus the solid bodies within the flow simulation closely match those used in the physical setup. This was not the case for the modified UP213 cell lid, where the physical cell was created from spare parts and the solid bodies in the flow simulation software were shapes representing those parts.

The cell, referred to as the Enterprise Cell and shown in Figure 13, has an improved internal geometry and allows movement of the sample via magnetic coupling of the sample stage to an XY manipulator. The sample stage is housed within the outer cell.

The outer cell volume, c.a. 117 cm\textsuperscript{3}, is much larger than the modified UP213 cell lid to accommodate larger sized samples. The design also minimises turbulence around the Sniffer induced by edges of other components that lie in the path of the gas flow, smoothing the flow around the Sniffer.

Figure 13 - Reproduced schematic drawing of the Enterprise Cell, the new outer cell for the Sniffer\textsuperscript{70}
The Sniffer sits on axis to the inlet c.a. 0.1 mm above the sample surface, held in place by a bar that extends across the cell, perpendicular to the inlet. The Sniffer-sample distance can be varied between 0 and 0.2 mm by placing stainless steel spacer disks under the sample or by placing spacers between the Sniffer and bar. Fixing the Sniffer to the bar, rather than suspending it by a stainless steel tube, ensures the Sniffer is parallel to the sample surface and cannot freely rotate.

2.3.5 Total Transport Volume

When coupled to the DCI the Sniffer the total transport volume, from ablation site to injection in the ICP, is much smaller than conventional cell. For example the Zircon cell, described in a later chapter, is a small volume ablation cell c.a. 3.0 cm$^3$ that connects to a conventional ICP injector c.a. 2.0 cm$^3$ (2.0 mm injector) via Tygon tubing (1/8” I.D., typical length 200 cm) c.a. 15.8 cm$^3$ to give a total transport volume of 20.8 cm$^3$, the cell representing 14% the total volume. Compared to the Sniffer cell volume of 0.005 cm$^3$ and transport tubing (250 µm I.D., typical length 40 cm) c.a. 0.020 cm$^3$ to give a total transport volume of 0.025 cm$^3$, where the cell represents 20% of the total volume.
2.3.6 Modelled Gas Flow for the Modified UP213 Cell Lid

The PC hardware used to simulate the flow is given in Table 1.

<table>
<thead>
<tr>
<th>Hardware</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processors</td>
<td>2 x Intel(R) Xeon(R) CPU E5640 (2.67GHz )</td>
</tr>
<tr>
<td>Memory</td>
<td>16367 MB / 8388607 MB</td>
</tr>
<tr>
<td>Operating system</td>
<td>Windows 7 Service Pack 1 (Build 7601)</td>
</tr>
<tr>
<td>CPU speed</td>
<td>2661 MHz</td>
</tr>
</tbody>
</table>

The CAD geometry from Solidworks is used to compute the volume of interest (an internal or external flow relative to the components) and produces a rectangular computational domain encompassing solid and fluid regions. The fluid region is the internal volume of the cell through which the helium gas flows and the solid region is the components.

The computational domain is automatically divided into cubes of finite volume by intersecting planes, resulting in a mesh. Further refinement of the mesh at solid-fluid boundaries results in smaller volume cubes to more accurately predict and model the flow at these regions. Small and narrow features such as the injector tubing are also refined. These cubes are defined as fluid cells (those that occupy only fluid volume), solid cells (those that occupy only solid volume) and partial cells (those that occupy fluid and solid volume).

Navier-Stokes equations are then used to solve the movement of the fluid through these cells. The formulations are of mass, momentum and energy conservation for fluid flows and are used within a Cartesian coordinate system within the cells. Discrete terms within these cells are defined e.g. fluid velocity, fluid density, buoyancy (gravitational factor), thermal enthalpy and the diffuse heat flux. The viscous stress and Reynolds stress factors are also calculated as products of dynamic and turbulent eddy viscosity coefficients as well as the turbulent kinetic energy and dissipation. Laminar and turbulent flow can be calculated using dynamic viscosity and the density of the fluid to calculate the diffusion of momentum (dispersion), which when combined with velocity and length is used to calculate the Reynolds number and thus how the fluid flows through that cell.
Numerical solutions are then used by integrating the equations over a cell and approximating these solutions to a cell centre value. This value is then applied to the faces of the adjoining cells to propagate the flow through the model.

Particle tracking can be performed once the flow has been calculated. Particles are injected into the fluid flow from a sketch point or component face and their trajectories and velocity can be calculated.

2.3.6.1 The Model

The CAD geometry used in the flow simulations is shown as a 2-dimensional representation in Figure 12 and a 3-dimensional CAD representation in Figure 14. The Sniffer was placed on-axis relative to the cell gas inlet as it was believed that this would generate optimum flow conditions. Two simulations were performed to investigate the effect of Sniffer-sample surface distance on particle residence time. The two distances were set at 50 and 200 µm.

A fused silica tube (250 µm I.D., 350 µm O.D. and 300 mm long) was placed recessed in the Sniffer outlet 4.6 mm from the centre point of the laser port, to mimic the DCI inlet and tubing in an experimental setup. This position is not optimum and the DCI inlet should be placed as close to the ablation site for optimum performance, however this was not practically achievable in this setup due to build constraints and costs.

The stainless steel tubing used to support the sample tray was removed to reduce model complexity and thus simulation time.
Figure 14 – 3-dimensional CAD image of the Sniffer and modified UP213 cell lid, the model is semitransparent and the optical window clamp removed for clarity.

The mesh refining criteria, physical features and thermodynamic conditions are given in Table 2. These inputs are used to determine the accuracy of the mesh i.e. the number of cubes around small features and solid-fluid interfaces, and the physical properties of the model.

The software automatically refines the mesh to generate a flow region that predicts the fluid flow through the model whilst minimising simulation time. However, for regions where there is a narrow gap (relative to the rest of the model) between components e.g. Sniffer-sample gap, or where the curvature of a component piece is significant, the automatic refinement fails and does not accurately predict the flow. As such the critical conditions: small solid features refinement, curvature refinement, characteristic number of cells across a narrow channel and minimum height of narrow channels, must be manually investigated to solve the flow simulation with a higher degree of accuracy. In Table 2 values of 2, 2, 2 and 0.5 mm for the respective critical conditions resulted in a single cell crossing two solid boundaries between the sniffer-sample gap resulting in a slower flow rate than that predicted when at least three cells between components was used.
Table 2 – Flow simulation mesh refining criteria, physical features and thermodynamic conditions

<table>
<thead>
<tr>
<th>Refinement criteria</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small solid features refinement level</td>
<td>5</td>
</tr>
<tr>
<td>Curvature refinement level</td>
<td>5</td>
</tr>
<tr>
<td>Curvature refinement criterion</td>
<td>0.800 rad</td>
</tr>
<tr>
<td>Tolerance refinement level</td>
<td>4</td>
</tr>
<tr>
<td>Tolerance refinement criterion</td>
<td>0.050 mm</td>
</tr>
<tr>
<td>Refine fluid cells</td>
<td>On</td>
</tr>
<tr>
<td>Level of refining fluid cells</td>
<td>2</td>
</tr>
<tr>
<td>Refine partial cells</td>
<td>On</td>
</tr>
<tr>
<td>Level of refining partial cells</td>
<td>4</td>
</tr>
<tr>
<td>Refine solid cells</td>
<td>Off</td>
</tr>
<tr>
<td>Advanced narrow channel refinement</td>
<td>On</td>
</tr>
<tr>
<td>Characteristic number of cells across a narrow channel</td>
<td>5</td>
</tr>
<tr>
<td>Narrow channels refinement level</td>
<td>5</td>
</tr>
<tr>
<td>The minimum height of narrow channels</td>
<td>0.050 mm for 200 µm</td>
</tr>
<tr>
<td></td>
<td>0.020 mm for 50 µm</td>
</tr>
<tr>
<td>The maximum height of narrow channels</td>
<td>Off</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical features</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravitational effects</td>
<td>In Y-plane at 9.8 m/s^2</td>
</tr>
<tr>
<td>Flow type</td>
<td>Laminar and turbulent</td>
</tr>
<tr>
<td>Default roughness</td>
<td>10 µm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermodynamic conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Static Pressure</td>
<td>101325 Pa</td>
</tr>
<tr>
<td>Temperature</td>
<td>293.2 K</td>
</tr>
</tbody>
</table>

Helium was used as the simulated fluid and injected normal to the inlet, shown in Figure 14, at a flow rate of 120 mlmin⁻¹. The flow was set to be initially turbulent with a pressure and temperature of 101325 Pa and 293.2 K respectively, and was not fully developed before injections. This was modelled as initial experimentation limited flow rate to 120 mlmin⁻¹, at this flow rate the maximum safe outer cell pressure of 10 P.S.I. was reached. Higher flow rates have been modelled but
showed distorted flow trajectories within the micro-chamber. A static pressure outlet was placed at the end of the DCI (300 mm opposite the inlet) and set at an initial pressure and temperature of 101325 Pa and 293.2 K respectively.

### 2.3.6.2 200 µm Gap Distance Between Sniffer and Sample Surface

The final number of cubes used in the mesh to compute the flow simulation is given in Table 3.

<table>
<thead>
<tr>
<th>Table 3 – Final mesh computation for 200 µm Sniffer gap distance</th>
<th>Number of cubes and their characterisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total cells</td>
<td>3279988</td>
</tr>
<tr>
<td>Fluid cells</td>
<td>1281183</td>
</tr>
<tr>
<td>Solid cells</td>
<td>913758</td>
</tr>
<tr>
<td>Partial cells</td>
<td>1085047</td>
</tr>
</tbody>
</table>

A 2-dimensional representation of the computed mesh in the y-plane (see Figure 14 for plane reference) for the outer and Sniffer cell is shown in Figure 15A and in the z-plane in Figure 15B. As can be seen by the number of smaller rectangles in magnified section of Figure 15A) there is a high level of refinement around the sharp points at the Sniffer entrance, as is the refinement within the injector tube. The same can also be seen in the z-plane, magnified section of Figure 15B, where the same level of refinement is used for the gap between Sniffer and sample surface. This results in a more accurate prediction of flow in these critical areas. More accurate predictions are required at sharp edges and small gaps as this is where the gas will experience change in direction, turbulence and higher pressures.
Figure 15 – Two cut plots showing the 2-dimensional computed mesh for the outer cell and Sniffer cell at a 200 µm gap distance. A) the Y-plane and C) in the Z-plane, both plots have are accompanied with magnified pop-outs centred around the Sniffer for clarity.
The gas flow trajectories from the inlet (point of gas injection) are shown in Figure 16A and B. The trajectories depict the most likely paths for the main bulk of gas flow from the inlet.

**Figure 16** – Gas flow trajectories colour scale truncated from 0 to 0.1 ms⁻¹, A) viewed in the Y-plane with a magnified view of the Sniffer and B) an isometric cut-view with outer cell removed for clarity.
A large proportion of the fast flowing gas (that greater than 0.5 ms\(^{-1}\)) from the centre of the gas inlet deviates slightly when entering the main volume of the outer cell, Figure 16A, but then converges back to the micro-chamber inlet. Flows off-centre from the inlet deviate further, spreading around the outer cell walls and converge back to the micro-chamber by travelling around to the entrance of the micro-chamber or by flowing between the Sniffer and sample surface and entering from underneath the Sniffer.

Computing power limits the number of trajectories that can be computed and thus visualisation of the minor flows around the Sniffer consumes larger amounts of computer memory. However, by selecting the face of a component, gas flow trajectories in contact with that face can be investigated and their start and end position traced. This enables visualisation of minor gas flow otherwise not shown when trajectories are made to emanate from the gas inlet. This has been used to generate the images shown in Figure 17, Figure 18 and Figure 19 where the flow trajectories have been generated from the bottom of the Sniffer, through the laser port and around the edges of the micro-chamber respectively.

![Image](image.png)

**Figure 17** – Gas flow trajectories that contact the bottom of the Sniffer, truncated colour scale from 0 to 1 ms\(^{-1}\), sectioned model and angled view in the Z-plane.

The flow entering the Sniffer from underneath, near the micro-chamber outlet, can be seen more clearly in Figure 17. Although not shown, these flows start on the outer edges of the gas inlet of the outer cell, travelling around the outer cell walls.
This flow is important, as shown later from particle simulations it lifts the ablated particulate into the micro-chamber outlet. This ensures the gas flow does not carry particulate out of the micro-chamber and into the outer cell for recirculation and minimises particle interaction with micro-chamber walls.

The gas flow down the laser port, see Figure 18, travels at *c.a.* 0.2 ms⁻¹ and provides a downward positive pressure into the micro-camber. From this it can be inferred that this pressure and flow hinder ablation plume expansion and keep particulate within the micro-chamber. More complex modelling, beyond the capability of this software, would be required to confirm this and would need to include plasma expansion and particle formation conditions.

![Figure 18 – Gas flow trajectories that contact the walls of the laser port, truncated colour scale from 0 to 1 ms⁻¹, sectioned model and viewed in the Z-plane](image)

The gas flow along the micro-chamber walls, see Figure 19, increases from around 0.2 to 0.7 ms⁻¹ when moving from the micro-chamber inlet to the outlet. It has been postulated that this flow and its velocity also hinder ablation plume expansion and minimise sample contact with the walls of the Sniffer and helps to retain particulate within the micro-chamber.
The gas velocity within the micro-chamber, see Figure 20, ranges from 0.8 ms$^{-1}$ at the entrance to 10 ms$^{-1}$ at the micro-chamber outlet. This increase in velocity ensures fast washout of the micro-chamber. The viewing area, the ablation site, has a much smaller velocity distribution between 0.8 and 1.5 ms$^{-1}$. As well as ensuring a fast washout (as the distance to the Sniffer outlet is roughly 1 mm from the centre of the viewing area) it also minimises the differences in spatially related washout, giving a more uniform response across the potential ablation area, as is shown with particle simulations later.

The sample surface and thus sample tray are above the centre point of the gas inlet. The effect this has on the gas flow is highlighted in Figure 20B. Although there is a uniform response in the Z-plane within the viewing area of the micro-chamber, zones above this, closer to the laser port, show a varied response. The flow velocity prior to the micro-chamber inlet has a fast region of gas that curves from the top of the outer cell and down into the entrance.
As well as visualising trajectories and velocities the average velocity at the end of the fused silica tubing (representing the DCI) was calculated to be 118.7 m s\(^{-1}\). A maximum gas velocity of 220 m s\(^{-1}\) was calculated at the centre of this tube.
2.3.6.2.2 200µm Sniffer-Sample Gap – Particle Trajectories and Residence Times

Two particle injection studies were performed for a 200 µm gap, to investigate flow trajectories, residence times and velocity. The first particle injection was positioned within the laser accessible area of the micro-chamber; that visible through the laser port and described here as the viewing area. For details of injection point number and relative position see Figure 21.

Figure 21 – Injection point position by number within the viewing area

Particles were injected into the fluid flow from the sample surface to investigate particulate trajectories when formed close to the sample surface due to limited plume expansion by increased cell pressure. The plume radius under these conditions is unknown; particle injection from the sample surface was employed as a worst case scenario. Glass was specified as the particle material, as NIST glass is a common test material for laser ablation, (mass flow rate 1.23x10⁻¹⁰ kgs⁻¹) for three particle sizes: 10, 100 and 1000 nm diameter. The particles were not given an initial velocity as modelling of plume expansion dynamics has not been performed for these conditions and thus initial speed and direction are unknown. Wall conditions were set to ideal reflection.
Figure 22 – Particle injection into fluid flow within the micro-chamber for a 200 µm gap distance, A), Y-plane, 0-0.4 ms$^{-1}$, B) Y-plane, 0-20 ms$^{-1}$ and C) Z-plane, 0-0.4 ms$^{-1}$
It is clear in Figure 22A and B that the simulated particle trajectories for all particle diameters converge towards the centre of the micro-chamber outlet and begin to lift from the sample surface, Figure 22C, after leaving the viewing area. These trajectories agree with expected paths inferred from gas flow modelling in section 2.3.6.2.1. The lift of the particles into the outlet highlights the role and importance of the counter gas flow, Figure 17, between the Sniffer and sample lifting the sample into the micro-chamber outlet.

Figure 22A shows that the particle velocity from all injections points within the viewing area was around 0.2 ms\(^{-1}\), by the time the particles reach the micro-chamber outlet, Figure 22B, the velocity had increased to between 7.7-9.2 ms\(^{-1}\).

<table>
<thead>
<tr>
<th>Position</th>
<th>Residence time (ms)</th>
<th>Average velocity (ms(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>9.7 9.4 7.1</td>
<td>31.4 32.4 42.9</td>
</tr>
<tr>
<td>#2</td>
<td>10.3 10.0 7.7</td>
<td>29.6 30.5 39.6</td>
</tr>
<tr>
<td>#3</td>
<td>11.0 10.7 8.4</td>
<td>27.7 28.5 36.3</td>
</tr>
<tr>
<td>#4</td>
<td>8.8 8.5 6.1</td>
<td>34.6 35.8 49.9</td>
</tr>
<tr>
<td>#5</td>
<td>10.2 3.9 7.7</td>
<td>29.9 - 39.9</td>
</tr>
<tr>
<td>#6</td>
<td>9.8 9.5 7.2</td>
<td>31.1 32.1 42.3</td>
</tr>
<tr>
<td>#7</td>
<td>9.6 9.4 7.2</td>
<td>31.7 32.4 42.3</td>
</tr>
<tr>
<td>#8</td>
<td>10.2 10.0 7.9</td>
<td>29.9 30.5 38.6</td>
</tr>
<tr>
<td>#9</td>
<td>10.1 3.7 7.6</td>
<td>30.2 - 40.1</td>
</tr>
<tr>
<td>#10</td>
<td>2.8 8.9 6.7</td>
<td>- 34.2 45.5</td>
</tr>
<tr>
<td>#11</td>
<td>9.1 8.8 6.5</td>
<td>33.5 34.6 46.9</td>
</tr>
<tr>
<td>#12</td>
<td>10.2 3.8 7.6</td>
<td>29.9 - 40.1</td>
</tr>
<tr>
<td>#13</td>
<td>2.8 2.8 6.6</td>
<td>- - 46.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>9.9 9.5 7.3</th>
<th>30.9 32.3 42.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.D</td>
<td>0.6 0.7 0.6</td>
<td>1.9 2.3 3.8</td>
</tr>
</tbody>
</table>

Shaded values are particles that did not reach the DCI outlet (end of fused silica)

*Averages and standard deviation are calculated omitting shaded values*

- Average velocity not calculated
From modelling the particle trajectories the residence time (the time taken to reach the DCI outlet from injection point), path length and average particle velocity are known, see Table 4. Most of the particles reached the DCI outlet within the total gas flow simulation time and their fate listed in the simulation as ‘opening’, meaning they escaped. Those that did not, particles number 10 and 13 at 10 nm diameter and number 5, 9, 12 and 13 at 100 nm diameter (shaded grey), most likely were caught in a turbulent region of the flow. Their fate was listed as ‘maximum steps in cell’, and is an indication that the equations pertaining to the flow in a particular cell caused the particle to remain within it for an excessive number of steps beyond the end of the simulation. Once a maximum number of steps within a given cell has been reached the particle is determined to be stationary and thus it’s transit through the model complete. The path length of these particles, c.a. 4 mm, suggests that they stopped at the point where the DCI inlet meets the gas flow. At this point the DCI presents a flat face to the gas flow (due to its thickness). As the gas velocity around the edges of the Sniffer outlet are much slower than the centre, see Figure 20A, this flat face will cause the formation of eddy regions, see Figure 23, these swirls can trap particulate and in practice would result in a longer residence time and a longer tail to signal response.

The initial injection point of these particulate was off-centre, relative to the laser port, and towards the micro-chamber outlet. This indicates that there may be the presence of two strong flows, one in through the entrance of the micro-chamber and the other from between the Sniffer and sample gap, which creates a region with poor or turbulent initial conditions that affects the 100 nm particle most as smaller particles travel quickly so the time within poor flow regions (turbulent) is negligible and the larger particles are affected less by deviations in the flow.
The residence time for all three particle diameters that reached the DCI outlet ranges between 6.1 and 11 ms, with a uniform distribution across the viewing area within particle diameters; 6.1, 7.3 and 8.9% R.S.D. for 10, 100 and 1000 nm respectively.

As expected particle 3, the furthest from the micro-chamber outlet, had the longest residence time of 11 ms at 10 nm particle diameter. However, particle 4 had the shortest residence time of 6.1 ms for a particle diameter of 1000 nm. The ablation distance from micro-chamber outlet has a minimal but noticeable effect on particle residence.

The average particle residence time for different particle diameters is similar for 10 and 100 nm particle diameters, 9.9 and 9.5 ms respectively, but is much shorter for the 1000 nm diameter particles at 7.3 ms. This is an indication that the smaller particle diameters experienced a small amount of turbulence along their path that increased their residence time. This mostly likely occurred at the point where the DCI inlet meets the Sniffer outlet.

The average velocity of each particle was calculated from the residence time and the path length, Table 4. As expected, for a constant path length the particles with the shortest residence time gave the fastest average velocity. However, this average velocity includes the velocity of the particle at all points along the path and the dynamics of what occurs as the particles leave the micro-chamber or cross from the Sniffer outlet into the DCI inlet are not characterised.
A second particle injection was used to investigate the effect on particle residence time and trajectories when particles began their transit to the DCI from outside of the micro-chamber; simulating as if the plume expands outside of the micro-cavity.

The position of injection point for particles outside the Sniffer is shown in Figure 24A. The same particle conditions and diameters were used for this injection as for those performed within the viewing area.

**Figure 24** – Particle injection outside the Sniffer for a 200 µm gap: A) injection point position by number outside the sniffer in the Y-plane and B) angled Z-plane, both colour scales 0-1.0 ms$^{-1}$
Particles that were injected on-axis to the micro-chamber outlet, numbers 1, 2, 4, 6 and 9, followed a straight line path into the micro-chamber and then curved up into the outlet, Figure 24B. All three particle diameters at these injection locations reached the DCI outlet. For positions 1, 2 and 4 the 1000 nm particle diameter had the shortest residence time, at position 9 they were roughly equal and at position 6 the 1000 nm particle had a much longer residence time than 10 or 100 nm, see Table 5. As can be seen in Figure 16, the position of the sample surface is off-axis to the gas inlet, causing the flow trajectories to curve up before sweeping back down on the surface. This causes low gas velocity around the edge of the sample leading to particle diameter related differences in transport efficiency.

Table 5 – Particle residence time and average velocity from particle injection outside the Sniffer for 200 µm gap

<table>
<thead>
<tr>
<th>Particle Ø</th>
<th>10 nm</th>
<th>100 nm</th>
<th>1000 nm</th>
<th>10 nm</th>
<th>100 nm</th>
<th>1000 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#1</td>
<td>15.3</td>
<td>14.9</td>
<td>13.6</td>
<td>20.0</td>
<td>20.5</td>
<td>22.5</td>
</tr>
<tr>
<td>#2</td>
<td>120.6</td>
<td>120.3</td>
<td>118.1</td>
<td>2.5</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>#3</td>
<td>297.6</td>
<td>297.8</td>
<td>294.3</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>#4</td>
<td>60.5</td>
<td>60.2</td>
<td>57.9</td>
<td>5.1</td>
<td>5.1</td>
<td>5.3</td>
</tr>
<tr>
<td>#5</td>
<td>293.9</td>
<td>294.1</td>
<td>302.2</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>#6</td>
<td>889.5</td>
<td>893.4</td>
<td>1016.5</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>#7</td>
<td>2193.1</td>
<td>2210.3</td>
<td>2639.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>#8</td>
<td>2126.6</td>
<td>2133.3</td>
<td>2451.7</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>#9</td>
<td>3104.8</td>
<td>3104.5</td>
<td>3104.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Shaded values are particles that did not reach the DCI outlet (end of fused silica)
- Average velocity not calculated

Particles injected perpendicular to the micro-chamber outlet and on the outer edge of the sample deviated away from the outlet towards the opening of the micro-chamber, their path took a sharp turn once the edge of the opening was reached. The flow velocity perpendicular to the micro-chamber outlet is much slower than on-axis. Only one particle from these positions, number 8 at 10 nm, reached the DCI outlet. The fate of particles 7 and 8 at other diameters returned as ‘maximum steps in cell’, with the maximum path length again ending at the point where the Sniffer outlet meets the DCI inlet. It is believed the eddy regions, previously
described, were the cause of the particle fate. Figure 25 shows the particle trajectories as ribbons. Although not clear, some of the ribbons at the Sniffer outlet-DCI inlet point curl around themselves, an indication of an eddy point.

