Development of novel calibration strategies for laser ablation inductively coupled plasma mass spectrometry

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Development of Novel Calibration Strategies for Laser Ablation Inductively Coupled Plasma Mass Spectrometry

By

Ciaran O'Connor

A Doctoral Thesis

Submitted in partial fulfillment of the requirements for the reward of the degree of

Doctor of Philosophy of Loughborough University

June 2007

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Thesis Abstract

Calibration has been termed the "Achilles heel" of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). This is down to the fact that Certified Reference Materials (CRMs) do not exist for the majority of sample types and the detrimental effects of elemental fractionation and the matrix dependency of the ablation process.

This thesis investigates the potential for two calibration strategies: one based upon the online additions of aqueous calibration standards; the other, upon the pressing of powders into discs utilising organic chromophores that absorb at the lasing wavelength of 213 nm. Finally, deviations of the above strategies have been devised enabling the absolute quantitation technique of isotope dilution to be employed.

All the strategies investigated have been validated by analysis of a wide range of CRMs including: glasses, plastics, metals, soils, sediments and powdered plant matter.

Throughout this project, useful insights into fundamental ICP and ablation processes have been obtained. The online additions strategy allowed investigation into mass loading induced matrix effects, and the relative merits of utilising a wet plasma rather than a dry; whilst the pressed powder approach allowed examination of fundamental, absorption related ablation processes.
Acknowledgements

I would like to acknowledge The Valid Analytical Measurement (VAM) Program for financial support throughout the duration of this project; LGC (Teddington, Middlesex, UK) for provision of the UP213 Laser Ablation System and Thermo Fisher Scientific (Winsford, Cheshire, UK) for provision of the VG PG ExCell ICP-MS instrument on which this work was performed.

My sincerest thanks go to Barry Sharp for having faith in me and for giving me the opportunity to become a member of the Analytical Atomic Spectroscopy Research Group. Thank you for your guidance, time and patience throughout the duration of this project – I really hope you are pleased with the outcome.

I would like to extend my appreciation to members of the Analytical Atomic Spectroscopy Research Group, past and present; Helen Reid, Mark Landon, Pete Winship, Sam Kerr, and Dhinesh Asogan. Thank you for making the last four years so special – I have loved every moment because of you.

I would also take this opportunity to express my gratitude to members of the Specialised Techniques Laboratory at LGC for accommodating me on my visits; namely Peter Evans for sparing his precious time and for being such a great industrial contact and friend.

Finally I would like to thank my fiancée Karen Tappenden and my family for their love and support.
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<td>Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>AES</td>
<td>Atomic Emission Spectrometry</td>
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<tr>
<td>BCS</td>
<td>British Chemical Standards</td>
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<tr>
<td>CE</td>
<td>Capillary Electrophoresis</td>
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<td>CRM</td>
<td>Certified Reference Material</td>
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<td>DC</td>
<td>Direct Current</td>
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<td>DIN</td>
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<td>Direct Sample Insertion</td>
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<td>Department of Trade and Industry</td>
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<td>ERM</td>
<td>European Reference Material</td>
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<td>HG</td>
<td>Hydride Generation</td>
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<td>Infra Red</td>
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<td>LASER</td>
<td>Light Amplification by Stimulated Emission of Radiation</td>
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<tr>
<td>LC</td>
<td>Liquid Chromatography</td>
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<td>Relative Sensitivity Factor</td>
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<tr>
<td>SN</td>
<td>Solution Nebulisation</td>
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<tr>
<td>St. Dev.</td>
<td>Standard Deviation</td>
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<tr>
<td>TIMS</td>
<td>Thermal Ionisation Mass Spectrometry</td>
</tr>
<tr>
<td>TOF</td>
<td>Time of Flight</td>
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<tr>
<td>TRA</td>
<td>Time Resolved Analysis</td>
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<tr>
<td>USN</td>
<td>Ultra Sonic Nebulisation</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>VAM</td>
<td>Valid Analytical Measurement</td>
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<td>WEEE</td>
<td>Waste Electrical and Electronic Equipment</td>
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Thesis Objectives
The Valid Analytical Measurement Program

The analytical measurement is of major economic significance and is essential to ensuring quality of life with over £7 billion spent annually on chemical analysis in the UK. However, evidence suggests that many analytical measurements are not fit for purpose and that poor quality data represent a major cost and risk to business and society.

The Valid Analytical Measurement (VAM) Program helps organisations in the UK to carry out analytical measurements competently and accurately. The program enables the UK to demonstrate the comparability of analytical measurements with those of its trading partners and provides working laboratories with the ‘tools’ needed to implement best practice and demonstrate the reliability and integrity of their results.

The VAM program is one of the portfolio of programs supporting the development of the UK’s National Measurement System (NMS). The NMS is the UK’s national infrastructure and measurement laboratories which delivers world-class measurement science and technology and provides traceable and increasingly accurate standards of measurement for use in trade, industry, academia, and government.

The VAM program covers the field of ‘analytical measurements’, which are carried out widely by industry, for example, to assure the composition of manufactured products, in process control, and in research and development.

VAM Principles

The six VAM principles enable organisations to implement best practice and make valid measurements. They are designed to control all factors that might affect the reliability of analytical results, thereby reducing the cost and risk of unreliable measurements. The six principles are:

1. Analytical measurements should be made to satisfy an agreed requirement.

2. Analytical measurements should be made using methods and equipment which have been tested to ensure they are fit for purpose.
3. Staff making analytical measurements should be both qualified and competent to undertake the task.

4. There should be a regular independent assessment of the technical performance of a laboratory.

5. Analytical measurements made in one location should be consistent with those elsewhere.

6. Organisations making analytical measurements should have well defined quality assurance procedures.

Objectives of Research

Since its development in the late 19th century, mass spectrometry (MS) has become a very powerful measurement tool in the laboratory; so much so that it underpins much of the VAM work on high accuracy measurements. An important area of VAM research is looking at possible industrial applications of modern mass spectrometry techniques.

One such modern mass spectrometric technique is Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). However, the LA analytical process is affected by many variables that must be understood and controlled in order to produce a robust methodology. For example, calibration has been termed the ‘Achilles heel’ of LA-ICP-MS, namely due to a lack of certified reference materials (CRMs) for the majority of sample types. Without these CRMs, calibration is severely hampered by elemental fractionation and the fact that ablation rates vary dramatically between sample and standard of only slightly differing matrix.

By working in collaboration with LGC (Teddington, Middlesex, UK) strategies will be developed for calibration and validation of LA-ICP-MS, with a view to developing chemical standards and reference materials for analysis of solid samples. For the sake of clarity, this major objective can be broken down in several smaller aims:

1. A critical review of the LA literature, with particular emphasis on the factors that affect the robustness of the analytical process for quantitative measurement by ICP-MS.
2. Identification of key sample types where quantitative measurement by LA-ICP-MS provides benefits over conventional analytical techniques.

3. Investigation into the performance of LA as a sample introduction device for the materials identified above.


5. Investigation into methods of sample measurement by LA-ICP-MS to include the use of isotope dilution calibration.

6. Investigation into the coupling of LA to multi-collector instrumentation for isotope dilution analysis/isotope ratio measurements.
References

www.vam.org.uk

Accessed on 12.10.2006
Chapter One

An Introduction to Inductively Coupled Plasma Mass Spectrometry
Introduction

Since the first coupling of an Ar Inductively Coupled Plasma (ICP) and a mass spectrometer over twenty years ago, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has become an exceptionally powerful technique for elemental analysis. Due to continuous instrumental and procedural development, the technique is now capable of providing accurate and precise measurements of elements across the periodic table, in a wide variety of sample matrices at ultra-trace levels.

Along with the wide range of analytes and sample matrices that the technique can handle, ICP-MS has found such widespread use due to its relative speed and simplicity; its high sensitivity for the majority of elements and its wide dynamic range. Importantly, ICP-MS is capable of providing qualitative and quantitative data, and isotopic analysis rather than just elemental analysis, unlike other forms of atomic spectrometry.

Below follows a general introduction into ICP-MS, with an emphasis on the requirements for sample introduction to the ICP using laser ablation (LA).
Instrumentation

ICP-MS instrumentation can be divided into subsystems for the purpose of ease of description. The sample introduction system enables transportation of the gaseous, liquid or solid sample into the ICP. The plasma source, where vaporisation of the sample is followed by atomisation and finally ionisation to efficiently form the ionic species required. The interface region, which enables a ‘stepping down’ from the atmospheric pressures encountered by the ions in the ICP, to the vacuum pressure of the analyser and detector. The ion focusing system, which steers and focuses the ion beam by a series of electrostatic lenses. The mass analyser where the ions of interest are separated from the remaining ion beam and finally the detection system where the ions of interest are converted to an electronic signal. Figure 1 shows a schematic of a typical ICP-MS instrument.

![Schematic of a typical ICP-MS instrument](image)

Figure 1 A schematic of a typical ICP-MS instrument.

Sample Introduction for ICP-MS

Sample introduction is the principal means by which the analyst can tailor the performance of the ICP-MS to particular analytical tasks. Whereas formerly sample
introduction was seen as a limiting part of the instrumentation, now it is this aspect that brings enormous versatility to the applications of these techniques. Interfaces for solid, liquid and gaseous samples have been described and in turn these have been coupled to a variety of separation techniques including Gas Chromatography (GC), Liquid Chromatography (LC), Capillary Electrophoresis (CE), and gel separations. Developments in sample introduction for the ICP source have been largely responsible for bringing about convergence between the historically separate fields of elemental and organic analysis.

General accounts of sample introduction have been provided by several authors including, for liquids: Browner, Montaser, Sharp and Mora; and for solids Durrant, Russo and Günther.

Gaseous Sample Introduction
The simplest method for introducing the sample into the ICP is via the gaseous phase, and this approach offers significant advantages over liquid or solid introduction. Firstly, transport efficiency is very close to 100%, which has the obvious effect of significantly improving detection limit. This is in contrast to solution nebulisation in which up to 95% of the sample goes to waste. Secondly, matrix interferences in the plasma are almost totally eliminated since the analytes are in the vapour phase and are removed from any potentially interfering elements in the sample matrix. Finally, because there is no need for desolvation or vaporisation steps within the ICP, the plasma energy is devoted to more efficient atomisation and ionisation processes, resulting in improved sensitivity and reduced detection limits.

The major drawback of gaseous sample introduction lies in its limited application. Many elements are not easily converted to the gaseous phase, but perhaps more importantly, the majority of samples naturally occur as liquids or solids.

Vapour Generation
Vapour generation is a method by which analytes present in a liquid, or sometimes a slurried solid sample, may be mixed with reagents that transform them into a gaseous species. The gaseous species may then be swept by a flow of Ar gas into the plasma for detection. There are several types of vapour that may be produced; for instance, Hg may
be reduced to its elemental form by stannous chloride and the Hg vapour produced is detected. This technique is usually termed ‘cold vapour generation’. The other main types of vapour produced are the hydride species, e.g. of As, Sb, Se and Pb, formed by reaction with sodium tetrahydroborate (also called sodium borohydride). This technique is referred to as hydride generation (HG).

Vapour generation of analytes into an ICP offers several advantages over conventional nebulisation. Since the analyte is transformed into a gaseous state, the advantages mentioned for gaseous sample introduction are applied. Inevitably, there are also disadvantages associated with sample introduction of gaseous analytes. One disadvantage is that different oxidation states of analytes can produce hydrides with different efficiencies (e.g. As$^{\text{III}}$ and As$^{\text{V}}$, with the lower oxidation state preferred). Another disadvantage of the HG technique is that the presence of some other metals (e.g. platinum group metals or some transition metals, namely Cu or Fe$^{\text{III}}$) in the sample may interfere with the HG process. Another drawback of vapour generation is that the excess hydrogen produced during the hydride formation process is also swept into the plasma, and may cause instability.

The instrumentation required for vapour generation is fairly minimal. Commercial units may be purchased, but effectively, they amount to a peristaltic pump, a switching valve, a mixing ‘T’ and a gas–liquid separator. A more detailed text discussing HG has been published by Dedina and Tsalev.83

Liquid Sample Introduction
Liquid sample introduction is by far the most common means for introducing the sample into the plasma. This form of sample introduction achieves excellent measurement accuracy and precision as a consequence of ease of sample handling, sample dilution and calibration. The liquid sample is dispersed into a fine ‘primary’ aerosol via the nebulisation process. Many processes have been invoked to produce the primary aerosol, but commercially pneumatic nebulisation and ultrasonic nebulisation are the only ones that have made significant impact and so the discussion here is restricted to these types of device.
Since the response of the ICP-MS is affected by the quality of this aerosol stream, a spray chamber is generally required to remove larger droplets, to form what is known as the ‘secondary’ aerosol. The cyclonic and the double pass are the most common types of spray chamber encountered in liquid sample introduction for ICP-MS and again the discussion is restricted to these devices.

Pneumatic Nebulisation
A wide variety of pneumatic nebuliser designs have been described, but here the focus is on devices that are commercially available and are therefore in widespread use.

Choosing between the various types depends on the application, but as a general guide, best sensitivity and highest signal-to-noise ratio is obtained from concentric designs, as shown in Figure 2, with high pressure and/or intermediate/reduced flow e.g. 100 µL min\(^{-1}\).

Figure 2 Configuration of a typical glass concentric pneumatic nebulisers courtesy of Meinhard Glass Products®.

Concentric nebulisers are usually constructed of one-piece, fused glass or polymer e.g. perfluoro-alkoxyalkane (PFA), or from sapphire orifices coupled with fused silica
capillaries. They come in standard format (as shown in Figure 2), recessed tip variant for high solids, micro-flow, high-pressure operation and direct injection. The direct injection nebuliser (DIN) dispenses with the spray chamber and injects the aerosol directly into the base of the plasma. This has the advantages of reducing both the dead volume, which is useful for high-resolution chromatographic couplings and the area of wetted surface which reduces memory effects (e.g. in ultra-trace applications). The drawbacks are setting up time and limited tolerance to high dissolved solids, which have precluded their widespread application.

Other popular pneumatic nebulisers include the cross-flow nebuliser and the Babington type nebulisers (Cone-Spray or v-groove) which are often used for applications involving high matrix content and high salt or particulate content.

Ultrasonic Nebulisation

Ultrasonic nebulisers (USNs) employ ultrasound waves in the range of 200 kHz – 10 MHz to provide the energy for droplet production, rather than the gas flow. Thus the injector flow can be optimised independently of the droplet production. The waves are generated normally to the surface of a piezo-electric crystal, which in analytical devices is bonded to a chemically resistant plate (e.g. fused silica), onto which the sample is introduced. Waves can only propagate in fluid media given an adequate depth of fluid. Therefore, a small but significant depth of liquid has to be created on the surface of the plate to allow a geyser to form from which the droplets are produced. This is usually accomplished by pumping the analyte onto the surface through a capillary tube.

For a 3 MHz crystal the average droplet size is 3 μm and so transport efficiencies of ~20% are achieved rising to close to 100% when coupled to a desolvation system. Desolvation is essential unless a micro-flow is fed to the plate, but stability is more readily achieved at higher flow rates.

The greater efficiency of analyte transport leads to a 10-fold improvement in detection limit providing the sample matrix is not complicated. However, cost is much higher, wash-out times are longer, memory effects can be a problem and precision is lower ~2 - 3% because of the instability of the droplet production process.
The Spray Chamber

The primary function of the spray chamber is to remove the larger droplets from the primary aerosol stream and allow only those that can be fully processed by the plasma to remain. The fate of droplets in a spray chamber is determined by: the particle density which impacts on droplet coalescence, notably in the near field immediately after the nebuliser; the gas flow pattern and the degree to which particles are entrained in it. Small particles, <1 \mu m, are fully entrained in the gas flow and follow its flow paths, although they can be lost by Brownian diffusion through the static boundary gas attached to the chamber walls. Larger particles do not equilibrate their velocities with the gas flow and therefore tend to intercept on surfaces when the gas flow turns.

The market is dominated by the double-pass or Scott-type design and the cyclonic design. Generally, the double-pass chamber provides the finest aerosol, whereas the cyclonic design offers higher efficiency, but with a slightly broader particle size distribution. Materials are generally, glass, silica or polymer usually PFA. An important consideration, particularly for non-wettable surfaces, is to ensure a smooth drainage from the chamber without the generation of noise spikes due to pressure pulses.

Desolvation

Desolvation adds complexity and cost to the sample introduction system and changes the characteristics of the plasma. Without desolvation, the solvent, mostly water, dominates the plasma loading and only small perturbations are caused by the sample matrix. With desolvation a 'dry' plasma is produced, but variable sample matrix will in turn produce varying plasma loading. Although with MS detection, chilled spray chambers (typically 1–5 °C) are commonly used to reduce the vapour loading to reduce solvent related interferences, full desolvation should only be used for specific purposes. Desolvation is employed to: reduce the solvent load with high efficiency nebulisers such as the ultrasonic design, to improve the transport efficiency and to remove or reduce spectral interferences. Desolvation is also employed to produce a dry aerosol for calibration in LA experiments in which aqueous calibration standards are desolvated then combined with the aerosol generated by LA of the sample, in a standard additions type calibration strategy.
Solid Sample Introduction

Solid sampling introduces three main advantages over the use of liquid introduction. Firstly, the sample preparation time and sample handling time are reduced which minimises the likelihood of contamination from other samples or reagents. Secondly, because no solvent is present, a dry plasma results in which molecular ion spectral interferences are much reduced (although one of the findings of this thesis is that there are significant benefits to using wet plasmas in some circumstances). Thirdly, some solid samples, such as ceramics and precious metals are very difficult to digest or to keep in solution for liquid introduction; solid sampling presents a novel solution to this problem. Finally, solid sampling techniques are capable of providing data which would be near impossible by solution introduction; namely spatially resolved information and depth analysis. The major drawback of solid sampling introduction is calibration, which is restricted by the lack of CRMs for the majority of sample types. Direct sample insertion, electrothermal vaporisation, arc and spark ablation and laser ablation have all been used to introduce the solid sample into the ICP.

Direct Sample Insertion

Direct sample insertion (DSI) can be used to introduce a solid sample directly into the ICP. The solid sample is typically ground into a fine powder and placed onto the tip of a probe which is subsequently directly inserted into the plasma. Typically, the insertion probe is made of a material such as graphite, tantalum or tungsten and is guided into the ICP via a modified torch in which the injector tube is replaced by a central quartz channel. Energy transfer from the ICP results in rapid heating of the insertion probe and subsequent vaporisation of the analyte. Since this is a very efficient form of sample introduction, the sensitivity achieved by DSI is extremely high. Acquired data should always be time resolved, as differential vaporisation occurs due to: sample matrix composition, analyte volatility and other instrumental parameters.

The technique was reviewed in 1990 by Karanassios and Horlick99 and then again, more recently, by Sing.100
Electrothermal Vaporisation

Sample introduction by electrothermal vaporisation (ETV) is a method that has evolved from atomic absorption (AA) measurements. Instead of direct nebulisation of a liquid sample, a small volume of liquid (10 – 100 μl), or a few milligrams of solid material, is introduced directly into an electrothermal atomiser. The atomiser is then heated resistively, by passing an electrical current through it. A ramped temperature program is used in which the sample (if it is a liquid) is first dried, and then the temperature is raised so that as much of the potentially interfering matrix is removed as possible whilst ensuring that the analytes are not lost. Finally, a high-temperature vaporisation step follows in which the analytes are removed from the electrothermal atomiser and enter a gas stream which transports them to the plasma. It is important to note that atomisation is not required in plasma source spectrometry and indeed it is quite difficult to conduct reactive free atoms through connecting tubing. Micro-particulates or stable molecular vapours are the preferred forms for introduction to the ICP.

The technique has the advantage of being capable of determining analytes in very small volumes of sample (~100 μl), as well as separating them from many potential interferences. In addition, transport efficiency to the plasma tends to be very high, leading to improved sensitivity and improvements in LOD of at least an order of magnitude. However, the procedure is very slow. As well as taking time to weigh (in the case of solid samples) the sample into the vaporiser, each of the stages of the temperature program requires a finite time. This technique produces a transient signal and so, as with LA and chromatography, a sequential scanning optical spectrometer may be fast enough to determine only one analyte per injection, and therefore simultaneous instruments are preferred. Modern quadrupole mass spectrometers however do have sufficient scanning speed to carry out multi-element scans on signals lasting of the order of a few seconds. Since sample introduction is normally by a micro-pipette, precision is typically 3 – 5% rather than the 1% normally associated with sample introduction using a nebuliser.

Commercial instrumentation is available, although many laboratories manufacture their own vaporisers, often from redundant systems that had been used for atomic absorption spectrometry (AAS) measurements. Metal vaporisers may be used instead of carbon and
a brief discussion of these has been presented by Nobrega and co-workers\textsuperscript{101} whilst a good example of the application of ETV-ICP-MS using a metal vaporiser has been published by Parsons \textit{et al.}\textsuperscript{102}

Reviews of ETV-ICP-MS have been prepared by Martin-Esteban and Slowikowski\textsuperscript{103} and by Vanheacke \textit{et al.}\textsuperscript{104} The analysis of micro-samples, using techniques such as ETV as a sample introduction method, has also been discussed recently by Todoli and Mermet.\textsuperscript{105}

Arc and Spark Ablation
Arc and spark ablation is a process in which a quantity of the solid sample is removed by an electrical discharge before entrainment in a carrier gas and transportation to the ICP. The technique has recently been reviewed by Gunther.\textsuperscript{82} The distinction between arc and spark ablation arises from the nature and duration of the electrical discharge. A spark is defined as an intermittent electrical discharge that lasts between 1 μs and 1 ms, and is low current/high voltage in nature. Sparks remove only a small fraction of a sample and generate ions because of their high energy. An arc, is a more continuous, high current/low voltage discharge, that generally removes a large fraction of the sample.

Ablation is typically performed in an Ar atmosphere, since this is beneficial to both the discharge and the ICP. The sample is transported through connective tubing, either directly into the ICP or via a settling chamber to remove larger particulates by gravitational settling.

The major disadvantage of these forms of solid sample introduction is that the sample must be, or made to be, electrically conducting. Samples that are not naturally conducting must be made so by the addition of a pure conducting material such as copper powder or graphite. This sample preparation procedure eliminates the advantages related to minimised sample handling inherent in other forms of solid sampling.
Laser Ablation

In 1985 Gray first realised that the material produced via LA could be transported to the ICP for efficient atomisation and ionisation.\textsuperscript{106} The analyte ions were detected by MS so creating the technique of LA-ICP-MS. Twenty years later, LA is the most versatile solid sampling technique for ICP-MS, and the general principle of the technique has not changed. To avoid repetition the reader’s attention is diverted to Chapter 2 which describes the technique of LA-ICP-MS in greater detail.

The Plasma Source\textsuperscript{107}

The ICP has long been recognised as a good source of ions due to its high temperature, in the vicinity of 7000 K. This enables the analysis of the vast majority of the elements within the periodic table, since most elements are ionised in the plasma to some extent.

The basic components used to generate and sustain the ICP are: a plasma torch, a radio frequency (RF) power supply, a RF coil and a supply of plasma gas.

The Plasma Torch

The plasma torch consists of three concentric tubes commonly constructed from quartz, known as the outer, middle and sample injector. The tubes can either be connected in a one-piece design or a demountable design in which the outer and the middle tubes are separate to the sample injector. The plasma gas, usually Ar, flowing at around 12 - 17 L min\textsuperscript{-1}, passes between the outer and middle tubes, whilst a second Ar gas flow of around 1 L min\textsuperscript{-1} passes between the middle tube and the sample injector. The purpose of this secondary gas flow is to change the position of the base of the plasma, relative to the location of the middle tube and the sample injector. It is the third gas flow through the sample injector, of around 1 L min\textsuperscript{-1}, that carries the sample aerosol from the sample introduction system and physically ‘punches’ a hole through the ICP to form the central channel. The plasma torch is mounted horizontally and positioned centrally between the RF coil, approximately 10 – 20 mm from the sample cone.

Plasma Generation and Plasma Properties

Ar flows tangentially between the outer and middle tubes of the plasma torch. A load coil, typically of copper, connected to a RF power supply, surrounds the top-end of the
torch. When RF power is applied to the coil, a current oscillates within at a frequency of 27 or 40 MHz, corresponding to the frequency of the RF generator. This oscillation of current within the coil induces a large electromagnetic field to be set up in the top-end of the torch. A high voltage spark is applied to the Ar, inducing the removal of electrons from some Ar atoms. These electrons are subsequently accelerated in the intense magnetic field leading to ionisation of further Ar atoms by collision. This collision induced ionisation continues in a cascade effect forming an inductively coupled plasma discharge. The plasma discharge is maintained within the torch and RF coil by a continued supply of RF energy by the inductive coupling process. Now that the plasma has been formed and can be sustained; it is ready for the introduction of the sample containing gas flow through the sample injector.

It is important to understand the different heating zones and regions of the ICP in order to explain the processes of sample vaporisation, atomisation and ionisation. The regions of the ICP are shown in Figure 3.

![Figure 3 The heating zones of an ICP discharge.](image)

The sample aerosol containing gas flow is introduced into the ICP via the sample injector tube. As this gas flow exits the injector tube it is traveling at such a velocity that
it physically punches a hole through the centre of the ICP discharge. The sample undergoes a number of physical changes as it passes through the preheating zone and radiation zone, before it finally emerges as positive ions in the normal analytical zone. Generally, when a nebuliser and spray chamber is employed, the analyte elements will be in the form of metal salts in droplets of solution. The first step is desolvation of the droplet. Once the solvent molecules have been stripped away, small, solid particulates exist. These particulates move further into the plasma and particulate shrinking occurs as vaporisation of the particulate is achieved. The next steps are atomisation into discrete, ground state atoms, followed by ionisation via a collisional ionisation mechanism with electrons, principally derived from the Ar plasma gas.

**The Interface Region**

The major problem encountered in the mid 1980s regarding the development of ICP-MS was the efficient extraction of the ions from the ICP, at atmospheric pressure (760 Torr), into the mass analyser at vacuum pressure (10⁻⁶ Torr).

**Description of the Interface**

The ion extraction problem was eventually solved by ‘stepping’ down from atmospheric pressure to vacuum in two steps rather than one, in a complex interface region. Figure 4 is a schematic of the interface region, showing the processes involved at each stage. The first step is to pass the ions through an orifice in a metal disc, of approximately 1 mm. This metal disc is known as the sampler cone and is usually constructed from Ni, although Al, Cu or Pt are sometimes used. The region behind the sampler cone is known as the expansion region and is maintained at a pressure of around 2 Torr with the use of a rotary pump. Gas flow through the sampler orifice has been estimated to be as large as 1 - 2 L min⁻¹ since approximately 100% of the sample carrier gas passes through. Shortly after passing through this orifice, the gas reaches supersonic velocities as rapid adiabatic expansion occurs, forming a region known as the zone of silence; this rapid expansion gives the ions a forward velocity.
About 1 cm behind the sampler cone lies a second cone, known as the skimmer cone. Similar to the sampler, this cone is constructed from Ni, although Al, Cu or Pt have also been used, the main difference being that it is often more tapered with a smaller orifice around 0.5 mm. The function of this secondary cone is to ‘skim’ the plasma, allowing approximately 1% of the sample through its orifice and into the vacuum region of the instrument.

**Ion Focusing and Steering**

The role of the ion focusing system is to transport as many analyte ions from the interface region to the mass analyser, whilst rejecting as many of the matrix or non-analyte species as possible in the attempt to minimise space charge effects. ‘Space charge effects’ is the term used to describe the defocusing effect of large quantities of matrix ions, particularly when the matrix ions are heavier than the analyte ions. A secondary role, but just as crucial, is the removal of neutral particulates, neutral species and photons from the ion beam which would reduce system performance by signal instability and increased backgrounds.
The lens system

Ion focusing is achieved by employing a series of electrostatically controlled, metallic plates, barrels or cylinders that focus the ion beam into the desired shape and steer the ion beam by electrostatic interaction into the mass analyser. Quadrupole instruments require a natural circular ion beam to function optimally; whereas sector instruments require a rectangular beam shape which can be achieved using supplementary lenses. Many instruments possess an extraction lens that sits just behind the skimmer and electrostatically extracts the ions from the interface region. This extra lens has the effect of increased ion transmission, particularly for lower mass ions which would otherwise be pushed from the ion beam due to space charge effects.

The Mass Analyser\textsuperscript{108,109}

This section of the instrument is where the ions are separated according to their mass-to-charge ratio $(m/z)$ and is therefore responsible for mass discrimination. The mass analyser sits between the ion optics and the detector and is typically maintained at a vacuum of $10^{-6}$ Torr to minimise the ion energy spread caused by collisions with gas molecules.

Several types of mass analyser have been utilised in ICP-MS including the quadrupole which was the first mass analyser used in ICP-MS in 1983. Problems encountered with analysis of difficult ions and difficult sample matrices led to the development of further mass analysers for ICP-MS such as the Magnetic Sector Analyser (MSA), the Electrostatic Sector Analyser (ESA), and the Time of Flight (TOF).