![Particle paths curl back on themselves, spiralling in an Eddy](image)

**Figure 25 – Particle injection outside of the Sniffer for a 200 µm gap**

Particles injected perpendicular to the micro-chamber outlet and half way between sample diameter and centre point again deviated but flowed under the Sniffer to enter the micro-chamber. Only the 1000 nm particles at positions 3 and 5 did not reach the DCI outlet.
2.3.6.3 50 μm Gap Distance Between Sniffer and Sample Surface

Flow simulation conditions were set the same as for 200 μm gap distance, only the minimum channel height was changed from 0.05 mm to 0.02 mm. The final mesh generated to simulate the flow was similar to that for a 200 μm gap, but the number of cells between the Sniffer and sample were reduced, see Table 6.

<table>
<thead>
<tr>
<th>Number of cubes and their characterisation</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total cells</td>
<td>3369889</td>
</tr>
<tr>
<td>Fluid cells</td>
<td>1224572</td>
</tr>
<tr>
<td>Solid cells</td>
<td>1059748</td>
</tr>
<tr>
<td>Partial cells</td>
<td>1085569</td>
</tr>
</tbody>
</table>

The simulated gas flow trajectories follow the same pattern as shown for the 200 μm gap, there being a more dominant flow through the entrance of the micro-chamber and less entering from the sides and between the Sniffer and sample.

![Figure 26 – Gas velocity cut plots in A) truncated colour scale 0-20 ms⁻¹ cross-section in the Z-plane, velocity contour arrows included and C) in the Y-plane truncated colour scale0-2 ms⁻¹](image-url)
When visualising the gas velocities as a cut-plot at a 50 µm gap, see Figure 26, significant differences can be seen from the velocities at a 200 µm gap. Viewing in the z-plane, Figure 26A, shows that the velocities exceeding 1.0 ms$^{-1}$ now extends from the micro-chamber entrance to outlet; a faster average gas flow within the chamber, across the sample surface and down the laser port. However, the flow velocity is no longer consistent, parallel to the sample surface, as slower region can be seen at the start of the viewing area.

The flow velocity exceeding 5.0 ms$^{-1}$, see Figure 26B, extends further into the micro-chamber from the outlet. The flow around the sharp edges of the micro-chamber entrance has also been altered, as the faster velocities are stronger relative to the gas inlet, such that the perpendicular flow is much slower.

The calculated maximum and average gas velocity at the outlet were the same as for the 200 µm gap distance simulation.

2.3.6.3.1  50 µm Sniffer-Sample gap – Particle Trajectories and Residence Time
Two particle injection studies were performed within the 50 µm gap simulation. Particle injection conditions and locations were the same as for the 200 µm gap in section 2.3.6.2.2., 13 points within the viewing area and 9 points outside of the Sniffer.

The particle velocity within the viewing area, around 0.5 ms$^{-1}$ see Figure 27A, was higher than for the 200 µm gap. However, by the micro-chamber outlet the particles had not accelerated as much as in the 200 µm gap simulation, reaching c.a. 6.2 ms$^{-1}$. This can be attributed to the reduce lifting-flow from between the Sniffer and sample. The particulate followed a much closer path to the Sniffer outlet walls, resulting in a much sharper path angle and ultimately slowing them down.
Figure 27 – Particle injection into fluid flow within the micro-chamber at a gap distance of 50 µm, A), Y-plane, 0-1.0 ms\(^{-1}\) and B) Z-plane, 0-20 ms\(^{-1}\)

The average particle velocity was calculated from the path length and residence time, see Table 7. The residence time ranged from 5.6-10.1 ms, almost 1 ms quicker than at a 200 µm gap. There was fairly good agreement across the viewing area within particle diameters, 0.5, 0.6 and 0.5 standard deviation of the average for 10, 100 and 1000 nm respectively. The average particle velocities were followed a similar pattern as for the 200 µm gap, where the residence time for 10 and 100 nm being very similar and 1000 nm much faster. However, although faster more 100 nm particles did not reach the DCI outlet. The path length of these particles suggests they were trapped in the eddy region where the DCI inlet meets the Sniffer outlet. The 100 nm particulate is more likely to become trapped within the eddy regions. The 1000 nm particulate has enough mass that when it enters the region its momentum and thus the centrifugal force generated, will more than likely carry it out of the spiral. The smaller lifting-flow causes particulate from the sample surface to be closer to the Sniffer outlet wall and thus be forced more into the eddy regions.
Table 7 – Particle residence time and average velocity from particle injection within the viewing area for 50 µm gap

<table>
<thead>
<tr>
<th>Position</th>
<th>Particle Ø</th>
<th>10 nm</th>
<th>100 nm</th>
<th>1000 nm</th>
<th>10 nm</th>
<th>100 nm</th>
<th>1000 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>10 nm</td>
<td>9.2</td>
<td>8.8</td>
<td>6.3</td>
<td>33.1</td>
<td>34.6</td>
<td>48.4</td>
</tr>
<tr>
<td>#2</td>
<td>100 nm</td>
<td>9.6</td>
<td>9.3</td>
<td>6.7</td>
<td>31.8</td>
<td>32.8</td>
<td>45.5</td>
</tr>
<tr>
<td>#3</td>
<td>1000 nm</td>
<td>10.1</td>
<td>9.8</td>
<td>7.2</td>
<td>30.2</td>
<td>31.1</td>
<td>42.4</td>
</tr>
<tr>
<td>#4</td>
<td>10 nm</td>
<td>8.5</td>
<td>8.1</td>
<td>5.6</td>
<td>35.8</td>
<td>37.6</td>
<td>54.3</td>
</tr>
<tr>
<td>#5</td>
<td>100 nm</td>
<td>9.7</td>
<td>3.2</td>
<td>7</td>
<td>31.4</td>
<td>-</td>
<td>43.5</td>
</tr>
<tr>
<td>#6</td>
<td>1000 nm</td>
<td>9.2</td>
<td>2.6</td>
<td>6.4</td>
<td>33.1</td>
<td>-</td>
<td>47.6</td>
</tr>
<tr>
<td>#7</td>
<td></td>
<td>9</td>
<td>2.6</td>
<td>6.4</td>
<td>33.8</td>
<td>-</td>
<td>47.6</td>
</tr>
<tr>
<td>#8</td>
<td></td>
<td>9.5</td>
<td>3.1</td>
<td>6.9</td>
<td>32.1</td>
<td>-</td>
<td>44.2</td>
</tr>
<tr>
<td>#9</td>
<td></td>
<td>9.4</td>
<td>2.8</td>
<td>6.6</td>
<td>32.4</td>
<td>-</td>
<td>46.2</td>
</tr>
<tr>
<td>#10</td>
<td></td>
<td>8.7</td>
<td>8.4</td>
<td>6</td>
<td>35.0</td>
<td>36.2</td>
<td>50.8</td>
</tr>
<tr>
<td>#11</td>
<td></td>
<td>9.5</td>
<td>2.9</td>
<td>6.6</td>
<td>32.1</td>
<td>-</td>
<td>46.2</td>
</tr>
<tr>
<td>#12</td>
<td></td>
<td>2.2</td>
<td>2.2</td>
<td>5.9</td>
<td>-</td>
<td>-</td>
<td>51.6</td>
</tr>
<tr>
<td>#13</td>
<td></td>
<td>8.8</td>
<td>8.4</td>
<td>5.9</td>
<td>34.6</td>
<td>36.2</td>
<td>51.6</td>
</tr>
</tbody>
</table>

$\bar{x}$ | 9.3 | 8.8 | 6.4 | 32.9 | 34.8 | 47.7 |

S.D | 0.5 | 0.6 | 0.5 | 1.6 | 2.4 | 3.6 |

Shaded values are particles that did not reach the DCI outlet (end of fused silica)

* Averages and standard deviation are calculated omitting shaded values
- Average velocity not calculated

Particle injection outside of the Sniffer varied, when compared to the 200 µm gap injection, dependent on distance from the micro-chamber, see Table 8. Particles closer to the micro-chamber had a shorter residence time whilst those further away had a much longer residence time. Although not clear from the gas flow trajectories or cut-plots, the small difference of gas flow outside the sniffer has a significant effect on particle transport.
Table 8 – Particle residence time and average velocity from particle injection outside the Sniffer for 50 µm gap

<table>
<thead>
<tr>
<th>Position</th>
<th>Residence time (ms)</th>
<th>Average velocity (ms⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 nm</td>
<td>100 nm</td>
</tr>
<tr>
<td>#1</td>
<td>13.1</td>
<td>12.8</td>
</tr>
<tr>
<td>#2</td>
<td>52.0</td>
<td>51.7</td>
</tr>
<tr>
<td>#3</td>
<td>301.5</td>
<td>301.3</td>
</tr>
<tr>
<td>#4</td>
<td>962.6</td>
<td>962.5</td>
</tr>
<tr>
<td>#5</td>
<td>298.8</td>
<td>298.8</td>
</tr>
<tr>
<td>#6</td>
<td>1041.6</td>
<td>1041.3</td>
</tr>
<tr>
<td>#7</td>
<td>2749.2</td>
<td>2744.8</td>
</tr>
<tr>
<td>#8</td>
<td>2774.6</td>
<td>821.3</td>
</tr>
<tr>
<td>#9</td>
<td>31271.1</td>
<td>31260.1</td>
</tr>
</tbody>
</table>

Shaded values are particles that did not reach the DCI outlet (end of fused silica)
- Average velocity not calculated

Flow simulations were used as an insight into the flow dynamics of the Sniffer cell and potential particle residence times. However, physical complications limited the how accurately the modified UP213 cell lid represented that modelled (optimum design).

The Sniffer was placed off-axis relative to the gas inlet. When modelled the flow trajectories were similar as seen in for the on-axis models, but the main flow was skewed, see Figure 28A. A particle injection study performed with these simulated flow dynamics using the same initial particle conditions as set for the on-axis 50 µm and 200 µm gap simulations (only one particle diameter of 100 nm), see Figure 28C, showed that particles from the sample surface would exit the micro-chamber under the outlet, recirculate around the Sniffer exit the micro-chamber outlet after entering from the laser port and micro-chamber entrance.

Ensuring the Sniffer remained parallel to the sample surface was also difficult due to is suspension on a stainless steel tube. The sample height was also difficult to control and was measured before analysis.

Therefore the results from the flow simulation were for an optimised configuration.
Figure 28 – Flow trajectories for the Sniffer off-axis relative to the gas inlet A) in the Y-plane, B) isometric and C) a particle study viewed in the Z-plane, black arrows indicate the particulate path.
2.3.6.4 The Enterprise Cell

Recent modelling of the gas flow within the Enterprise Cell has shown that for a 100 µm gap distance and helium flow rate of 200 ml min$^{-1}$, the average particle residence time from within the Sniffer to an outlet distanced on-axis at 88 mm was 4 ms$^{70}$. Flow trajectories and velocity cut-plots for the outer cell show a very similar flow compared to the modified UP213 cell lid. The flow within the Sniffer was also similar to flow trajectories and velocities shown here for the modified UP213 cell lid in section 2.3.6.2.1. The performance of the Sniffer cell within the Enterprise outer cell can thus be inferred from these models.
2.4 Conclusions

A LA-ICP-MS interface has been designed that consists of a laser ablation cell, a single transport tube (from ablation point to plasma) and a new injector, as a single whole unit.

The design utilises a cell within cell design to capture the ablation plume and to situate the cell outlet as close as possible to the ablation site by development of a micro-chamber, reducing the effective cell volume to 0.005 cm$^3$ whilst maintaining a much larger volume in the outer cell to hold the sample. The gas flow dynamics of the Sniffer cell have been modelled within a modified UP213 cell lid and particle injection studies performed within this simulation. Flow simulations have shown that gas trajectories converge on the Sniffer with minimal turbulence in critical zones to create:

- A fast gas velocity within the micro-chamber that sweeps through the micro-chamber volume and sample surface
- A counter flow at the opposing end of the chamber to lift flow into the outlet
- A positive pressure down through the laser port to hinder ablation plume expansion and particulate escape

These flow dynamics result in a fast washout of the micro-chamber when a 30 cm path length to the ICP is incorporated. This has been confirmed by performing particle injection studies into the simulation, resulting in residence times of <10 ms. However the temporal spread of particulate from a single laser shot, equating to the peak width that would be detected, has not been modelled as this is beyond the scope of this project. Particle transport modelling performed by Bleiner and Bogaerts showed that the minimum time width of a single laser pulse, described as a time-of-flight type profile, can be calculated by dividing the transport distance by the carrier gas terminal velocity. Using the average gas velocity from both gap distance models of 118 m$^{-1}$ and transport length of 300 mm, gives a minimum width of 0.0025 s. However, this model does not take into account the spread of particulate in the ablation plume, which in the Sniffer cell is assumed to be reduced as a result of the background pressure of the sample gas.

The overall transport volume has been reduced by the design of a DCI torch, where the injector and transport tubing are one piece of fused silica. The interface reduces aerosol dilution and temporal aerosol broadening. The DCI also facilitates
the movement of the injection point of sample aerosol closer to the plasma, past its noisy base and recirculation regions.

The flow simulation and particle injection studies show that the design is practically operational and the design can be fabricated for experimental testing.
2.5 Further Work

Experimental testing of the interface has been performed to confirm the modelling performed here, see later chapters.

Flow simulations of the gas trajectories within the micro-chamber of the Sniffer have shown that the Sniffer-sample gap distance to be critical for particle transport, especially if particles emanate from close to the sample surface. Further modelling is required to find an optimum distance. However, this will be related to the gas volume flow rate introduced into the system. As only one gas volume flow rate was modelled (due to practical limits of the modified UP213 cell lid) a multivariate study of volume flow rates and Sniffer-sample distances within the Enterprise cell need to be modelled to identify an optimum design.

Edge effects also need to be investigated to identify if the flow dynamics within the micro-chamber are altered by a change in the flow in the outer cell. For example, how close could the edge of the sample tray be to the micro-chamber before distortion of the flow dynamics within it occur?

To fully understand the complexities of the flow within such a small volume, computational fluid dynamics needs to be used to incorporate the effects that the pressure waves from laser ablation will have on the flow and particle residence times (based on plume expansion in a pressurised system).

The inner Sniffer cell relies on the gas flow dynamics in the outer cell, based on its relative position, to develop flow dynamics within the micro-chamber. A new design of the Sniffer cell, see Figure 29, could be used to further improve washout of the micro-chamber by introducing a sample gas flow directly into the micro-chamber. The outer cell would still provide a chamber for exclusion of atmosphere, but the gas flow dynamics within the micro-chamber would be largely independent of the surrounding flow. The density of the outer cell flow would need to be larger than the gas used in the micro-chamber, so argon as the outer cell flow would be preferable.
The mixing of two gases generally results in a turbulent flow that extends far beyond their meeting point, as such the proposed new design shown in Figure 29 may lead to unfavourable flow through the Sniffer cell micro-chamber. The angle of the sample gas inlet relative to the sample surface may also result in unfavourable flow conditions. This could result in ejection of particulate out of the micro-chamber, leading to recirculation and ultimately longer washout times. Therefore a closed micro-chamber Sniffer design is also proposed, see Figure 30, in which the sample gas inlet lies parallel to the sample surface. The use of a curtain gas in the outer cell would still be required to effectively contain the micro-chamber and provide lift of particulate into the sample gas flow.
Figure 30 – A) Schematic drawing of a new closed Sniffer cell design (the inner cell) and B) an isometric representation of the Sniffer cell, partially transparent for clarity, where sample gas is fed directly into the micro-chamber.
Chapter 3 Experimental Evaluation of a High-Speed, High-Efficiency, LA-ICP-MS Interface

3.1 Introduction

LA-ICP-MS is becoming an increasingly important tool for bio-imaging, single particle analysis and depth profiling. These applications utilise single laser shot pulses to provide pixel information of the sample, which are then used to generate a sample map or image depicting elemental distribution. It is therefore important that pulses are resolved from one another by determining the washout time of a laser ablation interface and spacing successive laser pulses by this time period by altering the repetition rate. This ensures information does not mix and pixels remain un-blurred so that image resolution is the same as the laser spot size.

As previously discussed current laser ablation cell designs limit the practicality of the technique as commercially available cell designs have long washout times e.g. 700 ms to 1% of peak maximum \(^7\), resulting in a very long analysis time. Temporal spreading of the ablation plume also results in a reduction of sensitivity and limit of detection (due to a poorer signal-to-noise ratio); important when considering the concentration of elements within the cell of a tissue section or within the small volume of micro-particulate.

As discussed in Chapter 2, a LA-ICP-MS interface has been designed to minimise transit time and temporal broadening of particulate from ablation point to introduction into an ICP. By reducing the spread of the package (the particulate from the ablation plume) the total sampling time is reduced and a higher sensitivity achieved.

3.1.1 Data Processing

The software Igor Pro (version 6.1.2.1, WaveMetrics, Oregon, USA) was used to process the peak profiles obtained from the Sniffer-DCI interface. The software was used to either integrate the area under the peak or find the equations of curves fitted to the peak profile. Curve fitting is performed by an iterative process,
where the software tries various values for the unknown curve coefficients and computes the chi-squared value for the fit; repeating to find the lowest chi-squared value.

### 3.1.2 Data Acquisition

When acquiring data for laser ablation the normal data output is in a Time Resolved Analysis (TRA) format i.e. as time increased along the x-axis the signal intensity is recorded in the y-axis, see Figure 32 as an example.

### 3.1.3 Peak Characteristics

The detection of resolved pulse information takes the form of individual peaks separated by background intensity, in a time resolved format. To evaluate the performance of the interface the following important peak characteristics were determined for each peak and averaged to generate a ‘typical’ peak profile for a set condition:

- Peak height/maximum (aerosol density)
- Peak area (total transported aerosol)
- Sensitivity
- Interface washout time
- Full Width at Half peak Maximum (FWHM)
- Peak width (aerosol dispersion)

The maximum peak height and area were used as direct measures of the interface transport efficiency. Dividing the peak maximum (counts s$^{-1}$) by the analyte concentration in the solid (parts per million) was used to calculate the sensitivity (counts s$^{-1}$ ppm$^{-1}$).

Washout times of LA-ICP-MS interfaces have been reported using many different criteria such as 10% peak maximum$^{55,56}$ or 3% signal area$^{62}$. In this report an exponential decay curve is fitted from the peak maximum to the baseline, see Equation 12, and rearranged, see Equation 13, to calculate the time at which the peak decays to 10% of its maximum. Where $N_1$(10% peak maximum in counts s$^{-1}$) is
the quantity at time $t$, $N_o$ is the initial quantity (the peak maximum) and $\tau$ is the time constant.

$$N_t = N_o \cdot e^{-t/\tau}$$  \text{Equation 12}

$$t = -\left[\ln\left(\frac{N_t}{N_o}\right) \cdot \tau\right]$$  \text{Equation 13}

$$\lambda = \frac{1}{\tau}$$  \text{Equation 14}

Quoting the washout time at 10% of the peak maximum allows easy comparison with existing cells. The decay constant, $\lambda$, is also given, as this describes the slope of the peak decay and can be used to better compare different interfaces. This is calculated from the time constant, see Equation 14.

The point of half-maximum on the peak rise edge was calculated from the equation of a straight line, plotted from the start of the peak rise to the peak maximum. The point of half maximum on the trailing peak edge was calculated from the equation of the exponential decay curve, fitted from the peak maximum to the baseline. The difference between the two points gave the FWHM.

The full peak width was used as a measure of the temporal spread of the entire ablation plume. The aspect ratio of the peak, calculated by dividing the peak height by the width, has also been used as a description of the signal structure, where a higher value indicates a better signal-to-background ratio.\(^{53}\)

\subsection*{3.1.4 Instrumentation}

A commercially available UP-213 laser ablation system (ESI, New Wave Research Division, Huntingdon, Cambridgeshire, UK) was used to deliver a laser beam to the sample surface. The UP-213 is a solid state Nd:YAG laser operating at 213 nm ($5^{th}$ harmonic of 1064 nm) with a 4 ns pulse duration. Details of the cell used are given in each sub-section. A pressure monitor was placed prior to the ablation cell inlet to monitor the back pressure when altering gas flows.
An Element XR magnetic sector field ICP-MS (Thermo Scientific, Bremen, DE) was used to monitor isotopic signal response from the laser induced ablation plume. Details regarding the coupling of the ICP-MS to the ablation cell and the sampling regime used for each experiment are detailed in each sub-section. The Element XR SF-ICP-MS has two detectors to provide a larger dynamic range, a Faraday cup and a Secondary Electron Multiplier (SEM). The SEM has two modes of operation, counting and analogue. Software controls limit the minimum sample time to 1.1 ms in analogue mode and 0.1 ms in counting.
3.2 Signal Response from the Sniffer-DCI Interface Using the Modified UP213 Lid as the Outer Cell

3.2.1 Coupling the DCI and Sniffer via Multiple Tubes of Varying Diameter

The custom alpha cell was fitted to the standard cell brackets. This outer cell housed the inner Sniffer cell and was coupled to the ICP-MS using the DCI. As described in section 2.3.2 the first Sniffer-DCI interface iteration was initially constructed such that the injector and transport tubing were constructed using multiple tubes of differing diameter. In this design the sample transport tubing, from micro-chamber to DCI outlet, was constructed as shown in Figure 31. The total transport distance from micro-chamber outlet to DCI tip of 426 mm and volume of 0.08 cm$^3$ (excluding the micro-chamber volume).

![Figure 31 – Schematic drawing of the multiple transport tubing used in the initial Sniffer-DCI configuration.](image)

For initial experiments the safe maximum working pressure was set at 34.47 kPa (approximately 5.0 lbf/in$^2$). The sheath tube used in these experiments had an internal diameter at the tip of 2.0 mm.

The laser and ICP-MS operating conditions are given in Table 9. Optimisation of ICP-MS parameters were performed by monitoring $^{238}$U using a 20 Hz laser repetition rate and DCI extension of 0 mm to promote pulse mixing and minimise variability due to resolved pulsed data. The mass spectrometer dwell time was reduced to match that of the data acquisition method. However, even at this repetition rate and short dwell time the signal intensity varied significantly as a
result of monitoring partially resolved pulses and from variation in the laser ablated mass.

Four different Sniffer-cell sample flow rates were tested to establish an optimum flow rate \textit{i.e.} maximum sample transport with minimal sample dilution. This was determined by maximum peak intensity (counts s$^{-1}$). These flow rates were tested with the DCI in the 0 mm position (in-line with the end of the sheath-gas tube).