The Quadrupole Mass Analyser

The quadrupole was historically the first analyser used in ICP-MS instruments and to this date is still the most common, found in over 90% of all ICP-MS produced. Quadrupole technology is considered to be very mature and robust.

The analyser consists of four identical rods of stainless steel or molybdenum, often with an anti-corrosion ceramic coating, arranged in a perfect square arrangement as shown in Figure 5. Ideally, the rods are hyperbolic rather than circular in shape, of 15 – 20 cm in length and around 1 cm in diameter. Pairs of opposing rods are connected together.
electrically to a combination of RF and Direct Current (DC) electrical supply. Ions enter the region between the four rods with a low velocity, such that as they pass through the rods they are affected by the RF oscillations. The more oscillations to which an ion is subjected to, the greater the achievable resolution. In order for the quadrupole to act as a mass filter and allow only ions of a particular $m/z$ to pass through, a calculated value of DC plus RF must be applied, leading to a region of stability through which only the selected $m/z$ can pass. The ratio between DC and RF is usually maintained constant at a fixed RF frequency. In this scenario, ions of the selected mass are subject to a few oscillations, but will exit from the ends of the rods. Ions of higher or lower $m/z$ will either impact with the rods or pass through the spaces between them.

![Figure 5](image)

**Figure 5** A schematic of a quadrupole mass analyser.

Since the quadrupole can only allow ions of one $m/z$ to pass through for a given set of RF and DC voltages, it can only act as a sequential analyser. However, quadrupole instruments are considered to be fast sequential and are thus more than capable of handling the fast transient peaks encountered during laser ablation analysis. Settling times between mass jumps is typically between 0.1 - 2 ms, although these times are reducing with technological development. Employing a dwell time of 8 to 20 ms allows efficient use of the mass analyser, enabling 100 intensity recordings per second. The number of sweeps per second is dependent upon the number of isotopes at which data is
acquired; a greater number of isotopes results in fewer overall possible sweeps per second.

**Magnetic Sector Mass Analyser**

Magnetic sector analysers were historically the first kind of analyser used in mass spectrometry and are now playing an important role in ICP-MS. Ion separation is based upon the fundamental principle that a moving charge, in this case a positive ion, will travel in a curved path in the presence of a magnetic field. This operating principle is shown in Figure 6.
Figure 6 Schematic of a MSA (A) working as a mass filter for sequential detection and (B) for ‘dispersive’ mass separation for simultaneous detection.

When all ions have the same kinetic energy, it can be shown that the paths of heavier ions (higher m/z) are less deflected than those of lighter ions. In the magnetic sector analyser, ions are accelerated with several kilovolts of energy, with higher energies potentially yielding better sensitivity and resolution. The ion energies are much higher than those used with quadrupole analysers and complicates the design of the instrument since one end of the instrument must be at a high potential when compared to the other end. The m/z selected by the magnetic sector analyser is dependent upon: the magnetic
field strength \((H)\), the radius \((r)\) and the accelerating voltage \((V)\), in the relationship shown in Equation 1.

\[
\frac{m}{z} = \frac{H^2 r^2}{2V} \quad (1)
\]

In single detector instrumentation, the radius is fixed and the instrument can select the desired \(m/z\) by varying the magnetic field strength \(H\), or the accelerating voltage \(V\). In multi-collector instrumentation, the magnetic field strength \(H\) and the accelerating voltage \(V\) are selected so that various ions impact on different detectors positioned at various positions i.e. various radii. These mass analysers are very slow, due to required changes in magnetic field strengths. However, the speed is beginning to improve as better laminated magnets and magnet power supplies are developed. Magnetic sector analysers are rarely solely used in ICP-MS due to the slow scanning speed associated with changing the magnetic field strengths and in practice they are typically combined with an ESA to significantly reduce this scanning speed due to the increased speed in jumping electrically from one peak to another.

**Electrostatic Sector Analyser**

Technically, this device is not a mass analyser at all, but an energy filter. These devices are normally used in conjunction with a magnetic sector analyser. The ESA consists of two curved conducting plates, between which the ions must pass, onto which a potential difference is applied. The separation process is somewhat similar to magnetic sector analyser, with ions moving too fast impacting with the outside wall and ions moving too slow being pulled into the inside wall. Only ions of the correct energy will exit between the two plates for detection.

**Double Focusing Instrumentation**

When an electrostatic analyser is used in conjunction with a magnetic sector analyser, in a double focusing ICP-MS instrument, two configurations are possible. If the electrostatic analyser is placed before the magnetic sector analyser, typical of multi-collector instrumentation since the dispersive section is the final section, then the configuration is known as Nier-Johnson. If the setup is reversed, with the magnetic sector placed before the electrostatic analyser, then the configuration is known as
Reverse Nier-Johnson; such instrumentation is more suited to sequential detection since the ESA is the final section allowing faster scanning of the mass spectrum.

Using such double focusing instrumentation, scanning over a limited mass range of 20% is possible by using a fixed magnetic field strength and simultaneously scanning the electrostatic analyser with the accelerating potential. Some instrumentation allows an elegant combined magnetic sector analyser and electrostatic analyser scan in which the magnetic sector is analyser is scanned linearly, whilst a saw tooth wave form is applied to the electrostatic analyser. This mode of scanning allows for very efficient data acquisition.

The major advantage offered by double focusing instrumentation is superior resolution and sensitivity in comparison to quadrupole and other instrumentation. However, there is a trade off between the two and changing from low (300) to high (10,000) resolution incurs more than a 100 fold loss in sensitivity. The most recent improvements in sensitivity came with the use of a shield torch to reduce the ion energy variation leading to much improved transmission. The background is typically very low due to the long, curved ion path efficiently eliminating photons. This lower background leads to lower detection limits; however, this improvement is reduced at the low integration times often used in LA sampling. Although the scanning speed is becoming shorter with technological development, sector field instrumentation is still slower than quadrupole technology and may be unsuitable for the measurement of rapid transient signals, such as those found in LA analysis.

Multi-Collector Instrumentation
Multi-collector instruments are an example of sector instrumentation. These instruments avoid the need for changes in magnetic field strength by incorporating a number of detectors, enabling truly simultaneous detection of ions over a limited mass range. Because of their truly simultaneous nature of detection, multi-collector instrument lend themselves to the precise measurement of isotopic ratios.

Time of Flight
The TOF analyser is the latest analyser to be used in ICP-MS and is now found in commercially available instrumentation. The separation principle is perhaps the
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simplest of all the mass analysers discussed. Figure 7 shows a schematic of a TOF instrument. In such instrumentation, ions from the ICP are collected in discrete packets for a period of time. These packets of ions are then accelerated by several thousand volts before entering a flight tube, typically 1 m in length.

![Schematic of TOF instrument](image)

**Figure 7** A schematic of a time of flight instrument.

Since the kinetic energy \((KE)\) of the ions is dependent upon their mass \((m)\) and velocity \((v)\), and all the ions have been given the same kinetic energy by the accelerating potential \((U)\), then ions of different mass will have different velocities \((v)\). This principle is then used to separate ions of differing \(m/z\) in the time \((t)\) domain over a fixed flight path distance \((D)\).

\[
KE = \frac{mv^2}{2} \tag{2}
\]

\[
\frac{m}{z} = \frac{2Ut^2}{D^2} \tag{3}
\]

As shown in Figure 7, ions of differing \(m/z\) are accelerated into the flight tube; because of their differing velocities they reach the detector at different times, with the lightest
ions reaching the detector first and the heavier ions reaching the detector last. With a path length of 1 m, one complete spectrum can be acquired every 50 μs, two to three orders of magnitude faster than a quadrupole. This analyser has the characteristics of a simultaneous device and hence the benefits of sampling each ion at the same time can be obtained. Sensitivity of TOF instrumentation is typically an order of magnitude less than quadrupole instrumentation due to the smaller fraction of ions that are used. When the issue of sensitivity is corrected, it will be because of the unique ability to sample ions generated in the plasma at the same time that will lead to growth of TOF instrumentation. Ultimately, TOF instrumentation will have major implications in the measurement of rapid transient signals such as those obtained from LA,\textsuperscript{110-115} the measurement of precise isotopic ratios and rapid multi-element determinations especially where sample volume is limited.

**Ion Detection\textsuperscript{108,109}**

Ion detection takes place at the tail end of the instrument, in which the ion beam intensity is converted to a number, either in pulse counting or digital mode in which ions are counted or in analogue mode in which the ion beam current is converted to a potential which is in turn converted to a useable number by analogue-to-digital circuitry.

For low intensity signals, the digital mode of detection is superior since it offers better stability and lower detection limits. For higher intensity signals, greater than 1,000,000 counts s\textsuperscript{-1}, pulse pile up or dead time corrections degrade the quality of the analytical data using this mode of detection and the analogue mode becomes superior in capability. Ideally, an instrument should possess a detector capable of performing both modes of ion detection, since the different modes are optimum at different ion intensities. In order to use both modes of detection simultaneously a cross calibration is required, which converts the analogue value into an equivalent digital count rate, by making measurements where both modes of detection are operational.

Various types of detectors have been used in ICP-MS including: the channel electron multiplier, the discrete dynode electron multiplier, and faraday collectors.
Electron Multipliers

The channel electron multiplier was for a long time the most common detector used in ICP-MS. The device consists of a one-piece, glass cone with a high resistance coating. A high potential of a few kilovolts is applied to one end of the device. Once an ion impacts on the first surface of the device, several electrons are released. Each subsequent impact of electrons has the effect of increasing the net electron current flow, until at the end of the cone a current pulse of multiple electrons can be collected. The resulting current pulse is counted in the digital mode or the combined current is measured in the analogue mode.

Channel electron multipliers are of moderate cost and possess a finite lifetime of around a year, depending upon frequency of use since they are subject to deterioration with each successive ion impact.

The discrete dynode electron multiplier is based upon the same principle as the channel electron multiplier, except that it uses discrete dynodes to perform the electron multiplication process as shown in Figure 8. In this case, a resistor chain is used to apply separate and varying potential to each dynode. The main advantage offered by this system is the lack of need for a high resistance coating, leading to a more reliable device. Also, when in analogue mode, the analogue signal can be taken off at an intermediate dynode, with no necessary change in applied potentials or removal of the applied potential at later dynodes.

![Figure 8 A schematic of a discrete dynode electron multiplier.](image-url)
Both types of electron multipliers have the advantage of low noise and are subsequently found in most single detector instruments. Although they can be operated in both digital and analogue mode, if the applied potential is not reduced when high ion intensities are encountered, then a much reduced detector lifetime can be expected. For this reason instruments should be operated to pass over very intense ion signals where analytical data is not required.

Faraday Collectors
The Faraday collector is the detector of choice for multiple collector instruments, since the operating principle produces high stability and linearity allowing the use of multiple collectors simultaneously. For each ion that impacts within the ‘cup’ an electron flows through a resistor, creating a potential difference across it. The principle of operation is shown in Figure 9.

![Figure 9](image-url)  
*Figure 9 Schematic of a Faraday cup detector or DC analogue detector and measurement circuitry.*

The downside of this detector is that there is no control over the applied voltage or gain of the detector, meaning that Faraday ‘cups’ are only suitable for high ion intensities. For this reason if a Faraday cup is the sole detector then the sensitivity of the instrument will be severely compromised. To increase the sensitivity of ICP-MS instruments equipped with Faraday collectors and to increase the linear dynamic range of the instrument, discrete dynode electron multipliers are often added to be used in
conjunction with the Faraday collectors. Another drawback of this system of detection is that Faraday cups are limited to relatively slow scan rates due to the time constant used in the DC amplification process used to measure the ion current. This makes Faraday collectors limited in their ability to handle rapid transient peaks, such as those derived from LA analysis.
Limitations of ICP-MS Analysis\textsuperscript{116}

Although ICP-MS is known to produce excellent Limits of Detection (LOD) for a vast array of elements, analysis is often hindered to a certain degree by two types of interferences: spectroscopic and non-spectroscopic. Both classes of interference can be reduced by a variety of techniques which include modification in sample preparation, sample introduction and variation in ICP-MS parameters.

Spectroscopic Interferences

Spectroscopic interferences can be defined as an enhancement of the analyte signal caused by atomic or molecular ion species of the same \textit{m/z} as that of the analyte species. This class of interference can occur for various reasons and are sub-categorised accordingly.

\textbf{Isobaric Interferences}

Signals originating from different isotopes, at the same \textit{m/z}, can be observed. These overlapping isotopic signals are referred to as isobaric interferences and cannot be resolved using typical quadrupole technology. One example where an isobaric interference is detrimental to analysis is in the determination of \textsuperscript{114}Cd which is 'overlapped' by \textsuperscript{114}Sn.

\textbf{Polyatomic Ion Interferences}

Ionic molecular species, known as polyatomic ions, can also interfere with the \textit{m/z} signal of the analyte isotope. Such polyatomic ions can be detected as the result of either atomisation survival within the ICP or formation from atomic ions and neutral species within the ICP interface region via combination or ionisation reactions. One important polyatomic interference is \textsuperscript{32}O\textsubscript{2}\textsuperscript{+}, which interferes in the analysis of \textsuperscript{32}S. Another is the presence of \textsuperscript{31}NOH\textsuperscript{+} which appears at the same \textit{m/z} as the \textsuperscript{31}P isotope, making P determination less successful by quadrupole ICP-MS.

Since LA analysis typically avoids the risks associated with the use of a solvent, an LA mass spectrum will possess a lower background due to a reduction in polyatomics derived from the use of the solvent.
Doubly Charged Ion Species

Doubly charged species can be formed under certain plasma conditions for some elements, particularly those elements possessing a low second ionisation enthalpy. The signal for such an ion in the mass spectrum will appear at a \( m/z \) half that of the same isotope carrying a single charge and will therefore cause interferences in lower regions of the mass spectrum. One example of a doubly charged ionic species interfering in analysis is the determination of \(^{69}\text{Ga}\), which can be hindered by the presence of \(^{138}\text{Ba}^{2+}\).

Techniques to Alleviate Spectral Interferences

Higher Resolution

It may be possible to separate an interfering signal from the analyte signal by employing instrumentation with a higher resolution. Resolution is defined by equation 4, where \( \Delta m \) is the peak width, in mass units, of an interference free peak at 5% of the peak height.

\[
\text{Resolution} = \frac{m}{\Delta m} \quad (4)
\]

Alternatively, if two neighboring peaks have equal intensity, \( h \), \( \Delta m \) is defined as the mass difference necessary to achieve a valley height between the peaks of 0.1 \( h \). This is known as the 10% valley definition. Although these definitions are in theory equivalent, the first is much more useful in practice as it is rare to find neighboring peaks of equal intensity.

Quadrupole instrumentation is typically capable of a resolution of around 400, sufficient to separate signals of ions one mass unit apart, but insufficient to resolve spectral interferences. Double focusing mass analysers are capable of much higher resolution, typically offering a maximum resolution of between 10,000 and 12,000. However, operating these mass analysers at higher resolution is accompanied by a reduction in ion transmission leading to reduced sensitivity, but is still typically better or equal to quadrupole instrumentation.

Sample Preparation

Whenever possible, nitric acid should be the only acid used in sample preparation. Since, H, N and O species are all present in the plasma and entrained atmospheric gases,
then no further interferences are introduced to the spectrum by employing nitric acid. In contrast, the use of hydrochloric, phosphoric and sulfuric acids can lead to the introduction of many further and varied interfering species which results in a significantly more complicated mass spectrum.

Chemical separation of the analyte and interfering species is often a viable strategy for reducing spectroscopic interferences and chelating or ion exchange resins have been employed for this purpose.

Sample Introduction
Desolvation can be used as an effective technique for reducing the polyatomic interferences that may arise in the spectrum due to the presence of water and other solvent molecules. Oxides, hydroxides and nitrides can all be reduced whilst simultaneously increasing the analyte signal.\(^\text{119}\)

Sample introduction techniques that avoid complex digestion of the sample and hence avoid interferences derived from the presence of a solvent, are useful in reducing polyatomic interferences. Such techniques include: ETV, HG, slurry nebulisation, desolvation, DSI and LA.

Plasma Variables
Mixed gas plasmas, involving the addition of N\(_2\), H\(_2\), He or Xe to the main Ar stream, have been reported to reduce the signal intensity observed for many polyatomic ions.\(^\text{120}\) The choice of secondary gas is dependent upon the application, namely the analyte species and the interferent to be reduced.\(^\text{121}\)

The operation of a plasma at lower than normal power, resulting in lower plasma temperature, has been successfully applied in the reduction of argon based molecular ions.\(^\text{122-124}\) This background can be greatly reduced, particularly at \(m/z\) 40, enabling measurement of isotopes that were impossible with conventional quadrupole ICP-MS parameters. Typically, under these ‘cold plasma’ conditions the ICP forward power will be set around 600 W, in contrast to a typical forward power of around 1300 W for routine analysis. It may be necessary to employ a grounded metal shield, positioned
between the torch and RF coil to reduce the formation of molecular ions due to a secondary discharge, which can occur under such plasma conditions.\textsuperscript{125}

Collision/reaction cells
Collision cells are a source of chemical resolution and utilise ion-molecule chemistry to remove or reduce polyatomic interferences. They have the secondary effect of thermalising the ions, reducing the ion energy spread and consequently increasing transmission to the detector. Collision/reaction cells consist of a multipole, acting as an ion guide, to which a reaction gas or gases, such as H\textsubscript{2}, NH\textsubscript{3} and O\textsubscript{2}, is applied at low pressure.\textsuperscript{126-128} As well as reducing the impact of interference from polyatomic ions, collision cells have been used to overcome isobaric interferences, by either selectively reacting the interfering element to move it away from the isotope of interest or selectively reacting the analyte element and moving it to a clear part of the mass spectrum.\textsuperscript{128}

Typically, LA of solid samples results in a dry aerosol. Such dry aerosols are very low in O\textsubscript{2}\textsuperscript{+} and H\textsuperscript{+}, which are the major species responsible for polyatomic ion interferences formed within the plasma and within the ion extraction region. However, the abundance of doubly charged species is similar to those encountered in solution nebulisation work. Many samples, typically geological in nature, contain appreciable numbers of oxygen atoms, which can lead to polyatomic interferences. This is prevalent in the case of rare earth element (REE) determination in Ba rich glass samples, in which BaO causes problematic interferences on the REE. These interferences, combined with the fact that many interferences related to the presence of Ar remain, have meant that collision cells have found widespread use, even with the dry aerosols typical of LA analysis.\textsuperscript{129-134}

Mathematical Corrections
The measurement of polyatomic interferences and multiply charged ions at alternative isotopes can be used to correct the analyte signal in a similar way to isobaric interferences. Methods such as multiple linear regression and principle component analysis can be used to great effect, as long as the interferences arising from a particular matrix are known in detail.\textsuperscript{135-138}
Non-Spectroscopic Interferences

Non-spectroscopic interferences can be defined as any change in signal intensity, that results from the physicochemical properties of the sample. Again, this class of interference, often termed ‘matrix effects’, can occur for various reasons and are sub-categorised accordingly. They are caused by concomitant species in the sample and also by the ICP-MS instrumentation itself. Processes such as sample transport, ionisation within the plasma, ion extraction and the behavior of ions within the ion beam, are all influenced, leading to variations in analyte sensitivity.

Presence of Easily Ionisable Elements

If the sample matrix contains a large quantity of elements exhibiting relatively low ionisation enthalpies (such as Na, K, Ca, Rb and Cs) then a change in the ionisation equilibrium of the ICP can result. Such changes can result in a decline in sensitivity, due to ionisation suppression of analytes of higher ionisation enthalpy.\(^{139}\)

Sample Deposition

The analyte signal may become suppressed over a period of time due to deposition of sample matrix on the sampler, skimmer or ion lenses. This can be problematic for ‘high matrix’ samples and can lead to significant deposition on the skimmer orifice, affecting the ion beam behind and subsequently reducing the observed signal intensity.\(^{140}\)

Older laser systems used for LA, generated large quantities of ablated material, consisting primarily of large particulates that cannot be fully processed by the ICP. Hence this problem was commonly encountered when employing such older LA systems. Newer LA systems typically have a much lower ablation rate and produce particles with a much smaller mean diameter; hence this problem is no longer commonly encountered with these systems.

With regular instrumental maintenance, such as cleaning of sampler, skimmer and lenses this problem can be more easily avoided.

Space Charge Effects

The term ‘space charge effects’ is used to describe a mutual repulsion amongst ions, caused by a predominance of positive or negative ions. As plasma species (positive
ions, electrons and neutral atoms or molecules) are transported through the skimmer cone orifice a separation of charge occurs as electrons rapidly diffuse from the ion beam, leading to the ion beam possessing a net positive charge. Electrostatic repulsion influences the ion trajectory, potentially causing a loss in analyte sensitivity. These ‘space charge effects’ can be particularly severe if the matrix ions are of a higher mass than the analyte ions, since the positive matrix ions repel the analyte ions from the ion beam, resulting in a detrimental effect on analyte sensitivity.

Nature of the Sample
The physical properties of the sample and the nature of the sample introduction system can all contribute to the occurrence and extent of non-spectroscopic interferences.

The introduction of gaseous samples of high vapour pressure can vary the width of the central channel within the ICP, affecting the local temperature and ionisation capability. If this vapour pressure is sufficiently high, then the plasma may be destabilised causing plasma ‘flicker’ and subsequent high Relative Standard Deviations (RSDs) or even be fully extinguished. Similar effects are observed upon introduction of a volatile liquid sample, such as samples containing ammonia, where upon vaporisation within the ICP, the same considerations mentioned above apply.

The efficiency of introduction of analytes within a liquid matrix, into the ICP is dependent upon factors such as: viscosity, surface tension, density and vapour pressure; hence matrix matching of sample and standard is essential to provide good quality analytical data. For solid introduction, particularly LA, even slight changes in matrix composition can lead to dramatic variations in ablation rate and the size of the particles produced by the ablation process; since exact matrix matched standards are not available for the majority of sample types, these matrix effects are often a limiting factor for quantification.

Techniques to Alleviate Non-Spectral Interference
Many of the same techniques used to alleviate spectral interferences can be used to alleviate non-spectral interferences. These include; a chemical separation of the analyte of interest from the matrix, utilising an alternative sample introduction technique such as flow injection and desolvation to reduce the number of matrix ions reaching the
plasma. Finally it is vital that matrix matching of sample and standards is performed to ensure constant plasma conditions; this approach used in conjunction with internal standardisation should ensure good quality analytical data is achieved.
Data Acquisition

Data acquisition is an important consideration for ICP-MS, particularly when utilising laser ablation as a sample introduction technique, whether it be for quantitative elemental determinations, spatial resolution or isotopic analysis. For LA-ICP-MS it is important that the data is acquired as a function of time i.e. it is time resolved; hence, the situation is a little more complicated than for the steady state signals produced by solution sample introduction.

The ability to acquire data as a function of time and to observe the data while it is being acquired is termed 'real time data acquisition.' Real time data acquisition is imperative in LA-ICP-MS, since it is through examination of this data that sample heterogeneity is elucidated and the ability to optimise laser operating parameters is achieved. Efficient data acquisition protocols are determined by several factors including: spectrometer sweep time, spectrometer settling time, dwell time, the number of sweeps per reading, and the number of points or channels per spectral peak.

Spectrometer Sweep Time
Spectrometer sweep time can be defined as the total time required for the acquisition of intensity information for all selected masses. This is an important factor since clearly it is pointless to waste time acquiring data at masses where the information generated is of no use. For this reason, particularly for LA analysis in which the signals obtained are generally noisy, the list of masses should be kept as short as possible to minimise the sweep time, allowing heterogeneity in the sample to be observed. For TOF instruments, the sweep time is very short, typically 50 μs; whilst for truly simultaneous instruments such as MC, the sweep time is equivalent to the total time of analysis. For MC instrumentation, this analysis needs to be broken down into smaller intervals to observe signal variation with respect to time, that is, to become time resolved.

Spectrometer Settling Time
Since quadrupole and single sector instrumentation are sequential in operation there is inevitably a period of time ‘wasted’ between acquisitions whilst the mass analyser and detector settle between changes in mass and ion signal; this is known as the
spectrometer settling time. Quadrupole instruments are fast peak hopping and achieve a relatively constant settling time between mass jumps of 0.1 - 2 ms. Single sector instruments are slower, with the settling time being dependent upon the particular set of masses chosen for monitoring and can be as high as 1 ms per mass. This longer time can be attributed to the delay associated with changes in magnetic field strength. The term settling time has no significance when TOF and MC instrumentation are involved.

**Dwell Time**

Dwell time can be defined as the time used acquiring data at a particular mass. Usually, this time is kept constant for every mass selected, although most software allows different dwell times to be used for different masses. In order to allow heterogeneity in the sample to be observed, when performing LA-ICP-MS, dwell times should be kept as short as possible. However, as the dwell time is reduced, leading to a reduction in sweep time, the fraction of time 'wasted' on settling is increased; hence the selection of dwell time is typically a compromise between these two factors. Generally, 80 - 90% of the total sweep time should be used for data acquisition.

**Number of Sweeps per Reading**

This term describes the combination of a number of sweeps to form a reading. At first this may seem disadvantageous for LA applications, since the time resolved nature of the acquisition is reduced; however, the advantages gained include an increase in sensitivity and a separation in signal information from the noise by averaging sweeps. Again the selection of the appropriate number of sweeps is a compromise between two factors, to effectively reduce noise whilst maintaining information regarding sample heterogeneity.

**Number of Points per Spectral Peak**

Sequential instrumentation can be operated to acquire data at various points across the peak of interest as well as at the point of maximum intensity, allowing a true integration. However, the best choice is always one point per peak for a variety of reasons. Firstly, the maximum signal is obtained since the peak is higher than the mean of the points before, at and after the peak. Secondly, the change in intensity with mass calibration is minimised, since there is a larger change in intensity as a function of mass.
off peak rather than on peak. Thirdly, by employing one point per peak the fraction of
time wasted on settling is reduced. Finally, utilising one point at the peak maxima
achieves the best abundance sensitivity, reducing interferences from neighboring
masses.
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Chapter Two
An Introduction to Laser Ablation Inductively Coupled Plasma Mass Spectrometry
Introduction

It is a fact that many ‘real samples’ are solids and thus have to undergo a digestion procedure, often involving multiple steps, in order to prepare them for introduction into an analytical instrument. Such sample preparation techniques increase the likelihood of contamination from other samples and reagents; and also the occurrence of interferences such as molecular ion spectral interference e.g. ArO+. Solid sampling reduces sample preparation time and sample handling, thus diminishing the risk of such contamination. Interferences derived from the use of a solvent are also absent since no solvent is required. Hence, solid sampling for analytical techniques such as ICP-MS has been a long term goal of analytical research.

Initially, the laser provided both the sampling source and the source of excitation and ionisation by using the laser-induced plasma for optical emission and atomic absorption. It was Gray in 1985, who realised that a laser ablated aerosol could be transported with high efficiency to the superior excitation and ionisation source, the ICP. Hence Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) was born. The paper demonstrated detection limits of less than 1 μg g\(^{-1}\) using high-powered lasers that generating large craters of 0.5 - 0.7 mm in diameter. Twenty years later, LA is now the most versatile solid sampling technique for ICP-MS. The technique of LA has been thoroughly reviewed by a number of authors, including: Durrant, Russo and Gunther.

The advantages of LA are well known. Firstly, any type of solid sample can be ablated for analysis, such as conducting and non-conducting inorganic and organic compounds, either as solids or powders. In general there are no sample size requirements except that the sample must fit in the ablation cell; typically, analysis by LA requires a much smaller amount of sample than is often required for solution analysis. Importantly, ablation with a focused laser beam enables spatial characterisation of heterogeneity within samples, typically offering micrometer (μm) resolution both in terms of lateral direction and depth. As mentioned, sample preparation and the use of a solvent is not required meaning the risks of contamination and interferences are reduced.
The drawbacks associated with LA-ICP-MS are also well known. Namely a lack of CRMs for the majority of sample types, to enable the calibration required for accurate and precise quantification. This calibration requires certified reference materials that need to exactly match the sample in terms of matrix composition and are typically hard to acquire or fabricate. Without such standards, ‘elemental fractionation’ has major implications for accurate chemical analysis. The development of reliable, possibly universal calibration standards is thus of great interest and will enable LA to achieve its primary goal of quantitative analysis.

**Elemental Fractionation**

There seems to be no formal definition of the phenomenon described as elemental fractionation, which causes a variation in the relative elemental signal response. Elemental fractionation is massively detrimental to obtaining good data quality, since it means that the observed instrumental response may not be representative of the elemental composition of the sample.

Previously, elemental fractionation was attributed to processes occurring during the ablation process itself; however, it is now known that elemental fractionation can occur at three main points in a typical LA-ICP-MS measurement; the ablation process, the transport process and the atomisation/excitation process within the plasma itself. Recent research has focused upon relating the occurrence of elemental fractionation to the size of particles produced during the LA process, with a shift towards smaller particles causing a reduction in elemental fractionation. The size of particles produced at the ablation process has been shown to not only be dependent upon the absorption and physicochemical properties of the sample, but on the instrumental parameters such as laser wavelength, pulse duration, fluence and carrier gas.