A sample gas flow of 0.130 Lmin$^{-1}$ produced peaks with the highest average peak intensity. This flow rate produced a back pressure close to the safe maximum working pressure, thus DCI extensions were investigated at this flow rate. ICP operating parameters were optimised as in the flow rate investigation and were held constant for each extension.
<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spot diameter</strong></td>
<td>55 μm, aperture imaged</td>
</tr>
<tr>
<td><strong>Laser energy/Fluence</strong></td>
<td>0.220 mJ equating to 9.20 J/cm²</td>
</tr>
<tr>
<td><strong>Sample</strong></td>
<td>NIST SRM 611 Trace Elements in Glass (450 ppm nominal concentration)</td>
</tr>
<tr>
<td><strong>Sample gas (helium)</strong></td>
<td>Flow rate 0.050, 0.075, 0.100 and 0.130 Lmin⁻¹ resulting and resulting back pressure</td>
</tr>
<tr>
<td><strong>Sampling strategy</strong></td>
<td>1 Hz repetition rate, down-hole ablation, 30 second dwell time (equating to 30 single pulses), samples pre-ablated 60 shots</td>
</tr>
<tr>
<td><strong>Sniffer-sample distance</strong></td>
<td>Estimated as 300 μm, exact distance cannot be given as Sniffer was not parallel to the sample surface, measured from the back of Sniffer to the sample surface</td>
</tr>
</tbody>
</table>

|                  |                                                                 |
| **ICP-MS operating parameters** |                                                              |
| **Cool gas**     | 15.5 Lmin⁻¹                                                   |
| **Auxiliary gas** | 0.85 Lmin⁻¹                                                  |
| **Plasma RF power** | 1300 W                                                       |
| **Sheath gas**   | 1.00 Lmin⁻¹                                                   |
| **DCI extension (relative to sheath gas tube tip)** | -15, 0, 2, 4, 6, 8, and 10 mm for 0.130 Lmin⁻¹             |
| **Acquisition parameters** | $^{232}$Th and $^{238}$U, low resolution, 5% mass window, 0.01 s sampling time and 1 channel equating to 0.01 s dwell time, 5% peak top integration window, E-scan, Triple detection mode |
|                  | 0.020 seconds per sweep                                       |
3.2.1.1 Varying the Sample Gas Flow for the Sniffer-DCI Interface

The peak characteristics for the Sniffer-DCI (alpha outer cell) interface at varied flow rates are given in Table 10 and five typical baseline resolved peaks for each flow rate are shown in Figure 32A 0.050, B 0.075, C 0.100 and D 0.130 Lmin⁻¹. The peak characteristics have been determined for the $^{238}$U signal response. This isotope is a commonly used for characterisation of ICP-MS signals as it provides the largest sensitivity (compared to lower mass elements) due to smaller mass bias effects. No significant difference was observed between $^{232}$Th and $^{238}$U.

The peak height increased as the flow rate increased improving the signal-to-noise ratio. However the peak area also increased as flow rate increased, thus at low flow rates the particle transport efficiency was poor, compared to higher flow rates, resulting in only a proportion of the ablated mass reaching the ICP. The washout time became much shorter as the flow rate was increased 327 ms down to 86 ms, for 0.050 and 0.130 Lmin⁻¹ respectively, bettering the washout time of commercial cells. The peak width also became shorter at higher flow rates showing an overall improved transport efficiency and signal-to-noise ratio.

Table 10 – Typical peak characteristics from the Sniffer-DCI interface (alpha outer cell) at varied sample gas flow rates

<table>
<thead>
<tr>
<th>Peak characteristics</th>
<th>Flow rate (Lmin⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.050</td>
</tr>
<tr>
<td>Peak max. (counts s⁻¹)</td>
<td>2.01 x 10⁵</td>
</tr>
<tr>
<td>Area (counts)</td>
<td>1.41 x 10⁴</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>450</td>
</tr>
<tr>
<td>(counts/ppm)</td>
<td></td>
</tr>
<tr>
<td>Washout time (s)*</td>
<td>0.327</td>
</tr>
<tr>
<td>$\lambda$ (s⁻¹)**</td>
<td>7.70</td>
</tr>
<tr>
<td>FWHM (s)</td>
<td>0.142</td>
</tr>
<tr>
<td>Peak width (s)</td>
<td>0.490</td>
</tr>
</tbody>
</table>

*10% of peak maximum, ** the decay rate

However, the FWHM seems to be the shortest at 0.075 Lmin⁻¹. This was falsely created due to a complex bimodal peak profile (see next paragraph for details); see Figure 32B, where large satellites occur after the peak has decayed to less than 10%. These large satellites could be caused by the formation of a complex flow within the Sniffer micro-chamber at 0.075 Lmin⁻¹ causing a significant proportion
of the ablation plume to recirculate. As the FWHM was calculated based on curves fitted to the initial peak maximum, the width was reduced as a significant proportion of the ablated mass lies within a second maximum of the peak. The effect was also seen at 0.050 Lmin⁻¹, but at a reduced intensity.
Figure 32 – Peak profiles of $^{238}$U for the Sniffer-DCI interface (using the alpha cell) at flow rates: A) 0.050, B) 0.075, C) 0.100 and D) 0.130 L\(\text{min}^{-1}\). The x-axis has been truncated to between 20 and 25 seconds to show the peaks profiles in detail.

Bi-modal peaks can also be seen in Figure 32D, however, rather than resulting from large signal spikes in the tail of the peaks the peak splitting occurs around the peak maximum. Recent modelling and experimental comparison of a new laser ablation cell reported peak splitting of single pulse data\(^6\) due to turbulence induced particle-size separation within a y-piece gas connector. The connector prolonged the residence time of the particles with a diameter $\leq$200 nm as they became caught up in the complex flow patterns within the turbulent region. In the configuration reported here the Sniffer was not parallel to the sample surface. This may have created a more complex flow pattern than seen from modelling, resulting in a particle-size related separation. The particle transport tubing was constructed of different tubes of varying diameter; as such the flat cross sections of the tubes will have obstructed flow and resulted in turbulence where one tube meets another.

A flow rate of 0.130 L\(\text{min}^{-1}\) produced the highest peak maximum and best transport efficiency, however, flows beyond this could not be tested as the maximum safe-working pressure had been reached. As such an optimum flow rate could not be determined; DCI extension tests were performed at 0.130 L\(\text{min}^{-1}\).
3.2.1.2 Extending the DCI at a 0.130 Lmin⁻¹ Flow Rate

![Figure 33](image)

Figure 33 – Example peak profiles for the Sniffer-DCI interface (alpha cell) at a 0.130 Lmin⁻¹ flow rate and varied DCI extensions. Profiles have been offset by 0.3 seconds on the x-axis and by 2 x 10⁵ counts s⁻¹ on the y-axis for clarity.

Typical peak profiles for the Sniffer-DCI interface at varied DCI extensions are shown in Figure 33. The average peak area, see Figure 34A, decreased as the DCI was extended towards the plasma as did the peak maximum, see Figure 34B. The plasma conditions for the Sniffer-DCI interface were optimised at a 0 mm extension and held constant for subsequent extensions, thus the operating parameters will not have been optimum for those extensions. For example when extending the DCI, the transit time of particulate through the plasma will be shorter, therefore time dependant processes such as particle processing (atomisation) and ionisation will be affected. This means that although the same mass of material with the same concentration of analyte will be transported to the ICP the subsequent peak area and height will be reduced.

The peak area decrease was fairly linear with increasing DCI extension (R² of 0.9886), however the peak maximum, a measure of aerosol density, does not follow the same trend. The aerosol density was similar for 2, 4 and 6 mm, but the variation between maximum, as indicated by error bars, was largest at 4 and 6 mm extensions. As previously described these extensions lie within the regions of gas mixing and plasma induced turbulence.
The relative standard deviation, see Table 11, shows the variation of the peak area and maximum with changes in DCI extension. The most significant variation in peak maximum and area was observed when particulate was injected into the noisy base of the plasma (4-6 mm). As previously discussed a noisy, turbulent region exists at the base of the plasma, occurring relative to the first turn in the load coil. Once this noisy region was overcome, however, the variation was much smaller. At a 10 mm extension the variation in peak area was lower than at a 0 mm extension, but the variation in peak maximum much higher.
Table 11 – The percentage relative standard deviation associated with the average peak area and maximum for the Sniffer-DCI interface at 0.130 Lmin\(^{-1}\) at varied DCI extensions

<table>
<thead>
<tr>
<th>Peak characteristics</th>
<th>DCI extension (mm)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak max. %RSD</td>
<td></td>
<td>16.0</td>
<td>11.0</td>
<td>41.4</td>
<td>37.5</td>
<td>19.8</td>
<td>24.1</td>
</tr>
<tr>
<td>Peak area %RSD</td>
<td></td>
<td>7.1</td>
<td>5.5</td>
<td>9.3</td>
<td>18.7</td>
<td>10.1</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Washout times at 2 and 6 mm although similar to each other were much longer than washout times for other DCI extensions, see Table 12. Two different processes may have resulted in increasing the washout time at these extensions. Turbulent mixing of the sample gas and auxiliary gas in a standard torch occurs in the region directly after the sheath-gas tube. At 2 mm particles were injected directly into this turbulent region, which could result in a particle-size related increase in residence time within the plasma. At a 6 mm DCI extension the particulate exiting the DCI would be injected into the turbulent region at the plasma base, again resulting in a particle-size related residence time within the plasma.

Table 12 – Peak characteristics for the Sniffer-DCI interface (alpha cell) for a 0.130 Lmin\(^{-1}\) flow rate at varied DCI extensions

<table>
<thead>
<tr>
<th>Peak characteristics</th>
<th>DCI extension (mm)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washout time (s)*</td>
<td>0.081</td>
<td>0.107</td>
<td>0.063</td>
<td>0.102</td>
<td>0.072</td>
<td>0.058</td>
<td></td>
</tr>
<tr>
<td>λ (s(^{-1}))</td>
<td>27.5</td>
<td>21.2</td>
<td>29.0</td>
<td>27.1</td>
<td>33.3</td>
<td>43.5</td>
<td></td>
</tr>
<tr>
<td>FWHM (s)</td>
<td>0.043</td>
<td>0.070</td>
<td>0.045</td>
<td>0.059</td>
<td>0.063</td>
<td>0.056</td>
<td></td>
</tr>
<tr>
<td>Peak width (s)</td>
<td>0.232</td>
<td>0.235</td>
<td>0.236</td>
<td>0.239</td>
<td>0.169</td>
<td>0.156</td>
<td></td>
</tr>
<tr>
<td>Aspect ratio (x 10^6, counts s(^{-2}))</td>
<td>10.8</td>
<td>7.84</td>
<td>8.00</td>
<td>7.45</td>
<td>7.08</td>
<td>7.45</td>
<td></td>
</tr>
</tbody>
</table>

*10% of peak maximum

The FWHM was shortest at 0 mm, increasing to a maximum at 2 mm extension and then decreased again as the DCI was extended further. The peak width however decreased for 8 and 10 mm extension. This gave an overall consistent aspect ratio for extensions past 0 mm, see Table 12.
It was later discovered that large gas leaks occurred when using multiple tubes for the particle path; also large dead volumes were present where the tubing connected to one another and potential eddy regions where tubing faces were perpendicular to the flow path. These physical factors increased particle washout time and created particle-size related temporal separation. From the results obtained the flow modelled through the Sniffer cell and subsequent residence time of particles does not match the experimental results. This suggests that dead volumes increased particle residence times or that particles were ejected into the outer cell where they re-circulated before exiting via the micro-chamber outlet.

The data acquisition method was too slow to clearly describe the peak shapes, as single point (the peak maximum) represented 31-40% of the total peak area. In some profiles the peak maximum was flat topped (trapezoidal), described by two consecutive data points. However these peaks had a lower peak maximum compared to peaks described by a single data point, indicating that the true peak maximum had been missed during data acquisition.

### 3.2.1.3 Other Investigations Using the Multiple Tube Design

The effect of changing the sheath-gas tube internal diameter was also investigated. A 10-fold decrease in peak maximum was observed when using a 1.0 mm compared to a 2.0 mm internal diameter injector. However the results were inconclusive.

The effect of the distance between the Sniffer and sample surface was also investigated. An optimum distance, where peak maximum was highest, of around 300 µm was observed. However as the Sniffer was not parallel to the sample surface exact distances could not be confirmed.

At this point damage to the lasing medium (the rod) of the UP213 resulted in bimodal peak shapes. As the laser is aperture imaged the damage resulted in a cold or hot spot within the ablation site, this can cause changes in the interaction of the laser beam and solid and lead to ablation mechanisms that create an unfavourable, larger particle size distribution. The second peak became more prominent as the hole depth of the ablated spot increased. As such subsequent investigations focused on improving peak shapes and minimising peak widths by improvements in design.
3.2.2 Coupling the DCI and Sniffer via one Transport Tube of a Single Diameter

The transport tubing from micro-chamber outlet to the DCI tip was modified to become a single piece of fused silica tubing, as described and modelled in Chapter 2, c.a. 350 mm in length. The use of a single transport tube helped to ensure the interface was sealed from atmosphere and did not leak. However, by excluding the transport tube as a potential source of leaks the flow rate was halved at the maximum safe working pressure of 34.47 kPa. As such off-line testing was performed and a new maximum safe working pressure of 68.95 kPa (approximately 10 lbf/in²) was used, at a flow rate of 0.120 L/min⁻¹.

3.2.2.1 Initial Investigations with a Single Continuous Transport Tube

Initial experiments showed that the new single continuous transport tube had minimised particulate escape; when using the same conditions described in 3.2.1.2 the signal intensity saturated the SEM. As such the signal was attenuated, by switching from low resolution to medium resolution to yield a signal roughly 8% of the original intensity. The data acquisition time resolution used for initial characterisation of the peak profiles was too long, resulting in little information describing the peak maximum. The minimum sample time of the SEM was used to improve the time resolution of the data. Instrument parameters are given in Table 13. Only one isotope, $^{238}$U, was monitored. This ensured the magnet settling time was only a consideration for the first sweep as for successive sweeps the magnet current was held stationary (no cycling) at a value corresponding to $^{238}$U. Using a single isotope also ensured the duty cycle was maximised.

The DCI was extended to 2 mm past the sheath-gas tube to investigate the washout time and peak width. The ICP-MS operating conditions were optimised as in section 3.2.1.1; however the signal appeared noisy, making optimisation difficult. The noise of the signal was caused by monitoring partially resolved pulses and variation in the ablated mass.

As the operating parameters were considered to be multivariate, a simplex optimisation procedure was employed to find the optimum operating parameters. Simplex optimisation generates a series of nodes in multidimensional space, where each node is the response of the system at varied operating conditions. The nodes
are joined by vertices such that algorithms can then be used to discard the worst response and predict a new node (set of operating conditions). This new node is evaluated and the algorithms applied again such that the worse response is discarded and the simplex moves towards conditions that yield an optimum response.

However, the variation in peak height due to variation in ablated mass and long data acquisition times (relative to the peak maximum duration) made optimisation via this method impractical. A uni-variate approach was then adopted and typical operating parameters gauged over successive experiments.
Table 13 – Laser and ICP-MS operating parameters to investigate the use of a single transport tube

<table>
<thead>
<tr>
<th>Laser system operating parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot diameter</td>
</tr>
<tr>
<td>Laser energy/Fluence</td>
</tr>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>Sample gas (helium)</td>
</tr>
<tr>
<td>Sampling strategy</td>
</tr>
<tr>
<td>Sniffer-sample distance</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ICP-MS operating parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cool gas</td>
</tr>
<tr>
<td>Auxiliary gas</td>
</tr>
<tr>
<td>Plasma RF power</td>
</tr>
<tr>
<td>Sheath gas</td>
</tr>
<tr>
<td>DCI extension (relative to sheath gas tube tip)</td>
</tr>
<tr>
<td>Acquisition parameters</td>
</tr>
</tbody>
</table>

3.2.2.1.1 Peak Profile and Characteristics from Initial Investigation of Using a Single, Continuous Transport Tube

Peak characteristics from the initial investigation into using a single continuous transport tube are given in Table 14, the percentage relative standard deviation has been calculated for the peak maximum and area from an average of 10 peaks.
Signal intensities in medium resolution were 8% of that measured in low resolution. In order to compare the peak characteristics of the single continuous tube with the multiple-tube configuration the signal needs to be multiplied by the attenuation ratio (12.5) and the difference in spot diameter ratio (0.3025, assuming ablation depth was constant for all spot sizes). This gives an average peak maximum of $4.66 \times 10^6$ counts s$^{-1}$, a peak area of $4.66 \times 10^3$ counts and a sensitivity of $1.03 \times 10^4$ counts s$^{-1}$/ppm. This was a twofold increase in transport efficiency compared to the same conditions using multiple tubes to transport the particulate.

### Table 14 – Peak characteristics for the Sniffer-DCI interface at a 2 mm extension and sample flow rate of 0.120 Lmin$^{-1}$ using a single continuous transport tube. Signal has been attenuated using medium resolution

<table>
<thead>
<tr>
<th>Peak characteristics</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak maximum (counts s$^{-1}$)$^\wedge$</td>
<td>1.23 x 10$^6$ 60.2</td>
</tr>
<tr>
<td>Peak area (counts)$^\wedge$</td>
<td>1.23 x 10$^3$ 17.6</td>
</tr>
<tr>
<td>Sensitivity (counts s$^{-1}$/ppm)$^\wedge$</td>
<td>2700</td>
</tr>
<tr>
<td>Washout time (s)$^*$</td>
<td>0.015</td>
</tr>
<tr>
<td>$\lambda$ (s$^{-1}$)</td>
<td>144.7</td>
</tr>
<tr>
<td>FWHM (s)</td>
<td>0.007</td>
</tr>
<tr>
<td>Peak width (s)</td>
<td>0.098</td>
</tr>
<tr>
<td>Aspect ratio (counts s$^{-2}$)</td>
<td>1.26 x 10$^7$</td>
</tr>
</tbody>
</table>

$^\wedge$ Average of 10 pulses
$^*$10% of peak maximum

The slope of the peak decay, described by $\lambda$, has become much sharper. This leads to a washout time of 15 ms. Due to an increase in the aerosol density (peak maximum) and reduction in washout the FWHM was 7 ms; comparable to in-torch ablation were peaks reported to be baseline resolved with a 4 ms FWHM.  

The whole peak width has been reduced to less than 100 ms (baseline resolved). However this peak width was longer than expected, considering the FWHM and washout time. The 10 single peaks have been averaged to generate a ‘typical’ peak profile, see Figure 35. This profile shows the long tail of the peak, for which after 15 ms was less than 10% the height of the peak maximum. This tail was caused by particle-size related temporal separation as small satellites can be seen in the individual peak (smoothed out by averaging in Figure 35). There was a significant shoulder on the peak decay of the averaged peak profile (present in all 10 peaks).
This again could be related to particle-size related temporal separation. These separations could result from turbulence, as described in section 3.2.1.2, where the DCI inlet meets the Sniffer outlet. The diameter of the fused silica was 0.14 mm smaller than the Sniffer outlet and as such will not lay concentric or tight to the Sniffer. This gap will cause gas turbulence around the DCI inlet and a potential dead-volume.

Employing multiple connecting tubes from ablation site to introduction into the plasma yields a gas flow path with multiple turbulence inducing regions, thus increasing particle size related temporal spread. The potential for particle loss is also increased due to potential problems associated with temporarily connecting tubes i.e. dead volume regions with push fit connectors. As such it was concluded that a smooth connection-free path using a single tube would yield optimum flow conditions for particle transport.

The initial signal rise was represented by two consecutive data points (baseline to peak maximum) the maximum peak intensity was represented by a single data point and the peak decay was significantly influenced by the peak tail as only a few data points describe the initial slope. The time resolution of the data acquisition was too long to clearly describe the peak shape around maximum intensity.
The method was modified from that used in the initial investigation, see 3.2.1, to acquire data at a time resolution of 0.0003 s (the isotope dwell time). However, the output of data (time per sweep) was at a rate of every 0.003 seconds, equivalent to a duty cycle of 10%. In section 3.2.1, where two isotopes were being monitored, the duty cycle was 90% (a true time per sweep of 0.022 seconds).

Using low resolution for method development and data acquisition was favoured over medium resolution due to large variation in signal intensity as a result of sampling position on the Gaussian peak shape in medium resolution.
3.2.2.2 Data-Acquisition Method Development with a Single Continuous Transport Tube

Conventional transient data-acquisition using the minimum time parameters in the Thermo software results in a data point (the time per sweep) every 0.003 s, although the dwell time was set at 0.0003 s, as discussed in section 3.2.2.1.1. This long time per sweep limits the time resolution of the data and thus the accuracy of the peak profiling, as such a different method of acquiring data was investigated to try and improve time resolution.

The conventional method (software controlled), referred to here as the averaged channels per peak transient signal, of monitoring a single ion, averages the signal intensity of a number of channels per mass peak (the minimum being three for single ion monitoring) to yield a single data point per isotope from one sweep of the mass range. The new method, referred to here as the raw channels per peak transient signal, increased the number of channels per mass peak to the software limited maximum and a mass window set such that the measured channels would still be within the flat top of the mass peak profile. The raw channel intensities were then used to describe the transient nature of the signal by stitching consecutive sweeps together and building a continuous temporal signal at a much shorter time resolution.

The instrument parameters used to investigate the new data acquisition method and comparison with a conventional method are given in Table 15.
Table 15 – Laser and ICP-MS operating parameters to investigate data acquisition method development

**Laser system operating parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot diameter</td>
<td>55 μm, aperture imaged</td>
</tr>
<tr>
<td>Laser energy/Fluence</td>
<td>5.00 J/cm²</td>
</tr>
<tr>
<td>Sample</td>
<td>NIST SRM 611 Trace Elements in Glass (450 ppm nominal concentration)</td>
</tr>
<tr>
<td>Sample gas (helium)</td>
<td>Flow rate 0.120 Lmin⁻¹ resulting in a back pressure of 68.95 kPa</td>
</tr>
<tr>
<td>and resulting back pressure</td>
<td></td>
</tr>
<tr>
<td>Sampling strategy</td>
<td>1 Hz repetition rate, down-hole ablation, 5 second dwell time (equating to 5 single pulses), samples pre-ablated 60 shots</td>
</tr>
<tr>
<td>Sniffer-sample distance</td>
<td>Estimated as 300 μm, exact distance cannot be given as Sniffer was not parallel to the sample surface, measured from the back of Sniffer to the sample surface</td>
</tr>
</tbody>
</table>

**ICP-MS operating parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cool gas</td>
<td>15.5 Lmin⁻¹</td>
</tr>
<tr>
<td>Auxiliary gas</td>
<td>0.90 Lmin⁻¹</td>
</tr>
<tr>
<td>Plasma RF power</td>
<td>1320 W</td>
</tr>
<tr>
<td>Sheath gas</td>
<td>1.340 Lmin⁻¹</td>
</tr>
<tr>
<td>DCI extension (relative to sheath gas tube tip)</td>
<td>-10, 2, 12 and 16 mm for 0.0001 s sample time</td>
</tr>
<tr>
<td></td>
<td>2 and 12 mm for 0.0002 and 0.0005 s sample time</td>
</tr>
<tr>
<td>Acquisition parameters</td>
<td></td>
</tr>
<tr>
<td>Raw channels per mass peak transient signal</td>
<td>²³⁸U, low resolution, 20% mass window, 1000 channels per peak at 0.0001, 0.0002 or 0.0005 s sampling time equating to 0.020, 0.200 or 0.500 s dwell time respectively, E-scan, SEM in counting mode</td>
</tr>
<tr>
<td>Averaged channels per mass peak transient signal</td>
<td>²³⁸U, low resolution, 10% mass window, 0.0001 s sampling time and 30 channels per peak equating to 0.0003 s dwell time, 10% average integration window, E-scan, SEM in counting mode</td>
</tr>
</tbody>
</table>
3.2.2.2.1 100 µs Raw Channels per Mass Peak Transient Signal

The raw channel data using a 100 µs sampling time (time per channel) was used to generate a transient signal containing the information from 5 laser ablation events. The data acquisition parameters were set to generate 200 channels per mass peak, however only 184 were actually monitored. The time per sweep was 23.1 ms giving a duty cycle of 80%. Thus the settling time of the first channel per mass peak and the subsequent settling time for each channel resulted in a total of 4.7 ms where data were not collected. This creates gaps within the transient data resulting in missing data for some peak profiles; these gaps have not been included in the stitched data presented here. However, individual peaks were averaged giving a typical peak profile with the aim of smoothing out profile distortion due to missing data. Alternatively large data sets could be generated so that only peaks that fall within one entire sweep of the mass spectrum are used. The peak characteristics were determined from the average peak profile; see Table 16, for a 10 mm DCI retraction (10 mm inside the sheath-gas tube relative to the tip) and a 2 mm extension respectively.