**Elemental Fractionation During the Ablation Process**

Fractionation is known to be strongly element dependent and hence attempts have been made to compare the degree of fractionation with elemental properties such as; melting point, boiling point, vapour pressure, atomic and ionic radius, charge and speciation.
It has been shown that elements with lower melting points and high volatility are often enriched in the vapour phase meaning that the vapour produced by LA of the sample is not representative of the sample itself.\(^8\-10\) This arises since the ablation process often involves a thermal mechanism. It is the electrons within the atoms of the sample that directly absorb the incident laser energy. This energy is subsequently distributed throughout the solid lattice as heat, inducing melting and vaporisation of the sample material. Strong fractionation can arise since different chemical elements have different latent heats of vaporisation; thus some elements are transferred into the vapour phase more readily than others upon application of incident laser energy.

Kuhn and Günther’s studies on elemental fractionation within laser induced brass aerosols,\(^8\) highlighted the dependency of fractionation on elemental properties. Among alloys, brass is thought of as one of the more difficult to analyse, due to the large differences in melting (Cu, 1083 °C; Zn, 420 °C) and boiling (Cu, 2567 °C; Zn, 907 °C) points of Cu and Zn. They showed a particle size dependent fractionation of Cu and Zn in the aerosol produced. Those particles larger than 100 nm primarily consisted of Cu, whereas particles smaller than the lowest measurable particle size fraction or vapour were highly enriched with Zn. Sputtered material remaining further away from the ablation crater was depleted in Zn and was attributed to the laser induced plasma heating and vaporising ejected particles. Since Zn is more volatile than Cu, it was enriched in the gas phase and was therefore depleted in the particles. The resultant Cu signal was greatly reduced since the larger Cu enriched particles did not vaporise and ionise fully within the ICP.

Jeffries \textit{et al.}\(^11\) discussed a possible relationship between fractionation and the ionic radius, charge and melting temperature of elements using both an IR and UV laser. They showed that upon use of an IR laser, the degree of fractionation in the rare earth elements strongly correlated to the ionic radii of the element within the sample.

It has been shown by Chen\(^12\) that the degree of fractionation depends also upon the ionisation enthalpies of the elements within the sample, namely the sum of the first and second ionisation enthalpy. In this study more low ionisation energy elements were found in an ablated mass than higher ionisation elements.
A link between fractionation and elemental speciation or chemical form has been observed. A fractionation study during LA of Mg compounds with different chemical forms was performed. The results obtained can be related to the melting temperatures or on the ease of decomposition, of the compound. For instance, the response factor was lowest for the MgO form, which has a melting point of 2826 °C, whilst MgSO₄ and MgF₂ have melting points of 1127 and 1263 °C respectively. A non-stable form, Mg(CH₃CO₂)₂, gave the highest response factor. A similar result was obtained for Al analysis, where the lowest response factor corresponded to the most stable compound, Al₂O₃, with a melting point of 2054 °C.

Studies performed by Mank and Mason suggested that the degree of fractionation is determined by the shape of the crater formed by the ablation process. In this study fractionation effects were investigated throughout the ablation of deep craters i.e. >200 μm, in a silica based glass matrix. Mank and Mason concluded that fractionation became more significant as the crater aspect ratio was increased. Crater aspect ratio is described as the ratio between the depth and diameter of the crater. The elemental fractionation index showed a change when this aspect ratio exceeded 6:1.

The increased degree of elemental fractionation can be attributed to a change in the aerosol transport mechanism with a change in depth. Larger diameter craters exhibit less elemental fractionation than small diameter ablation craters, when ablated to the same depth. These smaller craters show a greater degree of enrichment towards some elements towards the later stages of the ablation process. This enrichment occurs due to interaction between the ablated material and the surface walls in the upper and intermediate regions of the crater as the ablated material attempts to escape the crater. Thus, a much greater amount of material is removed directly from larger craters without recombination and adherence to crater walls.

An exact mechanism for the dependence of fractionation on crater geometry is not known although it is possible that a plasma confined within a deep crater contributes to the sampling process and leads to strong fractionation i.e. the ablation mechanism is primarily non-thermal at the sample surface but changes to a plasma dominated thermal mechanism with a greater depth.
It is also plausible that fractionation effects could be attributed to the actual irradiance of the laser beam decreasing as the crater deepens due to changes in effective area exposed to the laser beam. As laser irradiance is increased, crater geometry changes from a flat bottomed (at shallow depths), to an increasingly convoluted profile with the same number of laser pulses. In this scenario the ablation crater deepens and the aspect ratio of the crater increases, consequently the surface area of the crater walls increase. Laser irradiance on the side wall of the crater is smaller than that at the crater bottom.

**Elemental Fractionation During the Transport Process**

Elemental fractionation processes are known to occur during transport of the ablated material to the detection system. It is thought that the sources of elemental fractionation during such transportation may be attributed to selective vapour condensation on tubing walls, or even on selective nucleation of species on different sized particles. It is the size and shape of the particles produced that governs these two effects and hence the transport efficiency of the particle and its chemical composition are particle size dependent. It is often the origin of the particles that determine their size and chemical composition; for instance, larger particles are believed to originate from melt flushing of the heated liquid layer and hence their composition is often significantly different from the bulk.

The presence of enriched particles has been demonstrated by Outridge et al. Such particles were enriched in certain elements including Pb, Bi, Zn, Au and Ag, by LA of NIST 610 glass. The study showed that different particle sizes can possess greatly different elemental composition. Two mechanisms were described which could explain the formation of these pure elemental particles. Firstly, volatilisation of low melting point/boiling point elements within the melted region of the sample, together with post ablation condensation of low melting point/boiling point element vapour. Secondly, zone refinement, in which virtually instantaneous migration and segregation of elements during the melting of the sample occurs, providing an elementally enriched target, from which molten droplets are ejected.
The occurrence of this zone refinement has been proven by Cromwell and Arrowsmith.\textsuperscript{19} Refinement of Pb during the ablation of brass occurred and it was suggested that the Pb had erupted from Pb rich inclusions below the crater surface, which had in turn been formed during ablation, by the migration of the Pb in the liquid phase of the ablating sample.

Hence the size distribution of particles produced by LA greatly affects the degree of fractionation observed. It has already been shown that different sized particles may possess a different chemical composition, since some may become enriched. This source of fractionation is amplified as smaller particles and vapour may often diffuse onto the ablation chamber walls as well as the walls of the connective tubing used throughout the transport system. Larger particles can settle out due to the effects of gravity and hence are prevented from reaching the ICP.

**Elemental Fractionation Within the Plasma**

The operating conditions of the ICP itself have a significant effect on the measured elemental ratios under constant ablation conditions. The degree of elemental fractionation occurring within the ICP depends not only on the particle size distribution of the aerosol but on the ionisation efficiency of the plasma itself. Even though the ICP is a very powerful and efficient ionisation tool, the vaporisation, atomisation and ionisation efficiencies change with the local temperature of the ICP. Differences in the sample load can therefore alter the ICP temperature and hence alter the vaporisation and ionisation efficiencies. This effect is especially pronounced for elements with a high first ionisation enthalpy.\textsuperscript{20} In fact, recent studies have highlighted that the laser ablated aerosol structure itself can have a significant impact on elemental fractionation.\textsuperscript{21-24} The laser ablated aerosol can be subdivided into three parts:

1. The fraction that remains within the ablation cell or transport system, referred to as immobile.

2. The fraction that is transported to the ICP but is not completely vaporised, atomised and ionised, referred to as incomplete.
3. The fraction that is completely transported, vaporised, atomised and ionised, referred to as complete.

Whether the ICP causes elemental fractionation will therefore depend upon the mass ratio of incomplete to complete particles. When this ratio is small, almost every particle will be fully vaporised, atomised and ionised by the plasma, and the ion number density will reflect the stoichiometry of the laser ablated aerosol. When the incomplete fraction increases, an increasing number of particles will not be fully vaporised, atomised and ionised, and a preferential vaporisation of elements with higher volatility will alter the relative composition of atoms and ions within the ICP, leading to plasma based elemental fractionation. This process is shown in Figure 10.

ICP induced elemental fractionation can be reduced by optimising the ICP parameters, including forward power, sampling depth, and carrier gas flow and composition, to give sufficiently high gas temperature within the central channel of the ICP. It is important to realise that optimum conditions for minimising plasma based elemental fractionation may differ greatly to those conditions required for optimum sensitivity.

The LA process is responsible for the initial particle size distribution of the laser ablated aerosol. Most of the particle loss within a typical LA-ICP-MS system occurs within the ablation cell, and the transported fraction is vaporised, atomised and ionised to a highly variable degree within the plasma. Therefore all observations of elemental fractionation, in particular contradictory results for different instrumentation, have at least some relation to the particle size distribution and its treatment within the ICP.
Figure 10 (a) Silicate particle is less than 150 nm and is completely vaporised by the plasma leading to a vapour cloud that is representative of the sample i.e. no plasma based fractionation (b) Silicate particle is greater than 150 nm and is not completely vaporised by the plasma; this leads to selective vaporisation of volatile elements from the particles large surface area, inducing plasma based fractionation.²²

Another source of fractionation within the ICP is produced via element specific matrix effects. Matrix elements with a lower second ionisation potential than the first ionisation potential of Ar may show severe matrix effects.²⁰, ²⁵, ²⁶ It is possible to reduce these matrix effects by substituting the Ar carrier gas for He. The interference mechanism is not yet fully understood, although it is thought to involve the interaction between doubly charged matrix ions and argon species.
The Ablation Process

Ablation is a frequently used term for material removal by intense laser light, and originates from the Latin “ablatum”, which means “taken away”. The term laser ablation (LA) is generally used in a broad sense to denote any laser induced material removal.

The interaction between an incoming laser beam and a solid surface is complicated and remains poorly understood. This is due to the fact that the absorption process and the subsequent material ejection are characterised by different processes which usually even occur simultaneously and are shown below:

1. The laser light strikes the solid and interacts with the electrons. After a period of tens of ps the electrons and atoms equilibrate, which leads to strong heating of the irradiated volume.

Figure 11 A representation of the interaction between a high-power, highly-focused laser beam and a solid surface.
2. Material from the heated volume is ejected and continuously absorbing energy from the laser, resulting in the formation of an expanding one dimensional plasma plume.

3. After the termination of the laser pulse the plume expands adiabatically in all three dimensions. If the expansion takes place in a vacuum, the plume atoms will eventually flow away with a constant velocity.

4. If the expansion occurs in a background gas, as is typically the case, the high plume pressure initially drives the expansion as if it were in a vacuum. After several μs the plume propagation is completely determined by the interaction of the plume atoms with the atoms and molecules of the ambient gas.

Particle Formation Processes

Many mechanisms have been proposed to explain mass removal from the ablation site and subsequent particle formation. A recent review by Hergenroder describes the extent of current research and knowledge.

If the particle distribution of a laser generated aerosol is measured, two distinct fractions can be observed, implying that at least two mechanisms exist in conjunction for particle formation processes. Two models produced by Hergenroder, have been proposed to explain the mechanisms involved in the formation of both particle size fractions. The first model describes the formation of the larger particles above the size of 100 nm. This model is based upon the ejection of particles via plasma initiated Kelvin-Helmholtz instabilities within the melt layer after the laser pulse. However, the model suggests that this hydromechanical mechanism cannot explain the existence of particles smaller than 100 nm, and thus a second model is proposed for the generation of this smaller particle size fraction. This second model proposes a gas-to-solid particle mechanism, based upon nucleation and condensation of sub nanometer clusters. These liquid clusters, collide and coalesce within the laser induced plasma to form larger particles, before solidification. Subsequently, the solid particles collide to form larger agglomerates.
Chapter Two

Instrumentation

The laser (Light Amplification by Stimulated Emission of Radiation) was created in the 1960s and rapidly attracted the attention of analytical chemists due to its potential sampling capabilities. Optical energy is built up in the laser cavity which contains the laser medium and is subsequently released in a very short time as a laser pulse. Lasers are capable of producing coherent, collimated, monochromatic pulses of energy of very short duration at specific wavelengths, which range from the ultraviolet (UV), through the visible, to the infrared (IR), depending upon the laser medium used. Since laser light allows a highly focused energy pulse of high peak power, they are particularly well suited to LA.

A typical LA-ICP-MS system consists of a laser, an ablation stage, a transfer system, in conjunction with an ICP-MS instrument. Figure 12 shows a schematic of a typical LA-ICP-MS setup. The laser is used to ablate material from the sample, which is placed on a mechanically adjustable ablation stage. The transfer system transfers the ablated material to the detection system, the ICP-MS.
Figure 12 A schematic of a typical LA-ICP-MS system, showing the sample introduction (laser ablation) region, transport region and detection (ICP-MS) region.

**Laser Action**

To produce laser emission, an excited state must be stimulated, so that it emits a photon, by radiation of the same frequency. The more photons that are present the greater probability of the emission. One essential requirement of laser action is the existence of a metastable exited state, an excited state with a long enough lifetime for it to participate in stimulated emission. Another requirement is the existence of a greater population in the metastable state than in the lower state where the transition terminates, for then there will be a net emission of radiation. Because at thermal equilibrium the opposite is strictly true, it is necessary to achieve this population inversion in which there are more molecules in the upper state than in the lower.

One way of achieving this population inversion can be seen in Figure 13. The molecule is excited to an intermediate state $I$, which then gives up some of its energy non-radiatively and changes into a lower state $A$. The laser transition is the return of $A$ to the
ground state $X$. Since three energy levels are involved this type of laser action is termed a ‘three-level laser system’.

![Diagram](https://via.placeholder.com/150)

Figure 13 The transitions involved in basic laser action. The pumping pulse populates the intermediate state $I$, which in turn populates the lower state $A$. The laser transition is the stimulated emission $A \rightarrow X$.

The disadvantage of the three-level laser system is that it is difficult to achieve a population inversion, since so many ground-state molecules must be converted to the excited state by the pumping action. This problem is avoided in a four-level laser system, such as the Neodymium doped Yttrium Aluminium Garnet (Nd:YAG), whose transitions are shown in Figure 14, by having the laser transition terminate in a state $A'$ rather than the ground state. Because $A'$ is initially unpopulated, any population in $A$ results in a population inversion. Moreover, this population inversion is more easily maintained, if the $A' \rightarrow X$ transition is rapid, for these transitions will deplete any population in $A'$ that stems from the laser transition, and keep the state $A'$ relatively empty.
Figure 14 A Nd:YAG laser four level energy diagram. Because the $A'$ energy level is not the ground-state, then it is initially unpopulated meaning that a population inversion is more easily attained.

**Types of Lasers**

The basic requirement of the laser is to provide energies of sufficiently high power density (typically in excess of $10^7$ W cm$^{-2}$) at the lens focus to ablate and vaporise diverse sample matrices. A precise and representative sampling process is desirable for bulk analysis; whilst in order to perform microanalysis or spatial discrimination, focusing the laser beam to a small spot size i.e. 10 - 20 μm is necessary. Carbon dioxide, nitrogen, excimer, ruby and Nd:YAG lasers have all successfully been used for the technique of LA, although the market is now dominated by the Nd:YAG and excimer.

**The Nd:YAG Laser**

The Nd:YAG laser is the most commonly used source for LA. This laser has a fundamental frequency of 1064 nm and has largely replaced the ruby laser which was used previously. The Nd:YAG laser consists of a Nd doped Yttrium Aluminium Garnet rod a few millimetres in diameter. When sufficient power is available, Nd:YAG lasers may be frequency tripled, quadrupled or quintupled and operated at the third (355 nm), fourth harmonic (266 nm) and fifth harmonic (213 nm);$^{40}$ whilst a Nd:YAG operating at 193 nm has recently become commercially available.$^{41,43}$ In contrast to ruby lasers,
Nd:YAG lasers may be operated at medium (10 - 20 Hz) or high (1 - 5 kHz) repetition rates without an associated loss of power. Since the laser is reasonably priced and reported by users and manufacturers to be both robust and reliable without extensive maintenance, the Nd:YAG laser is a powerful ablation tool. The flash lamp is the only part of a solid laser medium system which requires routine maintenance and must be replaced when it no longer provides enough energy since it loses intensity with prolonged use.

The Excimer Laser
Excimer lasers have also been successfully used for LA applications. Such lasers emit very short wavelength pulses which more readily induce photo-ejection of electrons; hence these lasers are capable of sustaining laser induced plasmas at low pulse energies. Excimer lasers, such as the XeCl and ArF which operate at 308 and 193 nm respectively, are capable of delivering pulses of 0.1 - 1 J at repetition rates of 300 Hz. Previously, the major disadvantage of excimer lasers was that they both lacked mode structure and displayed poor spatial coherence. This meant that they were not able to be focused to small spot sizes and were often unsuitable to applications involving spatial profiling. However, this problem was removed by involving a more complex laser optics system. The main advantage of these lasers is that the crater size produced, as well as the ablated particle size distribution tends to be more uniform than those produced from other lasers.

The Laser Wavelength
There is a widespread discussion concerning the ‘best’ wavelength to use for LA. Wavelength is known to be a very important variable based on the sample’s optical penetration depth as well as photon energy required for bond breaking within the sample. The amount of laser energy incident upon a sample is dependent upon the wavelength of the laser; this laser energy controls the ablation yield and thus the resulting signal response. Since UV radiation can be focused to a smaller spot size than longer wavelength radiation (such as visible or IR), and the fact that UV is more highly absorbed by the majority of sample types, UV lasers are almost exclusively used for LA purposes.
Generally speaking, the use of shorter laser wavelength (UV) is advantageous since it offers higher photon energies for more efficient bond breaking and ionisation of the solid sample, as well as reducing the fractionation process. This occurs since ablation can involve thermal and/or non-thermal processes, depending upon the wavelength of laser used. In a thermal process, the electrons within the sample directly absorb the incident laser light. This energy is transferred to the atomic lattice inducing melting and vaporisation of the sample material. Different chemical elements have different latent heats of vaporisation and thus strong fractionation is induced via this mechanism. When a shorter wavelength is used the ablation is not so dependent on this thermal mechanism. Instead, when the photon energy is higher than the bonding energy between atoms, the laser radiation can directly break the atomic lattice. This non-thermal mechanism induces ion and atom ejection without heating effects, thereby greatly reducing fractionation.\textsuperscript{44,45}

The laser beam can interact with the expanding plume of plasma which is created at the early stage of the ablation process. When this occurs, the laser energy can be strongly absorbed or strongly reflected by the plasma. This process is known as plasma shielding and is known to be strongly dependent upon the wavelength of the laser used. Again shorter wavelength lasers are preferred since they are able to penetrate the plasma with greater efficiency, reducing plasma shielding and directly initiating bond breaking within the sample. Shorter wavelengths thus enable a larger ablation rate and less fractionation.\textsuperscript{46,47}

The influence of laser wavelength on analytical performance has been investigated by many research groups,\textsuperscript{27,43,48-51} although comparison data from such investigations can often be misleading since the comparisons of wavelengths are often for different samples, different laser energies and spot sizes, different ablation cell designs, flow rates and often ICP-MS conditions. For a fair comparison all laser, sample and system parameters should be similar.

The Laser Mode
Pulse lasers can operate in either the free running mode or a Q-switched mode. The free running mode, which is the simplest mode of laser operation, produces relatively long
laser pulse widths (typically 10 -100 μs) and has in the past been used successfully for LA-ICP-MS. If employed, this operating mode can cause significant cratering of the sample and ejection of material primarily as particulates.

The Q-switched mode tends to produce laser pulses of much shorter duration and at a much higher peak power. For this reason the Q-switched laser is thought to yield a greater proportion of material in the vaporised state. They use an optical switch (Q-switch) to concentrate the laser output energy into giant pulses.

In Q-switching, a shutter is placed in the cavity which prevents reflection between the mirrors. This leads to little stimulated emission (referred to as low Q), and allows a large population inversion to build up. When the shutter is opened (high Q), this large population inversion is "swept" out of the cavity as a single, high intensity pulse. Q-switching can give pulse lengths down to about 5ns, with pulse energies in excess of 3 J. The mechanism is shown in Figure 15.

![Figure 15 The principle of Q-switching. (a) Low Q, the excited state is populated while the cavity is non-resonant. (b) High Q, the resonance characteristics are suddenly restored, and the stimulated emission emerges as a giant pulse.](image)

Typically, ablation yields are significantly lower using the Q-switched mode by one or two orders of magnitude although signal strength at the detector is only reduced by one
order of magnitude. As well as sensitivity and precision there are also practical aspects of equal importance to consider including build-up of particulate matter in the ablation cell, transport lines and inlet system of the ICP-MS system. Generally speaking, Q-switched lasers are now preferred to the free running laser because of an improved ‘coupling’ with the sample surface.

**Laser Pulse Duration**

Previous LA work utilised nanosecond pulsed laser systems. However, there is now a trend towards shorter laser pulses of femtosecond duration\(^ {35, 36, 53-70}\) due to evidence suggesting a potential for reduced elemental fractionation.

The processes involved in the ablation of material from a sample e.g. a metal, must first be considered. The free electron gas of the metal is rapidly heated due to the effect of the laser pulse. The energy of this hot electron gas is then subsequently transferred to the sample lattice and thermalised in the bulk. The actual mechanism for removal of the material is thought to be thermal melting and evaporation or some kind of explosive evaporation. The electron heating and thermalisation is thought to take approximately 100 fs with cooling of the hot electron gas and energy transfer to the lattice lasting a few ps. Thermal diffusion into the bulk takes place at a time of \(10^{-11}\) s and finally the onset of thermal melting and subsequent ablation occurs after \(10^{-10}\) s.\(^ {53, 54}\)

Hence a laser pulse with duration longer than a few ps will interact with different transient states and with the plasma formed above the sample surface (plasma shielding occurs). Under such circumstances the main part of the material is evaporated from the molten metal and fractionation occurs due to preferential volatilisation of different elements within the sample with different melting temperatures.\(^ {53, 54} \)

In comparison, if ablation involves a laser of pulse duration no longer than 100 fs then the laser only interacts with the electron sub-system of the sample. The laser pulse is long over before the sample undergoes any changes in thermodynamic state. In this scenario most of the laser energy is transferred into the sample and converted into kinetic energy of the ablated material. Due to the high intensity of the femtosecond laser pulse and the short pulse duration in comparison with the phonon relaxation time of the
sample, the laser and material interaction involves nonlinear processes. Multi-photon and tunneling ionisation processes dominate the interaction and heating of the sample lattice is minimised. Sample heating is a major cause of elemental fractionation and is greatly reduced in femtosecond ablation.\textsuperscript{53, 54}

As discussed another major contributor to elemental fractionation and energy loss is plasma shielding. Since a femtosecond laser pulse cannot interact with the plasma leaving the sample surface all the laser energy is deposited in the sample surface region. The femtosecond laser pulse ceases before the material can escape the sample surface and hence no interaction occurs.\textsuperscript{53, 54} Femtosecond LA is becoming more popular and is now used for many applications due to the ability to ablate extremely well defined craters whilst greatly reducing elemental fractionation effects and its use has been recently reviewed by Hergenroder\textsuperscript{57}.

**Laser Beam Profile**

Another factor that can influence mass removal from the sample surface during LA is the laser beam spatial energy profile. Nd:YAG lasers usually possess a Gaussian beam profile and hence can be easily focused to a small beam area; whereas excimer lasers generally possess a flat top beam profile.

The laser beam spatial energy profile greatly affects the shape of the ablation crater formed. Using a Gaussian profile the crater becomes cone-like after hundreds of pulses;\textsuperscript{71} whereas using a flat top beam profile i.e. an excimer laser, will generally produce straight wall craters. Both Nd:YAG and excimer lasers are capable of producing flat bottom craters if the correct imaging optics are employed.

It has been shown that the shape of the crater walls produced in the ablation influences the depth resolution and that fractionation may become more significant with the development of the ablation crater.\textsuperscript{15, 71} The degree of elemental fractionation is not strictly related to the beam profile employed and cannot be completely eliminated by employing a flat top laser beam profile.
Laser Focusing and Steering

In order for LA to be effective, the energy of the laser must be directed and focused upon the sample of interest which is contained inside an ablation cell. Mirrors and prisms are used to direct the laser beam to the sample. Such mirrors will often have a dielectric optical coating on a highly polished substrate. These produce very high reflectivity for the design wavelength, in excess of 99% at the specified angles of incidence and reflection and also have high transmission for other wavelengths. Mirrors such as this are thought of as very robust and long lasting.

Once the beam has been directed towards the sample it must then be focused onto a small area of the sample surface. For a Nd:YAG laser the spot size can be controlled by adjusting the laser focus and the incident energy simultaneously; whereas in most excimer systems an aperture imaging system is often used in which the spot size is defined by the size of the focused image of an aperture placed at an appropriate position within the optical path. When changing the aperture size the spot size changes proportionally whilst maintaining a constant energy density on the sample surface.

There are two main types of focusing objective used, refracting and reflecting. Within each type a wide range of models are available; the choice of which depends on its analytical application and subsequent requirements such as, wavelength and power, magnification, focal spot size, working distance and finally cost.

Refracting Focusing Lenses

Refracting focusing lenses are potentially less robust than reflecting objectives since they are much more prone to damage through absorption by impurities or imperfections. In order to reduce damage specialist materials such as UV grade synthetic fused silica (or other UV transmitting materials) must be used. Although not providing high focusing or visual imaging performance due to various lens aberrations, simple single element lenses are readily available at relatively low cost and are considered consumables by many users.

Cemented multi-element refracting lenses provide much improved focusing and imaging properties and work well for most low power, IR and visible systems. The
major drawback to such lenses is that the organic cements used in their construction are extremely susceptible to laser damage. Air spaced compound lenses with very good focusing and imaging properties are available with high laser handling properties, even in the UV and come highly acclaimed by many users.

Reflecting Objectives
Reflecting objectives are an alternative to standard refracting lenses. When appropriate dielectric reflective coatings are applied on a visible light reflective surface, such objectives can be applied to high power laser applications, whilst maintaining imaging capabilities. Such objectives are potentially very long lived. Other advantages associated with their use are that they provide very high magnification and long working distances. Working distance is described as the distance between the lens or its mount and the point of focus. Very good visual imaging is obtainable since these objectives have an absence of chromatic aberrations. Chromatic aberration is the focusing of different wavelengths at different distances.

The use of reflecting objectives has some major disadvantages however. With a standard dielectric coating they can only be used at one wavelength and they suffer an inherent transmission loss, whilst producing a strongly convergent beam with a small depth of focus. Such reflecting objectives are typically very expensive.

The Ablation Cell
In general an ablation cell must consist of a window, an ablation chamber and an adjustable platform on which the sample sits. This cell must allow the laser energy to enter and become focused upon the sample. It must also contain ports for the entry and exit of a carrier gas that is used to sweep the ablated material into the ICP. The cell is gas tight to avoid sample losses and the introduction of atmospheric gases. The use of a wide variety of ablation cells has been described in the literature e.g. the ‘Arrowsmith type’ ablation cell,72 the ‘Jet Cell’ as described by Jackson,73 the High Efficiency Aerosol Dispersion (HEAD) cell as described by Pisonero74 and even cryogenically cooled cells for biological applications and ablation of gel plates.75 However, there is still room for improved cell design, especially for specific analytical applications.
Ablation Cell Volume

It is desirable to have fast and efficient transport of the sample from the ablation cell and this can normally be achieved with good gas flow dynamics; typically small chambers with high gas flow velocities are used. However, it is also desirable to have a cell which provides adequate volume for dilution and mixing of the sample pulses in order to achieve a fairly stable input into the ICP. Importantly, the cell design must allow flushing of the cell to remove residual atmospheric gas following swapping of samples, otherwise a mixed gas plasma will temporarily occur.

The most important requirement of an ablation cell is that it must be capable of accommodating the sample. Ideally the cell should be capable of accommodating several samples as well as calibration and reference materials to avoid regular opening of the cell and therefore provoking less constant ICP operating conditions. There are cases when the cell volume needs to be kept to a minimum in order to avoid over dilution of the sample; this is especially the case for the analysis of very small samples such as fluid inclusions. The volume of the ablation cell used depends very much on the application and the nature and size of the sample involved.

Ablation Cell Windows

The ablation cell must contain a window that allows entry of the laser energy so that it can be focused upon the sample of interest. The window must be transparent to the laser wavelength; optical quality glass is used to achieve this or for UV lasers synthetic fused silica. When high energy lasers are used, back reflections may cause harm to the laser system and for this reason the window is often mounted at a small angle to the incident laser beam. This is not necessary for low energy applications.

If the laser operator wishes to observe transparent samples using transmitted light then a second window is required that is transparent to visible light. This is placed in the bottom of the cell. Good ablation cell design will incorporate a method of easily replacing the cell windows in case of damage.