Table 16 – Peak characteristics obtained from the raw channels per mass peak transient signal method from the average profile at -10 and 2 mm DCI extension, 0.120 Lmin⁻¹, 100 µs time resolution

<table>
<thead>
<tr>
<th>Peak characteristics</th>
<th>DCI extension</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-10 mm %RSD</td>
<td>2 mm %RSD</td>
<td></td>
</tr>
<tr>
<td>Peak max. (counts s⁻¹)</td>
<td>2.61 x 10⁶</td>
<td>31.9 %</td>
<td>3.36 x 10⁶</td>
</tr>
<tr>
<td>Area (counts)</td>
<td>6.06 x 10⁴</td>
<td>11.6 %</td>
<td>7.99 x 10⁴</td>
</tr>
<tr>
<td>Sensitivity (counts/ppm)</td>
<td>5800</td>
<td>7500</td>
<td></td>
</tr>
<tr>
<td>Washout time (s)*</td>
<td>0.0044</td>
<td>0.0376</td>
<td></td>
</tr>
<tr>
<td>λ (s⁻¹)</td>
<td>493.9</td>
<td>47.8</td>
<td></td>
</tr>
<tr>
<td>FWHM (s)</td>
<td>0.0028</td>
<td>0.0086</td>
<td></td>
</tr>
<tr>
<td>Peak width (s)</td>
<td>0.0101</td>
<td>0.0909</td>
<td></td>
</tr>
<tr>
<td>Aspect ratio (counts s⁻²)</td>
<td>2.58 x 10⁸</td>
<td>3.70 x 10⁷</td>
<td></td>
</tr>
</tbody>
</table>

*10% of peak maximum

The peak maximum and area were larger for a 2 mm DCI extension compared to when the DCI was retracted within the sheath gas tube. Thus an increase in transport efficiency was seen when extending the injector towards the plasma by 2 mm. The lower peak maximum and area in the retracted position were caused by dilution of the sample aerosol by the sheath gas. This is indicated by the higher
percentage RSD of the five peaks as a result of turbulent mixing within the sheath gas tube. As the overall peak width is similar at both positions the increase in peak maximum at the 2 mm extension was not a result of a reduction in the transit time of the particulate. Extensions past the turbulent gas mixing region and the turbulent plasma base are expected to reduce peak widths further and improve sensitivity. The FWHM in the retracted position was shorter than that reported for in-torch ablation, 2.7 ms and 4 ms \(^{37}\) respectively. However at a 2 mm extension, the FWHM was double that for in-torch ablation at 8.6 ms. Washout time was also faster in the retracted position (higher \(\lambda\)). The differences were caused by a change in the peak profile when at a 2 mm DCI extension; see Figure 36 and Figure 37.

![Figure 36](image)

**Figure 36** – Peak profiles for a -10mm extension at a 0.120 L\(\text{min}^{-1}\) flow rate, obtained using the raw channels per mass peak transient signal method A) five individual pulses offset consecutively by 0.01 s on the x-axis and 1 x 10\(^6\) counts s\(^{-1}\) on the y-axis and B) the average peak profile from the 5 separate pulses
Figure 37 – Peak profiles for a 2mm extension at a 0.120 Lmin\(^{-1}\) flow rate, obtained using the raw channels per mass peak transient signal method A) five individual pulses offset consecutively by 0.05 s on the x-axis and 1 \(\times\) 10\(^6\) counts s\(^{-1}\) on the y-axis and B) the average peak profile from the 4 separate pulses (peak 1 excluded due to failing the Grubbs test based on peak maximum).

The averaged peak shape has two distinct peak maxima when the DCI was retracted in the sheath gas tube, taking the form of two convoluted Gaussian peaks. This was similar to the peak shapes reported by Tanner and Günther for in-torch ablation \(^{63,64}\), where the presence of two convoluted Gaussian peaks were a result of the aerosol formation process. The formation of multiple peak splitting was also reported by Gurevich and Hergenröder and attributed to vortices, created by turbulent flow, separating the particulate \(^{55}\). Temporal differences due to particle-size related turbulent separation was reported by Autrique \textit{et al} \(^{61}\). Within this configuration a turbulent region could exist where the DCI inlet meets the
Sniffer outlet; due to a non-concentric loose fit of the fused silica. This was seen within the modelled flow; a smaller number of particles did not escape the system from simulated injections. This could also be a result of turbulent mixing of the sample aerosol with the sheath gas in the sheath-gas tube. However, the peak maximum for peaks 1, 2, 3 and 5 at a 2 mm extension, see Figure 37A, show small peaks and troughs surrounding a single maximum, there was also a large second peak in peak 5. The more complex peak shape at a 2 mm DCI extension, compared to a retracted position, suggests that the cause was a combination of effects. The main influence was the turbulence induced by the mixing of gases in the torch and the turbulent region at the base of the plasma; up-stream effects such as turbulence at the DCI inlet have less of an effect. Further extensions towards the plasma (where plasma parameters are optimised at each distance) need to be investigated to identify if peak splitting was reduced once the base of the plasma has been passed.

Two other extensions of the DCI, 12 and 16 mm, were investigated at 100 µs time resolution, see Figure 38. The stitched data showed large portions of missing data within the peak profile. The signal intensity was much larger than at distances of -10 and 2 mm. The maximum signal intensity before the SEM becomes saturated in counting mode is \(5 \times 10^6\) counts per second. The SEM will also switch off if the count rate increased by more than \(2 \times 10^5\) counts per second within 1 ms. Figure 38A and B show that count rates exceed the saturation limit at the data point prior to the missing data. As such peak profiles at these extensions could not be investigated. The same occurred for peak profiles at time resolutions of 200 and 500 µs.
Figure 38 – Peak profiles for A) 12mm and B) 16 mm extensions at a 0.120 L/min flow rate, obtained using the raw channels per mass peak transient signal method, five individual pulses offset consecutively by 0.05 s on the x-axis and $1 \times 10^6$ counts s$^{-1}$ on the y-axis.

This new data acquisition method improved the time resolution of the transient data, allowing a more accurate description of the peak profiles generated by the Sniffer-DCI interface. However, 4.7 ms worth of transient data was missed every sweep, limiting the accuracy of the data acquisition as vital peak information may be lost within this period. Processing of the data was very time consuming as successive sweeps needed to be stitched and peaks needed to be searched for within a mass of raw data.
3.2.2.2 200 and 500 µs Raw Channels per Mass Peak Transient Signal

The time per channel was increased to 200 and 500 µs at a 2 mm DCI extension; see Table 17 for typical peak characteristics from the average of 5 separate peaks. The washout to 10% peak maximum, the FWHM and the peak width all increase with increasing time per channel, resulting in a lower aspect ratio. This is expected for fast pulses as increasing the time per channel decreases the time resolution.

Table 17 – Peak characteristics obtained from the raw channels per mass peak transient signal method from the average profile at 2 mm DCI extension, 0.120 Lmin⁻¹, 200 and 500 µs time resolution

<table>
<thead>
<tr>
<th>Peak characteristics</th>
<th>Time resolution (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>Sensitivity (counts/ppm)</td>
<td>6200</td>
</tr>
<tr>
<td>Washout time (s)*</td>
<td>0.0645</td>
</tr>
<tr>
<td>λ (s⁻¹)</td>
<td>30.8</td>
</tr>
<tr>
<td>FWHM (s)</td>
<td>0.0202</td>
</tr>
<tr>
<td>Peak width (s)</td>
<td>0.1393</td>
</tr>
<tr>
<td>Aspect ratio (counts s⁻²)</td>
<td>1.99 x 10⁷</td>
</tr>
</tbody>
</table>

*10% of peak maximum

The mean peak area did not change significantly at the different time resolutions, however the standard deviation was smaller at longer times per channel, see Figure 39A. The peak maximum did not significantly differ at different time resolutions, however the error associated with the average peak maximum increased as the time per channel increased, see Figure 39B.
Figure 39 – A) the average peak area and B) the average peak height from 5 separate peaks at time per channel of 100, 200 and 500 µs. Errors are given as the standard deviation of the mean.

The raw channels per mass peak method provides sufficient time resolution to describe the peak profiles from the Sniffer-DCI. However the data processing was time consuming and would not be practical for larger data sets, such as the information required for bio-imaging. The method uses successive sweeps to generate transient signal data, as there was a required settling time between the sweeps a gap in the transient information was created. This gap was much larger than between successive channels and as such can distort the data.
3.2.2.2.3 Averaged Channels per Mass Peak Transient Signal

The peak characteristics from peak profiles obtained by conventional data acquisition at a 2 mm DCI extension were also determined for comparison with the new method, see Table 18.

| Table 18 – Peak characteristics obtained from the averaged channels per peak transient signal method from the average profile at 2 mm DCI extension, 0.120 Lmin⁻¹ |
|----------------------------------------------------------|----------|----------|
| Peak characteristics                                    | 0 mm DCI extension | %RSD     |
| Peak max. (counts s⁻¹)                                  | 9.08 x 10⁴    | 22.4 %   |
| Area (counts)                                           | 1.75 x 10²    | 18.2 %   |
| Sensitivity (counts/ppm)                                | 200        |
| Washout time (s)*                                       | 0.032      |
| λ (s⁻¹)                                                 | 71.6       |
| FWHM (s)                                                | 0.0175     |
| Peak width (s)                                          | 0.0869     |
| Aspect ratio (counts s⁻²)                               | 3.88 x 10⁶  |

*10% of peak maximum

The peak maximum and area were lower than for the raw channel data. The peak profiles, see Figure 40, show an irregular shape compared to those seen previously under the same conditions, see section 3.2.2.1. As the conventional data acquisition was performed after the raw channels per peak experiments the DCI was believed to be damaged due to thermal stress induced at 16 mm extensions towards the plasma, confirmed by visual inspection of the DCI tip.
Figure 40 – Peak profiles for a 2mm extension at a 0.120 Lmin⁻¹ flow rate, obtained using the averaged channels per peak transient signal method A) five individual pulses offset consecutively by 0.05 s on the x-axis and 2 x 10⁴ counts s⁻¹ on the y-axis and B) the average peak profile from the 5 separate pulses
3.3 Signal Response from the Sniffer-DCI Interface, Using the Enterprise Cell as the Outer Cell

As described in chapter 2, the Enterprise cell, a purpose built outer cell, has been designed and fabricated. The new cell facilitates movement of samples in the x and y axis via magnetic coupling of the sample stage to an x-y manipulator. The Sniffer cell, housed in the Enterprise, was coupled to the DCI and the peak profiles from this configuration investigated.

3.3.1 Instrumental Parameters and Sniffer-DCI Configuration

The Sniffer was made parallel to the sample surface by fixing it to the support bar of the Enterprise cell, floating the Sniffer above the sample surface by c.a. 100 µm. The DCI inlet was fixed to the Sniffer c.a. 3 mm from the outlet, and was a total length of 460 mm.

The safe maximum working pressure within the cell was set at 100 kPa, higher than the modified UP213 cell lid due to much stronger fixings and fabrication. Optimisation of ICP operating parameters was conducted as in section 3.2.2, see Table 19.

A lower concentration standard, NIST SRM 613 (nominal 50 ppm concentration for trace elements), and a smaller laser spot diameter were used to attenuate the signal as the same conditions and sample used in section 3.2.2 saturated the SEM in counting mode. The sample was prepared by polishing the surface to a finish of Rₐ of 0.2 µm.

The averaged channels per peak data acquisition method was used, with a longer time per channel compared to section 3.2.2.2, as data acquisition development had not been fully investigated at the time of testing this cell. The dwell time per mass peak was set at 4 ms, however the time per sweep was 7.1 ms giving a duty cycle of 56%.
Table 19 – Laser and ICP-MS operating parameters used to investigate the peak profiles from the Enterprise cell

<table>
<thead>
<tr>
<th>Laser system operating parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot diameter</td>
<td>8 μm, aperture imaged</td>
</tr>
<tr>
<td>Laser energy/Fluence</td>
<td>0.007 mJ equating to 13.00 J/cm²</td>
</tr>
<tr>
<td>Sample</td>
<td>NIST SRM 613 Trace Elements in Glass (50 ppm nominal concentration)</td>
</tr>
<tr>
<td>Sample gas (helium) and resulting back pressure</td>
<td>Flow rate 0.050, 0.100 and 0.150 Lmin⁻¹ resulting in a back pressure of 38.06, 67.57 and 93.77 kPa respectively</td>
</tr>
<tr>
<td>Sampling strategy</td>
<td>2 Hz repetition rate, down-hole ablation, 15 second dwell time (equating to 30 single pulses), samples pre-ablated 60 shots</td>
</tr>
<tr>
<td>Sniffer-sample distance</td>
<td>100 μm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ICP-MS operating parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cool gas</td>
<td>15.5 Lmin⁻¹</td>
</tr>
<tr>
<td>Auxiliary gas</td>
<td>1.08 Lmin⁻¹</td>
</tr>
<tr>
<td>Plasma RF power</td>
<td>1330 W</td>
</tr>
<tr>
<td>Sheath gas</td>
<td>1.350 Lmin⁻¹</td>
</tr>
<tr>
<td>DCI extension (relative to sheath gas tube tip)</td>
<td>-12, 0, 2, 4, 6, 8, 10 and 12 mm</td>
</tr>
<tr>
<td>Acquisition parameters</td>
<td>²³⁵U, low resolution, 2% mass window, 0.001 s sampling time and 200 channels per peak equating to 0.004 s dwell time, 2% average integration window, E-scan, SEM in counting mode</td>
</tr>
</tbody>
</table>
3.3.2 Peak Profiles and Characteristics Using the Enterprise Cell

The 30 single peak profiles from each extension at a given flow rate were averaged to generate a typical peak profile for that condition. The data from a 0.150 Lmin\(^{-1}\) flow rate showed no significant difference from that at a 0.100 Lmin\(^{-1}\), as a result of poor time resolution of the data. This limits the level of detail within the peak profile and smooths out any significant differences. As such only the data from 0.050 and 0.100 Lmin\(^{-1}\) flow rates are presented, see Figure 41. The poor time resolution was also apparent at these flow rates. The peaks at a DCI extension consist of a single large data point at the maximum, accounting for 75-81% and 83-88% of the peak area for 0.050 and 0.100 Lmin\(^{-1}\) respectively. With the DCI retracted the peak maximum accounts for 26% and 45% of the peak area.

![Figure 41 – Peak profiles for varied extension of the DCI, Enterprise cell configuration, at a flow rate of A) 0.050 and B) 0.100 Lmin\(^{-1}\). Peaks have been successively offset by 0.05 seconds on the x-axis and 1 x 10\(^5\) counts per second on the y-axis for clarity](image)
The peak profiles show only one peak maximum and the presence of a second peak or peak splitting was not observed. However, due to the poor time resolution and resulting accuracy of the peak profile representation it is inconclusive if using the Enterprise cell has eliminated this feature.

The average peak maximum at a given DCI extension is shown in Figure 42A and B for flow rates of 0.050 and 0.100 Lmin\(^{-1}\) respectively.

**Figure 42** - The average peak maximum for the Enterprise configuration Sniffer-DCI interface at A) a 0.050 and B) a 0.100Lmin\(^{-1}\) flow rate for varied DCI extensions, errors bars are given as 95% confidence intervals. The dotted lines represent the end of the sheath gas tube at 0 mm, the first and second turn of the load coil at 5.3 and 9.3 mm respectively.
The peak maximum does not significantly differ between the two flow rates; however both show a similar trend with changing DCI distance. The peak maximum at a flow rate of 0.100 Lmin\(^{-1}\) was similar for distances of -12 and 0 mm. However, at 0.050 Lmin\(^{-1}\), confidence intervals overlap, but a small increase in the average peak maximum was seen. Between these two distances turbulent mixing of the sample aerosol and the sheath gas most likely occurs. At the higher flow rate the gas velocity of the sample aerosol, when exiting the DCI, will be much higher. This in turn reduces the residence time of particulate in the sheath-gas tube and thus the effect of turbulent mixing.

Past the end of the sheath-gas tube the peak maximum increased as the DCI was extended towards the plasma. At 2 mm the DCI tip was within the turbulent mixing zone of the sheath gas and auxiliary gas \(^{66,68}\), at extensions of 4 and 6 mm the tip enters the noisy recirculation region at the base of the plasma \(^{66}\); the location of the first turn in the load coil. Once the DCI was pushed past these regions the highest peak maximum was achieved at an 8 mm extension for a flow rate of 0.050 Lmin\(^{-1}\). However, at 0.100 Lmin\(^{-1}\) the average peak maximum decreases slightly at this extension as a result of the higher particulate velocity and reduced particle processing, confirmed by a similar trend shown for the peak area in Figure 43.

Past an 8 mm extension the average peak maximum was reduced significantly at both flow rates. Again this was due to a shorter residence time of the particulate within the plasma resulting in a reduction in particle processing of the sample aerosol. Interestingly this drop coincides with the second turn of the load coil, around 10 mm, after which the average peak maximum starts to increase again at 12 mm. The reduction in peak maximum was a combination of reduced residence time and the possible presence of another complex flow region. This region could be similar to that seen at the first load coil turn and promote recirculation of particulate. The modelling performed by Helmut et al \(^{66}\) reported a small turbulence within the region of the second turn as a result of recombination of the recirculation regions induced at the base of the plasma converging on the central sample stream.

The load coil used in the investigations reported here was wrapped three times around the torch with a spacing of 1-2 mm between coils, much closer than the model used by Helmut et al. ICP modelling by Punjabi et al \(^{72}\) reported that the
spacing of the load coil affects the flow patterns and temperature distribution of the plasma. By placing turns in the load coil closer together a downstream recirculation region becomes larger, this affects the upstream flow and enhances the recirculation region.

After being exposed to these extensions slight devitrification of the DCI injector tip occurred, however the tip did not melt. Modelling of the ICP has shown the temperature of the centre of the plasma to be dependent on the injector gas flow rate; at a flow rate of 0.4 Lmin$^{-1}$ the model predicted a temperature of 1000-2000 K in-line with the second turn of the load coil 66.

Figure 43 – The average peak area for the Enterprise configuration Sniffer-DCI interface at A) a 0.050 and B) a 0.100Lmin$^{-1}$ flow rate for varied DCI extensions, errors bars are given as 95% confidence intervals.
The peak area shows a similar trend as was shown for the peak maximum when extending the DCI towards the torch, see Figure 43. The peak area at 0 mm was much lower than at -12 or 2 mm, however as previously discussed the peak maximum was similar to -12 mm, which suggests a particle size dependant loss of sample material occurred. Modelling of the peak shape in relation to particle washout time by Autrique et al, reported peak splitting; where 100% of the larger particulate diameter ranging from, 300 nm to 5 µm, represented the first maximum in the split peak and 88% of the smaller particulate diameter, ranging from 1-200 nm, represented the second. The split was a result of gas mixing induced turbulence. As the sheath-gas tube tapers at -10 mm the sheath gas flow velocity will be highest at the 0 mm position. This in turn will result in more turbulent mixing of the sample aerosol and sheath gas at a 0 mm position and potential loss of the smaller particle sizes. Thus the peak area will be lower, but the peak maximum similar as the larger, unaffected particulate accounts for this.

The percentage RSD of the peak maximum and area, see Table 20, were much higher than those given in 3.2.2.1.1 using the modified UP213 cell lid. This was a result of poor time resolution and description of the peak profile. As the peak widths were much shorter, see Table 21 and Table 22, capturing the true peak maximum and area using a longer integration time becomes more difficult. The profile becomes temporally blurred, resulting in more variability in the determined peak maximum and area. However, as the peak maximum increased as the DCI was extended towards the plasma the percentage RSD got smaller for both flow rates. The opposite effect was seen for the peak area.
Table 20 – The percentage relative standard deviation associated with the average peak area and peak maximum for the using the Enterprise cell at 0.050 and 0.100 Lmin\(^{-1}\) at varied DCI extensions

<table>
<thead>
<tr>
<th>DCI extension (mm)</th>
<th>-12</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0.050 Lmin(^{-1})</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak max. %RSD</td>
<td>82</td>
<td>70</td>
<td>62</td>
<td>55</td>
<td>54</td>
<td>55</td>
<td>65</td>
<td>61</td>
</tr>
<tr>
<td>Peak area %RSD</td>
<td>19</td>
<td>49</td>
<td>43</td>
<td>43</td>
<td>44</td>
<td>44</td>
<td>49</td>
<td>44</td>
</tr>
<tr>
<td><strong>0.100 Lmin(^{-1})</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak max. %RSD</td>
<td>97</td>
<td>68</td>
<td>67</td>
<td>66</td>
<td>69</td>
<td>74</td>
<td>64</td>
<td>69</td>
</tr>
<tr>
<td>Peak area %RSD</td>
<td>38</td>
<td>61</td>
<td>56</td>
<td>59</td>
<td>60</td>
<td>66</td>
<td>60</td>
<td>62</td>
</tr>
</tbody>
</table>

The peak characteristics from varying the DCI extension when using the Enterprise outer cell configuration at flow rates of 0.050 and 0.100 Lmin\(^{-1}\) are given in Table 21 and Table 22 respectively.

Table 21 – Peak profile characteristics for varied DCI extensions using the Enterprise outer cell at a flow rate of 0.050 Lmin\(^{-1}\)

<table>
<thead>
<tr>
<th>DCI extension</th>
<th>-12</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (counts/ppm)</td>
<td>5300</td>
<td>8780</td>
<td>15400</td>
<td>18200</td>
<td>19300</td>
<td>20000</td>
<td>7610</td>
<td>7700</td>
</tr>
<tr>
<td>Washout time (s)*</td>
<td>0.0537</td>
<td>0.0076</td>
<td>0.0075</td>
<td>0.0064</td>
<td>0.0064</td>
<td>0.0063</td>
<td>0.0068</td>
<td>0.0069</td>
</tr>
<tr>
<td>(\lambda) (s(^{-1}))</td>
<td>42</td>
<td>301</td>
<td>305</td>
<td>359</td>
<td>358</td>
<td>362</td>
<td>335</td>
<td>333</td>
</tr>
<tr>
<td>FWHM (s)</td>
<td>0.0193</td>
<td>0.0058</td>
<td>0.0058</td>
<td>0.0055</td>
<td>0.0055</td>
<td>0.0054</td>
<td>0.0056</td>
<td>0.0056</td>
</tr>
<tr>
<td>Peak width (s)</td>
<td>0.1305</td>
<td>0.0262</td>
<td>0.0278</td>
<td>0.0252</td>
<td>0.0254</td>
<td>0.0253</td>
<td>0.0239</td>
<td>0.0240</td>
</tr>
<tr>
<td>Aspect ratio (x10(^7), counts s(^{-2}))</td>
<td>0.152</td>
<td>1.25</td>
<td>2.07</td>
<td>2.70</td>
<td>2.85</td>
<td>2.96</td>
<td>1.19</td>
<td>1.20</td>
</tr>
</tbody>
</table>

*10% of peak maximum
Table 22 – Peak profile characteristics for varied DCI extensions using the Enterprise outer cell at a flow rate of 0.100Lmin\(^{-1}\)

<table>
<thead>
<tr>
<th>DCI extension</th>
<th>-12</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (counts/ppm)</td>
<td>9240</td>
<td>8840</td>
<td>15100</td>
<td>17100</td>
<td>18000</td>
<td>17500</td>
<td>8520</td>
<td>8720</td>
</tr>
<tr>
<td>Washout time (s)*</td>
<td>0.0245</td>
<td>0.0048</td>
<td>0.0053</td>
<td>0.0055</td>
<td>0.0050</td>
<td>0.0049</td>
<td>0.0046</td>
<td>0.0047</td>
</tr>
<tr>
<td>λ (s(^{-1}))</td>
<td>95</td>
<td>477</td>
<td>432</td>
<td>419</td>
<td>456</td>
<td>468</td>
<td>502</td>
<td>484</td>
</tr>
<tr>
<td>FWHM (s)</td>
<td>0.0110</td>
<td>0.0050</td>
<td>0.0051</td>
<td>0.0052</td>
<td>0.0086</td>
<td>0.0050</td>
<td>0.0049</td>
<td>0.0050</td>
</tr>
<tr>
<td>Peak width (s)</td>
<td>0.0687</td>
<td>0.0192</td>
<td>0.0217</td>
<td>0.0224</td>
<td>0.0213</td>
<td>0.0209</td>
<td>0.0185</td>
<td>0.0190</td>
</tr>
<tr>
<td>Aspect ratio (x10(^7), counts s(^{-2}))</td>
<td>0.503</td>
<td>1.72</td>
<td>2.61</td>
<td>2.84</td>
<td>3.16</td>
<td>3.13</td>
<td>1.72</td>
<td>1.72</td>
</tr>
</tbody>
</table>

*10% of peak maximum

Comparing these characteristics with those determined for the modified UP213 cell lid at a DCI extension of 2 mm, section 3.2.2.1.1, shows a significant improvement in aerosol transport.

The total peak width (baseline resolved) was five times shorter when using the Enterprise cell. As a smaller spot size was used compared to the investigation in section 3.2.2.1.1, the initial ablation plume diameter was smaller for the Enterprise cell investigation. This may have also contributed to the reduction in peak width. However the modelling conducted in Chapter 2 showed that the dispersion of particulate across the laser viewing area resulted in a difference in residence time of 1-2 ms (dependant on the proximity to the micro-chamber outlet). As the Sniffer was fixed parallel to the sample surface the flow dynamics were believed to match the modelled flow patterns more closely. Thus particulate was contained within the micro-chamber and plume dispersion minimised, resulting in a shorter peak width and higher peak maximum.
The washout time to 10% of the peak maximum was also greatly reduced, twice as quick at a 0.050 Lmin\(^{-1}\) flow rate and three times as quick at a flow rate of 0.100 Lmin\(^{-1}\). The FWHM at both flow rates was also much shorter. However, the accuracy of these values was limited by the time resolution. At all DCI extensions the calculated FWHM and washout time were less than the data acquisition sweep time (7.1 ms), the time between data points. The washout time and FWHM were shorter than the sweep time as the characteristics were calculated using an exponential decay curve, fitted from the peak maximum to the baseline. As only a few data points account for the bulk of the peak area, the less intense but numerous data points that make up the peak tail result in a poor curve fit around the peak maximum.

Direct comparison of the aspect ratio shows a two-fold improvement; however the spot size was smaller and analyte concentration lower when investigating peak profiles using the Enterprise cell. An improvement in the aspect ratio can be inferred from the peak width and the sensitivity (a function of analyte concentration and peak maximum). The sensitivity increased almost five-fold at a 2 mm DCI extension. Sensitivity at an 8 mm DCI extension and 0.050 Lmin\(^{-1}\) flow rate was 20,000 counts s\(^{-1}\)/ppm, similar to in-torch ablation (integration time of 0.5 ms) \(^37\).

The Enterprise cell showed a significant improvement in aerosol transport efficiency when compared to the modified UP213 cell lid.
3.4 Comparing the DCI Performance to that of a Standard Injector for the Zircon Cell

3.4.1 The Zircon Laser Ablation Cell
The practicality of coupling the DCI to an existing laser ablation cell was investigated. The chosen cell, described by Horstwood et al\textsuperscript{52}, was designed following the work of Bleiner and Günther\textsuperscript{53}. The cell is tear drop in shape, with the gas inlet positioned at the point of the tear and the sample outlet at the wide angle curvature of the bottom, see Figure 44.

![Figure 44 – Schematic drawing of the Zircon cell.](image)

The cell contains two pucks, sealed by an o-ring, on which a sample or standard is placed and is pushed into the cell such that when a 1 mm thick sample is placed inside, the sample surface is at the same height as the cell bottom. This ensures gas flow entering the cell sweeps across the surface and isn’t perturbed.

The gas outlet is a standard \(\frac{1}{8}\)" internal diameter barbed gas connector.

3.4.2 Instrumental Parameters and Interface Configuration
Details of the laser ablation and ICP-MS parameters and sampling regime are given in Table 23.
When using a standard injector (2.0 mm I.D.) the cell outlet was directly coupled with Tygon tubing (1/8” I.D., ¼” O.D.). The tubing extended 15 cm from the cell to a y-piece connector where an argon make-up gas was introduced with the sample aerosol. The transport length from the y-piece to injector base was 40 cm and connected to the injector via a 12/5 ball joint.

When coupling the DCI to the cell, the fused silica tubing (360 µm outer diameter, 250 µm internal diameter, Supelco, untreated fused silica tubing, Sigma-Aldrich Company Ltd., Dorset, UK) was sheathed with PEEK tubing (400µm I.D. and 1/8” O.D.) which in turn was sheathed in Tygon tubing (1/8” I.D. and ¼” O.D.) and held together using a hose clip. The sampling end of the DCI was placed at the bottom of the tear-drop curve; see Figure 44, giving a total transport length of 50 cm. The 2.0 mm standard injector was used as the sheath gas tube for these experiments.
<table>
<thead>
<tr>
<th><strong>Laser Ablation System</strong></th>
<th>ESI, New Wave Research Division, Huntingdon, UK</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System</strong></td>
<td>Solid State Nd:YAG, UP-213</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>213 nm, 5th harmonic of 1064 nm, 4 ns pulse duration</td>
</tr>
<tr>
<td><strong>Spot diameter</strong></td>
<td>100 μm, aperture imaged</td>
</tr>
<tr>
<td><strong>Laser energy/Fluence</strong></td>
<td>0.700 mJ equating to 9.00 J/cm²</td>
</tr>
<tr>
<td><strong>Sample</strong></td>
<td>NIST SRM 611 Trace Elements in Glass</td>
</tr>
<tr>
<td><strong>Helium sample gas</strong></td>
<td>0.025 (DCI and 1/8&quot; Tygon tubing)</td>
</tr>
<tr>
<td></td>
<td>0.05, 0.1, 0.2, 0.4 and 0.8 Lmin⁻¹ (Tygon tubing only)</td>
</tr>
<tr>
<td><strong>Sampling strategy</strong></td>
<td>4 x tracks (450 μm, 120μm spacing) at 5 μms⁻¹</td>
</tr>
<tr>
<td></td>
<td>translation</td>
</tr>
<tr>
<td></td>
<td>Repetition rate 10 Hz</td>
</tr>
<tr>
<td></td>
<td>30 second wash out delay between each line</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>ICP-MS</strong></th>
<th>Thermo Scientific, Bremen, DE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System</strong></td>
<td>Element XR Magnetic Sector Field ICP-MS</td>
</tr>
<tr>
<td><strong>Cool gas</strong></td>
<td>15.5 Lmin⁻¹</td>
</tr>
<tr>
<td><strong>Auxiliary gas</strong></td>
<td>0.85 Lmin⁻¹</td>
</tr>
<tr>
<td><strong>Plasma RF power</strong></td>
<td>1300 W</td>
</tr>
<tr>
<td><strong>Make-up argon gas</strong></td>
<td>Varied to maintain a constant total gas flow rate of 1.55 L min⁻¹ when combined with helium sample gas</td>
</tr>
<tr>
<td><strong>Sheath gas when using the DCI</strong></td>
<td>1.00 Lmin⁻¹</td>
</tr>
<tr>
<td><strong>DCI extension (relative to sheath gas tube tip)</strong></td>
<td>-15, 0, 2, 4, 6, 8, and 10 mm</td>
</tr>
<tr>
<td><strong>Acquisition parameters</strong></td>
<td>²³⁸U, low resolution, 40% mass window, 0.01 s sampling time and 10 samples per peak equating to 0.04 s dwell time, 40% integration window averaged across peak, E-scan, Triple detection mode</td>
</tr>
</tbody>
</table>
3.4.3 Signal Profiles from the DCI-Zircon cell and Standard Configuration

3.4.3.1 Cell Pressure

The back pressure of the cell was monitored with change in sample gas flow rate, see Table 24.

Table 24 – Change in back pressure from the Zircon Cell when altering the sample gas flow rate using the two injector types

<table>
<thead>
<tr>
<th>Injector/transport configuration</th>
<th>Sample gas flow rate (Lmin⁻¹)</th>
<th>Pressure (PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard injector and 3/8&quot; Tygon tubing</td>
<td>0.025</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>0.050</td>
<td>0.15</td>
</tr>
<tr>
<td>DCI, 250 µm I.D.</td>
<td>0.100</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>0.200</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>0.400</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>0.800</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>0.050</td>
<td>1.76</td>
</tr>
</tbody>
</table>

When the DCI was coupled to the Zircon cell the pressure increased of the order of tenfold the pressure at the same flow rate with the standard transport configuration. However, it was observed when using the DCI at a flow of 0.050 Lmin⁻¹ the sample became defocused over time. This indicated that the pressure within the cell was enough to force the sample puck down and thus cause the cell to leak losing sample aerosol and entraining atmosphere. DCI experiments were therefore conducted at 0.025 Lmin⁻¹.

3.4.3.2 Average Signal Intensity and Signal Area for NIST 611

The signal profiles for the standard injector (red) and the DCI at a 4 mm extension (blue), at a flow rate of 0.025 Lmin⁻¹ are shown in Figure 45, the DCI trace has been offset by an order of magnitude for clarity. The noise of the DCI signal was typical for all positions (extended and retracted).
The signal was averaged after the initial rise and before the signal washout to give an average signal intensity and a standard deviation for each ablation track. From this the percentage R.S.D was calculated for each individual track and averaged to give a mean signal noise at each condition; presented in Table 25.

As can be seen in Table 25, when using the DCI the average noise was less than when using the standard injector at the same flow rate. When using the standard injector an argon makeup gas was introduced, this increased noise due to the turbulent mixing involved.

The increased pressure within the laser cell when using the DCI also helps to confine the ablation plume and reduce mixing within the cell, reducing noise related to particle spread; however this effect was expected to be minimal.
Table 25 – The average signal noise for the DCI and the standard injector at 0.025 Lmin\(^{-1}\) helium flow rate

<table>
<thead>
<tr>
<th>DCI extension (mm)</th>
<th>Track 1</th>
<th>Track 2</th>
<th>Track 3</th>
<th>Track 4</th>
<th>(\bar{\tau})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-15</td>
<td>39</td>
<td>28</td>
<td>35</td>
<td>20.1</td>
<td>31</td>
</tr>
<tr>
<td>0</td>
<td>25</td>
<td>25</td>
<td>20</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>23</td>
<td>13</td>
<td>20</td>
<td>18</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>43</td>
<td>24</td>
<td>20</td>
<td>28</td>
</tr>
<tr>
<td>6</td>
<td>23</td>
<td>43</td>
<td>28</td>
<td>33</td>
<td>32</td>
</tr>
<tr>
<td>8</td>
<td>15</td>
<td>19</td>
<td>18</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>10</td>
<td>19</td>
<td>18</td>
<td>30</td>
<td>46</td>
<td>22</td>
</tr>
<tr>
<td>2.0mm Injector</td>
<td>43</td>
<td>40</td>
<td>40</td>
<td>41</td>
<td>41</td>
</tr>
</tbody>
</table>

The noise reduced when extending the DCI from inside the sheath tube to 4mm past the tip. Between 4 and 6 mm extension the noise increased. This region lies at the base of the plasma, the previously discussed noisy region, thus an increase in noise was expected. Extensions past this (8 and 10 mm) showed a reduction in noise as expected, but were not lower than a 2 mm extension.

Table 25 also shows that although the individual ablation tracks were on average less noisy for the DCI, the variation of the noise between different ablation tracks was much larger. As the injector was hard coupled to the cell, cell movement can cause small variations in the injector position relative to the plasma and of the overall transport tubing orientation. The flow through the cell using standard conditions (0.8 Lmin\(^{-1}\), atmospheric pressure) has been modelled, but not described here, and it was found that the time taken for a particle to exit the cell was spatially dependent. Due to the pressure increase when using the DCI, these spatial dependent transport efficiencies will differ more than at atmospheric pressure due to an increase in turbulence. Thus the variability in noise between track positions for the same conditions was more significant. In this configuration the DCI inlet was flush to the end of the Zircon cell outlet and presents a large flat surface around it, providing area for possible eddy formation. This will also affect transport efficiency dependent on ablation position within the cell.
The average signal intensity and total counts for various DCI positions and the standard injector are shown in Figure 46A and B.

At 2 mm past the sheath gas tube the signal intensity and area was more than double than at 0 mm; an indication that transport efficiency was improved by extending the injector. Comparing the 2mm DCI extension to the standard injector at the same flow rate shows a 46% increase in total signal area and a 40% increase in signal height.

Extending the DCI further than 2 mm resulted in a reduction in signal intensity and area compared to the standard injector. ICP parameters such as sheath gas...
flow rate, z-position (the distance of the torch from the cones) and power were held constant for each extension and as such the operating conditions were not optimised for each extension. For example at a 10 mm extension the particulate would have had a shorter residence time within the plasma causing a reduction in atomisation and thus ionisation efficiency. The signal intensity and area reduced from a 2 to 6 mm extension, but increased after extending further (8 and 10 mm). This was an indication that the noise and recirculation at the plasma base had been negated.

<table>
<thead>
<tr>
<th>Sample gas flow rate (Lmin⁻¹)</th>
<th>Track 1</th>
<th>Track 2</th>
<th>Track 3</th>
<th>Track 4</th>
<th>Percentage R.S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>27</td>
<td>27</td>
<td>26</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>0.10</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>0.20</td>
<td>16</td>
<td>17</td>
<td>16</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>0.40</td>
<td>19</td>
<td>16</td>
<td>18</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>0.80</td>
<td>22</td>
<td>20</td>
<td>21</td>
<td>31</td>
<td>23</td>
</tr>
</tbody>
</table>

However, when the flow rate was increased using the standard injector the signal noise reduced to percentages similar to the DCI, see Table 26. Improvements were also seen in the signal intensity and the signal area; see Figure 47A and B respectively. Therefore operation of the Zircon cell, when coupled to the DCI, cannot be performed at the optimum gas flow rate for the cell and any improvements in sample transport to the torch and through the plasma were hindered by lack of efficiency in the cell at sub-optimal conditions.
For the DCI to work efficiently and at optimum conditions, a cell capable of running at low flow rates whilst maintaining transport efficiency through it is required. Thus for large single cell ablation chambers the DCI does not offer significant advantages as it needs to be operated at flow rate that is not optimum for particle transport through the large cell volume. However, for other cell in cell type designs that can operate efficiently at lower flow rates, the DCI could improve cell performance.
3.5 Conclusion

The Sniffer-DCI interface was shown to produce a peak profile from a single laser pulse with a width of less than 30 ms and washout time to 10% of the peak maximum in less than 10 ms. So for imaging applications a laser repetition rate of 33 Hz could be used to generate fully resolved pixel information or 100 Hz repetition rate for a 10% peak maximum resolved signal. Compared to current research cells with a 100 ms washout time to 10% peak maximum sample mapping can be completed in 10% of the time.

Investigations have shown a twofold improvement in transport efficiency and peak width when using one continuous sample transport tube, from close to the ablation site to the ICP, when compared to using multiple tubes of a continuous diameter. This was a result of improved flow dynamics along the aerosol path by a reduction in potential dead volumes and eddy regions.

An increase in the peak maximum and area has been shown when using the Enterprise cell as the outer-housing to contain the inner Sniffer cell. Thus by placing the Sniffer cell parallel to the sample surface an improvement in transport efficiency has been shown. Investigations using the Enterprise cell also showed improvements in sensitivity and FWHM, 20,000 counts s\(^{-1}\)/ppm and 5.4 ms respectively at a 8 mm DCI extension. This is comparable to that seen for in-torch ablation where the sample aerosol is created at the base of the plasma and transport distance is essentially 0 mm. The sensitivity was roughly 20,000 counts s\(^{-1}\)/ppm and the FWHM reported as 4 ms. However the accuracy of the values reported for the Sniffer-DCI is limited by the time resolution of the data acquisition.

The peak profile has also been shown to change with different distances relative to the sheath gas tube, conventionally the injector tube. By increasing the DCI tip from within the sheath-gas tube towards the plasma, an increase in peak maximum and area was observed complimented by a reduction in peak width and FWHM. The highest peak maximum of \(7.47 \times 10^5\) counts s\(^{-1}\), for an 8 \(\mu\)m diameter spot on NIST 612, was observed at an 8 mm extension.

An improved data acquisition method was also investigated and found to improve the time resolution of the peak profiles by reducing the time per data point output to 100 \(\mu\)s. However the processing of the data is time consuming and not
practically applicable for large data sets such as those obtained from bio-imaging and rendered the instrument to single ion monitoring. A multi-collector instrument with SEM detectors is required to implement the same method for multiple ion monitoring.

Based on the peak characteristics the Sniffer-DCI interface is currently undergoing patent application.
3.6 Future Work

The peak maximum and thus sensitivity of the interface has been determined, however this can vary between instruments and makes comparison with other laser ablation interfaces difficult. Thus the efficiency of the interface as a function of the ablated mass compared to the number of ions detected needs to be investigated.

Determining the transport efficiency in this manner will also give an insight into potential particle-Sniffer wall interaction, which could be significant given the small volume of the micro-chamber. It has been reported by Bleiner and Günther that a circular cell design of radius 0.8 cm and volume of 0.25 cm³ resulted in splattering of ablated particulate onto the cell walls, resulting in longer washout times. The flow dynamics and gas velocity were not reported for this cell design and as such turbulent flow could also be the cause of this increase in aerosol spread. The ablation plume expansion was reported by Koch et al in which the plume evolution was visualised over time. The plume reached a maximum height of 6 mm from the sample surface. However this investigation was conducted in a large cell using a larger spot diameter and laser energy. The gas within the cell was static and at atmospheric pressure. This is far from the dynamic environment in which conventional laser ablation is conducted. Further to their work on laser induced ablation plume expansion, Koch et al investigated the effect of high repetition rate on the plume dynamics. It was reported that at high laser-pulse repetition rates a local pressure gradient built up within the plume expansion region resulting in a complex macroscopic flow pattern of the expanding aerosol. Loss of ejected material from deposition on cell walls was also investigated and it was reported that at high repetition rates only a 1% loss of ejected mass occurred.

Numerical calculations based on particle travel with the laser induced shock front by Gurevich and Hergenröder reported a maximum diameter of 2 mm for the initial laser ablation particle cloud under atmospheric pressure using 1 mJ laser energy. Modelling by Bogaerts et al reported a plume maximum of c.a. 2 mm 600 ns after laser irradiance of the sample surface under atmospheric pressure, Chen et al reported that this distance is significantly reduced as the background pressure is increased creating a much hotter plasma. Reports of plume expansion seems to vary considerably dependant on the initial laser parameters, the background gas and pressure and the local flow dynamics surrounding the ablation.
site. As such the flow within this specific configuration will need to be investigated by visualisation of the plume or by modelling to assess wall interaction and potential particle loss. This will also aid in assessing if the peak widths characterised in this report are representative of the expected peak widths, as such investigation into the initial ablation plume diameter will need to be conducted.

Modelling of the DCI and its extensions would useful to fully understand and complement the findings reported here. Current models of the ICP by Lindner et al. have been useful in identifying recirculation regions, however the effect the DCI has on these regions and potential down-stream effects are not understood.

A practical data acquisition method is currently under development in which the SEM signal will be monitored directly and data processing will become less complicated and time consuming. This will facilitate practical improvements in time resolution and thus allow further investigation and characterisation of the peak profiles generated when using the Enterprise cell. With improved time resolution, optimisation of the interface at different DCI extensions and different Sniffer-sample distances can be investigated.
Chapter 4 Laser Ablation of a Sample In Liquid – LASIL

4.1 Introduction

Many real world samples have a varied, complex and unknown matrix composition, e.g. nuclear waste sludge from storage ponds. Conventional analysis of these sample types involves dissolution by a strong acid, followed by multiple dilution steps to reduce concentrations of hazardous elements to a measurable and safe level. However, this can be expensive, as large volumes of waste are generated requiring treatment and controlled disposal and any spatial information regarding elemental distribution is lost.

Solid sampling by LA can be used as an alternative to conventional ‘wet’ analysis methods. This technique offers many advantages over wet analysis methods, such as: a smaller waste volume, the facility to acquire spatial as well as bulk information and direct coupling to analytical instrumentation, e.g. ICP-MS, reducing sample preparation and analysis time. However, due to the complex and unknown matrix composition of some samples LA-ICP-MS has certain disadvantages. Calibration by matrix matching becomes difficult or expensive due to the sample complexity and by on-line additions the analysis becomes time consuming in order to overcome the heterogeneity of the sample and generate bulk concentration information.

The analysis is also fraught with complications if the sample is hazardous e.g. high concentrations of radioactive elements. In this instance the generation of an aerosol by LA requires strict control of the containment and transport of the particulate, often requiring expensive custom and complex engineering to facilitate the analysis.

LASIL was developed as an alternative to existing LA and wet chemistry (dissolution and dilution) techniques, allowing for analysis of samples with complex matrices and containment of any potential hazardous materials.

LASIL has previously been performed with the sample completely submerged within a liquid. As well as trying to replicate and improve this technique, LASIL within a liquid droplet upon the sample surface was also developed.
4.1.1 The LASIL Mechanism

LASIL is a technique where laser induced ablation occurs at a solid-liquid interface, where the sample is submerged or a liquid droplet is placed on the sample surface. The liquid medium is transparent to the laser wavelength to ensure maximum laser energy transport to the sample and minimise any laser-liquid interactions. The mechanism described here is for the processes that occur for a laser with a nanosecond pulse width and assumes a flat sample surface. The mechanism does not account for translational laser ablation where the surface becomes angled as the laser rasters across new material.

The laser energy couples with the sample converting it into a liquid/vapour. This causes localised vaporisation of the surrounding liquid, oscillation of the sample surface and the release of energy as a shockwave which all lead to the formation of a gaseous micro-cavity that surrounds the ablation site and expands into the liquid. The formation of the micro-cavity is advantageous in that it reflects energy released in the shockwave back onto the ablation site, which in a gaseous media dissipates energy into the surrounding environment. Thus LASIL leads to a more efficient energy coupling between laser and sample as energy transfer to the surrounding environment is reduced.

Part of the laser induced liquid/vapour is ejected and confined within the micro-cavity as an ablation plume/plasma; a small amount of material can pass into the liquid in the initial ejection. The expansion of the micro-cavity occurs faster than that of the ablation plume, resulting in the diameter of the micro-cavity becoming much larger than the plume diameter, inhibiting further material transfer to the liquid. Confinement of the ejected material in the micro-cavity results in a smaller ablation plume/plasma compared to that generated at a solid-gaseous interface, leading to an increase in the pressure and temperature. This increase can be over an order of magnitude higher than ablation in a gaseous atmosphere.

The mechanisms of material ejection and particle formation of laser ablated matter at a solid-liquid interface are not yet fully understood. However, recent investigations have shown that due to the increased pressures and temperature within the micro-cavity the percentage mass of matter ejected via phase explosion is smaller than that at the same laser operating conditions in a gaseous...
atmosphere. Material ejection is dominated by fragmentation and vaporisation mechanisms, so that particle formation occurs via condensation or cooling of small liquid drops. Particle diameters can be expected to be less than tens of nanometer and particle size distribution to be much smaller than that from laser ablation in a gaseous atmosphere.

After the initial expansion of the micro-cavity the plasma cools, resulting in a particulate-filled vapour bubble. The quenching time of the plasma confined by liquid is much shorter than that generated in a gaseous atmosphere. This effectively limits the particle diameter and size distribution to the nanometer range when using laser pulse durations of less than 20 ns. Provided the micro-cavity forms close or on an immersed solid surface, as with laser ablation at a solid-liquid interface, it will elongate perpendicular to the solid surface, and the radius of the bubble will increase with increasing laser energy. The micro-cavity continues to expand until a maximum radius is reached, after which it begins to distort, shrink and finally collapse. This collapse is caused by decay in the interior pressure of the cavity from plasma cooling and an increasing radius, resulting in a lower pressure than the surrounding water. If the initial micro-cavity radius is large enough during the collapse phase, the micro-cavity can rebound from the sample surface into a re-growth phase to a smaller radius than the initial expansion. The growth-collapse oscillation continues until a radius is reached at which re-growth no longer occurs. The time taken for the collapse is increased, compared to a bubble generated in free solution, due to the elongation relative to the solid surface.

During collapse of the micro-cavity, micro-jets form that impinge upon the sample surface, adding a mechanical mechanism for removal of material. The micro-jets also inhibit particle agglomeration by clearing the ablation site of ejected particulate, ensuring a free path for the next incoming laser pulse. Mechanical stress, induced by the micro-jets, can lead to fracture or hydrodynamic removal of particles from a melt zone. Thermal convection and bubble induced liquid motion also aid in the removal of particulate from the ablation site when nano-second pulse lengths and repetition rates below 1 kHz are used.