The Sample Stage

In a typical ablation cell the sample sits on an adjustable platform within the cell. This adjustable platform allows precise positioning of the sample within the cell in the X, Y
and Z directions and is typically under computer control. With such an adjustable platform, displacements as small as a few microns can readily be achieved without any difficulty. The adjustable platform allows different tasks such as depth profiling, spatial profiling, surface and bulk analysis when combined with precise timing between individual laser pulses.

The Transfer System

The sensitivity of an ICP-MS instrument partly depends on the amount of material successfully transported from the ablation site to the plasma source for ionisation. A measure of this is the transport efficiency. In addition to the transport efficiency, the particle size distribution of the aerosol produced has a pronounced affect on the sensitivity of the instrument. This effect on sensitivity occurs since the size of the particle has an influence on the ionisation capabilities of the plasma.

Ablated material is transferred to the ICP via a carrier gas along a length of plastic tubing. Both the nature of the carrier gas used to sweep the ablated material into the ICP, and the length of connective tubing play a part in the transport efficiency achieved by the system. Several studies have indicated that the efficiency of transportation can vary from 10 to 20%, with efficiencies of up to 40% being reported. However, such efficiencies are notoriously difficult to determine with any accuracy.

Effect of the Carrier Gas

The ablation chamber is flushed with an inert gas in order to transport the ablated material to the ICP. Ar and He have been employed to do this, with the latter gas providing improved ablation and transport rates, with a reduction in background. 17, 39, 76

Horn et al. 39 investigated the influence of the carrier gases, Ar, He and Ne on particle size distribution and transport efficiency of laser induced aerosols. Their results illustrated the differences in particle size distribution transported in Ar, He and Ne atmospheres using both 193 and 266 nm laser wavelengths for ablation.

It was found that ablation in a He atmosphere produced significantly smaller particles on all materials tested, for both wavelengths and thus an associated gain in instrument sensitivity was recorded using He as a carrier. It was also shown that the gas
environment may contribute to the control of condensational or coagulation growth of particles after the laser impact. Hence, the use of Ar, He or Ne could influence the growth of particles condensing from the vapour. The study showed that the laser induced plasma is significantly smaller in He than with Ar. This combined with the higher thermal conductivity of He, allows a faster spread of thermal energy from the sampling site, leading to a rapid end in condensational growth of particles and a subsequent shift towards smaller particle size distribution occurs. 39

**Connective Tubing**

Both the length and internal diameter have an affect on the transport efficiency of ablated material. Large diameter tubing has the advantage of an increased ratio of gas volume to tubing wall area, minimising the number of sample particles that collide with the tubing wall and are subsequently lost, leading to a reduction in system sensitivity. Conversely, a narrow tubing diameter may also be desirable since it provides an increase in linear gas velocity which reduces the time used to transport the ablated material consequently reducing loss of sample due to gravitational settling. In reality, it is necessary to reach a compromise between the two extremes resulting in reasonably efficient sample transfer.

It is necessary to regularly change the transfer tubing so that memory effects can be reduced. These memory effects arise as sample becomes deposited upon the walls of the tubing, providing a long term, source of contamination. The frequency of change depends very much on the type of sample and the volume of sample ablated. A need for tubing change is often indicated by spurious spikes in the gas blank signal.

**Ancillary Equipment**

It is necessary to have some means of viewing the sample during LA. Viewing of the sample is vital not only to allow careful selection of the sampling sites, but to observe the ablation process itself. In a typical LA system this is achieved through the use of a TV camera and monitor. Many of the systems available facilitate focusing of the laser by configuring the TV optics so that the laser is focused on the sample when the sample height is adjusted to produce a focused TV image. More sophisticated systems,
particularly those used for high resolution sampling, incorporate a microscope into the laser sampler, providing a wide range of additional viewing capabilities.
Sample Requirements

The major advantage offered by LA sampling is that it is extremely versatile in its sample requirements, allowing almost all materials to be efficiently ablated. The only prerequisite is that the sample type be compatible with the ablation cell used.

Sampling by LA can be divided into two types; bulk sample analysis, in which the beam is focused into a spot generally larger than 100 µm and microprobe analysis, in which the beam is focused into a spot diameter generally smaller than 100 µm. Table 1 shows a comparison of the two sampling techniques.

Table 1 Characteristics of the two sampling strategies offered by LA-ICP-MS; bulk sampling and microprobe analysis.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Bulk sampling</th>
<th>Microprobe analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser pulse energy</td>
<td>10 - 100 mJ</td>
<td>Few mJ</td>
</tr>
<tr>
<td>Typical crater diameter</td>
<td>0.1 - 1 mm</td>
<td>5 - 100 µm</td>
</tr>
<tr>
<td>Volume sampled</td>
<td>0.0008 - 0.8 mm$^3$</td>
<td>100 - 800000 µm$^3$</td>
</tr>
<tr>
<td>Mass ablated</td>
<td>2 µg - 2 ng</td>
<td>0.25 ng - 2 µg</td>
</tr>
<tr>
<td>Typical detection limits</td>
<td>ppm – ppb - ppt</td>
<td>ppm – 10 ppb</td>
</tr>
</tbody>
</table>

Bulk Analysis

In bulk analysis of a sample the idea is to obtain a result representative of a large sample without the need for digestion. In this scenario it is presumed that the small quantity of material ablated and carried to the ICP-MS is representative of the whole sample. In order for this presumption to be valid the sample must be highly homogenous. Therefore samples for bulk analysis are often homogenised.

Microprobe Analysis

Microprobe analysis is a very exciting application of LA and is enabled due to the focusing characteristics of lasers allowing sampling of very small areas. In this technique very small volumes of a sample are analysed so that instead of attempting to obtain a representative of the bulk sample, the compositions of many discrete portions that make up the larger sample are determined. This allows spatially resolved studies to become feasible with spatial resolution typically as low as 5 - 60 µm.
When using LA as a spatial resolution technique, the only real concern of sample preparation involves being able to visually identify the target for ablation. Hence thin wafers of the sample are often mounted on a glass slide to allow transmitted light viewing or polished sections for reflected light viewing. Another concern is the presence of any polishing materials such as Pb, trapped in any imperfections within the sample surface. Such materials can be removed by ultrasonic cleaning of the sample.
Calibration Strategies

Unfortunately there is no universal method of calibration for LA-ICP-MS and hence accurate and precise quantitative analysis remains a challenge for a wide variety of sample types. Many types of calibration strategies exist, although generally these can be classified into the following groups.

Matrix Matched External Calibration

To allow accurate quantitative analysis by LA-ICP-MS matrix matching of the external standards and the sample is extremely important. This is due to the fact that the ablation rate of the target can vary greatly with even slight changes in the target matrix. Ablation rate is defined as the mass of sample ablated per laser pulse and even a small difference in the target matrix can result in variations of around 50%. Quantitative analysis employing external calibration requires reference materials that are closely matrix matched to the sample type, with respect to elemental composition and physicochemical characteristics.

Although certified reference materials are available for some applications, including glasses and metals, they certainly do not cover all types of sample matrix. Because of this lack of certified reference materials, many laboratories prepare their own matrix matched, in-house calibration standards, typically by one of two approaches.

The first approach is fusion to form a glass bead. In this approach, high temperatures are generally required to melt and fuse the sample or standard. Since the homogenisation occurs in the liquid phase, this type of sample preparation results in a highly homogenous glass bead; however the high temperature involved can be detrimental as it often results in the loss of volatile analytes from the bead. If a flux is used, such as lithium metaborate, then these temperatures can be reduced, minimising analyte loss due to volatility; although, the use of an extra reagent increases the risk of contamination.

The second approach is to press a powdered sample into a disc. In this approach the sample is ground and homogenised, before subsequent pressing e.g. under pressure in a mechanical IR press. The use of binders, such as high molecular weight
alcohols and plastic resins including phenols or polyethylene can greatly improve the mechanical stability of the disc. Although less time consuming than the glass bead approach, pressed discs are often less homogenous in terms of elemental distribution since the homogenisation step does not occur in the liquid phase. However, the use of a mixer mill can now produce discs of adequate homogeneity for the majority of LA applications, especially if a large laser spot diameter is employed with either line or raster analysis.

External calibration is a technique of quantification that is particularly well applied to samples with a metallic matrix and external calibration is often considered relatively easy for such sample types. There is a broad range of metal standards widely available, which are considered to closely match many sample types in terms of physical and chemical properties. Such standards must be carefully chosen to match the sample of interest so that elemental fractionation does not occur or is similar in the standard and sample alike.

These above studies have shown that since the ablation yield can vary by as much as 50% between sample and standard, poor analytical data is obtained unless the calibration standards are prepared to exactly match the sample or an internal standard element is used to correct for these large differences in ablation yield. A major advantage of standard preparation of this type is that it facilitates addition of internal standard elements, isotope spikes or even matrix modifiers to improve the absorption characteristics of the standard.

**Internal Standardisation**

Even where such reference materials, which closely match the sample of interest, are available, calibration by this method still often results in poor analytical data. A much more robust method of calibration can be achieved through the addition of an internal standard. The use of such an internal standard allows a correction to be applied to the differing ablation yields between the reference material and the sample of interest. Matrix effects and signal drift within the ICP-MS can also be corrected for with this technique of calibration. This latter correction is of particular relevance to bulk
sampling using LA-ICP-MS whereupon vigorous ablation often results in heavy loading of the ICP, often resulting in significant matrix effects and instrumental drift.

Direct solid analysis of a sample in the natural state requires the use of a naturally occurring internal standard. In such circumstances, the internal standard of known concentration is often the major constituent of the sample matrix. The concentration of the internal standard may have been determined via an alternative technique or via estimation from the known stoichiometry of the material; the latter is mostly of importance in geological applications. Frequently the major constituents of such naturally occurring materials are of low atomic mass and consequently do not allow corrections for ICP-MS matrix and drift corrections. However, for microanalysis, whereupon the amount of ablated material is small, such matrix and drift effects can be considered insignificant. Therefore, this method of calibration can provide accurate results.

A good internal standard will have similar ablation characteristics to the elements that are being determined and because of the mass dependency of matrix and drift effects in ICP-MS analysis, the internal standard should ideally be in the mid-mass range and also have a similar ionisation potential to the analyte of interest. It is extremely important that the element used as an internal standard be homogenously distributed throughout the matrix.

Dual Sample/Standard Introduction

It is possible to mix the carrier gas flow from the LA cell, before entering the ICP, with an aerosol generated by standard solution nebulisation. In this scenario, standard reference materials can be introduced via solution nebulisation simultaneously with the ablated material from the sample. The major advantage with this method of calibration is that it offers great flexibility with respect to the composition of the reference materials used, whilst also facilitating optimisation of the ICP-MS operating conditions. Hence dual sample-standard introduction is often an attractive alternative to finding suitable matrix matched solid reference materials.
Chapter Two

The plasma produced with conventional LA is 'dry' relative to that produced using 'wet' sample introduction procedures. The advantages of employing a dry plasma (such as reduced oxide interferences) are therefore somewhat reduced when using this method of calibration. In order to reduce such solvent related interferences and regain some of the advantages of employing a dry plasma, the solution aerosol can be desolvated before entering the ICP. However, the plasma formed in this case has a variable composition, dependent upon the matrix of the ablation target; hence, a variable sample matrix will produce varied sample loading. When no desolvation is employed, resulting in a wet plasma, plasma conditions are standardised since water is always the dominant plasma species. Water dominates the plasma loading and only small perturbations are caused by the sample matrix, leading to reduced matrix effects. This method of calibration is described in greater depth in chapter three.

Direct Liquid Ablation

Recent trends in LA-ICP-MS have highlighted the necessity of high spatial resolution, typically requiring craters of less than 10 \( \mu \text{m} \) to be ablated. For this purpose most in-house produced solid reference materials are not adequate since the trace element content is typically heterogeneous in distribution at such scales. As discussed, dual sample-standard introduction techniques have been developed and successfully applied. However, drawbacks associated with this technique include; interferences due to oxide formation (arising from wet solution nebulisation) and reduced sensitivity due to dilution of the dry laser aerosol. Severe matrix effects may arise from the totally different forms in which the sample and standard material enter the ICP. Work has been performed to assess the calibration capability of direct ablation of liquid standard solutions. Calibration via this technique is limited by the two totally different matrices involved and subsequently totally different ablation characteristics. However the method has the advantage that standards are very easily produced, are totally homogenous in their trace element distribution and offer a clean, renewed surface for ablation every time. Hence spatial resolution analysis is not limited by the heterogeneity of reference materials.

Günther et al. demonstrated the potential for direct liquid ablation as a calibration strategy for LA-ICP-MS. In this study different solutions were used for the quantitative
analysis of NIST 610 and 612 glasses. Fractionation and matrix effects were investigated with the use of high and low salinity aqueous calibration standards and finally the particle size distribution was monitored to interpret the ablation behavior of two such different matrices. Sodium was used as an internal standard for all elements and Yb as an internal standard for rare earth metals only. In this study 75 out of 96 determinations were within 10% of the expected values and there was no difference between the values based on Yb and Na as internal standards. Particle size distributions were measured and the contribution towards total ablated volume was calculated; this was used to explain the similar ablation characteristics of the liquids and solids.

Boue-Bigne et al.\textsuperscript{106} described the development of a new technique of calibration using direct liquid ablation. In this technique aqueous standards were ablated after the addition of a chromophore to modify their absorption characteristics. Using such a technique a more desirable coupling was achieved between the aqueous standards and the laser energy. The purpose of the chromophore was to improve laser energy coupling to the standards in such a way that the threshold ablation fluence was reached within the surface layers of the liquid, producing a much finer aerosol. The calibration was applied to NIST glass reference materials and also a sample of low density polyethylene (LDPE). It was found that the calibration was indeed possible and all calibration curves produced had a correlation coefficient greater than 0.993. Results obtained via this calibration technique were in good agreement with data obtained via digestion ICP-MS, furnace AA and previous work. The major advantage described by Boue-Bigne et al. is that simple variation of the additive concentration of chromophore allows the standard to be ablated at an energy that is optimal for the sample. This effectively means that the technique could be widely applicable to a variety of sample types.

The use of direct liquid ablation of standards provides many practical benefits. These include; aqueous standard solutions are much easier to prepare than solid standards, their elemental composition is much more readily varied, trace element distribution within the standard is homogeneous and they offer a renewed surface for ablation each time.
Isotope Dilution

The absolute quantitation technique of isotope dilution can be combined with the solid sampling tool of laser ablation. Two approaches have been demonstrated to perform this task.

The first approach as reported by Becker et al. uses the dual sample/standard approach as described in chapter three and hence the aqueous isotopic spike is introduced online using a nebuliser and spray chamber arrangement.

The second approach as developed by Heumann et al. incorporates the isotopic spike into a powdered sample before subsequent pressing into a disc.

To avoid repetition the readers attention is diverted to chapter five, in which the theory and application of Laser Ablation Inductively Coupled Plasma Isotope Dilution Mass Spectrometry (LA-ICP-ID-MS), is discussed in detail.
Chapter Conclusion

The review has provided an overview of LA for analytical chemistry with particular emphasis on its application to LA-ICP-MS. Attention has been focused upon methods of calibration and upon fractionation effects within LA; with particular emphasis being placed upon factors which affect the robustness of the analytical process for quantitative measurement by ICP-MS.

LA-ICP-MS has proved to be one of the most powerful analytical tools that can provide nearly non-destructive solid sampling and determine a large number of elements with low detection limits in a wide variety of sample types. Calibration of the technique still remains a challenge; however, with continued research LA will find many additional applications in analytical chemistry.
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Chapter Three

Online Additions of Aqueous Calibration Standards for Calibration of Laser Ablation Inductively Coupled Plasma Mass Spectrometry: Theory and Comparison of Wet and Dry Plasma Conditions

Work Published:

Chapter Abstract

This chapter describes the theory of online additions of aqueous standards for calibration of LA-ICP-MS. Establishment of a calibration curve enabled investigation of: fractionation, matrix effects, mass flow ratios and the relative merits of wet and dry plasma conditions for laser ablation sampling. It was found that a wet plasma was much more tolerant of increased sample loading and larger particle size, without reducing plasma robustness, leading to less severe and more constant mutual matrix effects. These findings indicate that the online addition of water is the preferred mode of operation for quantification by LA-ICP-MS.

The analytical performance of the method was validated by the analysis of three certified reference materials: National Institute of Standards and Technology (NIST) 612 Trace Elements in Glass, European Reference Material (ERM) 681 Trace Elements in Polyethylene and British Chemical Standards (BCS) No. 387 Nimonic 901 Alloy. Analysis of NIST 612 was performed under both wet and dry plasma conditions and the correlation with certified elemental concentrations was much better when a wet plasma was employed. Analyses of ERM 681 and BCS No. 387 were performed under wet plasma conditions, due to its proven advantages. The differences between the determined and certified elemental concentrations varied between 1 – 10% for the majority of elements, for all three certified reference materials.
**Introduction**

LA-ICP-MS has become the most versatile technique for the direct determination of trace elements in a wide variety of solid sample types. It has particular application for the determination of trace elements in sample types such as metals, rocks, polymers and ceramics, and avoids the risk of contamination associated with complex digestion procedures.

The limitations of LA-ICP-MS are well known; namely elemental fractionation and a lack of certified reference materials (CRMs) for the majority of sample types. ‘In-house’ synthetic standards can be prepared for this purpose, although their preparation is often time consuming and expensive, and they are frequently compromised by in-homogenous distribution of elemental composition. In the absence of solid calibration standards, aqueous calibration standards have been employed for quantification. Such aqueous standards can be ablated directly, with or without the presence of an organic chromophore to improve coupling between the laser and solution or more commonly they are introduced online via a nebuliser and spray chamber in what is referred to as the “dual sample/standard approach”.

**Dual sample/standard calibration**

The dual sample/standard approach, first proposed by Thompson *et al.*, can provide quantitative data in the absence of solid calibration standards. In this calibration approach, the aerosol generated by laser ablation of the target is combined with the aerosol generated by solution nebulisation of an aqueous calibration standard.

The limitation of this approach is the different sample and standard matrices that result in differing atomisation and ionisation characteristics within the ICP. Namely, ablated particles have larger mean diameters and size distributions than those particles produced by solvent evaporation from a wet aerosol. Consequently, these particles are vaporised along an extended region of the ICP, leading to wider ion density distributions along the central channel for LA in comparison to solution nebulisation.
The dual sample/standard approach, using a wet or a dry plasma, requires internal standardisation to compensate for the different mass transport rates of the two sample introduction sources. Consequently, an element of known concentration and homogenous distribution must be present in the sample. However, this may not be as restrictive as at first may seem, since a matrix element of known concentration (from stoichiometry or previous analysis) is often available.

In its simplest form, dual sample/standard introduction produces a wet plasma, leading to the possibility of spectral interferences such as oxides and hydroxides derived from the use of water as a solvent. In this context the term “wet” refers to a plasma in which the liquid phase aerosol and vapour phase water are present, i.e. the classical wet plasma produced in solution analysis. Normally, desolvation of the standard aerosol is employed so that it more closely matches the sample aerosol. However, the plasma formed in this case is referred to as being “dry”, and has a variable composition depending upon the matrix of the ablation target; hence variable sample matrix will produce varied sample loading. In contrast, a wet plasma produces more standardised conditions with a single dominant plasma species i.e. water; thus water dominates the plasma loading and only small perturbations are caused by the sample matrix leading to reduced matrix effects.

Whereas the absence of oxides and hydroxides may be necessary for the accurate determination of isotopic ratios, the standardised plasma conditions offered by employing a wet plasma may be of greater benefit for routine analysis by LA-ICP-MS. Koch et al. observed that the $^{65}$Cu/$^{66}$Zn ratio from brass using LA-ICP-MS with dry plasma conditions differed to the ratios obtained using wet plasma conditions. This was also confirmed by Boulyga et al. who reported that the $^{65}$Cu/$^{66}$Zn ratio obtained by LA-ICP-MS using wet plasma conditions, was closer to the ratio obtained with a traditional digest and solution based nebulisation, than using dry plasma conditions. These differences can probably be attributed to differential fractionation within the ICP, between dry and wet plasma conditions, due to different atomisation and ionisation conditions.
This work develops the theory of the online dual sample/standards technique and provides a comparison between the use of wet or dry plasma conditions. A strategy was devised using online, multi-point aqueous calibration, allowing the investigation of fractionation, matrix effects and characterisation of a mass flow ratio representing the ratio of mass transport between the two sources.

**Theory of Online Additions**

**Nomenclature**

- \( I \) = Intensity or ion count rate
- \( C \) = Concentration
- \( C_L^{s} \) = X-axis intercept at \( I = 0 \)
- \( S \) = Sensitivity
- \( m \) = Mass flow rate

**Superscript**

- \( s \) = Solid or sample
- \( L \) = Liquid standard
- \( S+L \) = Solid in the presence of the aqueous standard aerosol

**Subscript**

- \( I \) = Internal standard
- \( A \) = Analyte

Generally the calibration function for an ICP-MS instrument is written as:

\[
I = CS
\tag{5}
\]

The sensitivity \( S \) factor can be split into two terms; a *true instrumental sensitivity* term i.e. the response of the ICP-MS instrument per unit mass (strictly speaking molar quantities should be used since these directly represent the number of atoms sampled) of a specified element and a *mass flow rate* term representing the flux of sample or standard. Thus for an analyte in the sample substrate, Equation 5 becomes:

\[
I_A^S = m_A C_A^{s} S
\tag{6}
\]
Dimensional analysis of Equation 6 is instructive in understanding the meanings of the individual terms, thus:

\[
\frac{\text{counts}}{s} = \frac{g^S}{s} \times \frac{g^A}{g_A} \times \frac{\text{counts}}{s} \tag{6b}
\]

Note how the cancellation of dimensions is between, rather than within terms, indicating the inherent separation of sample and analyte quantities.

For online additions the overall intensity is the sum of the intensity contributions from the sample and from the standard, in accordance with a standard additions type calibration. Hence:

\[
I_A = m_A^L \frac{L}{L} C_A + m_A^S \frac{S+L}{S} C_A \tag{7}
\]

Note that two sensitivity terms are present; one, \(S_A^L\), representing the sensitivity of the aqueous calibration curve; and the other, \(S_A^{S+L}\), representing the sensitivity of the online additions calibration curve i.e. the sensitivity of the combined solid sample and aqueous standard. Plotting \(I_A\) against \(C_A\) yields a graph as shown in Figure 16, with slope of \(m_A^L S_A^L\) and intercept of \(m_A^S S_A^{S+L} C_A\).
Figure 16 A representation of the curves obtained by aqueous calibration and online additions calibration. In this simple scenario there are no mutual matrix effects, as indicated by the parallel curves, hence $S^L = S^{S+L}$.

Extrapolation of the online addition curve to $I_A = 0$, and rearrangement of Equation 7, yields the concentration of the analyte in the sample as:

$$C_A = \frac{m_A}{m_A} \times \frac{S_A}{S^{S+L}} \times C_A^{L,0} \tag{8}$$

$C_A^{L,0}$, which is negative, is taken directly from the graph, and it remains to determine the mass flow ratio $\frac{m_A}{m_A}$, since the sensitivity ratio $\frac{S_A}{S^{S+L}}$, can be calculated from the slopes of the two curves. It is this sensitivity ratio that can be used as a direct indicator of mutual matrix effects, i.e. two parallel curves indicate no mutual matrix effects, whereas any divergence or convergence indicates mutual matrix effects are occurring. The mass flow ratio can be determined by performing online additions for an internal standard element; hence, Equation 8 can be written as:
Knowing $C^S_I$, the mass flow ratio can be determined. For this to be useful in solving Equation 8, it is necessary to assume that:

\[
\frac{\dot{m}_L}{\dot{m}_S} = \frac{c^S_I}{s^L_I \times c^L_I|_0}
\]  

That is, there is no elemental fractionation between the internal standard element and the analyte, since differing mass flow ratios are a direct measure of elemental fractionation.
Experimental Instrumentation

A commercially available UP-213 Laser Ablation System (New Wave Research Inc., Huntingdon, Cambridgeshire, UK) operating in the deep UV (213 nm) was employed using He as a carrier gas due to its improved ablation and transport characteristics. Figure 17 shows the experimental arrangement used throughout the investigation. The sample aerosol from the LA system was combined with the standard aerosol from a PFA-100 μL Fixed Capillary Nebuliser (Elemental Scientific Inc., Omaha, Nebraska, USA) and custom made cyclonic spray chamber, using a polypropylene ‘Y’-piece (Fisher Scientific, Loughborough, Leicestershire, UK). With this arrangement a wet plasma resulted. When a dry plasma was required, the nebuliser and spray chamber was replaced with a MCN-6000 sample introduction system (CETAC Technologies, Omaha, Nebraska, USA) for desolvation of the standard aerosol. The two 1 m, Tygon™, sample introduction lines were combined, using a polypropylene ‘Y’-piece, 1 m before the ICP torch. A further cyclonic mixing vessel was placed immediately before the ICP torch. This was placed in the Peltier chamber of the PQ ExCell and was cooled to 5 °C as in standard operating mode. The gas flow, carrying the combined sample and standard aerosol, was introduced tangentially into this vessel to facilitate further mixing.

A VG PQ ExCell ICP-MS instrument (Thermo Electron Corporation, Winsford, Cheshire, UK) was used throughout the investigation. Optimisation of the torch-box position, lens voltages and nebuliser gas flow was performed before analysis, with respect to the 115In signal intensity obtained upon nebulisation of a 1 μg L⁻¹ solution. All optimisation was performed at 1350 W.

A He gas flow of 0.5 L min⁻¹ was found to give optimum sensitivity and a good peak shape upon single shot ablation of NIST 612 and importantly had no detrimental effects on the signal intensity obtained upon solution nebulisation when the two sample introduction sources were combined. This gas flow was increased to 0.7 L min⁻¹ for experiments involving the particle separation device.

Table 2 lists the experimental parameters employed. The laser conditions were chosen to represent those typically used in of bulk analysis by LA-ICP-MS.
Figure 17 The two different experimental setups employed: (A) aqueous standards introduced by standard solution nebulisation to produce a wet standard aerosol and (B) introducing the standard aerosol by solution nebulisation with desolvation to produce a dry standard aerosol.
Table 2 Experimental parameters used in the investigation.

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<th>Laser Ablation System</th>
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<td>ERM Trace Elements in Polyethylene 681</td>
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<td>BCS No. 387 Nimonic 901 Alloy</td>
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<td>Sample translation rate</td>
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<td>Peltier chamber temperature</td>
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<td>$^{47}$Ti, $^{52}$Cr, $^{55}$Mn, $^{89}$Co, $^{65}$Cu, $^{88}$Sr, $^{107}$Ag, $^{111}$Cd, $^{137}$Ba, $^{140}$Ce, $^{140}$Ce$^{18}$O, $^{205}$Tl, $^{206}$Pb, $^{208}$Pb, $^{238}$U, $^{238}$U$^{16}$O,</td>
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<td>No. of replicates</td>
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Sample Preparation

Solid Samples

NIST 612 (National Institute of Standards and Technology, Gaithersburg, Maryland, USA) Trace Elements in Glass was used when performing investigations into laser and plasma variables, due to its certification for a wide variety of trace elements. For method validation, NIST 612 Trace Elements in Glass, ERM 681 Trace Elements in Polyethylene and BCS No. 387 Nimonic 901 Alloy (42% Ni, 36% Fe, 12% Cr, 6% Mo and 3% Ti) were analysed. 1% HNO$_3$ (Romil Pure Chemistry, Cambridge, Cambridgeshire, UK) was employed as a cleaning solution prior to analysis.
Aqueous Standard Preparation

Aqueous calibration standards, in a 1% HNO₃ matrix, were prepared by serial dilution of elemental stock solutions (Fisher Scientific, Loughborough, Leicestershire, UK) using 18.2 MΩ cm⁻¹ purity water (Elga Lab Water, High Wycombe, Buckinghamshire, UK). These standards contained the following elements: Ti, Cr, Mn, Co, Cu, Sr, Ag, Cd, Ba, Ce, Tl, Pb and U at concentrations 0, 1, 2, 5 and 10 µg L⁻¹.

Online Additions

The online additions involved simultaneous introduction of aqueous calibration standard aerosols by solution nebulisation, with or without desolvation, and a laser ablated sample aerosol. In order to allow the investigation of matrix effects and calculation of the mass flow ratio, multiple calibration standards were used. The whole calibration series was nebulised (with He passing through the ablation cell) to yield a standard calibration curve. Then, ablation of the sample commenced and the aqueous calibration series was repeated, so that simultaneous introduction of sample and standard occurred. This procedure yielded two curves, as shown in Figure 1; one curve representing the contribution from the aqueous calibration standards only; and the other representing the contribution from the aqueous calibration standards in addition to the laser ablated sample aerosol. Comparison of the slope of the two curves enabled an investigation into the occurrence of mutual matrix effects, as explained above. The mean and standard deviation of the sensitivity ratios obtained from various isotopes (n = 14) was used as an indication of the extent and consistency of matrix effects.