Secondary bubble formation can occur at different times throughout the mechanism, where small bubbles rise from the ablation site to the liquid surface. Initially these bubbles are generated during plasma formation and development;
the liquid surrounding the micro-cavity becomes superheated by thermal convection and leads to the generation of vapour bubbles. These vapour bubbles can also be generated after collapse of the micro-cavity. These bubbles originate from diffusion of dissolved gases from the liquid into the expanding micro-cavity and vapour released during ablation. The rising bubbles can interact with the next incoming laser beam and hinder ablation by refraction or reflection and cause the laser beam to deviate from the intended ablation track.

The overall process of energy coupling, shock wave formation, plume formation, micro-cavity generation and micro-jet formation are relatively fast (ns time scale) such that the next laser beam-sample coupling is not inhibited, e.g. by plasma shielding. After cavity collapse the particulate is released 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 \( \approx 3 \times 10^{-8} \text{ms}^{-1} \) (in pure water).

### 4.1.2 Calibration

The suspended solid is collected and aspirated into an ICP-MS. Provided the particulate has a diameter less than 150 nm the ICP will completely atomise the solid; comparable to the efficiency with which solution droplets are processed. Calibrating the suspension against aqueous standards (prepared from inorganic salts of the analyte) can then be used to determine the concentration of analytes in the suspension.

Once the concentration of analyte in solution is known the concentration of analyte in the original solid sample can be calculated by two methods.

As discussed in the introduction quantification by similar LASIL methods have been reported, in which details of calibration can be found.

#### 4.1.2.1 Analyte Concentration from Ablated Mass

The mass of the analyte in solution is calculated from the concentration of the analyte in solution \((C_{AL})\) and the volume of the solution \((V_{L})\). The mass of material removed by the ablation process is calculated from the volume of material \((V_{S})\)
removed (by directly measuring the ablation crater) and the density \( (\rho_s) \) of the solid. The concentration of analyte in the solid \( (C_{AS}) \) is calculated by multiplying the ratio of the two masses by \( 10^6 \), to obtain a concentration in parts per million, as shown in Equation 15.

\[
C_{AS} = \left( \frac{C_{AL} V_L}{\rho_s V_S} \right) . 10^6
\]  

**Equation 15**

4.1.2.2 **Analyte Concentration using an Internal Correction Factor**

The analyte concentration in the solid is calculated by multiplying the analyte concentration in solution by the ratio of a known concentration of an element in the solid \( (C_{xs}) \) to its measured concentration in solution \( (C_{xl}) \), as shown in Equation 16.

\[
C_{AS} = \left( \frac{C_{xs}}{C_{xl}} \right) . C_{AL}
\]

**Equation 16**

To be able to use Equation 15 time consuming surface profiling of the sample must be employed to estimate the ablated volume and knowledge of the sample density must be known to allow calculation of the ablated mass. Thus Equation 16 was the preferred method of determining analyte concentration as it could be used by direct measurement of an element of known concentration. This equation is valid so long as fractionation between the element of known concentration and the analyte does not occur. This was investigated by determining the Th/U ratio and found not to occur during LASIL, see section 4.3.3.

4.1.3 **Test Material**

NIST 611 glass (National Institute of Standards and Technology, Maryland, U.S.A.) was chosen as a test material due to its high concentrations of analytes (nominal 500 mg/kg) and its common use as a calibration standard for laser ablation.

For experiments conducted in the custom built pot (see section 4.2 for details) the sample was washed with acetone followed by two washings of D.I. water.
Prior to droplet experiments the sample was sonicated in 2\% v/v nitric acid (Suprapure, Romil, Cambridge, UK) for 15 minutes. It had been observed that the NIST glass had an associated surface contamination probably induced by re-grinding. Re-grinding was performed with silicon carbide grit paper P1200 (particle size roughly 15 μm) followed by P2500 (particle size roughly 6 μm) followed by diamond paste (particle size roughly 6 μm).

### 4.1.4 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 samples off-line. Laser parameters are given in Table 27.

<table>
<thead>
<tr>
<th><strong>Table 27 – Details of laser parameters</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Laser Ablation System</strong></td>
</tr>
<tr>
<td>ESI, New Wave Research Division, Huntingdon, UK</td>
</tr>
<tr>
<td><strong>System</strong></td>
</tr>
<tr>
<td>Solid State Nd:YAG, UP-213</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
</tr>
<tr>
<td>213 nm, 5\textsuperscript{th} harmonic of 1064 nm</td>
</tr>
<tr>
<td><strong>Pulse duration</strong></td>
</tr>
<tr>
<td>4 ns</td>
</tr>
<tr>
<td><strong>Sampling strategy</strong></td>
</tr>
<tr>
<td>Line scan (for specific details refer to text)</td>
</tr>
<tr>
<td><strong>Spot diameter</strong></td>
</tr>
<tr>
<td>Set as 100 μm aperture imaged, actual image at sample surface measured after experiment</td>
</tr>
<tr>
<td><strong>Laser energy</strong></td>
</tr>
<tr>
<td>See specific experiment for details</td>
</tr>
<tr>
<td><strong>Solid sample</strong></td>
</tr>
<tr>
<td>NIST SRM 611 Trace Elements in Glass</td>
</tr>
<tr>
<td><strong>Translation rate</strong></td>
</tr>
<tr>
<td>See specific experiment for details</td>
</tr>
<tr>
<td><strong>Sampling medium</strong></td>
</tr>
<tr>
<td>See specific experiment for details</td>
</tr>
</tbody>
</table>

### 4.1.5 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 observed ablated spot diameter was smaller than the nominal value (set by software control at 100 μm diameter), 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 output read 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 scattering of the beam when interacting or passing through different surfaces.

As described later in the chapter, it is possible to use reagents to control unwanted side effects such as excessive bubble formation and where these are absorbing they compromise estimations of fluence, however, in the analytical data obtained from droplet LASIL, no additions were used and so the water may be treated as a transparent medium.

4.1.6 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).
4.2 LASIL in a Pot

A pot was designed and manufactured to establish the feasibility of LASIL as a sampling method; with a view to implementing a similar setup in an industrial setting. The pot was also used to investigate optimum ablation parameters. See Figure 48 for a detailed diagram and schematic of the LASIL pot.

![LASIL in a Pot Diagram](image)

**Figure 48 - A) Exploded CAD image and B) schematic representation of the LASIL pot**

The cell was manufactured from high density polyethylene (HDPE) (Albrook Engineering, Loughborough, UK) and incorporated a split ring clamp to hold the optical window (CVI Melles Griot, Onchan, UK) in place. This allowed the window height to be varied, providing two positions for the optical window; either immersed in the liquid or floating above it. The inner cell volume was designed to
house NIST glass such that it was completely submerged, whilst maintaining a minimum liquid volume.

The cell also incorporated two holes in the lid that sat above cut grooves in the base. This feature was used when the lid was screwed in place to fill the cell with liquid through one hole whilst air to escaped through the other. A volume of 2.5 ml liquid resulted in a 3 mm gap between sample and optical window, where the optical window was in contact with the liquid.

The pot was not used for quantitation investigations. Initial experiments with NIST 611 showed high background levels of transition metals e.g. zinc, copper and iron, which could not be reduced even after successive soaking and washing. This high background was attributed to three possible sources of contamination:

i. The tools used to machine the pot were made of metal and the oils used to lubricate the tools were not clean, thus transfer from tool to pot could have occurred.

ii. Before LASIL was attempted, focus and ablation of a sample were tested with no liquid in the pot using a brass standard; particulate generated by ablation could have collected on the pot walls.

iii. Due to the coarse finish of the pot it is likely that particulate may have been trapped within the grooves left by tooling.

Recoveries for analytes using the pot ranged from 20-60% for low energies and from 8-75% at high energies.

4.2.1 Methodology

4.2.1.1 Establishing Optimum Laser Parameters

Different laser parameters were tested using the custom pot to establish the optimum ablation conditions, determined by reduced bubble formation after complete cavity collapse and the production of uniform ablation tracks. A univariate optimisation approach was employed as observation suggested that the variables were overall, mutually independent.
The effects of translation and repetition rates were investigated at 1, 2, 5 and 10 \( \text{µm}^{-1} \) using 1, 5, 10 and 20 Hz for each speed. The laser energy and spot size were kept constant at 0.50 mJ and 100 µm respectively.

The effect of laser energy was investigated at set energies of 0.01, 0.50, 1.00, 2.00 and 2.45 mJ. The repetition rate, translation rate and spot size were kept constant at 10 Hz, 1 \( \text{µm}^{-1} \) and 100 µm respectively.

All experiments were conducted over a single raster distance of 0.5 mm in D.I. water. The sample was cleaned and the water replaced once a variable was changed to prevent laser interaction with any solid suspended in the liquid. The sample was placed in the same position to ensure the distance from the optical window to the sample surface i.e. the depth of liquid the laser traversed, remained the same.

### 4.2.1.2 Establishing an Optimum Ablation Liquid

As previously described, during the plasma lifetime and after cavity collapse the release of smaller vapour bubbles occurs. They rise to the surface of the liquid medium and during their transit can interact with the laser beam by causing either reflection or refraction. The problem was further exacerbated during operation with the pot as bubbles came to rest on the under-side of the optical window, directly in the laser beam path. To minimise bubble formation different solutions were tested using the custom pot.

The solutions tested were as follows: D.I. water, D.I. water partially degassed by bubbling nitrogen through for an hour, NaCl solution (1.7 \( \times \) 10\(^{-3}\) mol/l), Triton X100 solution (0.1% v/v), tetramethylammonium hydroxide (TMAH) solution (1 \( \times \) 10\(^{-3}\) mol/l), tetrabutylammonium chloride (TBACL) solution (4 \( \times \) 10\(^{-4}\) mol/l), methanol solution (1% v/v) and butanol solution (1% v/v).

A 100 µm spot size, 10 Hz repetition rate and 1 \( \text{µm}^{-1} \) translation rate were used to investigate liquid effects. Laser energies of 0.5 and 1.0 mJ were tested. Tracks were inspected visually and bubble formation monitored throughout the ablation process.
4.2.1.3 Imaging of Track Profiles
Profiles and 3-dimensional images of the tracks generated by performing LASIL in solutions of non-degassed D.I. water, degassed D.I. water and TBACl (4 x 10^{-4} mol/l) were generated. Ablated tracks were inspected using an InfiniteFocus measurement system (20x lens, Alicona, Kent, UK) non-contact, optical, 3-dimensional surface measurement. This is a microscope that collects multiple images at different focus points and builds a 3-dimensional image of the sample using algorithms. TalyMap (Taylor Hobson Ltd, Leicester, UK) was used to process the image data obtained. The images were then inverted for clarity, see Figure 49.

4.2.2 Results and Discussion

4.2.2.1 Determination of Optimum Solution and Laser Parameters by Visual Inspection and Surface Profiling of the Laser Tracks
The optimum laser parameters, those that reduced post cavity collapse bubble formation, were found to be 10 Hz repetition rate and a translation rate of 1 μm s^{-1}, but the same uniform track could be achieved at 20 Hz repetition rate and a translation rate of 2 μm s^{-1}. At faster translation rates, such as 10 μm s^{-1}, the track became non-uniform with the individual spots not overlapping sufficiently to give one continuous track. At low repetition rates, such as 1 Hz, the same problem occurred.

A laser energy of 0.50 mJ was found to minimise bubble generation whilst still giving a visible plasma. At higher laser energies the tracks became non-uniform due to the increased post cavity-collapse bubble generation and subsequent laser-bubble interaction. This may have also been caused by higher energy micro-jet impingement, thus lower energies/fluences were favoured.

Laser-bubble interaction was minimised by optimising the composition of the LASIL solution. The track profiles and images by surface profiling are shown for non-degassed water in Figure 49A; degassed water at a notional fluence of 14.9 J/cm² in Figure 49B and C and a notional fluence of 31.6 J/cm² in Figure 49D and E; and a 4 x 10^{-4} mol/l TBACl solution at a notional fluence of 46.5 J/cm² in Figure 49F and G.
Figure 49 – NIST glass surface profiling images, tracks inverted for clarity: A) a track image from non-degassed D.I. water; B) a track image and C) a track profile from degassed water at a notional laser fluence of 14.9 J/cm²; (d) a track image and (e) a track profile from degassed D.I. water at a notional laser fluence of 31.6 J/cm²; (f) a track image and (g) a track profile from 4 x 10⁻⁴ mol/l solution of TBACl at a notional laser fluence of 46.5 J/cm².
Ablating in non-degassed D.I. water resulted in a large number of post cavity-collapse bubbles being released, leading to reflection and refraction of the laser beam with the rising bubbles. This caused it to deviate from the intended track resulting in non-uniform tracks. The appearance of scattered small peripheral damage craters can also be seen around the main ablation track, see Figure 49A. Similar craters were observed under optimised conditions (see Figure 49B, D and F, but at reduced frequency.

Degassing the D.I. water prior to ablation generated a lower number of bubbles most of which appeared smaller in volume. This reduction was caused by the removal of dissolved gases, thus reducing the amount that could diffuse into the micro-cavity. The resulting tracks were uniform, with converging walls and flat bottoms (due to the beam profile).

To further hinder bubble formation surface tension reducing agents were added. The addition of 0.1% Triton X 100 inhibited ablation at the sample surface due to its high absorptivity at 213 nm. The addition of 1% methanol and 1% butanol caused boiling at the optical window-water interface, inhibiting the transmission of laser energy to the sample surface. The addition of NaCl only had a minimal effect on bubble number and volume. The addition of an organic salt greatly reduced the bubble volume and the number of bubbles generated. An increasing effect was observed with increasing size and hydrophobicity of the organic constituent. Of the solutions tested, TBACl was found to yield the least number of bubbles due to the molecule inhibiting the hydrogen bonding of the water molecules and thus reducing the surface tension on the bubbles. The track image and profile for LASIL in TBACl, Figure 49F and G respectively, show a smaller diameter and mean depth of ablation, but a more uniform track shape, compared to D.I. water even though it was performed at a higher notional fluence of 46.5 Jcm$^{-2}$. TBACl absorbs at 213 nm and thus reduces the intensity of laser light falling on the sample surface compared to using D.I. water, but even for equivalent fluences, it still reduced bubble formation.

The TBACl solution was not employed for quantification work; however, it may be useful in future work when using an open pot ablation.

The track profiles show that a reduction in laser energy led to a smaller ablation diameter and a reduction in the ablation depth. This may have been caused by
scattering reducing the fluence at the edge of the beam profile below the ablation threshold. It may also have been due to a reduction in micro-jet impingement, compared with that which occurred at higher energies, and which contributed to larger spot diameters.

Although problems with laser-bubble interaction occurred the pot concept is useful as it can be used to generate a homogenous sub sample representing the bulk material as the sample is completely immersed. This can be achieved by ablating across the entire sample surface or sampling points which then mix within the solution to generate the sub sample.
4.3 LASIL in a Free-Standing Droplet

Due to the contamination, poor recoveries and the large volume of liquid required to cover the sample when using the custom pot, the concept of performing LASIL in a droplet on the sample surface was investigated.

The droplet is also preferential as recent investigations have shown that reduction in water depth results in an increase in ablation efficiency attributed to a reduction in heat loss from micro-cavity to the allowing for a higher temperature rise within the cavity and thus an pressure upon cavity collapse. The droplet acts as a freestanding micro-chamber and maintained its shape, a flattened-spherical cap (roughly a sphere), due to surface tension and the limited wetting of the sample, see

Figure 50.
The droplet was placed on the sample surface using a pipette and collected by the same means.

For all droplet work the spot size had a good reproducibility at lower energies, varying from 32.9-34.3 μm using a selected image aperture size of 100 μm.

4.3.1 Methodology

4.3.1.1 Instrumentation

Analytes in LASIL samples and calibration standards were monitored using an Element XR ICP-SFMS (Thermo Scientific, Bremen, Germany). Operating conditions and sample introduction details are given in Table 28.
Table 28 - Details of ICP-MS operating parameters and sample introduction system

<table>
<thead>
<tr>
<th>ICP-MS</th>
<th>Thermo Scientific, Bremen, DE</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
<td>Element XR Magnetic Sector Field ICP-MS</td>
</tr>
<tr>
<td>Cool gas flow</td>
<td>15.5 L min⁻¹</td>
</tr>
<tr>
<td>Auxiliary gas flow</td>
<td>0.80 L min⁻¹</td>
</tr>
<tr>
<td>Sample gas flow</td>
<td>0.904 L min⁻¹</td>
</tr>
<tr>
<td>Resolution/Isotopes monitored/Segment</td>
<td>Low resolution: $^{28}$Si, $^{88}$Sr, $^{133}$Cs, $^{139}$La, $^{140}$Ce, $^{153}$Eu, $^{232}$Th, $^{238}$U</td>
</tr>
<tr>
<td>Resolution/Isotopes monitored/Segment time</td>
<td>60 ms for $^{28}$Si and 160 ms for all other isotopes</td>
</tr>
<tr>
<td>Plasma RF power</td>
<td>1250 W</td>
</tr>
<tr>
<td>Acquisition mode</td>
<td>E-Scan</td>
</tr>
<tr>
<td>Detector mode</td>
<td>Triple (secondary electron multiplier, counting and Faraday cup)</td>
</tr>
<tr>
<td>Sample introduction</td>
<td>Self aspirating PFA-ST nebuliser with a 0.25mm I.D. exchangeable capillary delivering a 100 µl min⁻¹ uptake (Elemental Scientific Inc., Omaha, USA). Twinnabar cyclonic spray chamber, volume 20 ml (Glass Expansion, Melbourne, AU)</td>
</tr>
</tbody>
</table>

4.3.1.2 Quantification in a Free-Standing Liquid Droplet

Initially different liquid volumes: 5, 10, 15, 25, 50 and 100 µl, were tested to determine a useful working droplet size (single spot ablation, 100 µm spot size, 10 Hz repetition rate, 0.1 mJ laser energy). It was found that ablation could be conducted in all but a 5 µl droplet, at this volume there was enough force from the shockwave to cause the droplet to explode. An experiment later conducted using a 193 nm laser showed that ablation could be achieved in 5 µl without the droplet exploding, however this was conducted at lower laser energy.

A 25 µl droplet of deionised water was placed onto the surface of the NIST611 glass by means of a micro-pipette and the droplet employed as a free-standing, micro ablation chamber. This was chosen as it gave enough coverage by the droplet to allow multiple line scans. LASIL was performed at laser energy of 0.084 mJ and a
spot size of 34.3 μm; notional fluence of 9.1 J/cm², to ablate 6 x 1 mm length tracks (at a repetition rate of 20 Hz and translation speed of 2 μm/s, equating to 60,000 shots). Ablation off-centre to the droplet was employed because this minimised bubble-laser interaction as the bubbles collected at the top of the droplet. The resulting solution was collected by means of a pipette and transferred to a 15 ml centrifuge tube. A 25 μl droplet was placed on the surface to collect any remaining particulate, collected and added to the same 15 ml centrifuge tube. The solution was diluted to 500 μl. 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 were prepared in non-degassed D.I. water and nitric acid. De-gassing was not required when in-droplet ablation was used.

4.3.1.3 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 from the calibration curve, using the formula given in Equation 1.

\[ y_{\text{min}} = b + 3s_E \]

Equation 17

Where \( y_{\text{min}} \) 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.

4.3.1.4 Preparation of Samples for Study of Particle Morphology
Samples were prepared as above, by LASIL in a liquid droplet. The experiment was performed using a spot size of 32.8 μm for 0.255 mJ; notional fluence of 30.1 J/cm² and 0.092 mJ; notional fluence of 10.9 J/cm². No post ablation chemistry samples were prepared. The sample with droplet was then placed in an AtmosBag, two handed, size M, closure type, zipper-lock (Sigma-Aldrich, Dorset, UK) to avoid 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). The area where the droplet had filtered through/dried was isolated and mounted on double-coated carbon-conductive SEM tab. The samples were imaged by scanning electron microscopy (SEM), using a Carl Zeiss 1530UP field emission gun scanning electron microscope (FEG-SEM).

4.3.2 Results and Discussion

4.3.2.1 Particle imaging

The images from SEM analysis are shown in Figure 51A and B for a notional fluence of 30.1 J/cm$^2$; C and D for a notional fluence of 10.9 J/cm$^2$ (D.I. water was used for both). Free particles, i.e. those not part of an agglomeration, or less than 200nm may have passed through the pores.
Figure 51 - SEM analysis of filtered particulate from a D.I. water droplet LASIL experiment at a notional fluence of 30.1 J/cm² (a) 10,000 times magnification and (b) 50,000 times magnification; a notional fluence of 10.9 J/cm² (c) 5,000 times magnification and (d) 50,000 times magnification.

At a higher fluence the particle size distribution was wide with significant variability in particle morphology. Three distinct particle shapes were evident: spherical particles in the nanometer range from condensates and those up to the micrometer range from ejection of melt; long, thin string-like structures associated with nano-material agglomeration or possibly melt liquid jet collapse; and large jagged particles associated with the mechanical removal of material by micro-jet impact on the sample surface or melt, 1-2 μm in size. Because these samples were subsequently nebulised for introduction into the ICP, additional particle size selectivity would have been introduced at that stage.

At the lower fluence the particle size was much smaller and more homogenous, see Figure 51C and D. Particles were less than 200 nm in size but formed larger agglomerates, possibly during the ablation process or drying and filtration. Long,
thin string-like structures associated with nano-material agglomeration were also present.

4.3.3 Analysis of NIST 611 by LASIL

From the standard solutions, calibration graphs were generated and from these the concentrations of analytes in the solution were calculated.

Table 29 - R-squared values for calibration graphs used to quantify LASIL solutions

<table>
<thead>
<tr>
<th>Isotope</th>
<th>R-squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{28}\text{Si}$</td>
<td>0.9958</td>
</tr>
<tr>
<td>$^{88}\text{Sr}$</td>
<td>0.9999</td>
</tr>
<tr>
<td>$^{133}\text{Cs}$</td>
<td>0.9998</td>
</tr>
<tr>
<td>$^{139}\text{La}$</td>
<td>0.9997</td>
</tr>
<tr>
<td>$^{140}\text{Ce}$</td>
<td>0.9998</td>
</tr>
<tr>
<td>$^{153}\text{Eu}$</td>
<td>0.9998</td>
</tr>
<tr>
<td>$^{232}\text{Th}$</td>
<td>0.9997</td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>0.9999</td>
</tr>
<tr>
<td>$^{52}\text{Cr}$</td>
<td>1.0000</td>
</tr>
<tr>
<td>$^{59}\text{Co}$</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

The ratio of uranium concentration in solution to uranium concentration in the solid was calculated and applied as an internal correction factor to calculate the concentration of analytes in the original solid (assuming that the ablation process did not give rise to fractionation), refer to Equation 16.

The errors given for the certified concentrations represent the 95% confidence interval quoted from the standard reference material certificate of analysis (National Institute of Standards and Technology, Maryland, U.S.A.). The errors for mean concentrations obtained from complied values are given as standard deviations ($1\sigma$) for the measurements (GeoReM database). See

Table 30 – Certified concentrations of analytes within NIST 611

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Concentration in the solid (ug/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{28}\text{Si}$</td>
<td>$3.27 \times 10^5 \pm 1.31 \times 10^4$</td>
</tr>
</tbody>
</table>
The uncertainties for the LASIL calculated values are 95% confidence intervals based on t-statistics and the standard error of the mean where $N = 6$.

Fractionation has also been investigated, where in this paper fractionation is defined as the production of analytical data that does not represent the stoichiometry of the sample composition\textsuperscript{19-21}. The uranium-thorium ratio is often used as means of determining if particle size related fractionation has occurred. The ratio has been reported as 1.05 for ablation techniques and 1.095 for solution nebulised\textsuperscript{22}. This ratio was used here as both elements are present in NIST 611 in roughly equal concentrations (461.5 ± 1.1 μg/g uranium and 457.2 ± 1.2 for thorium\textsuperscript{18}), have a similar first ionisation potential (6.1939 eV for uranium and 6.3067 eV for thorium\textsuperscript{23}), have similar masses but have a different boiling point (4407 K for uranium and 5061 K for thorium\textsuperscript{24}).