The Effect of Increasing Plasma Sample Load

Data were acquired under different ablation and plasma conditions, including: ablation crater diameter and plasma forward power. By increasing crater diameter and keeping the fluence constant, the ablated mass and consequently the sample loading of the plasma was increased. Further, since the fluence remained constant throughout the investigation, the ablation products should remain similar (particle size distribution etc.), leaving sample yield as the sole variable. Crater diameters of 15 – 110 µm were investigated. Experiments were performed using both standard solution nebulisation and solution nebulisation with desolvation to allow a comparison between wet and dry plasma conditions.
The Effect of Plasma Robustness

The effect of plasma robustness on matrix effects was investigated by performing online additions under varying ICP forward powers, within the range of 1100 – 1600 W. This investigation was performed using fixed carrier gas flows. Although forward power and injector flow are recognised as being interdependent variables, it was felt that in these experiments changing the Ar/He ratio and hence the transport properties of the delivery systems might introduce too many additional variables. All experiments were performed using both standard solution nebulisation and solution nebulisation with desolvation to allow a comparison between wet and dry plasma conditions.

The Effect of Particle Size

As discussed in chapter two, the size of particles produced at the ablation process are known to have an impact on the nature and extent of plasma based elemental fractionation. Particle separation was performed to remove the larger particles, known to be incompletely vaporised by the plasma.

Particle separation involved the use of a particle size separator as described by Figg et al.21 and used extensively by Gunther et al.,22-24 to determine the effect of removal of larger particles from the aerosol stream on the occurrence and extent of matrix effects. The device consists of a Tygon™ tubing insert with an internal diameter of 0.6 mm coiled around a glass rod of 4 mm diameter which separates particles based upon the effect of centrifugal forces. Larger particles experience a greater centrifugal acceleration and impact with the tubing wall, whereas smaller particles experience a smaller centrifugal acceleration and can pass through the device. An aerosol with a smaller mean particle size can be selected by increasing the carrier gas flow, reducing the coil diameter or reducing the tubing internal diameter. Figure 18 shows the separation processes involved, whereas Figure 19 is a photograph of the separation device employed.
Chapter Three

3. Larger particles impact on the tubing wall, leading to separation of large and small particles.

2. Larger particles experience a greater centrifugal force than the smaller particles, and move towards the tubing walls.

1. Aerosol stream from the LA process consists of a mixture of large and small particles as they enter the coil.

4. Resulting aerosol possesses a smaller mean particle size due to separation of larger particles.

Figure 18 Schematic of the separation process, wherein larger particles are separated from the aerosol stream due to increased centrifugal force.

Figure 19 A photograph of the separation device employed.

To ensure that the device was acting as a particle size selector, preliminary investigations were performed, using NIST 612. The particle separation device was placed 0.5 m before the ‘Y’-piece in the LA sample introduction line as shown in Figure 20. The He gas flow through the ablation cell was varied between 0.3 and 1.1 L min\(^{-1}\) to determine the highest gas flow that could be used to facilitate the efficient separation of large particles without being detrimental to elemental sensitivity.

The number of coils was varied between 0 – 30, and changes in sensitivity and elemental ratios obtained upon ablation of NIST 612 were monitored, in particular the ratios U/Pb and U/Th which are of interest in geochronology and are prone to elemental
fractionation making the accurate measurement of the isotopic ratio notoriously difficult.

![Diagram of experimental arrangement](image)

**Figure 20** The experimental arrangement employed for LA-ICP-MS using the particle separation device.

The online additions measurement was performed with the particle separation device placed in the LA sample introduction line, 0.5 m before the ‘Y’-piece, and the effect of the number of coils on matrix effects was investigated. Again, the mean and standard deviation of the sensitivity ratios obtained was used as an indicator for the extent and consistency of matrix effects. The investigation was performed using both wet and dry plasma conditions.

**Calibration Procedure**

Once the optimum ablation and plasma conditions were found, with respect to minimising matrix effects, the reference materials were analysed. First, using online simultaneous sample/standard introduction for an internal standard element, a mass flow ratio was calculated. Then, by performing online simultaneous sample/standard introduction for the analyte element and applying the mass flow ratio obtained from the internal standard element, $C_s^S$ was calculated from Equation 4.

For NIST 612 Trace Elements in Glass the analysis was performed under wet and dry plasma conditions and the quality of the data compared with the certified elemental concentrations. For NIST 612 the calibration procedure was also performed whilst employing the particle separation device in the LA line, using fifteen turns and a He gas flow of 0.7 L min$^{-1}$. Again this was performed under wet and dry plasma conditions.
Analyses of ERM 681 Polyethylene and BCS No. 387 Nimonic 901 Alloy were performed using wet plasma conditions only.

For analysis using a dry plasma, an ICP forward power of 1500 W was used; whereas, for a wet plasma 1300 W was applied. LA parameters were kept constant throughout the analysis: a fluence of 13 J cm\(^{-2}\), a frequency of 20 Hz, an ablation crater diameter of 80 \(\mu\)m and a sample translation rate of 10 \(\mu\)m s\(^{-1}\) were employed.
Results and Discussion

Variation in Ablation Crater Diameter

Increasing the ablated crater diameter whilst maintaining constant fluence (made possible by the 'true aperture imaging' capabilities of the UP-213) led to a proportional increase in ablated volume as indicated by the changes in the calculated mass flow ratio in Figure 21 and Figure 22. In contrast, simply increasing the fluence did not lead to a proportional increase in the ablated volume, as indicated in Figure 23; this can be attributed to a minimal increase in ablated volume past a rollover point. For this reason an optimum fluence for laser ablation is often found between the ablation threshold and the rollover point, as described in Figure 24; selecting this fluence will lead to high sensitivity with minimal elemental fractionation.

![Figure 21](image)

Figure 21 Changes in mass flow ratio upon variation in ablated crater diameter, calculated using $^{47}$Ti.
Figure 22 Changes in mass flow ratio upon variation in ablated crater volume, assuming a crater depth of 50 μm, calculated using $^{45}$Ti.

Figure 23 Changes in mass flow ratio upon variation in laser fluence, calculated using $^{206}$Pb.
Figure 24 The relationship between laser fluence and analyte signal intensity, attributed to non-proportional mass removal at fluences above the rollover point.

The online additions strategy was performed at differing ablated crater diameters i.e. successively introducing more ablated mass into the ICP to increase the sample loading of the plasma. The data obtained are presented in Table 3 and Table 4.

Table 3 Standard deviation and mean of sensitivity ratios obtained under varying ablated crater diameters, during the analysis of NIST 612.

<table>
<thead>
<tr>
<th>Ablated crater diameter (μm)</th>
<th>Standard deviation of sensitivity ratios (n=14)</th>
<th>Mean of sensitivity ratios (n=14)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet</td>
<td>Dry</td>
</tr>
<tr>
<td>15</td>
<td>0.005</td>
<td>0.012</td>
</tr>
<tr>
<td>30</td>
<td>0.009</td>
<td>0.024</td>
</tr>
<tr>
<td>55</td>
<td>0.022</td>
<td>0.036</td>
</tr>
<tr>
<td>80</td>
<td>0.029</td>
<td>0.072</td>
</tr>
<tr>
<td>110</td>
<td>0.040</td>
<td>0.106</td>
</tr>
</tbody>
</table>
Table 4 Degrees of UO\(^{2+}\) formation using a wet and dry plasma, with and without the presence of a laser ablated aerosol for varying ablated crater diameters. The ratio % UO\(^{1+}\)/% UO\(^{3+}\) thus represents any changes in the degree of oxide formation upon introduction of the ablated aerosol.

<table>
<thead>
<tr>
<th>Ablated crater diameter (µm)</th>
<th>Wet plasma oxide analysis</th>
<th>Dry plasma oxide analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% UO(^{1+})</td>
<td>% UO(^{3+})</td>
</tr>
<tr>
<td>15</td>
<td>1.40</td>
<td>1.37</td>
</tr>
<tr>
<td>30</td>
<td>1.41</td>
<td>1.50</td>
</tr>
<tr>
<td>55</td>
<td>1.39</td>
<td>1.39</td>
</tr>
<tr>
<td>80</td>
<td>1.43</td>
<td>1.36</td>
</tr>
<tr>
<td>110</td>
<td>1.41</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Increasing the ablated crater diameter had the effect of increasing the relative sensitivity above unity, and the standard deviation in the sensitivity ratios obtained. This effect was much more pronounced under dry plasma conditions than under wet plasma conditions as can be seen in Figure 25.

![Figure 25](image)

Figure 25 Standard deviation of sensitivity ratios obtained with differing ablated crater diameter, under (a) dry and (b) wet plasma conditions.

The laser was run at constant fluence, leading to increased mass transport to the ICP with increasing ablated crater diameter; consequently the sample loading of the plasma
was increased. Under dry plasma conditions, with higher sample loading it appears that the plasma became less robust, leading to more severe matrix effects. The elements were affected by a less robust ionisation source to different extents (due to properties such as first and second ionisation enthalpy and oxide bond strength etc.). The increased plasma loading manifested itself as an increase in sensitivity ratios and the standard deviation thereof, across the suite of elements studied.

The degree of variation in the sensitivity ratios with increased sample loading was much more constant under wet plasma conditions. It appears that the presence of water buffered the plasma against the detrimental effects of sample loading on plasma robustness. Importantly, the data indicates that there was no significant change in the extent of oxide formation upon the introduction of the laser ablated aerosol. This is shown by the absence of any significant change in sensitivity upon introduction of the sample aerosol, especially for the oxide forming elements Ce and U. Oxide and hydroxide formation would be expected if less robust plasma conditions existed. The fact that the level of oxides remained constant upon introduction of the sample aerosol again indicates that the presence of water was beneficial in maintaining robust plasma conditions. The best way to detect changes in oxide formation is to monitor the \( ^{140}\text{Ce}^{16}\text{O} / ^{140}\text{Ce} \) ratio; however this was not possible in this case as the ablation of the NIST glass produces several interfering species at the \( m/z \) 156. For this reason, the molecular ion \( ^{238}\text{U}^{16}\text{O}^+ \) (\( m/z \) 254) was monitored as an indicator as to the extent of oxide formation. Under wet plasma conditions there was no increase in the degree of oxide formation for U upon introduction of the ablated aerosol, indicating there was no significant change in plasma robustness. This can be seen in Table 4 wherein the ratio \% \( \text{UO}^{L} / \% \text{UO}^{S-L} \), (representing the degree of UO formation for standard introduction only, divided by the degree of UO formation for simultaneous sample and standard introduction) does not deviate from unity under wet plasma conditions. Under dry plasma conditions this ratio is more erratic and deviations from unity were obtained indicating that the dry plasma was more susceptible to changes in sample loading.

The more constant sensitivity ratios obtained under wet plasma conditions have implications when applying an internal standard element in a calibration by LA-ICP-MS. Using wet plasma conditions, it is more likely that data obtained from an internal
standard element will be representative of a larger suite of elements. The mean sensitivity ratio at an ablation crater diameter of 110 μm did not quite follow the trend, but the change was small and is not likely to indicate a true reversal of slope.

**Variation in Plasma Forward Power**

The online additions strategy was performed for varying ICP forward powers, with fixed LA parameters, to determine the effect of forward power on the severity of matrix effects for both wet and dry plasma conditions. The results can be seen in Table 5 and Table 6.

**Table 5 Standard deviation and mean of sensitivity ratios obtained under varying ICP forward power, during the analysis of NIST 612.**

<table>
<thead>
<tr>
<th>ICP forward power (W)</th>
<th>Standard deviation of sensitivity ratios (n=14)</th>
<th>Mean of sensitivity ratios (n=14)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet</td>
<td>Dry</td>
</tr>
<tr>
<td></td>
<td>0.050</td>
<td>0.159</td>
</tr>
<tr>
<td>1100</td>
<td>0.038</td>
<td>0.080</td>
</tr>
<tr>
<td>1200</td>
<td>0.011</td>
<td>0.064</td>
</tr>
<tr>
<td>1300</td>
<td>0.030</td>
<td>0.053</td>
</tr>
<tr>
<td>1400</td>
<td>0.035</td>
<td>0.052</td>
</tr>
<tr>
<td>1500</td>
<td>0.031</td>
<td>0.066</td>
</tr>
<tr>
<td>1600</td>
<td>0.031</td>
<td>0.066</td>
</tr>
</tbody>
</table>

**Table 6 Degrees of UO⁺ formation using a wet and dry plasma of varying forward power, with and without the presence of a laser ablated aerosol. The ratio % UO⁰⁺/ % UO⁵⁺ thus represents any changes in the degree of oxide formation upon introduction of the ablated aerosol.**

<table>
<thead>
<tr>
<th>ICP forward power (W)</th>
<th>Wet plasma oxide analysis</th>
<th>Dry plasma oxide analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% UO⁰⁺</td>
<td>% UO⁵⁺⁺</td>
</tr>
<tr>
<td>1100</td>
<td>7.21</td>
<td>7.92</td>
</tr>
<tr>
<td>1200</td>
<td>1.95</td>
<td>1.71</td>
</tr>
<tr>
<td>1300</td>
<td>1.52</td>
<td>1.52</td>
</tr>
<tr>
<td>1400</td>
<td>1.41</td>
<td>1.53</td>
</tr>
<tr>
<td>1500</td>
<td>1.30</td>
<td>1.18</td>
</tr>
</tbody>
</table>

As shown in Figure 26, under wet plasma conditions, the standard deviation of the sensitivity ratios was almost constant with respect to changes in ICP forward power. For dry plasma conditions, the variation in sensitivity ratios, was strongly related to the ICP forward power. This can be explained by differences in plasma robustness i.e. a low ICP forward power and high sample load yielded a less robust plasma, leading to severe
matrix effects. As stated above, under wet plasma conditions this effect was much less pronounced, confirming that the presence of water buffered against the detrimental effects of low plasma robustness. Again, the data indicated that the degree of oxide formation remained constant with varying ICP forward power, upon introduction of the laser ablated aerosol, when wet plasma conditions were employed. This is shown in Table 6 wherein the % UO\(^1\)/% UO\(^{5+}\) is more constantly close to unity than for dry plasma conditions (notwithstanding that the smaller ratios obtained for the dry plasma will lead to greater statistical variation).

![Figure 26 Standard deviation of sensitivity ratios obtained with differing ICP forward power, with both (a) dry and (b) wet plasma conditions.](image)

**The Effect of Particle Size Selection**

For previous analyses a He gas flow of 0.5 L min\(^{-1}\) was employed, since it led to optimum sensitivity and stability of both sample introduction lines. However, this gas flow would be too low to facilitate efficient particle separation\(^{21}\) and for the purpose of this investigation the gas flow was increased to 0.7 L min\(^{-1}\).
Increasing the gas flow through the ablation cell to 0.7 L min\(^{-1}\) did not have any detrimental effects upon the overall sensitivity of the system; however, any subsequent increase in gas flow would have led to a reduction in sensitivity for some elements, as can be seen in Figure 27. Interestingly, the change in He gas flow through the separation device effected the elements studied differently. It was seen that \(^{115}\text{In}\) and \(^{238}\text{U}\) behaved in a similar manner, with the sensitivity increasing to an optimum gas flow of 0.6 L min\(^{-1}\). After this optimum any increase in gas flow led to a sharp decrease in sensitivity. The shape of the \(^7\text{Li}\) curve was different to those obtained for \(^{115}\text{In}\) and \(^{238}\text{U}\); the sensitivity rose with increasing gas flow to produce an optimum of 0.8 L min\(^{-1}\). Although any subsequent increase in gas flow did lead to a reduction in sensitivity, the decline was much shallower in comparison to the other isotopes studied. This led to a much broader shaped peak for \(^7\text{Li}\).

![Figure 27](image.png)

Figure 27 A chart to show the change in signal intensity for three elements with varying He gas flow through the particle separation device.

This observation is in agreement with Rodushkin \textit{et al.}\textsuperscript{7,8} who determined the optimum carrier gas flow rates for various analytes for solution nebulisation and laser ablation. It was found that for laser ablation, the inter-elemental response varied greatly as a function of carrier gas flow, with elements of lower nominal mass and lower
vaporisation enthalpy peaking at higher gas flows. This result can be attributed to the existence of differing zones of maximum ion intensities within the ICP, related to the time required for vaporisation of a given analyte from the particles produced during laser ablation.

The fact that these zones of maximum ion intensities occur along an extended region of the plasma for particles produced by LA in comparison to particles produced by SN, was confirmed by calculating the mass flow ratio at different sampling depths. In Figure 28, as the ICP torch is moved closer to the sample cone, i.e. an increase in sampling depth, the mass flow ratio increases indicating that the larger particles produced by LA are not being as efficiently processed by the plasma and the ratio is dominated by the mass flux from the particles produced by SN.

![Figure 28 Changes in mass flow ratio upon variation of the ICP sampling depth, calculated from $^{47}\text{Ti}$](image)

Increasing the number of coils on the particle separation device led to a reduction in overall sensitivity for all elements studied, as seen in Figure 29. However, the response was element dependent since some elements were affected to a greater extent by altering the number of coils on the particle separation device. This is an indication that
the device was selectively removing particles based on their size and reducing plasma based elemental fractionation.

Figure 29 A chart to show the change in signal intensity for three elements with varying number of coils on the particle separation device, obtained upon ablation of NIST 612.

Figure 30 and Figure 31 show a decline in the measured ratios as the number of turns on the particle separation device is increased, before leveling out at around 15 turns. This data suggests that the device is functioning as a particle size separator and selectively removing the larger particles that are known to be a major contributor to plasma based elemental fractionation. The $^{238}\text{U}/^{232}\text{Th}$ ratio is often used to monitor elemental fractionation, and it is well accepted that an ideal ratio close to 1 is an indication that no fractionation is occurring. In this investigation the ratio is falling towards the desired ratio of 1, confirming that fractionation is being reduced by the selective removal or larger particles. By employing the particle separation device with 15 turns and a flow rate of 0.7 L min$^{-1}$, plasma based fractionation can be substantially reduced. The downside is that this reduction in fractionation is accompanied by a subsequent reduction in sensitivity of around 50%.
Figure 30 A chart to show the change in the $^{238}\text{U}/^{208}\text{Pb}$ ratio obtained upon ablation of NIST 612 with changes in the number of coils on a particle separation device.

Figure 31 A chart to show the change in the $^{238}\text{U}/^{232}\text{Th}$ ratio obtained upon ablation of NIST 612 with changes in the number of coils on a particle separation device.
Chapter Three

The online additions approach was performed whilst varying the number of turns on the particle separation device; again this was performed whilst employing a wet and a dry plasma to determine their relative merits. The data is presented in Table 7 and Table 8 graphically in Figure 32.

Table 7 Standard deviation and mean of sensitivity ratios obtained whilst varying the number of turns on a particle separation device, during the analysis of NIST 612.

<table>
<thead>
<tr>
<th>Number of turns</th>
<th>Standard deviation of sensitivity ratios (n=14)</th>
<th>Mean of sensitivity ratios (n=14)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet</td>
<td>Dry</td>
</tr>
<tr>
<td>0</td>
<td>0.049</td>
<td>0.164</td>
</tr>
<tr>
<td>5</td>
<td>0.031</td>
<td>0.069</td>
</tr>
<tr>
<td>10</td>
<td>0.018</td>
<td>0.050</td>
</tr>
<tr>
<td>15</td>
<td>0.013</td>
<td>0.022</td>
</tr>
<tr>
<td>20</td>
<td>0.008</td>
<td>0.016</td>
</tr>
<tr>
<td>25</td>
<td>0.012</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Table 8 Degrees of UO\(^+\) formation using a wet and dry plasma whilst varying the number of turns on a particle separation device, with and without the presence of a laser ablated aerosol. The ratio \(\% \text{UO}^+/\% \text{UO}^{2+}\) thus represents any changes in the degree of oxide formation upon introduction of the ablated aerosol.

<table>
<thead>
<tr>
<th>Number of turns</th>
<th>Wet plasma oxide analysis</th>
<th>Dry plasma oxide analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% UO(^+)</td>
<td>% UO(^{2+})</td>
</tr>
<tr>
<td>0</td>
<td>1.35</td>
<td>1.29</td>
</tr>
<tr>
<td>5</td>
<td>1.38</td>
<td>1.31</td>
</tr>
<tr>
<td>10</td>
<td>1.38</td>
<td>1.30</td>
</tr>
<tr>
<td>15</td>
<td>1.31</td>
<td>1.27</td>
</tr>
<tr>
<td>20</td>
<td>1.36</td>
<td>1.35</td>
</tr>
<tr>
<td>25</td>
<td>1.37</td>
<td>1.36</td>
</tr>
</tbody>
</table>
Figure 32 Standard deviation (n=14) of sensitivity ratios obtained whilst varying the number of turns on a particle separation device, during the analysis of NIST 612, under both (a) dry and (b) wet plasma conditions.

As the number of turns on the particle separation device was increased there was a decline in the standard deviation of the sensitivity ratios indicating a reduction in matrix effects upon introduction of the laser ablated aerosol. If large particles enter the ICP they can cause a significant energy demand, as the plasma unsuccessfully attempts to vaporise them. This energy demand can lead to a reduction in plasma robustness and means that severe matrix effects may prevail. When these larger particles were removed from the laser ablated aerosol stream they were prevented from entering the ICP. Hence, there was less of an energy demand on the plasma, which led to a more robust plasma and a reduction in matrix effects.

This effect was much more pronounced under dry plasma conditions than under wet plasma conditions, shown by the much steeper fall in standard deviation. As the number of turns on the particle separation device is increased, large particles that will require substantial energy expenditure for vaporisation in the plasma are selectively removed. As these particles were removed the plasma became more robust and matrix effects were reduced.
Once again the data would suggest that a wet plasma is more successful in overcoming the detrimental effects of the presence of large particles, as indicated by the overall lower standard deviation of sensitivity ratios and the shallower decline of the curve.

**The Effect of Water on Plasma Conditions**

The fact that the presence of water alters the fundamental properties of the plasma, such as temperature and electron density is well documented. However, the effects of water remain poorly understood, with experimental outcomes often depending upon the exact details of the sample introduction system and the total water flux and vapour/liquid ratio. It was beyond the scope of this investigation to quantify all of these parameters. Generally, plasma energy is consumed in the vaporisation and dissociation processes; however, this energy can be replaced by energy transfer from the outer regions of the plasma into the central channel, and the dissociation products (molecular hydrogen and oxygen) contribute to a local increase in thermal conductivity and heat transfer. The more robust conditions offered by employing a wet plasma have been observed in the present work. The wet plasma was more tolerant of variable sample loading and variable ICP forward powers, evidenced by more constant sensitivity ratios.

**Calibration**

Method validation was performed on NIST 612 Trace Elements in Glass, ERM 681 Trace Elements in Polyethylene and BCS No. 387 Nimonic 901 Alloy. The uncertainty quoted on all calculated concentrations is based upon the standard error (S\text{std}) associated with the whole calibration curve and is a very robust estimate of the uncertainty associated with each result. Thus, the concentration uncertainties were calculated from the regression line for a signal intensity of ± S\text{std}. This method ignores the uncertainties in the concentration values, which is justified in the case of the NIST 612 glass, since the relative uncertainties are only 10% of the LA data values, but not so valid in the case of ERM 681 Polyethylene.

**Analysis of NIST 612 Trace Elements in Glass**

Cobalt was chosen as an internal standard element for the analysis of NIST 612 Trace Elements in Glass, since it provided a mass flow ratio that was most representative of the other elements under both wet and dry plasma conditions i.e. the mass flow ratio
was close to the mean. This indicates that there was little fractionation between Co and
the other elements, with the possible exception of Ti (as indicated by differing mass
flow ratios). It should be noted that for the analysis of a ‘real’ sample this data would
not be available and it is unlikely that there would be such a choice of internal standard
element. However, here, since this data was available, then a selection of the best
internal standard was made. LA is no different to any other analytical technique in that
prior knowledge of the sample will improve data quality. The optimum ICP forward
powers obtained from the previous investigation were employed for the analysis i.e.
1300 W for the wet plasma analysis, although from previous investigation this was not
too critical and 1500 W for the dry plasma analysis. The data obtained can be seen in
Table 9 and Table 10.

Table 9 Data showing the certified elemental concentration, calculated mass flow ratio and
calculated elemental concentration using Co as an internal standard, performed under wet plasma
conditions with constant LA parameters.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Certified concentration with associated uncertainty (mg kg⁻¹)</th>
<th>Mass flow ratio</th>
<th>Calculated concentration with associated uncertainty (mg kg⁻¹)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁴⁷TI</td>
<td>50.1 ± 0.8</td>
<td>10982</td>
<td>63.3 ± 4.8</td>
<td>126</td>
</tr>
<tr>
<td>⁵³Cr</td>
<td>Not certified</td>
<td></td>
<td>36.4 ± 2.5</td>
<td>-</td>
</tr>
<tr>
<td>⁵⁵Mn</td>
<td>39.6 ± 0.8</td>
<td>14697</td>
<td>37.4 ± 1.9</td>
<td>94</td>
</tr>
<tr>
<td>⁵⁹Co</td>
<td>35.5 ± 1.2</td>
<td>13888</td>
<td>Internal standard</td>
<td>-</td>
</tr>
<tr>
<td>⁴⁴Cu</td>
<td>37.7 ± 0.9</td>
<td>16170</td>
<td>32.4 ± 2.6</td>
<td>86</td>
</tr>
<tr>
<td>⁴⁲Sr</td>
<td>78.4 ± 0.2</td>
<td>14896</td>
<td>73.1 ± 4.7</td>
<td>93</td>
</tr>
<tr>
<td>¹⁰⁷Ag</td>
<td>22 ± 0.3</td>
<td>13092</td>
<td>23.3 ± 3.5</td>
<td>106</td>
</tr>
<tr>
<td>¹¹¹Cd</td>
<td>Not certified</td>
<td></td>
<td>20.6 ± 0.9</td>
<td>-</td>
</tr>
<tr>
<td>¹³⁷Ba</td>
<td>41 ± Not quoted</td>
<td>17044</td>
<td>33.4 ± 1.2</td>
<td>81</td>
</tr>
<tr>
<td>¹⁴⁰Ce</td>
<td>39 ± Not quoted</td>
<td>13731</td>
<td>39.4 ± 2.6</td>
<td>101</td>
</tr>
<tr>
<td>²⁰⁵TI</td>
<td>15.7 ± 0.3</td>
<td>14386</td>
<td>15.2 ± 1.4</td>
<td>97</td>
</tr>
<tr>
<td>²⁰⁶Pb</td>
<td>38.57 ± 0.2</td>
<td>14338</td>
<td>37.4 ± 1.6</td>
<td>97</td>
</tr>
<tr>
<td>²⁰⁸Pb</td>
<td>38.57 ± 0.2</td>
<td>13863</td>
<td>38.6 ± 1.5</td>
<td>100</td>
</tr>
<tr>
<td>²³⁵U</td>
<td>37.38 ± 0.08</td>
<td>14042</td>
<td>37.0 ± 4.0</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td></td>
<td>14261</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>St. Dev.</td>
<td></td>
<td>1500</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>% RSD</td>
<td></td>
<td>11</td>
<td>11</td>
</tr>
</tbody>
</table>
Table 10 Data showing the certified elemental concentration, calculated mass flow ratio and calculated elemental concentration using Co as an internal standard, performed under dry plasma conditions with constant LA parameters.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Certified concentration with associated uncertainty (mg kg⁻¹)</th>
<th>Mass flow ratio</th>
<th>Calculated concentration with associated uncertainty (mg kg⁻¹)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁴⁷Ti</td>
<td>50.1 ± 0.8</td>
<td>21055</td>
<td>30.7 ± 3.0</td>
<td>61</td>
</tr>
<tr>
<td>⁵²Cr</td>
<td>Not certified</td>
<td></td>
<td>40.1 ± 3.2</td>
<td>-</td>
</tr>
<tr>
<td>⁵⁵Mn</td>
<td>59.6 ± 0.8</td>
<td>16193</td>
<td>34.4 ± 3.0</td>
<td>87</td>
</tr>
<tr>
<td>⁶⁵Cu</td>
<td>35.5 ± 1.2</td>
<td>14074</td>
<td>Internal standard</td>
<td>-</td>
</tr>
<tr>
<td>⁸⁸Sr</td>
<td>37.7 ± 0.9</td>
<td>11999</td>
<td>44.2 ± 7.1</td>
<td>117</td>
</tr>
<tr>
<td>¹⁰⁷Ag</td>
<td>84.4 ± 0.2</td>
<td>21065</td>
<td>52.4 ± 4.8</td>
<td>67</td>
</tr>
<tr>
<td>¹¹¹Cd</td>
<td>Not certified</td>
<td></td>
<td>27.5 ± 3.7</td>
<td>125</td>
</tr>
<tr>
<td>¹³⁵Ba</td>
<td>41 ± Not quoted</td>
<td>19549</td>
<td>30.0 ± 1.8</td>
<td>-</td>
</tr>
<tr>
<td>¹⁴⁰Ce</td>
<td>39 ± Not quoted</td>
<td>15618</td>
<td>35.1 ± 3.0</td>
<td>90</td>
</tr>
<tr>
<td>²⁰⁵Tl</td>
<td>15.7 ± 0.3</td>
<td>9667</td>
<td>22.9 ± 1.6</td>
<td>146</td>
</tr>
<tr>
<td>²⁰⁶Pb</td>
<td>38.57 ± 0.2</td>
<td>10258</td>
<td>30.7 ± 9.5</td>
<td>80</td>
</tr>
<tr>
<td>²⁰⁸Pb</td>
<td>38.57 ± 0.2</td>
<td>9869</td>
<td>32.2 ± 12.3</td>
<td>83</td>
</tr>
<tr>
<td>²³⁵U</td>
<td>37.38 ± 0.08</td>
<td>11336</td>
<td>23.8 ± 6.3</td>
<td>64</td>
</tr>
</tbody>
</table>

The results for the mass flow ratios indicate that there was a much greater signal contribution from the aqueous calibration standards than from the laser ablated aerosol. This is highlighted by the large values calculated for the mass flow ratio i.e. the ratio of flux between sample and standard. Values this large are indicative of the small amounts of ablated material transported to the ICP when employing such a LA system. This value means that an analyte concentration of tens of mg kg⁻¹ in the solid sample will correspond to a signal intensity equivalent to one µg L⁻¹ of analyte in the aqueous calibration standards. This may be disadvantageous in terms of absolute detection limit, but as shown here, limiting the plasma loading is beneficial for obtaining good quantitative data.

The analysis proved a lot more successful when wet plasma conditions were used. Generally, the agreement between the calculated and certified concentrations was much closer under the wet plasma conditions. Under wet plasma conditions, the majority of elements quantified were within 1 – 10% of the certified values. One exception was Ti, for which poorer data was obtained, but no explanation for this is available.
The matrix effects were less severe and less variable between elements when using a wet rather than a dry plasma, as a direct result, the mass flow ratios calculated were less elementally variable, indicating that they were subject to less fractionation. This simplifies the choice of an internal standard, since it is more likely that the chosen element will be more representative of the set. For this reason, more accurate data can be obtained from the online additions approach when wet plasma conditions are employed. This is shown in Figure 33 and Figure 34, wherein a better correlation between the calculated elemental concentrations and certified elemental concentrations was obtained under wet plasma conditions, shown by a slope close to 1 obtained when using a wet plasma and a slope well below 1 when using a dry plasma ($R^2_{\text{Wet}} = 0.89$ vs. $R^2_{\text{Dry}} = 0.60$).
Figure 33 The correlation between the calculated elemental concentrations and the certified elemental concentrations, using Co as an internal standard element, under wet plasma conditions.

Figure 34 The correlation between the calculated elemental concentrations and the certified elemental concentrations, using Co as an internal standard element, under dry plasma conditions.
Chapter Three

Calibration with Particle Separation
The calibration procedure was repeated with the addition of the particle separation
device placed in the LA line, utilising fifteen turns and a He gas flow of 0.7 L min$^{-1}$.
The data is presented in Table 11 and Table 12, and graphically in Figure 35 and Figure
36.

Table 11 Data showing the certified elemental concentration, calculated mass flow ratio and
calculated elemental concentration using Co as an internal standard, performed under wet plasma
conditions with constant LA parameters, employing the particle separation device.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Certified concentration with associated uncertainty (mg kg$^{-1}$)</th>
<th>Mass flow ratio</th>
<th>Calculated concentration with associated uncertainty (mg kg$^{-1}$)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{47}$Ti</td>
<td>50.1 ± 0.8</td>
<td>33091</td>
<td>53.5 ± 3.2</td>
<td>107</td>
</tr>
<tr>
<td>$^{52}$Cr</td>
<td>Not certified</td>
<td></td>
<td>40.4 ± 2.3</td>
<td>-</td>
</tr>
<tr>
<td>$^{55}$Mn</td>
<td>39.6 ± 0.8</td>
<td>38975</td>
<td>36.5 ± 3.0</td>
<td>92</td>
</tr>
<tr>
<td>$^{59}$Co</td>
<td>35.5 ± 1.2</td>
<td>34190</td>
<td>Internal Standard</td>
<td>-</td>
</tr>
<tr>
<td>$^{63}$Cu</td>
<td>37.7 ± 0.9</td>
<td>30428</td>
<td>40.9 ± 2.4</td>
<td>108</td>
</tr>
<tr>
<td>$^{88}$Sr</td>
<td>78.4 ± 0.2</td>
<td>37844</td>
<td>75.1 ± 3.9</td>
<td>96</td>
</tr>
<tr>
<td>$^{107}$Ag</td>
<td>22 ± 0.3</td>
<td>29840</td>
<td>22.4 ± 3.2</td>
<td>102</td>
</tr>
<tr>
<td>$^{111}$Cd</td>
<td>Not certified</td>
<td></td>
<td>33.5 ± 2.1</td>
<td>-</td>
</tr>
<tr>
<td>$^{133}$Ba</td>
<td>41 ± Not quoted</td>
<td>38770</td>
<td>35.4 ± 1.9</td>
<td>86</td>
</tr>
<tr>
<td>$^{140}$Ce</td>
<td>39 ± Not quoted</td>
<td>32727</td>
<td>39.7 ± 2.1</td>
<td>102</td>
</tr>
<tr>
<td>$^{206}$TI</td>
<td>15.7 ± 0.3</td>
<td>30735</td>
<td>15.3 ± 1.4</td>
<td>97</td>
</tr>
<tr>
<td>$^{208}$Pb</td>
<td>38.57 ± 0.2</td>
<td>33895</td>
<td>36.9 ± 1.9</td>
<td>96</td>
</tr>
<tr>
<td>$^{209}$Pb</td>
<td>38.57 ± 0.2</td>
<td>34139</td>
<td>38.1 ± 2.1</td>
<td>99</td>
</tr>
<tr>
<td>$^{235}$U</td>
<td>37.38 ± 0.08</td>
<td>35633</td>
<td>37.8 ± 2.6</td>
<td>101</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>34193</td>
<td></td>
<td>99</td>
</tr>
<tr>
<td>St. Dev.</td>
<td></td>
<td>3128</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>% RSD</td>
<td></td>
<td>9</td>
<td></td>
<td>7</td>
</tr>
</tbody>
</table>
Table 12 Data showing the certified elemental concentration, calculated mass flow ratio and calculated elemental concentration using Co as an internal standard, performed under dry plasma conditions with constant LA parameters, employing the particle separation device.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Certified concentration with associated uncertainty (mg kg(^{-1}))</th>
<th>Mass flow ratio</th>
<th>Calculated concentration with associated uncertainty (mg kg(^{-1}))</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{41})Ti</td>
<td>50.1 ± 0.8</td>
<td>22025</td>
<td>40.5 ± 3.1</td>
<td>80</td>
</tr>
<tr>
<td>(^{52})Cr</td>
<td>Not certified</td>
<td></td>
<td>48.7 ± 2.6</td>
<td>-</td>
</tr>
<tr>
<td>(^{54})Mn</td>
<td>39.6 ± 0.8</td>
<td>19570</td>
<td>34.9 ± 2.9</td>
<td>88</td>
</tr>
<tr>
<td>(^{58})Co</td>
<td>35.5 ± 1.2</td>
<td>17999</td>
<td>Internal Standard</td>
<td>-</td>
</tr>
<tr>
<td>(^{64})Cu</td>
<td>37.7 ± 0.9</td>
<td>17321</td>
<td>46.4 ± 6.0</td>
<td>123</td>
</tr>
<tr>
<td>(^{84})Sr</td>
<td>78.4 ± 0.2</td>
<td>19683</td>
<td>63.3 ± 3.7</td>
<td>81</td>
</tr>
<tr>
<td>(^{107})Ag</td>
<td>22 ± 0.3</td>
<td>16042</td>
<td>28.6 ± 3.9</td>
<td>130</td>
</tr>
<tr>
<td>(^{111})Cd</td>
<td>Not certified</td>
<td></td>
<td>28.6 ± 1.2</td>
<td>-</td>
</tr>
<tr>
<td>(^{137})Ba</td>
<td>41 ± Not quoted</td>
<td>21696</td>
<td>33.3 ± 2.3</td>
<td>81</td>
</tr>
<tr>
<td>(^{149})Ce</td>
<td>39 ± Not quoted</td>
<td>19044</td>
<td>32.6 ± 3.0</td>
<td>84</td>
</tr>
<tr>
<td>(^{208})Tl</td>
<td>15.7 ± 0.3</td>
<td>16997</td>
<td>15.0 ± 1.8</td>
<td>96</td>
</tr>
<tr>
<td>(^{206})Pb</td>
<td>38.57 ± 0.2</td>
<td>17210</td>
<td>38.0 ± 5.4</td>
<td>99</td>
</tr>
<tr>
<td>(^{208})Pb</td>
<td>38.57 ± 0.2</td>
<td>17333</td>
<td>36.3 ± 6.9</td>
<td>94</td>
</tr>
<tr>
<td>(^{238})U</td>
<td>37.38 ± 0.08</td>
<td>18225</td>
<td>31.2 ± 4.3</td>
<td>83</td>
</tr>
<tr>
<td>Mean</td>
<td>18595</td>
<td></td>
<td>18699</td>
<td>94</td>
</tr>
<tr>
<td>St. Dev.</td>
<td>10</td>
<td></td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>% RSD</td>
<td>10</td>
<td></td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>
Figure 35 The correlation between calculated elemental concentrations and certified elemental concentrations, with particle separation, using Co as an internal standard element and performed under wet plasma conditions.

Figure 36 The correlation between calculated elemental concentrations and certified elemental concentrations, with particle separation, using Co as an internal standard element and performed under dry plasma conditions.
When the particle separation device was placed in the LA line it improved the quality of the analysis, particularly when performed under dry plasma conditions. Under wet plasma conditions, there was no real improvement in the correlation of the calculated elemental concentrations and the certified elemental concentrations. This can be attributed to the fact that the wet plasma is capable of efficiently processing the particles produced at the LA stage, and therefore removal of larger particles with the particle separation device, led to no real improvement in plasma robustness.

Under dry plasma conditions, placing the particle separation device in the LA led to a dramatic improvement in the quality of the analytical data obtained. This is shown by an increase in gradient, from 0.4327 ($R^2 = 0.6011$) in Figure 34 to 0.6874 ($R^2 = 0.8379$) in Figure 36. This indicates a better correlation between the calculated elemental concentrations and the certified elemental concentrations, when employing a simple particle separation device, under dry plasma conditions.

This improvement in the quality of analytical data can be attributed to an increase in plasma robustness whilst employing the particle separation device. Under dry plasma conditions the ICP is not capable of processing all the particles produced by the LA stage, and large particles (particularly those greater than 150 nm in diameter) cause a high energy demand, leading to a reduction in plasma robustness, ultimately causing matrix effects and elemental fractionation. When these large particles were removed, using the particle separation device, there was an increase in plasma robustness, which led to a reduction in matrix effects and a consequent improvement in the quality of analytical data.

It is accepted that the effects observed could be attributed to a reduction in matrix loading of the plasma as more material is removed from the sample tube, and not be related to a change in particle size distribution. However, the observed change in elemental ratios would suggest that material was being removed in a particle size discriminate manner. Without access to particle sizing instrumentation this theory cannot be validated.
Analysis of ERM No. 681 Trace Elements in Polyethylene

Analysis of ERM No. 681 Polyethylene was undertaken as an example of a typical polymer sample. For this analysis Cd was chosen as an internal standard element, due to it being in the middle of the mass range investigated. The data obtained are shown in Table 13.

Table 13 Data showing the certified elemental concentration, calculated mass flow ratio, and calculated elemental concentration using Cd as an internal standard, performed under wet plasma conditions with constant LA parameters.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Certified concentration with associated uncertainty (mg kg⁻¹)</th>
<th>Mass flow ratio</th>
<th>Calculated concentration with associated uncertainty (mg kg⁻¹)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁶⁵Cr</td>
<td>17.7 ± 0.6</td>
<td>4974</td>
<td>17.5 ± 3.5</td>
<td>99</td>
</tr>
<tr>
<td>¹¹¹Cd</td>
<td>21.7 ± 0.7</td>
<td>4910</td>
<td>Internal standard</td>
<td>-</td>
</tr>
<tr>
<td>²⁰⁸Pb</td>
<td>13.8 ± 0.7</td>
<td>4813</td>
<td>14.1 ± 0.48</td>
<td>102</td>
</tr>
<tr>
<td>²⁰⁹Pb</td>
<td>13.8 ± 0.7</td>
<td>4869</td>
<td>13.9 ± 0.43</td>
<td>101</td>
</tr>
<tr>
<td>Mean</td>
<td>1493</td>
<td>101</td>
<td></td>
<td></td>
</tr>
<tr>
<td>St. Dev.</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% RSD</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The analysis proved successful and excellent agreement with the certified concentrations was obtained. When using Cd as an internal standard element, agreement within 2% of the certified concentrations was obtained for the quantification of Cr and Pb. Mass flow ratios were much smaller for the polyethylene than those obtained for the NIST glass. Since the output from the nebuliser generally remained constant for all three analyses, then the change in mass flow ratio must have been due to a large difference in the ablated mass transported to the plasma. The results indicate that much more polymer sample was transported, most likely due to increased coupling between the laser beam and the polymer.

Analysis of BCS No. 387 Nimonic 901 Alloy

Analysis of BCS No. 387 Nimonic 901 Alloy was undertaken as an example of a typical metal alloy sample. For this analysis Cu was chosen as an internal standard element. The data obtained are shown in Table 14.
Table 14 Data showing the certified elemental concentration, calculated mass flow ratio and calculated elemental concentration using Cu as an internal standard and performed under wet plasma conditions with constant LA parameters.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Certified concentration with associated uncertainty (mg kg⁻¹)</th>
<th>Mass flow ratio</th>
<th>Calculated concentration with associated uncertainty (mg kg⁻¹)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁵⁵Mn</td>
<td>250 ± Not quoted</td>
<td>4575</td>
<td>193 ± 4</td>
<td>77</td>
</tr>
<tr>
<td>⁵⁷Co</td>
<td>200 ± Not quoted</td>
<td>4703</td>
<td>198 ± 7</td>
<td>99</td>
</tr>
<tr>
<td>⁶⁵Cu</td>
<td>76 ± Not quoted</td>
<td>4660</td>
<td>Internal standard</td>
<td>-</td>
</tr>
<tr>
<td>²⁰⁶Pb</td>
<td>0.8 ± Not quoted</td>
<td>5107</td>
<td>0.73 ± 0.23</td>
<td>91</td>
</tr>
<tr>
<td>²⁰⁸Pb</td>
<td>0.8 ± Not quoted</td>
<td>4933</td>
<td>0.75 ± 0.19</td>
<td>95</td>
</tr>
<tr>
<td>Mean</td>
<td>-</td>
<td>4796</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>St. Dev.</td>
<td>219</td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>% RSD</td>
<td>5</td>
<td></td>
<td></td>
<td>11</td>
</tr>
</tbody>
</table>

Using Cu as an internal standard, the analysis proved successful in the quantification of Co and Pb, and good agreement with the certified concentration was obtained. The quantification of Mn was less successful. This was due to the fact that the certified concentration of Mn was very high in the reference material, producing a signal intensity above the linear range of the ICP-MS detector (especially when combined with the signal intensity from the aqueous calibration standards). This gave erroneous calibration data, leading to an inaccurate quantification. Mass flow ratios were similar to those obtained for the polymer sample, again indicating that there was an increased transport of metal sample to the plasma in comparison to the glass.
Chapter Three

Chapter Conclusion

Although dry plasma conditions may be beneficial when performing isotope ratio measurements by LA-ICP-MS due to reduced oxides and hydroxides, it has been shown that a wet plasma is more advantageous for routine analysis. The findings indicate that the online additions of water is the preferred mode of operation for quantification by LA-ICP-MS. Employing a wet plasma produces more standardised plasma conditions and buffers against the detrimental effects of sample loading, large particles produced at the ablation process and reduced plasma robustness. Furthermore, the exclusion of a desolvation system results in faster analysis time (due to reduced sample uptake, wash-in and wash-out times) and less expense (due to reduced analysis time, energy and gas requirements).

The theory presented in this chapter has enabled differentiation between “sensitivity” and mass flow. The calculation of a mass flow ratio is useful not only for calibration, but also as a measure of the relative flux between two sample introduction sources. The mass flow ratios reported indicate the very small amounts of material that are transported to the plasma from the ablation site when compared to the quantities introduced by a standard nebuliser and spray chamber. It has been shown that different samples can yield highly different mass flow ratios, related to the optical and physicochemical properties of the sample. Differences in the mass flow ratios between elements are a direct indication of the occurrence and extent of elemental fractionation.

This paper has shown that online additions of aqueous calibration standards without desolvation can produce rapid and ‘fit for purpose’ quantitative data in the absence of a CRM. The ability of this method to make such determinations has particular relevance with the introduction of the Restriction of the use of certain Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment (WEEE) Directives.36,37

The practical aspects of multi-point online additions calibration may make it more useful for method development than practical analysis, (as a pre-cursor to a single point calibration by normal internal standardisation) especially since it requires a large sample area of homogenous analyte and internal standard distribution and typically a ten minute time for sample analysis. For example, the method could be performed on a CRM to...
investigate fractionation and matrix effects, aiding the choice of internal standard (if a choice is available), before subsequent single point calibration on the real sample.
References


(23) P. Weis, H. Beck and D. Gunther, Characterizing ablation and aerosol generation during elemental fractionation on absorption modified lithium


(36) www.rohs.gov.uk

Accessed 12.04.2005

(37) www.dti.gov.uk

Accessed 12.04.2005
Chapter Four
Absorption Modified Pressed Powders for Calibration of Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Work Published:
Chapter Abstract

Powdered samples have been pressed, utilising a standard KBr infrared (IR) press, to produce mechanically stable 13 mm discs. Three organic based binders have been employed in this work; vanillic acid, pyrazinoic acid and nicotinic acid, chosen because of their high optical absorbance at the wavelength of the incident laser energy (213 nm). Poly(vinyl alcohol) (PVA) was employed as an example of a ‘non-absorbing’ binder and because its use has been described previously in the literature. Discs of various sample/binder compositions were prepared and their absorption properties characterised by diffuse reflectance spectroscopy. LA-ICP-MS was used to investigate the effect of different sample/binder compositions on signal sensitivity; whilst surface profilometry was performed on the resulting tracks to provide an estimate of the ablation depth achieved by the laser beam. It was found that discs prepared with vanillic acid had the highest optical absorbance at the wavelength of the laser system employed, resulting in a lower ablation depth and improved signal sensitivity probably through the formation of smaller particles during the ablation process.

Analysis of CRMs was performed using simple external calibration standards of similar and dissimilar matrix composition. It was found that discs produced using a 40% vanillic acid binder and a 60% sample composition gave superior quality analytical data when compared to the use of 40% PVA binder or no binder at all. These findings indicate the potential for fit-for-purpose quality analytical data to be obtained when employing external calibration standards, without internal standardisation and without exact matrix matching. These data also provide further evidence that standardisation of ablation conditions and mass flux to the plasma are pre-requisites for robust calibration, particularly in the absence of a suitable internal standard element.
Introduction

LA-ICP-MS has become the most versatile technique for the direct determination of trace elements in a wide variety of solid sample types. It has particular application for the determination of trace elements in sample types, such as metals, rocks, polymers and ceramics, and avoids the risk of contamination associated with complex digestion procedures.

The limitations of LA-ICP-MS are well known; namely elemental fractionation and a lack of CRMs for the majority of sample types. ‘In house’ solid synthetic standards are often prepared to allow external calibration; however, with such external standards it is especially important that the standard matches the sample in terms of matrix composition, since even a small difference in composition can lead to vastly different rates of ablation.

There are two common approaches to solid standard preparation. The first approach is fusion to form a glass bead or disc. The second approach is to press a powdered sample into a disc. These studies have shown that since the ablation yield can vary by as much as 50% between discs, poor analytical data is obtained unless the calibration standards are prepared to exactly match the sample or an internal standard element is used to correct for these large differences in ablation yield.

A major advantage of standard preparation of this type is that it facilitates addition of internal standard elements, isotope spikes or matrix modifiers. The use of matrix modifiers has been demonstrated by Boue-Bigne et al. to improve the analytical data obtained from the direct ablation of liquid calibration standards. The absorption coefficients of the standards were modified by the addition of organic chromophores so that they more closely matched those of the sample.

Matrix modification to improve the ablation efficiency has been achieved by addition of metal oxides in order to enhance the absorbance characteristics of the target. Weis et al. reported an extensive investigation into the addition of $Fe_2O_3$ as a matrix modifier to modify the absorption coefficient of lithium metaborate discs. It was found that the addition of $Fe_2O_3$ led to a greater absorption of the incident laser energy, leading to a
shorter optical penetration depth and a subsequent reduction in the size of particles produced by the ablation process. Lee et al.\textsuperscript{21} found that the addition of Triton-X\textsuperscript{TM} to samples pressed into discs led to increased sensitivity and suggested that this might be due to improved absorption of the laser energy.

Much work has been performed relating LA parameters to the particle size distribution of the generated aerosol and the effect upon figures of merit for ICP-MS. The parameters that have been investigated include; fluence, pulse duration, wavelength, carrier gas and absorption properties of the sample.\textsuperscript{25–39} However, it is important to understand that the particle size distribution created by the ablation process is not indicative of what reaches the ICP, since particles can change shape by processes such as vaporisation, condensation and agglomeration with other particles.\textsuperscript{40} The processes involved in the formation of particles from ablated matter are complex and remain poorly understood; however recent models, provided by Hergenroder,\textsuperscript{41–43} have helped to clarify this complexity and provide explanations for the different particle size fractions encountered.

This work reports a detailed investigation into the benefits of the addition of organic chromophores, simultaneously acting as binders, to powdered samples before subsequent pressing into discs. The organic chromophores chosen for this investigation, vanillic acid, pyrazinoic acid and nicotinic acid, are common Matrix Assisted Laser Desorption Ionisation (MALDI) matrices and were chosen due to their high absorbance at 213 nm, the wavelength of the laser ablation system employed. The other binder investigated in this work, poly(vinyl alcohol) (PVA), was chosen since it, and other high molecular weight alcohols and polymers, have been reported to act as effective sample binders.\textsuperscript{16, 44–48} Further, PVA is relatively non-absorbing in comparison to the ‘absorbing’ binders at the laser wavelength. The molecular structures of all four binders are shown in Figure 37; whilst Table 15 lists their $\lambda_{\max}$ values and associated molar absorptivities.\textsuperscript{49}
The addition of chromophores should improve the coupling between the laser beam energy and the sample, leading to an improved efficiency of ablation and the formation of smaller particles at the ablation site. The smaller particles are more efficiently transported to, and more fully processed by the plasma, leading to enhanced sensitivity and a reduction in elemental fractionation. It was anticipated that by incorporating the chromophores into the discs a more sample independent ablation process would result, offering the possibility of improved analytical data when using external calibration standards. This is of particular importance when no suitable internal standard is available.
Table 15 $\lambda_{\text{max}}$ values and molar absorptivities for various binders used in this investigation.\(^{49}\)

<table>
<thead>
<tr>
<th>Binder</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Molar absorptivity, $\varepsilon_{\text{max}}$ (L mol(^{-1}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanillie acid</td>
<td>217</td>
<td>22900</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>217</td>
<td>8610</td>
</tr>
<tr>
<td>Pyrazinoic acid</td>
<td>208</td>
<td>7960</td>
</tr>
</tbody>
</table>
Experimental

Solid Sample Preparation

The powdered sample, in this case a certified reference material, and the powdered binder: PVA (Fisher Scientific, Loughborough, Leicestershire, UK), vanillic acid, pyrazinoic acid or nicotinic acid (Alfa Aesar, Heysham, Lancashire, UK), were weighed out to yield a combined total mass of 0.40 g. Table 17 lists the required masses of sample and binder to produce discs of various sample/binder composition.

Two methods were employed for mixing of the two powders. The first was to simply combine the powders in a pestle and mortar and grind for a period of 10 min until a homogenous looking mixture was achieved. The second approach involved the use of a MM 200 mixer mill (Retsch, Leeds, Yorkshire, UK) to obtain a more homogenous mixture, utilising the parameters listed in Table 16. In this case, the mixture was weighed out directly into a 25 mL polystyrene sample vial with two, 9 mm polyamide beads. The mixture was homogenised for a period of 15 min at a frequency of 30 Hz.

0.25 g of the resulting mixtures of sample and binder were transferred to a standard infrared (IR) press using 13 mm dyes (Specac, Orpington, Kent, UK) and pressed into a disc using 10 tonnes of pressure for approximately 5 min. The resulting discs had a diameter of 13 mm and a thickness of 1.2 mm. This method of pressing produced discs of good mechanical stability and of good surface finish, as can be seen in Figure 38, especially as the ratio of binder to sample was increased.

Table 16 Experimental parameters used for powder homogenisation.

<table>
<thead>
<tr>
<th>Mixer Mill</th>
<th>MM 200 Mixer Mill</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball mill type</td>
<td></td>
</tr>
<tr>
<td>Frequency</td>
<td>30 Hz</td>
</tr>
<tr>
<td>Duration</td>
<td>15 min</td>
</tr>
<tr>
<td>Containment</td>
<td>25 ml polystyrene vials</td>
</tr>
<tr>
<td>Mixing balls</td>
<td>9 mm diameter polyamide</td>
</tr>
<tr>
<td><strong>Pestle and Mortar</strong></td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>5 cm Agate pestle and mortar</td>
</tr>
<tr>
<td>Duration</td>
<td>10 min</td>
</tr>
</tbody>
</table>
Early trials with PVA suggested that particle sizes of <50 μm were required for good ablation performance. The particle sizes used in this investigation were much smaller and were mostly in the 1 – 10 μm range, which is the range produced by the mixer mill (values taken from manufacturers specification for milling of soft powders).

![Digital photograph of a disc produced using vanillic acid as a binder and employing the mixer mill as a sample/binder mixing method.](image)

**Figure 38** Digital photograph of a disc produced using vanillic acid as a binder and employing the mixer mill as a sample/binder mixing method.

**Table 17** The required masses of binder and CRM required to produce discs of varying composition.

<table>
<thead>
<tr>
<th>% CRM</th>
<th>% binder</th>
<th>Mass of CRM (g)</th>
<th>Mass of binder (g)</th>
<th>Total mass of mixture (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>0.00</td>
<td>0.40</td>
<td>0.4000</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>0.04</td>
<td>0.36</td>
<td>0.4000</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0.08</td>
<td>0.32</td>
<td>0.4000</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>0.16</td>
<td>0.24</td>
<td>0.4000</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.24</td>
<td>0.16</td>
<td>0.4000</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>0.32</td>
<td>0.08</td>
<td>0.4000</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0.40</td>
<td>0.00</td>
<td>0.4000</td>
</tr>
</tbody>
</table>

**Instrumentation**

Table 18 lists experimental parameters for all the instrumentation used throughout this investigation. A commercially available UP-213 Laser Ablation System (New Wave Research Inc., Huntingdon, Cambridgeshire, UK) operating in the deep UV (213 nm) was employed using He as a carrier gas due to its improved ablation and transport characteristics.\(^{29,50,51}\) The He carrier gas was combined with an auxiliary Ar gas flow 1
m before the torch using a simple polypropylene ‘Y’-piece (Fisher Scientific, Loughborough, Leicestershire, UK). A further tangential mixing vessel was placed in the Peltier chamber of the ICP-MS to facilitate further mixing of the two gas lines. All gas lines used were constructed from 1 m lengths of 6 mm O.D. Tygon™ tubing (Fisher Scientific, Loughborough, Leicestershire, UK).

The LA system was coupled to a VG PQ ExCell ICP-MS instrument (Thermo Electron Corporation, Winsford, Cheshire, UK). Optimisation of the torch-box position, lens voltages, auxiliary Ar gas flow and LA carrier gas flow was performed before analysis, with respect to the $^{115}$In signal intensity obtained upon ablation of NIST 612 Trace Elements in Glass CRM. The LA parameters employed were used to reproduce the typical conditions encountered in bulk analysis by LA-ICP-MS.

Calibration experiments were performed both under ‘dry’ and ‘wet’ plasma conditions and the quality of analytical data compared to determine whether the more standardised plasma conditions offered by employing a ‘wet’ plasma led to an improvement in data quality, as has been previously reported. In this context the term “wet” refers to a plasma in which the liquid phase aerosol and vapour phase water are present, i.e. the classical wet plasma produced in solution analysis. This was achieved by combining the aerosol produced by solution nebulisation of 18.2 MΩ cm$^{-1}$ purity water (Elga Lab Water, High Wycombe, Buckinghamshire, UK) using a PFA-100 μL Fixed Capillary Nebuliser (Elemental Scientific Inc., Omaha, Nebraska, USA) and custom made cyclonic spray chamber, with the LA aerosol using the polypropylene ‘Y’-piece. Figure 39 shows the experimental arrangement employed.
Figure 39 A schematic of the system used for LA-ICP-MS analysis. A PFA nebuliser and custom made cyclonic spray chamber was employed to produce the more standardised wet plasma condition.