4.3.3.1 Quantification using the free-standing droplet

The measured element/uranium concentration ratios in the D.I. water solutions and the post-acidified solutions are given in Table 31 and Table 32 respectively. The ratios between replicates vary, however the ratios of the elemental concentrations to the concentration of uranium in solution were in good agreement with the ratios of the concentration of elements to the concentration of uranium in the solid. This shows that although variation between replicates occurred, possibly due to variation in focusing on the sample surface for each replicate, the intra-ratio of elements represented the stoichiometry of the sample and gave good
repeatability. The ratios for cobalt and chromium were not in good agreement with the expected ratios. This was due to high backgrounds in the water used.

Table 31 - Measured elemental composition of NIST 611 expressed as element-to-uranium concentration ratio (500 µl D.I. water). The average ratio to uranium within a replicate and the associated %RSD are also presented calculated from elements of similar concentration to uranium in the solid. Elements in grey were not used to calculate the average ratio because they have significantly different concentrations in NIST 611.

<table>
<thead>
<tr>
<th>Element</th>
<th>Replicate 1</th>
<th>Replicate 2</th>
<th>Replicate 3</th>
<th>Replicate 4</th>
<th>Replicate 5</th>
<th>Replicate 6</th>
<th>Expected ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>380</td>
<td>120</td>
<td>650</td>
<td>620</td>
<td>260</td>
<td>300</td>
<td>710</td>
</tr>
<tr>
<td>Sr</td>
<td>1.6</td>
<td>1.5</td>
<td>1.6</td>
<td>1.6</td>
<td>0.96</td>
<td>0.93</td>
<td>1.1</td>
</tr>
<tr>
<td>Cs</td>
<td>0.63</td>
<td>-</td>
<td>0.85</td>
<td>1.1</td>
<td>0.79</td>
<td>0.82</td>
<td>0.78</td>
</tr>
<tr>
<td>La</td>
<td>1.1</td>
<td>-</td>
<td>1.2</td>
<td>1.2</td>
<td>0.80</td>
<td>0.74</td>
<td>0.99</td>
</tr>
<tr>
<td>Ce</td>
<td>1.1</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>0.81</td>
<td>0.74</td>
<td>0.97</td>
</tr>
<tr>
<td>Eu</td>
<td>0.96</td>
<td>0.91</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>0.95</td>
<td>1.0</td>
</tr>
<tr>
<td>Th</td>
<td>1.2</td>
<td>1.1</td>
<td>0.86</td>
<td>0.80</td>
<td>0.95</td>
<td>0.92</td>
<td>0.99</td>
</tr>
<tr>
<td>U</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Cr</td>
<td>1.3</td>
<td>1.8</td>
<td>1.4</td>
<td>1.5</td>
<td>0.71</td>
<td>0.77</td>
<td>0.88</td>
</tr>
<tr>
<td>Co</td>
<td>1.7</td>
<td>0.71</td>
<td>1.2</td>
<td>1.2</td>
<td>0.35</td>
<td>0.41</td>
<td>0.88</td>
</tr>
<tr>
<td>Mean</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>0.91</td>
<td>0.86</td>
<td>1.0</td>
</tr>
<tr>
<td>%RSD</td>
<td>22</td>
<td>21</td>
<td>21</td>
<td>23</td>
<td>11</td>
<td>13</td>
<td>5.1</td>
</tr>
</tbody>
</table>
Table 32 - Measured elemental composition of NIST 611 expressed as element-to-uranium concentration ratio (500 µl post acidified). The average ratio to uranium within a replicate and the associated RSD are also presented calculated from elements of similar concentration to uranium in the solid. Elements in grey were not used to calculate the average ratio because they have different concentrations in NIST 611.

<table>
<thead>
<tr>
<th>Ratio to uranium</th>
<th>Replicate</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Expected ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>390</td>
<td>350</td>
<td>290</td>
<td>300</td>
<td>140</td>
<td>150</td>
<td>710</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>0.89</td>
<td>0.91</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>0.61</td>
<td>0.55</td>
<td>0.73</td>
<td>0.78</td>
<td>0.78</td>
<td>0.79</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>0.91</td>
<td>0.91</td>
<td>0.92</td>
<td>0.93</td>
<td>0.84</td>
<td>0.84</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>0.96</td>
<td>0.96</td>
<td>1.0</td>
<td>0.99</td>
<td>0.88</td>
<td>0.87</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>0.93</td>
<td>0.99</td>
<td>0.97</td>
<td>0.99</td>
<td>1.1</td>
<td>1.1</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>1.1</td>
<td>1.0</td>
<td>0.92</td>
<td>0.93</td>
<td>0.91</td>
<td>0.92</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.98</td>
<td>0.81</td>
<td>1.2</td>
<td>2.5</td>
<td>0.76</td>
<td>1.1</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.98</td>
<td>0.90</td>
<td>0.85</td>
<td>0.89</td>
<td>0.40</td>
<td>0.41</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>$\bar{x}$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.92</td>
<td>0.93</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>%RSD</td>
<td>12</td>
<td>7.2</td>
<td>6.8</td>
<td>7.6</td>
<td>11</td>
<td>11</td>
<td>5.1</td>
<td></td>
</tr>
</tbody>
</table>

Post acidification of the sample reduced the noise in the isotopic signals, see Table 33. The addition of acid to a solution containing nanometer and micrometer particulate has a dissolution effect aided by the large surface area. It has been established through work with nano-particles that whilst average signal intensity can be sustained (for the same mass load) into the $10^2$ nm size range, noise increases compared with dissolved samples, however here the signal intensity did increase by an order of magnitude for the post-acidified samples.
Table 33 – A comparison of the percentage RSD for signal intensities of post-acidified and non-acidified samples

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Post-acidified</th>
<th>Non-acidified</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{28}$Si</td>
<td>2.95</td>
<td>3.98</td>
</tr>
<tr>
<td>$^{88}$Sr</td>
<td>1.03</td>
<td>4.58</td>
</tr>
<tr>
<td>$^{133}$Cs</td>
<td>1.60</td>
<td>4.06</td>
</tr>
<tr>
<td>$^{139}$La</td>
<td>0.62</td>
<td>6.84</td>
</tr>
<tr>
<td>$^{140}$Ce</td>
<td>1.08</td>
<td>6.55</td>
</tr>
<tr>
<td>$^{153}$Eu</td>
<td>1.25</td>
<td>6.60</td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td>0.73</td>
<td>3.27</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>1.87</td>
<td>5.68</td>
</tr>
<tr>
<td>$^{52}$Cr</td>
<td>2.05</td>
<td>2.57</td>
</tr>
<tr>
<td>$^{59}$Co</td>
<td>2.30</td>
<td>2.37</td>
</tr>
</tbody>
</table>

The bar charts of calculated concentrations versus certified concentrations for the trace elements and main constituents in NIST 611 for D.I. water and post-acidified solutions are shown in Figure 52. The calculated values, obtained by averaging the results for the six replicates, are in excellent agreement with the certified values. The 95% confidence intervals shown on the bar chart in Fig 3a show good reproducibility of the technique, with significant improvement when samples are post-acidified.
Figure 52 - Bar charts showing the calculated concentrations versus the certified concentrations 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 six replicates 6 x 25 μl droplets at a notional fluence of 9.1 J/cm².

The uranium-thorium ratio for the six replicates was 1.06 ± 0.14 for D.I. water and 1.04 ± 0.07 for post-acidified solutions (error is based on the standard error between the six replicate ratios), in good agreement with the published ratio.
The calculated concentrations of silicon are shown in Figure 52B, and were not in good agreement with the certified value for either the D.I. water or post-acidified solutions. This was because silicon is likely to be favoured in the larger sized particles and therefore had poorer transport efficiency (relative to smaller particles) to the ICP. The data acquisition method used to monitor the analytes could have also been an influence, as the number of peaks per isotope was lower (6 compared to 8 for other elements at that resolution) for silicon and the sampling time of these peaks shorter (10ms compared to 20ms).

The calculated value for silicon in the post-acidified solution was low due to the insolubility of silicon in acidic environments. The confidence intervals for silicon were large for both D.I. water and post-acidified solutions, 77% and 38% of the average concentration respectively. The smaller interval for the post-acidified solution was most likely because the silicon that remained in solution was in a more uniform particle size distribution. Other media could be employed to allow quantification of silica, e.g. basic media to stabilise silicates or HF.
4.4 Conclusion

The advantages of using LASIL as a sampling technique are:

- Use as a calibration technique; generation of a solid suspension allows calibration against inorganic salt standards.
- The generation of the sample as a suspended solid allows matrices that are insoluble in ICP compatible solvents to be sampled and analysed.
- Control over the dilution of the sample (mass ablated to volume of liquid) at the point of sampling material reduces the waste volume. Advantageous if hazardous analyte concentrations are too high, or if analyte concentrations are low.
- Collection of laser ablation generated particulate in a liquid medium allows for post-chemistry of the sample to remove matrix interferences. This can be achieved by either sample matrix removal or extraction of the analytes of interest.
- Spatial averaging can be achieved by collecting particulate from multiple ablation sites across the sample in one droplet/pot to generate a homogenous sub-sample representing the bulk material.
- Through the mechanism of LASIL the power delivered by the laser beam to the sample is more efficiently coupled due to the cavity surrounding the ablation site acting as a miniature cell and reflecting energy released in the ablation shockwave back towards the sample surface. The cavity also increases the pressure and temperature of the resulting laser induced plasma.
- Heat diffusion from the ablation site to the surrounding sample is minimised by the cooling effect of the liquid medium, thus preventing damage to other areas of the sample.
- Containment of hazard
- Off-line sampling

Laser ablation of a sample in solution, LASIL, has been shown to produce stable suspensions of particles from a sample material permitting its analysis by conventional solution mode calibration. Post ablation chemistry yields true solutions that provide low noise signals and remove problems of particle size.
related fractionation, however, further work is required to investigate fractionation based on elemental volatilities, for a range of matrices and elements.

It has been shown that LASIL can be performed in a 25 µl isolated, free-standing droplet that acts as a micro laser cavity and is capable of providing 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 being carried out in air, off-line to the measuring apparatus.

NIST 611 has been analysed using the LASIL technique and the measured concentrations were in good agreement with the certified values. Measurements of the uranium/thorium ratio were very close to the expected value in the droplet based analysis.

LASIL provides an excellent means of analysing inhomogeneous samples as the collecting solution integrates the ablated material into a homogeneous solution phase (defined in this context as the particulate being evenly distributed throughout the solution). Further, the degree of dilution is controlled by the number of laser shots. Conventional acid digestion of materials often requires a large volume of solution followed by multiple dilution steps to achieve a measurable concentration which can be a problem when the waste is toxic, such as in nuclear applications. Where a larger sample is to be analysed and spatial averaging is required, a cell design might be preferred and, following recent experience \(^{16}\), it appears that a simple open pot without window immersion would be the preferred option.

It has also been shown that, if laser-gas bubble interaction occurs, it can be reduced by de-gassing the liquid. Further, the addition of an organic salt reduces the surface tension thus reducing both the size and number of bubbles. The laser-bubble interaction is circumnavigated in the droplet experiment by ablating off-centre to the droplet such that generated bubbles do not travel into the laser beam path.

In these experiments simple post-ablation acidification was employed but a myriad of possibilities exist for post ablation chemistries including the use of: acids, bases,
chromatographic beads to extract major or minor components, chromophore doped solutions to change the ablation characteristics etc.

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 stable suspended solid that if required is amenable for post ablation chemistry. Particles below 150 nm can be fully atomised, and thus potentially ionised by the ICP, allowing direct calibration with aqueous standards. As LASIL is an off-line sampling technique, the resulting solution is not confined to analysis by ICP-MS and other techniques such as TIMS could be used for its characterisation. In the case of TIMS, in-droplet, post ablation chemistry to remove the matrix would normally be required. Alternatively, post ablation chemical processing, e.g. addition of acid, can be used to dissolve the nano-scale particulate, or clean-up can be achieved using, e.g. single bead extraction techniques.
4.5 Future work

LASIL has been demonstrated as a feasible technique for the sampling of glass and calibration of the trace elements within. However, areas still require investigation to establish the technique as useable for samples on a regular basis.

The effect of wavelength on fractionation effects needs to be investigated, as literature suggests the LASIL mechanism leads to smaller particle size distributions. The mean particle size also needs to accurately defined, so that particle formation mechanisms can be understood.

The effects of droplet height and ability of the liquid to wet the sample surface needs to be further understood as this could lead to an improved reproducibility of spot size. The evaporation of the droplet also by heating effects from the LASIL mechanism and environmental factors needs to be investigated as this will affect the accuracy of determining the mass of analyte in solution.

At present LASIL is being employed as a technique in two funded projects at Loughborough University.

The first is determination of Rh, Pd, Ir, and Pt concentrations in pharmaceutical powders that do not readily dissolve in matrices compatible with ICP. Astra Zeneca has so far funded 2 MSc projects to pursue this project, with preliminary results being presented as a poster at the European Winter Conference on Plasma Spectrochemistry 88. This project has also lead to the development of a potential new calibration technique of doping powdered samples with nanoparticulate, rather than adding internal standards as a solution and trying to homogenise the solid.

The second ongoing project is being conducted at the British Geological Survey (BGS). LASIL is being used to sample rocks and the solution analysed by MC-ICP-MS for Sr isotopes. The rocks have a high calcium content which interferes with these isotopes and a cleanup step is being investigated post-ablation pre-analysis. This cleanup will involve partial/complete dissolution of the sample and extraction of the analyte using micro-capture beads. Initial experimentation has already been conducted in which ablation of NIST 611 was repeated using a 193 nm laser. It was found that LASIL could be conducted in a much smaller droplet size without it
violently expanding. It was also found that the signal was less noisey when compared to LASIL using a longer wavelength.
Chapter 5 References


57. S. M. Eggins, L. P. J. Kinsley, and J. M. G. Shelley, (1998), Deposition and elemental fractionation processes during atmospheric pressure


Addendum

After submission of this thesis further experimental work was conducted to improve peak profiling of single laser ablation events. This was achieved by updating the Thermo software and firmware on the Element XR such that the method described in section 3.2.2.2 could be utilised effectively.

The results from this further experimentation formed part of the discussion in the Viva. The results improved time resolution of data to a data point every 0.1 ms and allowed clear inspection and profiling of the resulting peaks from a single laser ablation event. The data describes peaks with a full width of 10-15 ms and FWHM ranging from 2.6-4.5 ms log normally distributed. As such discussions relating to complex peak shapes and peak splitting were discussed with regards to the old configuration and data acquisition methods and then the new data presented to show that those issues were resolved with the Enterprise cell configuration and data acquisition method.

The DCI-Sniffer technology has now patent pending, submitted by ESI NewWave Research Division on the 14th of February 2013 as provisional application number 61/764,976.
Appendices
# Appendix I – Personal Development and Conference Attendance

<table>
<thead>
<tr>
<th>Course/Conference/Activity</th>
<th>Skills</th>
<th>Date</th>
<th>Duration (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>workshop, Loughborough University)</td>
<td>Networking with industrial contacts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Meeting with Prof. Barry Sharp and Dr Helen Reid (Loughborough University)</td>
<td>Communication skills with supervisor</td>
<td>03/12/2008</td>
<td>0.5</td>
</tr>
<tr>
<td>Departmental safety course, (Dave Wilson, Safety Officer, Loughborough University)</td>
<td>Safety awareness</td>
<td>04/12/2008</td>
<td>0.5</td>
</tr>
<tr>
<td>Library tour and online publications guide (Ginny Franklin, Loughborough University Library)</td>
<td>Database usage and literature searching</td>
<td>05/12/2008</td>
<td>0.5</td>
</tr>
<tr>
<td>Postgraduate research students introduction (Loughborough University)</td>
<td>Networking with other postgraduates</td>
<td>14/01/2009</td>
<td>0.5</td>
</tr>
<tr>
<td>Meeting between two research groups to discuss the development of a new technique (Lough</td>
<td>Inter-collaboration of researchers</td>
<td>30/01/2009</td>
<td>0.5</td>
</tr>
<tr>
<td>borough University)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SolidEdge software training (Loughborough University)

Teaching skills: part A (Loughborough University)

Organisation and time management (Loughborough University)

Teaching skills: part B (Loughborough University)

Meeting to discuss project direction, Dave Wickenden from Magnox North (Loughborough University)

Teaching skills: part C

Presentation to another research group (Loughborough University)

COGER conference (Liverpool University)

Instrument training by industrial engineer, Dr Lothar Rottmann (Loughborough University)

<table>
<thead>
<tr>
<th>Activity</th>
<th>Location</th>
<th>Date</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computer Aided Design (CAD)</td>
<td></td>
<td>03/02/2009</td>
<td>0.5</td>
</tr>
<tr>
<td>Teaching</td>
<td></td>
<td>04/02/2009</td>
<td>0.5</td>
</tr>
<tr>
<td>Management of time and organisation</td>
<td></td>
<td>09/02/2009</td>
<td>0.5</td>
</tr>
<tr>
<td>Teaching to those with limited knowledge of the subject</td>
<td></td>
<td>11/02/2009</td>
<td>0.5</td>
</tr>
<tr>
<td>Communication skills with industrial contacts</td>
<td></td>
<td>23/02/2009</td>
<td>0.5</td>
</tr>
<tr>
<td>Demonstrating practical aspects to those with limited knowledge of the subject</td>
<td></td>
<td>11/03/2009</td>
<td>0.5</td>
</tr>
<tr>
<td>Presentation skills</td>
<td></td>
<td>03/04/2009</td>
<td>0.5</td>
</tr>
<tr>
<td>Professional communication</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Presentation skills</td>
<td></td>
<td>06/04/2009</td>
<td>2.0</td>
</tr>
<tr>
<td>Networking within academia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Professional communication</td>
<td></td>
<td>15/03/2009</td>
<td>1.0</td>
</tr>
</tbody>
</table>

5-188
<table>
<thead>
<tr>
<th>Event</th>
<th>Skill</th>
<th>Date</th>
<th>Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>SolidEdge V17 training tutorials followed (Loughborough University)</td>
<td>CAD advanced knowledge</td>
<td>24/04/2009</td>
<td>1.0</td>
</tr>
<tr>
<td>Presentation at a meeting for Work package 2 of the DIAMOND consortium (Leeds University)</td>
<td>Presentation skills</td>
<td>07/07/2009</td>
<td>1.0</td>
</tr>
<tr>
<td>Dinner with representatives from Sellafield Ltd and UKAEA (Dr Claudie Black and Dr Steve Black, Sellafield)</td>
<td>Informal discussion</td>
<td>05/08/2009</td>
<td>0.5</td>
</tr>
<tr>
<td>Tour of the facilities at Sellafield site and discussion of furthering the project (Sellafield)</td>
<td>Insight into the nuclear industry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIAMOND 2009 Conference (York Railway Museum)</td>
<td>Presentation within an industrial setting</td>
<td>06/08/2009</td>
<td>1.0</td>
</tr>
<tr>
<td>Thermo Scientific UK Summer Symposium, (Queen Elizabeth II conference centre, London)</td>
<td>Presenting in a commercial setting</td>
<td>10/06/2010</td>
<td>1.0</td>
</tr>
<tr>
<td>European Workshop on Laser Ablation (Kiel, Germany)</td>
<td>International conference</td>
<td>29/06/2010</td>
<td>5.0</td>
</tr>
<tr>
<td>Biennial National Atomic Spectroscopy Symposium (Cambridge, UK)</td>
<td>National conference</td>
<td>07/07/2010</td>
<td>1.0</td>
</tr>
<tr>
<td>Analytical Research Forum (Loughborough, UK)</td>
<td>National conference</td>
<td>26/07/2010</td>
<td>1.0</td>
</tr>
<tr>
<td>Event Description</td>
<td>Type</td>
<td>Date</td>
<td>Duration</td>
</tr>
<tr>
<td>-----------------------------------------------------------------------------------</td>
<td>-----------------------------</td>
<td>------------</td>
<td>----------</td>
</tr>
<tr>
<td>DIAMOND annual conference, Museum Of Science and Industry (Manchester, UK)</td>
<td>Sponsor related conference</td>
<td>15/12/2010</td>
<td>2.0</td>
</tr>
<tr>
<td>European Winter Conference on Plasma Spectrochemistry (Zaragoza, Spain)</td>
<td>International conference</td>
<td>30/01/2011</td>
<td>5.0</td>
</tr>
<tr>
<td>Meeting with BGS, Thermo and University of Liverpool</td>
<td>Meeting to discuss a national project</td>
<td>26/05/2011</td>
<td>1.0</td>
</tr>
<tr>
<td>Meeting with Astra Zeneca (Loughborough, UK)</td>
<td>Project meeting</td>
<td>13/07/2011</td>
<td>0.5</td>
</tr>
<tr>
<td>Meeting with Matt Horstwood, NIGL (Loughborough, UK)</td>
<td>Project meeting</td>
<td>01/11/2011</td>
<td>0.5</td>
</tr>
<tr>
<td>DIAMOND annual conference (Coventry, UK)</td>
<td>Sponsor related conference</td>
<td>14/12/2011</td>
<td>2.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td>35.5</td>
</tr>
</tbody>
</table>
Appendix II - Papers
This technical note describes the development of Laser Ablation of a Sample In Liquid (LASIL), a technique where the ablation occurs at a solid sample surface submerged in a liquid. LASIL can be performed in a 25 μl isolated, freestanding droplet that acts as a micro-laser cavity, to produce a suspended particulate that can be analysed either directly, or following in-droplet chemistry, by calibration against aqueous standards. The technique is robust and easy to implement being carried out in air, offline to the detection apparatus. The analytical characteristics of LASIL are its ease of quantification, containment of particles, the ease of generating suspended solids in solution from insoluble materials and the control over dissolution and dilution to generate measurable concentrations. NIST 611 (trace elements in glass) was employed as a test sample as it is a commonly used reference material in conventional Laser Ablation (LA) studies. Droplet LASIL allowed the quantification of trace elements in NIST 611 and also investigation of the particle sizes and shapes generated by the ablation process. Particle sizes were found to vary with laser fluence, with higher fluences producing a wider particle size distribution with greater variation in shape. The types of particles found were: jagged particles of 1–2 μm in diameter most probably created by micro-jet impingement, spherical nanometre sized particles from vapour condensation and melt ejection, and thin, string-like particles from particle agglomeration or liquid jet fragmentation. At lower fluences the particle morphology tended towards spherical shapes and formed agglomerates. At this small particle size (below 250 nm), Brownian motion ensures a very slow settling rate in the liquid medium yielding solutions that are stable for analysis over several days. Alternatively, as demonstrated here, post-ablation chemistry can be carried out in the droplet, e.g. acid dissolution, or clean up using micro-extraction techniques. The liquid droplet was analysed by inductively coupled plasma-mass spectrometry (ICP-MS) with calibration against aqueous standards. The ablation yield from the sample was normalised using the found versus known concentration of uranium in the sample and ratioing measured elemental concentrations to this factor. LASIL on a sample immersed in liquid facilitated the study of the effect of the solution composition on the LASIL process.

1. 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 at lateral resolutions down to ~4 micrometres, but at this scale only the major elements can be measured. The principal difficulty is calibration, as 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 represent the whole sample. The sample must be ablated in a raster mode, or at multiple sampling points, to overcome sample heterogeneity.

This technical note describes Laser Ablation of a Sample In Liquid (LASIL), a technique where the ablation occurs at a solid sample surface submerged in a liquid. The 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 which expands into the liquid. In front of the expanding ablation plume, energy is released as a shock wave which in gaseous media dissipates energy into the surrounding environment. In LASIL, vapourisation 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 which are
This overall process of energy coupling, plume formation, translation rate 1
The formation of micro-jets adds a mechanical mechanism for slow settling rate due to a Stoke's law terminal settling velocity of 3
Mechanical stress could lead to fracture 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, or clean-up can be achieved using, e.g. single bead extraction techniques.

Research has also been conducted on the effect of using femtosecond laser pulse widths when ablating a solid in a liquid medium, but as of yet no publications linked with quantification have been found.

2. Experimental
2.1 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 and an Element 2 XR SF-ICP-MS (Thermo Scientific, Bremen, Germany) was used to analyse the samples. Operating conditions and laser parameters are given in Table 1.

2.2 Calculating the fluence at the sample surface
Due to the increase in the refractive index when using a liquid medium, compared to a gaseous one, the observed ablated spot normally an order of magnitude higher than those experienced in a gaseous atmosphere. 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.

It has been reported that after the initial expansion of this micro-cavity the plasma cools and results in a vapour bubble. 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. The bubble can continue to expand until a maximum is reached after which it begins to distort, shrink and finally collapse due to the decay in the interior pressure from plasma shielding. The time taken for the collapse is increased due to the elongation relative to the solid surface. Very little work has been performed on particle formation from 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.

The formation of micro-jets adds a mechanical mechanism for removal of material, inhibits particle agglomeration and also clears the ablation site of ejected particulate for the next incoming laser pulse. Mechanical stress could lead to fracture or hydrodynamic removal of particles from a melt zone. Thermal convection and bubble induced liquid motion also aid in the removal of particulate from the ablation site when nano-second pulse lengths and repetition rates below 1 kHz are used. After collapse of the micro-cavity smaller bubbles become evident. These are created by diffusion of dissolved gases from the liquid into the expanding micro-cavity. The rising bubbles can hinder ablation due to 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 is relatively fast (ns time scale) such that the next laser beam-sample coupling is not inhibited, e.g. by plasma shielding. 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 x 10^-9 m s^-1 (in pure water). Provided that the particulate is <150 nm in diameter and thus the potential for ionisation in the ICP the resulting solution can be collected and analysed by ICP-MS against aqueous standards to determine the concentration of the elements 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, or clean-up can be achieved using, e.g. single bead extraction techniques.

Table 1 Instrumental parameters used in the investigation

<table>
<thead>
<tr>
<th>Laser ablation system</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Wavelength</td>
<td>Pulse duration</td>
<td>Repetition rate</td>
</tr>
<tr>
<td>Auxiliary gas flow</td>
<td>Sample gas flow</td>
<td>Plasma RF power</td>
<td>Isotopes monitored</td>
</tr>
<tr>
<td>Cool gas flow</td>
<td>Plasma energy</td>
<td>Spot diameter</td>
<td>Acquisition mode</td>
</tr>
<tr>
<td>Sample gas flow</td>
<td>Sampling time</td>
<td>Laser energy</td>
<td>Detector mode</td>
</tr>
<tr>
<td>Sampling strategy</td>
<td>Sampling medium</td>
<td>Wavelength</td>
<td>Sample introduction</td>
</tr>
</tbody>
</table>

This journal is © The Royal Society of Chemistry 2011


Downloaded by Loughborough University on 12 July 2011 from pubs.rsc.org | doi:10.1039/C0JA00144A

Table 1 Instrumental parameters used in the investigation

<table>
<thead>
<tr>
<th>Laser ablation system</th>
<th>Instrumental parameters used in the investigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>ESI, New Wave Research Division, Solid State Nd:YAG, UP-213</td>
</tr>
<tr>
<td>Wavelength</td>
<td>213 nm</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>4 ns</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>10 Hz for bulk cell and 20 Hz for droplet experiments</td>
</tr>
<tr>
<td>Sampling strategy</td>
<td>Line scan (for specific details refer to text)</td>
</tr>
<tr>
<td>Laser energy; spot diameter</td>
<td>Set as 100 μm aperture imaged, actual image at sample surface: droplet laser energy 0.084 mJ; 34.3 μm spot diameter. Particle studies laser energy: 0.255 mJ and 0.092 mJ; 32.9 μm spot diameter for both energies</td>
</tr>
<tr>
<td>Solid sample</td>
<td>NIST SRM 611 Trace Elements in Glass</td>
</tr>
<tr>
<td>Translation rate</td>
<td>1 μm s^-1 for bulk cell and 2 μm s^-1 for droplet experiments</td>
</tr>
<tr>
<td>Sampling medium</td>
<td>Deionised water 18 MΩ (degassed for bulk cell experiments), 2.5 ml for the bulk cell and 25 μl for the droplet experiments respectively</td>
</tr>
<tr>
<td>ICP-MS</td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>Thermo Scientific, Element 2 XR Magnetic Sector Field ICP-MS</td>
</tr>
<tr>
<td>Cool gas flow</td>
<td>15.5 L min^-1</td>
</tr>
<tr>
<td>Auxiliary gas flow</td>
<td>0.80 L min^-1</td>
</tr>
<tr>
<td>Sample gas flow</td>
<td>0.904 L min^-1</td>
</tr>
<tr>
<td>Plasma RF power</td>
<td>1250 W</td>
</tr>
<tr>
<td>Isotopes monitored</td>
<td>^28Si, ^44Ca, ^60Co, ^88Sr, ^137Cs, ^139La, ^140Ce, ^232Th, ^238U</td>
</tr>
<tr>
<td>Acquisition mode</td>
<td>Peak hopping</td>
</tr>
<tr>
<td>Detector mode</td>
<td>Triple (secondary electron multiplier, counting and Faraday cup)</td>
</tr>
<tr>
<td>Sample introduction</td>
<td>Self-aspirating PFA-ST nebuliser with a 0.25 mm ID exchangeable capillary delivering a 100 μl min^-1 uptake (Elemental Scientific Inc., Omaha, USA). Twinnabar cyclonic spray chamber, volume 20 ml (Glass Expansion, Melbourne, Australia)</td>
</tr>
</tbody>
</table>

This journal is © The Royal Society of Chemistry 2011

diameter was smaller than the nominal value (set by software control at 100 μm diameter) 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 scattering of the beam when interacting or passing through different surfaces.

As shown below, it is possible to use reagents to control unwanted side effects such as bubble formation and where these are absorbing they compromise estimations of fluence, however, in the analytical data obtained from the droplet work, no additions were used and so the water may be treated as a transparent medium.

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

2.4 Preparation of sample
NIST 611 (National Institute of Standards and Technology, Maryland, USA) was chosen due to its high concentrations of analytes (nominal 500 mg kg⁻¹) and its common use as a calibration standard for laser ablation. For the droplet experiment the sample was sonicated in 2% 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. Re-grinding was performed with silicon carbide grit paper P1200 (particle size roughly 15 μm) followed by P2500 (particle size roughly 6 μm) followed by diamond paste (particle size roughly 6 μm). The sample was prepared by washing with acetone followed by DI water for the custom cell experiment.

2.5 Design of a custom cell
A custom cell was designed and manufactured for preliminary experimentation, to allow LASIL to be performed by modifying the standard UP-213 platform. The cell was operated using a 2.5 ml solution to cover the sample.

The cell was used to investigate the LASIL process and was based on an immersed window to avoid the air–water interface. However, though valuable for parameter optimisation, the complexity of the cell design rendered it inappropriate for analytical work and therefore a chamber-less experiment, employing a 25 μl droplet as a freestanding, micro-ablation chamber, was used to obtain the analytical data. The use of a simple open pot chamber was reported recently by Okabayashi et al.

2.6 Establishing optimum laser parameters
Different laser parameters were tested using the custom cell to establish the optimum ablation conditions, determined by reduced bubble formation after cavity collapse and the production of uniform ablation tracks. A univariate optimisation approach was employed as observation suggested that the variables were to a first approximation independent.

The effect of translation rate was investigated at 1, 2, 5 and 10 μm s⁻¹ using 1, 5, 10 or 20 Hz repetition rates respectively (constant laser energy of 0.50 mJ). The effect of laser fluence was investigated at set energies of 0.01, 0.50, 1.00, 2.00 and 2.45 mJ (repetition rate was kept constant at 10 Hz and translation rate at 1 μm s⁻¹). All experiments were conducted over a line distance of 0.5 mm.

2.7 Establishing optimum ablation solutions
Different solutions were tested using the custom cell to establish the optimum medium in which to carry out ablation. The solutions tested were as follows: DI water, DI water partially degassed by bubbling nitrogen through for an hour, NaCl solution (1.7 × 10⁻³ mol l⁻¹), Triton X100 solution (0.1% v/v), tetramethylammonium hydroxide (TMAH) solution (1 × 10⁻³ mol l⁻¹), tetrabutylammonium chloride (TBACl) solution (4 × 10⁻⁴ mol l⁻¹), methanol solution (1% v/v) and butanol solution (1% v/v).

2.8 Imaging of track profiles
The profiles of the tracks ablated using solutions of non-degassed DI water, degassed DI water and TBACl (4 × 10⁻⁴ mol l⁻¹) were generated as were the 3 dimensional images of these tracks. Ablated tracks were analysed using a 20× lens on an InfiniteFocus (Alicona, Kent, UK) non-contact, optical, 3 dimensional surface measurement instrument; the measurement principle is based on focus-variation. The software used to process the data obtained from the instrument was TalyMap (Taylor Hobson Ltd).

2.9 Quantification in a freestanding liquid droplet
A 25 μl droplet of deionised water was placed onto the surface of the NIST 611 glass by means of a micro-pipette and the droplet employed as a freestanding, micro-ablation chamber. LASIL was performed at a laser energy of 0.084 mJ and a spot size of 34.3 μm; a notional fluence of 9.1 J cm⁻², to ablate 6 × 1 mm length tracks (at a repetition rate of 20 Hz and a translation speed of 2 μm s⁻¹, equating to 60 000 shots). Ablation off-centre to the droplet was employed because this minimised bubble–laser interaction as the bubbles collected at the top of the droplet. The resulting solution was collected by means of a pipette and transferred to a 15 ml centrifuge tube. A 25 μl droplet was placed on the surface to collect any remaining particulate, collected and added to the same 15 ml centrifuge tube. The solution was diluted to 500 μl. 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 of 2% v/v. Six replicates and four method blanks were prepared in non-degassed DI water and nitric acid. De-gassing was not required when in-droplet ablation was used.

2.10 Preparation of calibration standards
Calibration standards were prepared by serial dilution of multielement 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).
The limit of detection was calculated from the calibration curve, using the formula given in eqn (1).

\[ y_{\text{min}} = b + 3S_E \]  

(1)

where \( y_{\text{min}} \) 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.

2.11 Preparation of samples for study of particle morphology

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

The samples were imaged by scanning electron microscopy (SEM), using a Carl Zeiss 1530UP field emission gun scanning electron microscope (FEG-SEM).

3. Results and discussion

3.1 Determination of optimum solution and laser parameters by visual inspection and surface profiling of the laser tracks

The optimum laser parameters, those that reduced laser–bubble interaction, were found to be 10 Hz repetition rate and a translation rate of 1 \( \mu \text{m s}^{-1}\), but the same uniform track could be achieved at 20 Hz repetition rate and a translation rate of 2 \( \mu \text{m s}^{-1}\). At faster translation rates, such as 10 \( \mu \text{m s}^{-1}\), the track became non-uniform with the individual spots not overlapping sufficiently to give one continuous track. At low repetition rates, such as 1 Hz, the same problem occurred. A laser energy of 0.50 mJ was found to minimise bubble generation whilst still giving a visible plasma. At higher laser energies the tracks became non-uniform due to the increased bubble generation after cavity collapse and subsequent laser–bubble interaction. This may have also been caused by higher micro-jet impingement, thus lower energies/fluences were favoured.

Laser–bubble interaction, which was a problem in the custom cell, was minimised by optimising the composition of the LASIL solution, by visual inspection of the solution during the ablation and bubble formation after micro-cavity collapse. The track profiles and images from the surface profiling are shown for the non-degassed water in Fig. 1a; for the degassed water at a notional fluence of 46.5 J cm\(^{-2}\), but also a much more uniform track shape. TBACl does absorb at 213 nm, but even for equivalent fluences, it still reduced bubble formation. The TBACl solution was not employed for quantification work as this was performed in the droplet where the issue of laser–bubble interaction was overcome by ablating off centre to the droplet. However, it may be useful in future work when using an open pot ablation.

The track profiles show that a reduction in laser energy led to a smaller ablation diameter and a reduction in the ablation depth. This may have been caused by scattering reducing the fluence at the edge of the beam profile below the ablation threshold. It may also have been due to a reduction in micro-jet impingement, compared with that which occurred at higher energies, and which contributed to larger spot diameters.

For all droplet work the spot size had a good reproducibility at lower energies, varying from 32.9–34.3 \( \mu \text{m} \).

3.2 Particle imaging

The images from the SEM analysis are shown in Fig. 2a and b for a notional fluence of 30.1 J cm\(^{-2}\) and Fig. 2c and d for a notional fluence of 10.9 J cm\(^{-2}\) (DI water was used for both). Free particles, i.e. those not a part of an agglomeration, or less than 200 nm in size. Because these samples were subsequently nebulised for introduction into the ICP, additional particle size selectivity would have been introduced at that stage.

At the higher fluence the particle size distribution was wide with significant variability in the particle morphology. Three distinct particle shapes were evident: spherical particles in the nanometre range from condensates and those up to the micrometre range from ejection of melt; long, thin string-like structures associated with nano-material agglomeration or possibly melt liquid jet collapse; and large jagged particles associated with the mechanical removal of material by micro-jet impact on the sample surface or melt, 1–2 \( \mu \text{m} \) in size. Because these samples were subsequently nebulised for introduction into the ICP, additional particle size selectivity would have been introduced at that stage.
At the lower fluence the particle size was much smaller and more homogenous. Particles were less than 200 nm in size but formed larger agglomerates, possibly during the ablation process or drying and filtration. Long, thin string-like structures associated with nano-material agglomeration were also present.

3.3 Analysis of NIST 611 by LASIL

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

The errors given for the certified concentrations represent the 95% confidence interval quoted from the standard reference material certificate of analysis (National Institute of Standards and Technology, Maryland, USA).

The errors for mean concentrations obtained from compiled values are given as standard deviations (1σ) for the measurements (GeoReM database).

The uncertainties for the LASIL calculated values are 95% confidence intervals based on t-statistics and the standard error of the mean.

Fig. 1 (a) A track image from the non-degassed DI water; (b) a track image and (c) a track profile of the degassed water at a notional laser fluence of 14.9 J cm⁻²; (d) a track image and (e) a track profile of the degassed DI water at a notional laser fluence of 31.6 J cm⁻²; (f) a track image and (g) a track profile of 4 × 10⁻⁴ mol l⁻¹ solution of TBACl at a notional laser fluence of 46.5 J cm⁻².
Fractionation has also been investigated, where in this paper fractionation is defined as the production of analytical data that do not represent the stoichiometry of the sample composition.19–21 The uranium–thorium ratio is often used as means of determining if particle size related fractionation occurred. The ratio has been reported as 1.05 for ablation techniques and 1.095 for mining if particle size related fractionation occurred. The ratio of elements represented the stoichiometry of the sample and gave good repeatability. The ratios for cobalt and chromium were not in good agreement with the expected ratios. This was because of high blanks in the water used.

Post-acidification of the sample reduced the noise in the isotopic signals. The addition of acid to a solution containing nanometre and micrometre particulates has a dissolution effect aided by the large surface area. It has been established through work with nanoparticles that whilst average signal intensity can be sustained (for the same mass load) into the 10 nm size range, noise increases compared with dissolved samples,24 however, here the signal intensity did increase by an order of magnitude for the post-acidified samples.

The bar charts of calculated concentrations versus certified concentrations for the trace elements and main constituents in NIST 611 for DI water and post-acidified solutions are shown in Fig. 3. The calculated values, obtained by averaging the results for the six replicates, are in excellent agreement with the certified values. The 95% confidence intervals shown in the bar chart in Fig. 3a show good reproducibility of the technique, with significant improvement when samples are post-acidified.

The uranium–thorium ratio for the six replicates was 1.06 ± 0.14 for DI water and 1.04 ± 0.07 for post-acidified solutions (error is based on the standard error between the six replicate ratios), in good agreement with the published ratio.

The calculated concentrations of silicon are shown in Fig. 3b but were not in good agreement with the certified value for either the DI water or post-acidified solutions. This was because silicon is likely to be favoured in the larger sized particles and therefore had poorer transport efficiency (relative to smaller particles) to the ICP. The calculated value for silicon in the post-acidified solution was low due to the insolubility of silicon in acidic environments. The confidence intervals for silicon were large for both DI water and post-acidified solutions, 77% and 38% of the average concentration respectively. The smaller interval for the

### Table 2 Measured elemental composition of NIST 611 expressed as element-to-uranium concentration ratio (500 μl DI water). The average ratio to uranium within a replicate and the associated %RSD are also presented calculated from elements of similar concentration to uranium in the solid. Elements in bold were not used to calculate the average ratio because they have different concentrations in NIST 611.

<table>
<thead>
<tr>
<th>El</th>
<th>Replicate 1 Ratio to U</th>
<th>Replicate 2 Ratio to U</th>
<th>Replicate 3 Ratio to U</th>
<th>Replicate 4 Ratio to U</th>
<th>Replicate 5 Ratio to U</th>
<th>Replicate 6 Ratio to U</th>
<th>Expected ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>380</td>
<td>120</td>
<td>650</td>
<td>620</td>
<td>260</td>
<td>300</td>
<td>710</td>
</tr>
<tr>
<td>Sr</td>
<td>1.6</td>
<td>1.5</td>
<td>1.6</td>
<td>1.6</td>
<td>0.96</td>
<td>0.93</td>
<td>1.1</td>
</tr>
<tr>
<td>Cs</td>
<td>0.63</td>
<td>–</td>
<td>0.85</td>
<td>1.1</td>
<td>0.79</td>
<td>0.82</td>
<td>0.78</td>
</tr>
<tr>
<td>La</td>
<td>1.1</td>
<td>–</td>
<td>1.2</td>
<td>1.2</td>
<td>0.80</td>
<td>0.74</td>
<td>0.99</td>
</tr>
<tr>
<td>Ce</td>
<td>1.1</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>0.81</td>
<td>0.74</td>
<td>0.97</td>
</tr>
<tr>
<td>Eu</td>
<td>0.96</td>
<td>0.91</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>0.95</td>
<td>1.0</td>
</tr>
<tr>
<td>Th</td>
<td>1.2</td>
<td>1.1</td>
<td>0.86</td>
<td>0.80</td>
<td>0.95</td>
<td>0.92</td>
<td>0.99</td>
</tr>
<tr>
<td>U</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Cr</td>
<td>1.3</td>
<td>1.8</td>
<td>1.4</td>
<td>1.5</td>
<td>0.71</td>
<td>0.77</td>
<td>0.88</td>
</tr>
<tr>
<td>Eu</td>
<td>1.7</td>
<td>0.71</td>
<td>1.2</td>
<td>1.2</td>
<td>0.35</td>
<td>0.41</td>
<td>0.88</td>
</tr>
<tr>
<td>%RSD</td>
<td>12%</td>
<td>12%</td>
<td>12%</td>
<td>12%</td>
<td>9.1%</td>
<td>8.6%</td>
<td>1.0</td>
</tr>
</tbody>
</table>

This journal is © The Royal Society of Chemistry 2011 J. Anal. At. Spectrom., 2011, 26, 1294–1301 | 1299
post-acidified solution was most likely because the silicon that remained in solution was in a more uniform particle size distribution. Other media could be employed to allow quantification of silica, e.g. basic media to stabilise silicates or HF.

4. Conclusion

Laser Ablation of a Sample In Liquid, LASIL, has been shown to produce stable suspensions of particles from a sample material permitting its analysis by conventional solution mode calibration. Post-ablation chemistry yields true solutions that provide low noise signals and remove problems of particle size related fractionation, however, further work is required to investigate fractionation based on elemental volatilities, for a range of matrices and elements.

It has been shown that LASIL can be performed in a 25 μl isolated, freestanding droplet that acts as a micro-laser cavity and is capable of providing 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 being carried out in air, off-line to the measuring apparatus.

NIST 611 has been analysed using the LASIL technique and the measured concentrations were in good agreement with the certified values. Measurements of the uranium/thorium ratio were very close to the expected value in the droplet based analysis.

LASIL provides an excellent means of analysing inhomogeneous samples as the collecting solution integrates the ablated material into a homogeneous solution phase (defined in this context as the particulate being evenly distributed throughout the solution). Further, the degree of dilution is controlled by the number of laser shots. Conventional acid digestion of materials often requires a large volume of solution followed by multiple dilution steps to achieve a measurable concentration which can be a problem when the waste is toxic, such as in nuclear applications. Where a larger sample is to be analysed and spatial averaging is required, a cell design might be preferred and, following recent experience,16 it appears that a simple open pot without window immersion would be the preferred option.

It has also been shown that, if laser–gas bubble interaction occurs, it can be reduced by de-gassing the liquid. Further, the addition of an organic salt reduces the surface tension thus reducing both the size and number of bubbles. The laser–bubble interaction is circumnavigated in the droplet experiment by ablating off-centre to the droplet such that generated bubbles do not travel into the laser beam path.

In these experiments simple post-ablation acidification was employed but a myriad of possibilities exist for post-ablation chemistries including the use of: acids, bases, chromatographic beads to extract major or minor components, chromophore doped solutions to change the ablation characteristics, etc.

### Table 3

<table>
<thead>
<tr>
<th>Element</th>
<th>Replicate 1 Ratio to U</th>
<th>Replicate 2 Ratio to U</th>
<th>Replicate 3 Ratio to U</th>
<th>Replicate 4 Ratio to U</th>
<th>Replicate 5 Ratio to U</th>
<th>Replicate 6 Ratio to U</th>
<th>Expected ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>390</td>
<td>350</td>
<td>290</td>
<td>300</td>
<td>140</td>
<td>150</td>
<td>710</td>
</tr>
<tr>
<td>Sr</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>0.89</td>
<td>0.91</td>
<td>1.1</td>
</tr>
<tr>
<td>Cs</td>
<td>0.61</td>
<td>0.55</td>
<td>0.73</td>
<td>0.78</td>
<td>0.78</td>
<td>0.79</td>
<td>0.78</td>
</tr>
<tr>
<td>La</td>
<td>0.91</td>
<td>0.91</td>
<td>0.92</td>
<td>0.93</td>
<td>0.84</td>
<td>0.84</td>
<td>0.99</td>
</tr>
<tr>
<td>Ce</td>
<td>0.96</td>
<td>0.96</td>
<td>1.0</td>
<td>0.99</td>
<td>0.99</td>
<td>0.88</td>
<td>0.97</td>
</tr>
<tr>
<td>Eu</td>
<td>0.93</td>
<td>0.99</td>
<td>0.97</td>
<td>0.99</td>
<td>1.1</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Th</td>
<td>1.1</td>
<td>1.0</td>
<td>0.92</td>
<td>0.93</td>
<td>0.91</td>
<td>0.92</td>
<td>0.99</td>
</tr>
<tr>
<td>U</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Cr</td>
<td>0.98</td>
<td>0.81</td>
<td>1.2</td>
<td>2.5</td>
<td>0.76</td>
<td>1.1</td>
<td>0.88</td>
</tr>
<tr>
<td>Co</td>
<td>0.98</td>
<td>0.90</td>
<td>0.85</td>
<td>0.89</td>
<td>0.40</td>
<td>0.41</td>
<td>0.88</td>
</tr>
<tr>
<td>%RSD</td>
<td>12</td>
<td>7.2</td>
<td>6.8</td>
<td>7.6</td>
<td>6.8</td>
<td>5.1</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Fig. 3 Bar charts showing the calculated concentrations versus the certified concentrations for LASIL in DI water and in DI 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.
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 stable suspended solid that if required is amenable for post-ablation chemistry. Particles below 150 nm can be fully atomised, and thus potentially ionised by the ICP, allowing direct calibration with aqueous standards. As LASIL is an off-line sampling technique, the resulting solution is not confined to analysis by ICP-MS and other techniques such as TIMS could be used for its characterisation. In the case of TIMS, in-droplet, post-ablation chemistry to remove the matrix would normally be required.

Acknowledgements

This work was funded as part of the Decommissioning Mobilisation and Management Of Nuclear waste for Disposal (DIAMOND) consortium, funded by the Engineering and Physical Sciences Research Council (EPSRC). The authors would also like to thank Dr Richard White (CERAM Ltd, Stoke-on-Trent, UK), Mr Jagpal Singh, Mr John Bates (Loughborough University) and Mr Alan Albrook.

References