Table 18 Experimental parameters used for LA-ICP-MS measurements.

<table>
<thead>
<tr>
<th>Laser Ablation System</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type</strong></td>
<td>Solid state Nd:YAG, UP-213</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>213 nm</td>
</tr>
<tr>
<td><strong>Pulse duration</strong></td>
<td>4 ns</td>
</tr>
<tr>
<td><strong>Fluence</strong></td>
<td>2 J cm(^{-2})</td>
</tr>
<tr>
<td><strong>Repetition rate</strong></td>
<td>20 Hz</td>
</tr>
<tr>
<td><strong>Sampling strategy</strong></td>
<td>Raster</td>
</tr>
<tr>
<td><strong>Spot diameter</strong></td>
<td>110 μm</td>
</tr>
<tr>
<td><strong>Sample translation rate</strong></td>
<td>10 μm s(^{-1})</td>
</tr>
<tr>
<td><strong>He carrier gas flow</strong></td>
<td>0.80 L min(^{-1})</td>
</tr>
<tr>
<td><strong>Ar make up flow</strong></td>
<td>1.00 L min(^{-1})</td>
</tr>
<tr>
<td><strong>Binders</strong></td>
<td>Poly(vinyl alcohol) (PVA) Vanillic acid Nicotinic acid Pyrazinoic acid IMEP 14 Sediment CRM GBW 07311 Sediment CRM GBW 07401 Soil CRM NIST 8435 Whole Milk Powder</td>
</tr>
<tr>
<td><strong>Samples</strong></td>
<td></td>
</tr>
<tr>
<td><strong>ICP-MS</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Type</strong></td>
<td>PQ ExCell</td>
</tr>
<tr>
<td><strong>Auxiliary gas flow</strong></td>
<td>0.80 L min(^{-1})</td>
</tr>
<tr>
<td><strong>Cooling gas flow</strong></td>
<td>12.00 L min(^{-1})</td>
</tr>
<tr>
<td><strong>Plasma RF power</strong></td>
<td>1400 W</td>
</tr>
<tr>
<td><strong>Isotopes monitored</strong></td>
<td>(^{12})C, (^{40})Ca, (^{54})Cr, (^{55})Mn, (^{59})Co, (^{65})Cu, (^{107})Ag, (^{111})Ag, (^{137})Ba, (^{139})La, (^{153})Eu, (^{166})Er, (^{205})Tl, (^{206})Pb, (^{238})U</td>
</tr>
<tr>
<td><strong>Acquisition mode</strong></td>
<td>Peak hopping</td>
</tr>
<tr>
<td><strong>Detector mode</strong></td>
<td>Dual range</td>
</tr>
<tr>
<td><strong>Channels per peak</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>Dwell time</strong></td>
<td>100 ms</td>
</tr>
<tr>
<td><strong>No. of sweeps</strong></td>
<td>100</td>
</tr>
<tr>
<td><strong>No. of replicates</strong></td>
<td>50</td>
</tr>
</tbody>
</table>
Diffuse Reflectance analysis was performed on the discs to characterise their absorption properties. Reflectance spectroscopy is the study of light as a function of wavelength that has been reflected or scattered from a solid, liquid or gas. As photons enter a mineral, some are reflected from grain surfaces, some pass through the grain, and some are absorbed. The photons that are reflected from grain surfaces or refracted through a particle are said to be scattered. Scattered photons may encounter another grain or be scattered away from the surface so they may be detected and measured.

For the purpose of this investigation it was the reflectance of the discs at 213 nm that was of particular relevance since this coincided with the wavelength of the LA system employed. An Ocean Optics (Dunedin, Florida, USA) photo-diode array spectrometer operated in diffuse reflectance mode was employed in accordance with Table 19.

Table 19 Experimental parameters used for diffuse reflectance analysis.

<table>
<thead>
<tr>
<th>Diffuse Reflectance</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrometer</td>
<td>USB 2000</td>
</tr>
<tr>
<td>Light source</td>
<td>DH 2000</td>
</tr>
<tr>
<td>Reflectance probe</td>
<td>R400-7-SR-BX</td>
</tr>
<tr>
<td>Probe holder</td>
<td>RPH-1 probe holder</td>
</tr>
<tr>
<td>Integration time</td>
<td>1 s</td>
</tr>
<tr>
<td>Spectra average</td>
<td>5</td>
</tr>
<tr>
<td>Reflectance standard</td>
<td>WS-1 diffuse reflectance standard (PTFE)</td>
</tr>
<tr>
<td>Replicates</td>
<td>5</td>
</tr>
</tbody>
</table>

Surface profiling, of the craters produced during the laser ablation process, was performed using a custom made system employing a RM 600 laser stylus (Rodenstock, Munich, Germany) in accordance with Table 20. This is a non-contact laser stylus that uses dynamic focusing of the laser beam and the focus error signal to determine surface topography.
Chapter Four

Table 20 Experimental parameters used for surface profiling.

<table>
<thead>
<tr>
<th>Surface Profiling</th>
<th>Type</th>
<th>No. of points</th>
<th>Spacing</th>
<th>Vertical range</th>
<th>No. scans per sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RM 600 laser stylus</td>
<td>800</td>
<td>2 µm</td>
<td>±300 µm</td>
<td>5</td>
</tr>
</tbody>
</table>

Homogeneity Trials

In order to perform bulk analysis by LA-ICP-MS it is vital that the analyte is homogenously distributed throughout the sample. This is of particular importance when a binder is used, whether it is absorbing or not. For this reason an investigation into the homogeneity of the elemental distribution was performed, utilising the Transient Rapid Analysis (TRA) function of the ICP-MS. A dry plasma was used for this investigation.

Using the setup described in Figure 39 and the parameters listed in Table 18, the distributions of elements within discs produced by mixing in a pestle and mortar and discs produced by mixing in a MM 200 mixer mill were compared. For this investigation, three discs were analysed, consisting of GBW 07311 Sediment CRM and a vanillic acid binder. Their composition and mixing method is shown in Table 21.

$^{13}$C was used as an internal standard element to correct for differences in rates of ablation during the ablation of each track. The elemental distribution across the discs was monitored and the % RSD of the ratio of analyte signal intensity to $^{13}$C signal intensity was determined and used as an indication of homogeneity. The % RSD was determined over a range of 9 mm in the middle of the laser ablated track i.e. between the 3 and 12 mm points on the graphs produced.

Table 21 Composition and production method of discs used in homogeneity trials. GBW 07311 Trace Elements in Sediment CRM was used as a sample.

<table>
<thead>
<tr>
<th>Disc No.</th>
<th>Mixing method employed</th>
<th>Binder type</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disc 1</td>
<td>-</td>
<td>-</td>
<td>100% CRM</td>
</tr>
<tr>
<td>Disc 2</td>
<td>Pestle and mortar</td>
<td>Vanillic acid</td>
<td>40% Binder 60% CRM</td>
</tr>
<tr>
<td>Disc 3</td>
<td>Ball mixer</td>
<td>Vanillic acid</td>
<td>40% Binder 60% CRM</td>
</tr>
</tbody>
</table>
Effect of Different Disc Composition

Discs of varying composition were produced to determine the effects of different types and compositions of binders and samples. Three different 'absorbing binders' were chosen for this investigation due to their high absorptivity around the wavelength of the incident laser beam, as shown in Table 15: vanillic acid, nicotinic acid and pyrazinoic acid. PVA was chosen as an example of a 'non-absorbing' binder. GBW 07311 Sediment CRM was chosen as a sample in this particular investigation, since it is well characterised for a range of analytes. A series of discs with increasing CRM composition i.e. 0, 10, 20, 40, 60, 80 and 100% was produced for each combination of sample and binder.

LA-ICP-MS Analysis

These discs were analysed by LA-ICP-MS, using the parameters described in Table 18 and the setup shown in Figure 39, to determine the effects of differing binder type and binder composition on signal sensitivity and stability and to establish the optimum disc composition. In each case the laser beam was focused upon the disc surface. Response curves were plotted for all the isotopes monitored.

It should be noted that although the concentration of C was around 50% in the discs, the ablated mass produced by the UP-213 LA system was so small that no significant deposition was observed upon the cones, even in bulk analysis mode. For this reason no O₂ addition to the plasma was required.

Diffuse Reflectance Analysis

Diffuse reflectance analysis was performed, employing the parameters described in Table 19, on the same series of discs used for the LA-ICP-MS investigation, to determine the effect of differing binder type and binder composition on the absorption properties of the discs. The mean % reflectance at 213 nm was determined for each disc using five replicates. All reflectance measurements were made relative to a polytetrafluoroethylene (PTFE) diffuse reflectance standard.

The absorption properties of the pure binders were characterised by determining the mean % reflectance of '100% blank' discs, with respect to the PTFE standard.
Surface Profilometry

Surface profilometry was performed on the discs produced from 100% of each of the binders and the pure CRM, to determine the maximum ablated crater depth, produced during the LA process. This crater depth was used as an indication of the effective ablation depth achieved by the laser. It is recognised that optical absorbance was not the sole parameter affecting the data obtained in this investigation, and that the different physicochemical properties of the binders also affected the outcomes. However, the particle sizes of the binders used to press the discs were all similar and the press has been shown to produce discs of consistent density and hardness, so it was reasonable to assume that absorbance was the major factor determining the depth of the craters ablated.

Calibration and Analysis

To determine whether the presence of the organic chromophore offered any advantage when performing quantitative analysis by LA-ICP-MS, two simple calibration strategies based upon external calibration with and without internal standardisation were devised.

\[ C_A = \frac{I}{I_{Std}} \frac{I_{Std}}{C_{Std}} \]  \hspace{1cm} (11)

If an element of known concentration is available within the sample and standard, internal standardisation can be utilised yielding equation 12.
Calibration was performed using sample and standard discs produced from 100% CRMs, and from sample and standard discs produced from 60% CRM and 40% PVA or vanillic acid binder. Different combinations of discs were used as sample and external standard and the quality of data compared to determine the effects of the presence of the vanillic acid organic chromophore, in particular whether utilising vanillic acid offered an improvement in data quality over PVA or pure pressed sample/standard. These investigations were performed under both wet and dry plasma conditions to determine whether the use of wet plasma conditions offers any advantage with respect to standardising plasma conditions as observed in previous work.\(^{52}\)

Another set of calibrations were performed involving the use of a sample and a standard that were totally different in terms of their matrix composition. NIST 8435 Whole Milk Powder CRM was employed as either sample or standard with the other soil and sediment CRMs used previously. Again vanillic acid and PVA were used as a binder. This type of calibration was performed solely to verify the advantages offered by employing an absorbing binder, it is recognised that this deliberate 'mismatching' of sample and standard would not be employed for the analysis of a real sample. This series of calibrations were performed utilising 'dry' plasma conditions only.

It should be noted that for analysis of a 'real' sample, an internal standard element would normally be employed to correct for differences in ablation rates between the sample and the standard. In this investigation, the relative data quality between calibration sets, without internal standardisation, was more important than the absolute data quality with internal standardisation, to show the differences between the binders. However, since CRMs have been used as both samples and standards, then an internal
standard element was available. For this reason, data utilising $^{65}\text{Cu}$ as an internal standard element is also presented and is useful in providing a comparison of the data quality obtainable by this method.
Results and Discussion

Homogeneity Trials
The elemental distributions across the discs produced using the ball mixer were much more homogenous when compared to those produced using a simple pestle and mortar. This can be seen in Figure 40 and is numerically indicated by the much smaller % RSDs obtained for those discs as highlighted in Table 22. Importantly, discs produced from 100% CRM, with no subsequent homogenising stage, also showed poor homogeneity, indicating the importance of using a homogenising mixer mill even when no binder is employed, since the CRMs may not be as homogenous as is often assumed.

![Graph showing elemental distribution](image)
Figure 40 LA-ICP-MS analysis to determine the elemental distribution across discs: (1) produced from 100% sample, (2) 60% CRM and 40% vanillic acid binder mixed using a simple pestle and mortar, and (3) 60% CRM and 40% vanillic acid binder mixed using a MM 200 mixer mill. CRM was GBW 07311 Sediment.

It is vital that the distribution of analyte within the discs be as homogenous as possible in order to obtain good quantitative data. In the case of the ‘absorbing binders’ it is also
necessary to ensure that the sample and binder has been adequately mixed to facilitate an efficient coupling of the laser beam energy and the sample surface. It has been shown in this investigation that the use of a mixer mill is essential to provide a sufficient degree of mixing between sample and binder. All discs produced in this investigation were thus created using the mixer mill method described and not in a pestle and mortar which has been shown to produce an inadequate degree of mixing.

Table 22 % RSDs of (analyte signal intensity/¹¹²C signal intensity) ratio for discs 1 - 3. Discs 2 and 3 were prepared using a 60% CRM and 40% vanillic acid binder mixture.

<table>
<thead>
<tr>
<th>Type</th>
<th>% RSD of (Analyte Signal Intensity/¹¹²C Signal Intensity)</th>
<th>¹⁹⁹⁰La</th>
<th>¹⁹⁷⁰Pb</th>
<th>¹⁹⁷⁰U</th>
<th>Mean % RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disc 1 100% CRM</td>
<td></td>
<td>44</td>
<td>27</td>
<td>127</td>
<td>66</td>
</tr>
<tr>
<td>Disc 2 Pestle and Mortar</td>
<td></td>
<td>39</td>
<td>29</td>
<td>117</td>
<td>62</td>
</tr>
<tr>
<td>Disc 3 Retsch MM 200</td>
<td></td>
<td>26</td>
<td>13</td>
<td>26</td>
<td>22</td>
</tr>
</tbody>
</table>

Effect of Different Disc Composition

LA-ICP-MS Analysis

The use of vanillic acid as a binder led to increased sensitivity in comparison to the other binders investigated, as indicated by the steep climb and the high optimum of the curve in Figure 41 (although Figure 41 uses ²³⁸U as the analyte, all the analytes investigated, see the list in Table 18, gave the same result). Vanillic acid was followed by pyrazinoic acid and nicotinic acid in terms of overall sensitivity.

This correlated with the molar absorptivities of the compounds quoted in Table 15, in which vanillic acid is shown to possess a greater molar absorptivity when compared to pyrazinoic and nicotinic acid. Importantly, all three ‘absorbing binders’ showed a gain in sensitivity when compared to the use of ‘non-absorbing’ PVA.

The absorbing binders, vanillic acid, nicotinic acid and pyrazinoic acid, yielded distinct curves with optima around 60 - 80% CRM composition. The occurrence of these curves with distinct optima can be attributed to two competing factors. As the % of sample is increased, so does the analyte concentration within the disc, resulting in an increase in analyte signal intensity. However, as the % sample is increased, the % of absorbing chromophore is subsequently reduced, and consequently the absorbance properties of the discs at 213 nm. These two competing phenomena result in calibration curves with
distinct optima. Significantly, analysis of the series of discs produced using PVA yielded a straight line \((R^2 = 0.9994)\), as for a regular external calibration, rather than a curve, indicating the absence of any optical absorbance effect.

Figure 41 LA-ICP-MS data for discs produced using GBW 07311 Sediment as a sample and different binders of varying composition.

The presence of the vanillic acid changes the ablation characteristics of the discs considerably. Figure 42 shows the sensitivity obtained upon ablation of target discs of differing matrix composition, utilising varying energy density. When vanillic acid is employed as a binder, the ablation threshold of the disc is reached at a lower energy density. When no binder is used, or PVA is employed the ablation threshold of the discs occurs much later. Ultimately, this means that higher sensitivity can be obtained when the absorbing binder is present in the disc matrix.
Figure 42 LA-ICP-MS data at various laser energy densities for discs produced using 60% GBW 07311 Sediment as a sample, and 40% vanillic acid or PVA binder, or pure sample.

**Diffuse Reflectance Analysis**

The occurrence of the distinct curves in Figure 43 can be related to the optical properties of the binders employed. When an 'absorbing binder' was employed, as the concentration of sample, and consequently analyte, was increased there was a subsequent decrease in the absorbance of the sample surface (indicated by an increase in % reflectance) due to a reduction in absorbing binder concentration. There is a crossover point for the curves obtained from the analysis of pyrazinoic and nicotinic acid; as yet no explanation can be given, although it was observed that after pressing a pink tinge was often present on the surface of discs produced from pyrazinoic acid, indicating the occurrence of some unusual surface effects. Importantly, the data for PVA showed a slight decrease in reflectance as the sample concentration was increased, due to the fact that in this case the sample, GBW 07311 Sediment, had a greater absorptivity than the binder, PVA.
Figure 43 Reflectance data at 213 nm for discs produced using GBW 07311 Sediment as a sample and different binders of varying composition.

The diffuse reflectance data followed the same trend as the quoted molar absorptivities of the compounds and the LA-ICP-MS data described previously. Vanillic acid offered the greatest absorbance of the laser energy, followed by pyrazinoic and nicotinic acid. As expected, PVA has been shown to possess the lowest optical absorbance at the lasing wavelength and showed a greater degree of reflectance than the pure sample. This is shown in Table 23 and Figure 44.

Table 23 Reflectance data at 213 nm for discs produced from 100% of all the binders used in the investigation of discs produced from 100% GBW 07311 Sediment.

<table>
<thead>
<tr>
<th>Disc</th>
<th>Mean % Reflectance</th>
<th>Standard Deviation</th>
<th>% RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanillic acid</td>
<td>1.37</td>
<td>0.30</td>
<td>22.70</td>
</tr>
<tr>
<td>Pyrazinoic acid</td>
<td>2.40</td>
<td>0.33</td>
<td>8.68</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>5.26</td>
<td>0.40</td>
<td>7.57</td>
</tr>
<tr>
<td>GBW 07311 Sediment</td>
<td>8.48</td>
<td>0.40</td>
<td>4.72</td>
</tr>
<tr>
<td>PVA</td>
<td>11.19</td>
<td>0.96</td>
<td>8.58</td>
</tr>
</tbody>
</table>
Figure 44 Reflectance data at 213 nm for discs produced from 100% of all the binders used in the investigation and of discs produced from 100% GBW 07311 Sediment. Error bars are defined by one standard deviation either side of the mean.

Surface Profiling

Surface profiling of the laser ablated tracks showed that, as expected, ablation produced shallower craters in more absorbing matrices. These data are shown in Table 24 and Figure 45, whilst Figure 46 gives the profiles of one crater from each substrate, as a representation of the data obtainable by this technique. The depth of the craters produced correlated with the LA-ICP-MS and diffuse reflectance data already reported, in that the shallowest craters were produced in the most absorbing substrate, the vanillic acid. The deepest craters were produced in the least absorbing substrate, the PVA, as expected, and the disc prepared from the pure sample only. The crater depths indicate directly the depth of penetration of the laser beam before its intensity falls below the threshold intensity for ablation. Nicotinic acid and pyrazinoic acid gave similar, relatively shallow crater depths, indicating that they offer a similar optical penetration depth.
Table 24 Maximum crater depth measurements for discs produced from each of the four binders, obtained using surface profiometry.

<table>
<thead>
<tr>
<th>Disc</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Mean</th>
<th>SD</th>
<th>% RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanillic acid</td>
<td>86</td>
<td>93</td>
<td>81</td>
<td>87</td>
<td>86</td>
<td>87</td>
<td>4.2</td>
<td>4.8</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>96</td>
<td>86</td>
<td>91</td>
<td>105</td>
<td>108</td>
<td>97</td>
<td>9.4</td>
<td>9.7</td>
</tr>
<tr>
<td>Pyrazinoic acid</td>
<td>91</td>
<td>102</td>
<td>104</td>
<td>98</td>
<td>98</td>
<td>98</td>
<td>5.1</td>
<td>5.2</td>
</tr>
<tr>
<td>PVA</td>
<td>137</td>
<td>152</td>
<td>148</td>
<td>127</td>
<td>109</td>
<td>135</td>
<td>17.3</td>
<td>12.9</td>
</tr>
<tr>
<td>GBW 07311</td>
<td>120</td>
<td>130</td>
<td>113</td>
<td>131</td>
<td>119</td>
<td>123</td>
<td>6.9</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Figure 45 Surface profiling data showing the mean depth of crater ablated in discs produced from 100% of all the binders used in the investigation and of discs produced from 100% GBW 07311 Sediment. Error bars are defined by one standard deviation either side of the mean.

It would have been interesting to characterise the shape and maximum depth of the craters produced in discs containing sample rather than just the binders. However, access to the surface profiling instrumentation was restricted, and it was felt that that it was most important to characterise the craters produced in the four binders, and the pure sample. Figure 47 shows the loose correlation between the reflectance properties of the discs and the maximum crater depths produced during the ablation process. That this is only a loose correlation can be attributed to the fact that absorption of the incident laser energy was not the only parameter affecting the depth the ablation craters produced.
Other physicochemical properties such as hardness and particle size would have affected the crater depth produced. In Figure 47 it can be seen that Nicotinic acid does no quite follow the trend, in that its reflectance was slightly higher than anticipated. Again, no definitive explanation is available although it is possible that particle size affected the outcome of the reflectance measurements.

Although the greatest volume/mass of substrate was removed for the non-absorbing binder, the highest analytical sensitivity was obtained from the smallest crater volumes. The increased sensitivity offered by using an ‘absorbing binder’, such as vanillic acid, was almost certainly due to the production of smaller sized particles at the ablation site. Such smaller particles were more efficiently transported to, and processed by the ICP. Recent studies have shown that small particles are not necessarily produced directly from the laser/solid interaction, but more likely through secondary processes, namely by condensation of vaporised material.\textsuperscript{41-43} Nevertheless, a highly absorbing substrate results in a thinner melt layer and lower penetration depth, which in turn produces an aerosol with smaller particle sizes, and importantly an absence of larger particles that are not efficiently transported and processed by the plasma. Importantly, the generation of smaller particles during the ablation process is likely to reduce elemental fractionation occurring within the ICP which may be caused by selective volatilisation from the surface of large particles that are not fully vaporised. Therefore, the use of these absorbing binders should contribute to minimising the detrimental effects of elemental fractionation on quantitative analysis by L.A-ICP-MS, as well as providing the more obvious benefits offered by increased sensitivity.
A Vanillic acid. Maximum crater depth = 86 µm

B Pyrazinoic acid. Maximum crater depth = 89 µm

C Nicotinic acid. Maximum crater depth = 93 µm

D PVA. Maximum crater depth = 148 µm

Figure 46 (A-D) Examples of surface profiling of craters ablated in discs of: (A) vanillic acid (B) pyrazinoic acid (C) nicotinic acid and (D) PVA, showing the maximum ablated crater depth.
Figure 47 A chart to show the correlation between crater depth and reflectance. Again, the error bars are defined by one standard deviation.

**Calibration and Analysis**

The data obtained under ‘dry’ plasma conditions are shown in Table 25. The recoveries were consistently closer to 100% when vanillin acid was employed as a binder, compared to the use of a less absorbing binder or no binder at all. This outcome was true for all the elements studied with no outliers. When employing the vanillin acid, all external cross-calibrations resulted in recoveries well within ±10%. This was due to the chromophore dominating the ablation process rather than the sample. Unlike simple dilution of the sample, this ‘active substrate’ dilution/matrix matching enhanced sensitivity rather than reduced it. Vanillic acid yielded a signal response that was three times greater than when PVA was used.

External cross-calibration using discs of 100% CRM resulted in a broad range of recoveries (47 - 199%), indicating that the differences in sample matrix had large effects on the quality of data obtained. It is well documented that even small changes in sample matrix can lead to large variations in ablation rates and hence the poor quality data obtained by this type of cross-calibration was to be expected.
When the non-absorbing PVA was employed as a binder, the quality of the data declined even further and a larger range of recoveries was obtained (47 - 219%). This can probably be attributed to the dilution of the sample resulting in reduced sensitivity, since unlike vanillic acid, PVA does not offer an increase in target absorbance. This reduction in sensitivity meant that many analytes in the discs were at levels closer to their detection limits where the quality of analytical data was poorer.

Table 25 Calibration data showing the mean and % RSD of calibration recoveries using different combinations of discs as sample and standard. Obtained under ‘dry’ plasma conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard</th>
<th>Recovery Data 100% CRM (%)</th>
<th>Recovery Data 40% PVA (%)</th>
<th>Recovery Data 40% Vanilllic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>RSD</td>
<td>Mean</td>
</tr>
<tr>
<td>IMEP 14</td>
<td>GBW 07311</td>
<td>199</td>
<td>25</td>
<td>219</td>
</tr>
<tr>
<td>GBW 07401</td>
<td>GBW 07311</td>
<td>110</td>
<td>20</td>
<td>149</td>
</tr>
<tr>
<td>GBW 07311</td>
<td>IMEP 14</td>
<td>53</td>
<td>15</td>
<td>47</td>
</tr>
<tr>
<td>GBW 07401</td>
<td>IMEP 14</td>
<td>47</td>
<td>11</td>
<td>72</td>
</tr>
<tr>
<td>GBW 07311</td>
<td>GBW 07401</td>
<td>89</td>
<td>20</td>
<td>132</td>
</tr>
<tr>
<td>IMEP 14</td>
<td>GBW 07401</td>
<td>222</td>
<td>49</td>
<td>164</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>120</td>
<td>23</td>
<td>131</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td>74</td>
<td>-</td>
<td>63</td>
</tr>
<tr>
<td>% RSD</td>
<td></td>
<td>62</td>
<td>-</td>
<td>48</td>
</tr>
</tbody>
</table>

The fact that an absorbing binder such as vanillic acid does offer an advantage over the use of a non-absorbing binder, such as PVA, was confirmed by the repeat of the analyses under wet plasma conditions. Table 26 shows that the calculated recoveries were much closer to 100% when vanillic acid was used rather than PVA or no binder at all.

The quality of the analytical data obtained under wet and dry plasma conditions showed no significant differences. The recoveries were perhaps slightly better under wet plasma conditions, but the differences were not large enough to confirm the merits of employing a wet plasma for this type of calibration. Unlike previous work, the determining factor in this investigation was the difference in sample and standard matrix, resulting in variations in ablation yields during the ablation process and not during the vaporisation and ionisation processes occurring within the plasma i.e. plasma processes were secondary to the primary ablation processes. Here, by using a standardised and strongly absorbing matrix, the total plasma loading did not vary as much between samples and standards as when a dried nebuliser derived aerosol is used.
to calibrate the response from a laser ablated solid substrate (water is needed in this case to produce a single dominant plasma species).

Table 26 Calibration data showing the mean and % RSD of calibration recoveries using different combinations of discs as sample and standard. Obtained under 'wet' plasma conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard</th>
<th>Recovery Data 100% CRM (%)</th>
<th>Recovery Data 40% PVA (%)</th>
<th>Recovery Data 40% Vanilllic (%)</th>
<th>n=</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMEP 14</td>
<td>GBW 07311</td>
<td>Mean 178  RSD 15</td>
<td>Mean 231  RSD 22</td>
<td>Mean 253  RSD 20</td>
<td>6</td>
</tr>
<tr>
<td>GBW 07401</td>
<td>GBW 07311</td>
<td>115  125  55</td>
<td>100  120  24</td>
<td>90  115  6</td>
<td>6</td>
</tr>
<tr>
<td>GBW 07311</td>
<td>IMEP 14</td>
<td>69   49   20</td>
<td>104  120  24</td>
<td>110  130  6</td>
<td>6</td>
</tr>
<tr>
<td>GBW 07401</td>
<td>IMEP 14</td>
<td>59   75   55</td>
<td>111  130  6</td>
<td>110  130  6</td>
<td>6</td>
</tr>
<tr>
<td>GBW 07311</td>
<td>GBW 07401</td>
<td>92   130  71</td>
<td>98   110  7</td>
<td>100  120  6</td>
<td>6</td>
</tr>
<tr>
<td>IMEP 14</td>
<td>GBW 07401</td>
<td>174  149  41</td>
<td>94   110  6</td>
<td>100  120  6</td>
<td>6</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>114  119  44</td>
<td>102  120  6</td>
<td>110  130  6</td>
<td>6</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td>51   49   8</td>
<td>8    8</td>
<td>8    8</td>
<td></td>
</tr>
<tr>
<td>% RSD</td>
<td></td>
<td>45   41   8</td>
<td>8    8</td>
<td>8    8</td>
<td></td>
</tr>
</tbody>
</table>

The advantages of employing an absorbing binder are emphasised in Table 27, which shows the analytical data obtained by using a sample and standard that differed greatly in terms of matrix composition. Once again the vanillic acid binder yielded a considerable improvement in data over that obtained from the use of discs produced from 100% CRM and those produced using PVA as a binder.

Table 27 Analytical data showing the mean and % RSD recoveries using different combinations of discs as sample and standard. In this case the sample and standard were deliberately chosen to differ in terms of their matrix composition. IMEP 14 and GBW 07311 are sediments, GBW 07401 is a soil, whilst NIST 8435 is a powdered milk. The data were obtained under 'dry' plasma conditions. The title 'n=' represents the number of analytes quantified per calibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard</th>
<th>Recovery Data 100% CRM (%)</th>
<th>Recovery Data 40% PVA (%)</th>
<th>Recovery Data 40% Vanilllic (%)</th>
<th>n=</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST 8435</td>
<td>GBW 07311</td>
<td>286  291  55</td>
<td>158  160  16</td>
<td>115  130  6</td>
<td>5</td>
</tr>
<tr>
<td>NIST 8435</td>
<td>GBW 07401</td>
<td>314  294  53</td>
<td>165  160  16</td>
<td>110  130  6</td>
<td>5</td>
</tr>
<tr>
<td>NIST 8435</td>
<td>IMEP 14</td>
<td>232  212  98</td>
<td>166  180  12</td>
<td>110  130  6</td>
<td>4</td>
</tr>
<tr>
<td>GBW 07311</td>
<td>NIST 8435</td>
<td>41   40   33</td>
<td>66   80   20</td>
<td>100  120  6</td>
<td>5</td>
</tr>
<tr>
<td>GBW 07401</td>
<td>NIST 8435</td>
<td>36   33   44</td>
<td>68   80   20</td>
<td>100  120  6</td>
<td>5</td>
</tr>
<tr>
<td>IMEP 14</td>
<td>NIST 8435</td>
<td>78   61   62</td>
<td>72   80   45</td>
<td>110  130  6</td>
<td>4</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>165  155  61</td>
<td>116  130  6</td>
<td>110  130  6</td>
<td>6</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td>127  125  52</td>
<td>52    52</td>
<td>52    52</td>
<td></td>
</tr>
<tr>
<td>% RSD</td>
<td></td>
<td>77   80   45</td>
<td>45    45</td>
<td>45    45</td>
<td></td>
</tr>
</tbody>
</table>
Table 28 and Table 29 show the data obtained when $^{65}$Cu was employed as an internal standard element. There was a vast improvement in the quality of the analytical data from the calibrations performed using discs produced from 100% CRM and those produced from 40% PVA. This improvement is expected since the use of $^{65}$Cu as an internal standard element corrects for differences in ablation rates between sample and standard, which would have been significant when utilising 100% CRM or the PVA due to differences in target matrix. The quality of data did not improve for discs produced using vanillic acid since the standardised target matrix offered by these discs meant that rates of ablation were similar between sample and standard, and hence internal standard correction was not required. It is accepted that the data quality obtained using internal standardisation was actually reduced for the calibrations involving vanillic acid. No definitive explanation can be given for this, except that the homogeneity of the CRM's is questionable (as has already been shown in Figure 40). It is likely that for this particular disc the Cu was not distributed in a homogenous manner, resulting in poorer analytical data when utilising internal standardisation.

It would be possible to simply add internal standard elements as aqueous spikes, prior to the homogenisation and pressing stages. This is of particular interest for the analysis of samples where no prior knowledge of the sample is obtainable. This technique will be evaluated in a latter chapter, discussing the incorporation of isotopic spike solutions into the pressed discs.

It was subsequently realised that the use of an absorbing binder offered another major benefit for the analysis of pressed powders. As discussed previously, the analysis of pressed powders is often hampered by inhomogeneous distribution of elements. It is therefore of major importance that the sampling area is as large as possible, since a larger sampling area is statistically more likely to be representative of the whole sample. The UP-213 Laser Ablation System can deliver spot sizes up to 110 μm in aperture imaged mode, meaning that any changes up to this point are performed whilst maintaining constant energy density at the sample surface. It is possible to increase the spot size further, up to 250 μm, via beam expansion mode to improve the quality of data achievable for applications involving bulk analysis. However, an increase in spot size from 110 – 250 μm is accompanied by a large reduction in energy density at the surface.
For regular samples, this could prove problematic since the energy density may fall below the threshold value required for ablation. As has already been shown in Figure 42, utilising a binder that absorbs heavily at the lasing wavelength significantly reduces this threshold value, meaning that it would be possible to select the largest possible spot size available and still have enough energy density for efficient ablation. The consequence of this is that the use of vanillic acid allows analysis of a larger sampling area, reducing the detrimental effects of inhomogeneous analyte/internal standard distribution.

Table 28 Analytical data, using $^{65}$Cu as an internal standard element, showing the mean and % RSD recoveries using different combinations of discs as sample and standard. The data were obtained under ‘dry’ plasma conditions. The title ‘n=’ represents the number of analytes quantified per calibration. IMEP 14 and GBW 07311 are sediments whilst GBW 07401 is a soil.
Table 29 Analytical data, using 65Cu as an internal standard element, showing the mean and % RSD recoveries using different combinations of discs as sample and standard. In this case the sample and standard have been deliberately chosen to differ in terms of their matrix composition. IMEP 14 and GBW 07311 are sediments, GBW 07401 is a soil, whilst NIST 8435 is a powdered milk. The data were obtained under ‘dry’ plasma conditions. The title ‘n=’ represents the number of analytes quantified per calibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard</th>
<th>Recovery Data 100% CRM (%)</th>
<th>Recovery Data 40% PVA (%)</th>
<th>Recovery Data 40% Vanillic (%)</th>
<th>n=</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST 8435</td>
<td>GBW 07311</td>
<td>Mean 108, RSD 58</td>
<td>Mean 103, RSD 54</td>
<td>Mean 120, RSD 26</td>
<td>4</td>
</tr>
<tr>
<td>NIST 8435</td>
<td>GBW 07401</td>
<td>Mean 65, RSD 8</td>
<td>Mean 67, RSD 17</td>
<td>Mean 122, RSD 30</td>
<td>4</td>
</tr>
<tr>
<td>NIST 8435</td>
<td>IMEP 14</td>
<td>Mean 93, RSD 24</td>
<td>Mean 92, RSD 29</td>
<td>Mean 117, RSD 12</td>
<td>3</td>
</tr>
<tr>
<td>GBW 07311</td>
<td>NIST 8435</td>
<td>Mean 113, RSD 45</td>
<td>Mean 119, RSD 40</td>
<td>Mean 75, RSD 51</td>
<td>4</td>
</tr>
<tr>
<td>GBW 07401</td>
<td>NIST 8435</td>
<td>Mean 121, RSD 41</td>
<td>Mean 120, RSD 41</td>
<td>Mean 87, RSD 30</td>
<td>4</td>
</tr>
<tr>
<td>IMEP 14</td>
<td>NIST 8435</td>
<td>Mean 90, RSD 69</td>
<td>Mean 91, RSD 69</td>
<td>Mean 87, RSD 11</td>
<td>3</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>Mean 98, RSD 41</td>
<td>Mean 98, RSD 42</td>
<td>Mean 101, RSD 27</td>
<td>3</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td>20</td>
<td>20</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>% RSD</td>
<td></td>
<td>20</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>
Chapter Conclusion

This work has shown that by utilising a binder that absorbs strongly at the lasing wavelength of 213 nm, such as vanillic acid, rather than a non-absorbing binder such as PVA, excellent quality analytical data was obtained without the use of internal standardisation. By adding vanillic acid to the powdered sample of interest, an approximately three-fold gain in sensitivity was achieved over the use of PVA, leading to lower limits of detection and an improvement in quantitation. Importantly, the chromophores employed were successful as binders and produced discs of greater mechanical stability than by pressing the sample alone.

The data suggests that the mechanism for the increase in sensitivity was through the formation of smaller particles during the ablation process. Diffuse reflectance data showed that a greater absorptivity at the lasing wavelength was obtained by utilising vanillic acid as a binder. A greater absorption of the laser energy by the sample surface leads to a shorter effective penetration depth, as was shown by the surface profilometry. This allows a greater energy density to be achieved in the target, leading to the formation of smaller particles. Such particles are more efficiently transported to, and processed by the ICP, leading to an improvement in sensitivity and a reduction in plasma based elemental fractionation.

Employing vanillic acid as a binder introduces a degree of matrix matching between sample and standard, but more importantly, standardises the absorptivity of the matrix. This in turn leads to a standardisation of ablation conditions and mass flux to the plasma which are pre-requisites for robust calibration. Unlike the use of a traditional, non-absorbing binder, which simply dilutes the sample, this matrix matching is accompanied by an increase in sensitivity. The result is a substantial improvement in the quality of data obtained when using external calibration for LA-ICP-MS.

The use of absorbing chromophore binders has been shown to offer a robust calibration method for the quantitative analysis of powdered samples using simple external calibration. The data produced would be fit-for-purpose in many practical analytical
applications. The technique is simple and employs commonly available laboratory reagents and equipment.
References


Chapter 5
Isotopic Dilution for Quantitation by Laser Ablation
Inductively Coupled Plasma Mass Spectrometry
Chapter Abstract

Two techniques allowing the absolute quantitation technique of isotope dilution to be used in conjunction with laser ablation sampling have been developed. A detailed look at the theory and nomenclature is presented for both strategies. Both strategies are variations of the work previously described in chapters three and four, modified to allow the incorporation of an isotopic spike solution.

In the first technique for consolidated solids, introduction of the isotopic spike solution was via a nebuliser and spray chamber arrangement in accordance with the online additions approach. The second technique allowed incorporation of the isotopic spike in a powdered sample before subsequent pressing into a disc.

Importantly, the basic theory of isotope dilution is derived in a form that is suitable for LA-ICP-MS and enables it to be applied in various modes.

Both techniques have been validated by analysis of certified reference materials; NIST 612 glass for the online additions strategy; GBW 07311 Sediment, GBW 07401 Soil and NIST 1547 Peach Leaves for the pressed powder technique.
Introduction

The technique of isotope dilution mass spectrometry (ID-MS) was initially developed for elemental analysis during the 1950's using Thermal Ionisation Mass Spectrometry (TIMS). More recently Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has been used in conjunction with ID-MS for elemental analysis, since it offers the highest accuracy and precision, and typically requires much less sample preparation. Elemental ID-MS uses an enriched isotope of the target analyte as the optimal form of internal standardisation, the isotopic ‘spike’ being added at the earliest possible stage in the analytical process.¹,²

<table>
<thead>
<tr>
<th>Terminology</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spiking</td>
<td>Addition of an isotopically enriched material to a natural calibration standard or sample.</td>
</tr>
<tr>
<td>Blend</td>
<td>The mixture obtained by spiking a natural calibration standard or sample with an enriched material.</td>
</tr>
<tr>
<td>Spike isotope ratio</td>
<td>The ratio of the amounts of the natural and enriched isotopes in the material used for spiking.</td>
</tr>
<tr>
<td>Natural isotope ratio</td>
<td>The ratio of the amounts of the natural and enriched isotopes in either the natural calibration standard or the sample.</td>
</tr>
<tr>
<td>Blend isotope ratio</td>
<td>The ratio of the amounts of the natural and enriched isotopes in the blend.</td>
</tr>
</tbody>
</table>

ID-MS can be considered as a definitive method with definable uncertainty values because as a ratio measurement technique it can be described completely in terms of a measurement equation. This is reflected in the fact that it is widely used by national measurement institutes for the validation of CRMs.²

Optimum Spike Levels²

The exact signal matching approach to ID-MS involves an iterative adjustment procedure requiring isotopic ratio measurements for many gravimetrically prepared ‘blends’ containing the enriched (spike) isotope, and either the unknown sample or a natural calibration standard. This process culminates in calibration and sample blends that are exactly matched in that they have the same concentration of analyte isotope in the spiked sample and the spiked calibration standard. Ideally the ratio of the analyte...
isotope to the spike isotope in each sample and standard blend should be equal to 1. This results in low uncertainties, since systematic errors in the determination of the isotopic ratios are cancelled out under exactly matched conditions. However, this approach can become laborious as several iterations may be required, as well as the fact that it is not always feasible to achieve the blend isotope ratio of 1.

The approximate signal matching approach to ID-MS provides a less onerous alternative to the exact signal matching technique. This technique is essentially the same, but requires less iterations, whilst still retaining many of the advantages of the exact signal matching. In this approach, the two approximately matched sample and standard blend are run alternatively to provide a series of replicate measurements which can be averaged as with the exact signal matching approach.

Regardless of the calibration strategy employed there are a number of factors which must be considered to determine the optimum spike ratio and minimise error, whilst maximising the measurement precision for each ID-MS application. These factors include the 'error propagation' and the characteristics of the mass spectrometer (precision, ion counting uncertainty, background, linear dynamic range and detector dead time). This error propagation factor is a theoretical optimum for spiking samples to achieve the best precision for the ratio measurement, and can be calculated from the isotopic abundances in the natural sample and the isotopically enriched spike and is dependent upon the isotope system being employed.

As discussed above the optimum blend isotope ratio is as close as possible to 1, but achieving this often leads to practical problems e.g.

1. Samples with high analyte concentration require large quantities of expensive spike which is often impractical since the spike is only available as a dilute solution.

2. The uncertainty at very low analyte concentration is high since both isotope measurements may be close to detection limits leading to an imprecise isotope ratio measurement.
3. For some analytes the only desirable spike is radioactive, making it desirable to use very low analyte concentrations.

**Isotope Ratio Measurements using LA-ICP-MS**

ICP-MS will, for many elements, gradually replace TIMS as the method of choice for the direct determination of isotopic ratios in solid samples. This can be attributed to instrumental developments for both single and multi-collector ICP-MS. The major limitation for the determination of accurate and precise isotopic ratios by LA-ICP-MS lays in the instability of the ICP and the ablation process itself. Instrumental developments have therefore focused upon improving the ablation regime, the stability of the ICP, and the sample introduction of ablated matter into the ICP. A great deal of work has gone into the development of multiple ion detection systems.

The most frequently employed LA-ICP-MS systems utilise quadrupole technology. Using single collector instrumentation the uncertainty budget is dominated by the precision of measurement of the isotopic ratios. A key advantage of quadrupole instruments is their ability to scan rapidly across a broad mass range; however, for isotopic ratio measurements, individual isotopes are ideally monitored for a much longer time duration which may not be possible in LA measurements. Operating in peak jumping mode, the quadrupole is inherently unstable in its mass stability and therefore not suited to highly accurate and precise ratio measurements. Using optimised measurement strategies typical isotope ratio precisions between 0.1 and 0.5% RSD can be obtained. Incorporation of a collision cell can improve the isotope ratio precision for quadrupole instrumentation not only by the reduction of interferences, but by reducing the ion energy spread resulting in greater ion transmission.

Alternatively, Allen *et al.* utilised a twin quadrupole instrument for the simultaneous determination of LA-ICP-MS. This arrangement yielded an isotopic ratio measurement precision of 0.06 – 1% RSD for the measurement of $^{52}$Cr/$^{53}$Cr in a NIST 1263 steel reference material.

LA in combination with double focusing sector field instrumentation, with a single ion detection system is advantageous for accurate and precise isotope ratio measurements at trace and ultra-trace levels. This instrumentation offers flat-topped peaks when operated...
under low resolution conditions in comparison to quadrupole instrumentation, which allows for measurement precisions in the order of 0.1% RSD.\textsuperscript{5} If higher resolution is required then this measurement precision falls due to reduced sensitivity and loss of flat-top peak shape.\textsuperscript{6}

The best isotope ratio measurement precision for LA-ICP-MS, down to 0.005 %RSD, is possible by utilising sector field instrumentation with multiple ion collectors, for the simultaneous detection of mass separated ion currents.\textsuperscript{6} This instrumentation has opened the way for analysis of complex matrix samples by ID-MS, with uncertainties achievable by few other techniques. Walder\textsuperscript{7} first demonstrated the potential of LA-ICP-MS for direct, very high precision isotope ratio measurements on solid samples. This work demonstrated, by measuring Pb ratios in NIST glass, that LA-ICP-MS could provide isotope ratios in agreement with TIMS and of comparable precision. In this work, using craters of just 30 µm, % RSDs in the order of 0.09% were obtained whilst monitoring the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio. This pioneering work was followed by in-situ isotopic analysis of various elements in a wide variety of sample types using LA-ICP-ID-MS.\textsuperscript{8,9}

**Current Work**

In this work two approaches have been used allowing the absolute quantitation technique of isotopic dilution to be used in conjunction with LA-ICP-MS. ID-MS should prove to be a powerful quantification strategy for LA, especially in the absence of matrix matched CRMs. The ID-MS measurement corrects for fractionation effects since it relies on measurement of isotopes of the same element. If homogenous distribution of the spike and analyte is achieved, all fractionation effects are eliminated by the ratio measurement of the isotope diluted sample.

The first approach as reported by Becker \textit{et al.}\textsuperscript{10} uses the dual sample/standard approach as described in chapter three and hence the aqueous isotopic spike was introduced online using a nebuliser and spray chamber arrangement. The advantage of this method is the lack of necessary sample preparation; however the limiting factor is the different forms the sample and spike are introduced into the plasma in. Using this approach it is also difficult to ensure complete equilibrium between the sample and spike, greatly limiting the potential of the technique to deliver precise and accurate analytical data.
One further limitation is that the relative mass flux between the two sample introduction lines requires characterisation, meaning an internal standard element of known concentration is required within the sample. In previous work utilising solution nebulisation to introduce the isotopic spike solution, a relative sensitivity factor (RSF) was used to correct for the relative sensitivities of the two sample introduction sources. This RSF was not determined by ID-MS, and hence its use introduces a large uncertainty into the final analyte determination, eliminating the benefits of analyte determination by ID-MS. To maintain the benefits offered by ID-MS, the ID-MS process needs to be performed twice, once for the internal standard element to characterise the relative mass flux rates between the two sources, and again for the analyte element.

The second approach as developed by Heumann et al. incorporates the isotopic spike into a powdered sample before subsequent pressing into a disc as described in chapter four. The advantage of this technique is that only one sample introduction line is used, and in theory the relative mass flux between sample and spike is gravimetrically determined, such that an internal standard element is not necessary.

It is vital that the spike is added in such a way that homogeneity is achieved. In the work of Heumann et al. homogenization of the isotope-diluted sample was achieved by suspending the sample powder in the spike solution, followed by evaporation of the suspension to dryness. The resulting mixture was pressed into a disc using mechanical means. The detrimental effects of spike/analyte in-homogeneity were reduced by employing a special LINA-Spark-Atomiser laser system (Gothenburg, Germany). By focusing of the laser approximately 15 mm behind the sample surface and use of pulse energies up to 350 mJ, the isotope-diluted sample was first molten and then evaporated, which equilibrated the analyte with the spike. A large variety of different samples were analyzed by LA-ICP-ID-MS, including alkaline earth fluorides, sediments, and biological samples.

This work aims to tie the two LA-ICP-ID-MS approaches together and make them more approachable to the analyst not so familiar with ID-MS strategies. This is achieved using simplified and common nomenclature.
Theory and Nomenclature

Nomenclature

- $m$ = mass flow rate
- $A$ = Abundance %
- $C$ = Concentration

Superscript

- $^\text{Sample}$ = Sample e.g. NIST 612 or GBW 07311/07401
- $^\text{Spike}$ = Isotopically enriched spike solution e.g. NIST 983

Subscript

- $^1$ = Isotope 1
- $^2$ = Isotope 2
- $^\text{Element}$ = Element of interest e.g. elemental mass flow ratio
- $^F$ = Flux e.g. mass flux ratio

Online Addition of an Isotopic Spike to Determine Mass Flow Ratio

\[
\dot{m}_1 = \left( \dot{m}_{\text{Element}}^{\text{Spike}} \times A_1^{\text{Spike}} \right) + \left( \dot{m}_{\text{Element}}^{\text{Sample}} \times A_1^{\text{Sample}} \right)
\]  

\[
\dot{m}_2 = \left( \dot{m}_{\text{Element}}^{\text{Spike}} \times A_2^{\text{Spike}} \right) + \left( \dot{m}_{\text{Element}}^{\text{Sample}} \times A_2^{\text{Sample}} \right)
\]  

Taking ratios yields;

\[
\frac{\dot{m}_1}{\dot{m}_2} = \left( \frac{\dot{m}_{\text{Element}}^{\text{Spike}}}{\dot{m}_{\text{Element}}^{\text{Sample}}} \times A_1^{\text{Sample}} \right) + A_1^{\text{Sample}}
\]  

\[
\frac{\dot{m}_2}{\dot{m}_1} = \left( \frac{\dot{m}_{\text{Element}}^{\text{Spike}}}{\dot{m}_{\text{Element}}^{\text{Sample}}} \times A_2^{\text{Sample}} \right) + A_2^{\text{Sample}}
\]

Where $\dot{m}_1$ is the measured isotopic ratio and $\dot{m}_{\text{Element}}^{\text{Spike}}$ is the elemental mass flux ratio.

Substitution and multiplication yields;
Rearranging yields the elemental mass flow ratio as;

$$\frac{m_{\text{Sample}}}{m_{\text{Element}}} \cdot \frac{m_{\text{Spike}}}{m_{\text{Sample}}} \times A_2 = \left( \frac{m_{\text{Sample}}}{m_{\text{Element}}} \times A_2 \right) + \left( \frac{m_{\text{Sample}}}{m_{\text{Element}}} \times A_1 \right) + A_1$$

This elemental mass flow is not the same as the mass flux ratio since we need to account for the relative concentrations of the sample and spike e.g.

$$m_{\text{Element}} = m_{\text{Flux}} \times C_{\text{Element}}$$

$$m_{\text{Sample}} = m_{\text{Flux}} \times C_{\text{Sample}}$$

Thus;

$$\frac{m_{\text{Flux}}}{m_{\text{Sample}}} \cdot \frac{m_{\text{Spike}}}{m_{\text{Element}}} \times C_{\text{Element}} = \frac{m_{\text{Sample}}}{m_{\text{Element}}} \times C_{\text{Sample}}$$

This approach can be performed using an element of known concentration to determine the mass flow ratio. In a similar approach as used in chapter three, this mass flow ratio can be used in the quantification of an unknown element. So in effect the LA-ICP-MS method is performed twice, once using an internal standard element to determine the mass flow ratio, and once for the quantification of an unknown. Knowing the mass flow ratio allows calculation of the analyte concentration according to equation 21.
The same theory can be utilised for the pressed powder approach. In this scenario, the mass flow ratio is determined gravimetrically via gravimetric addition of the spike solution to the powdered mixture prior to pressing.

This method offers the advantage that no internal standard element is necessary to determine the mass flow ratio prior to analyte determination. That is to say that the LA-ICP-ID-MS procedure is only performed once and not twice as in the online additions procedure. This is a major advantage since no prior knowledge of the sample is required.

\[
C_{Sample} = \left( \frac{\frac{m_{Spike}}{m_{Sample}}}{\frac{m_{Spike}}{m_{Sample}}} \right) \]

(21)

**Pressed Powder Approach**

The same theory can be utilised for the pressed powder approach. In this scenario, the mass flow ratio is determined gravimetrically via gravimetric addition of the spike solution to the powdered mixture prior to pressing.

This method offers the advantage that no internal standard element is necessary to determine the mass flow ratio prior to analyte determination. That is to say that the LA-ICP-ID-MS procedure is only performed once and not twice as in the online additions procedure. This is a major advantage since no prior knowledge of the sample is required.
Chapter Five

Experimental

Instrumentation
A commercially available UP-213 Laser Ablation System (New Wave Research Inc., Huntingdon, Cambridgeshire, UK) operating in the deep UV (213 nm) was employed using He as a carrier gas due to its improved ablation and transport characteristics.\textsuperscript{15-17} Figure 48 shows the experimental arrangement used throughout the investigation. The sample aerosol from the LA system was combined with the standard aerosol from a PFA-20 μL Fixed Capillary Nebuliser (Elemental Scientific Inc., Omaha, Nebraska, USA) and custom made cyclonic spray chamber, using a custom made aerosol combination device. With this arrangement a wet plasma resulted. The two 1 m, Tygon\textsuperscript{TM}, sample introduction lines were combined, using the custom made device, 1 m before the ICP torch.

For the pressed powder approach, in order to reduce the detrimental effects of non homogenous distribution of sample and spike solution, the laser beam size was increased using the beam expansion mode of the UP213 Laser Ablation System. A feature of this 'auto-switchable' system is that spot sizes between 4 and 110 μm can be selected employing a constant energy density via true aperture imaging; when larger spot sizes are required, typically for bulk analysis, the beam can be expanded via beam expansion mode but with an associated loss in energy density. The presence of the vanillic acid, ensured that although the energy density was reduced using the 250 μm spot size, there was still sufficient energy to perform the ablation process. If no vanillic acid were present it is doubtful that the energy required for ablation could be achieved at this large spot size.

A Neptune multi-collector ICP mass spectrometer (ThermoFisher Scientific, Bremen, Germany) was used for the isotopic work to determine isotope ratios with superior isotope ratio precision. The instrument has a detector array that comprises of nine faraday detectors. Standard operating conditions used in this investigation are detailed in Table 31. A He gas flow of 0.7 L min\textsuperscript{-1} was found to give optimum sensitivity and a good peak shape upon single shot ablation of NIST 612 Trace Elements in Glass (NIST, Gaithersburg, USA), and importantly had no detrimental effects on the signal intensity.
obtained upon solution nebulisation when the two sample introduction sources were combined. Table 31 lists the experimental parameters employed. The laser conditions were chosen to represent those typically used in bulk analysis by LA-ICP-MS.

Figure 48 A schematic of the system used for LA-ICP-MS analysis. A PFA nebuliser and custom made cyclonic spray chamber was employed to introduce the isotopic spike solutions in the online additions approach.

Table 31 Experimental parameters used in the investigation.

<table>
<thead>
<tr>
<th>Laser Ablation System</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>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>Fluence</td>
<td>13 J cm$^{-2}$ (online additions approach)</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>20 Hz</td>
</tr>
<tr>
<td>Sampling strategy</td>
<td>Raster</td>
</tr>
<tr>
<td>Spot diameter</td>
<td>110 µm (online additions approach)</td>
</tr>
<tr>
<td></td>
<td>250 µm (pressed powder approach)</td>
</tr>
<tr>
<td>Solid samples</td>
<td>NIST 612 Trace Elements in Glass (online additions approach)</td>
</tr>
<tr>
<td></td>
<td>GBW 07311 Sediment (pressed powder approach)</td>
</tr>
<tr>
<td></td>
<td>GBW 07401 Soil (pressed powder approach)</td>
</tr>
<tr>
<td></td>
<td>NIST 1547 Peach Leaves (pressed powder approach)</td>
</tr>
<tr>
<td>Binder</td>
<td>Vanillic acid (pressed powder approach)</td>
</tr>
<tr>
<td>Sample translation rate</td>
<td>10 µm s$^{-1}$</td>
</tr>
<tr>
<td>He gas flow</td>
<td>0.7 L min$^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solution Nebulisation</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nebuliser</td>
<td>PFA-20 µL Fixed Capillary</td>
</tr>
<tr>
<td>Ar carrier gas flow</td>
<td>0.95 L min$^{-1}$</td>
</tr>
<tr>
<td>Spray chamber</td>
<td>Custom cyclonic</td>
</tr>
</tbody>
</table>
ICP-MS

<table>
<thead>
<tr>
<th>Type</th>
<th>Neptune Multicollector ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auxiliary gas flow</td>
<td>1.0 L min(^{-1})</td>
</tr>
<tr>
<td>Cooling gas flow</td>
<td>13.5 L min(^{-1})</td>
</tr>
<tr>
<td>Plasma RF power</td>
<td>1175 W</td>
</tr>
<tr>
<td>Isotopes monitored</td>
<td>(^{106})Cd, (^{111})Cd, (^{203})Tl, (^{204})Pb, (^{205})Tl, (^{206})Pb, (^{207})Pb, (^{208})Pb</td>
</tr>
</tbody>
</table>

Sample Preparation

Solid Samples

For the online additions approach, NIST 612 Trace Elements in Glass (NIST, Gaithersburg, USA) was used, since it is known to be homogenous and is well characterised for a wide range of analyte elements. No sample preparation was performed except the chemical cleaning of the glass surface with dilute nitric acid.

For the pressed powder approach, discs were prepared using the method described previously in chapter four. A blank disc was prepared from vanillic acid only, whilst ‘sample discs’ were prepared using 60% sample and 40% vanillic acid as described previously for optimum sensitivity. ‘Sample and spike blend discs’ were prepared using 60% sample and 40% sample but with the addition of the aqueous isotopic spike.

A disc was prepared, from vanillic acid only, but spiked with NIST 981 (NIST, Gaithersburg, USA) to produce a concentration of 5 mg L\(^{-1}\) within the final disc. NIST 981 is an isotopically characterised lead solution and this disc was prepared to determine the homogeneity achievable using the proposed spiking methodology.

Spike Incorporation into Absorption Modified Pressed Discs

One of the major advantages of producing pressed discs is that they allow the incorporation of an internal standard element to correct for differences in rates of ablation, or of an isotopic spike solution allowing quantitation by isotope dilution (ID). One important consideration, which is often a limitation in this type of sample preparation, is that the internal standard element or isotopic spike must be homogenously distributed throughout the disc surface.

This isotopic spike was added in aqueous form prior to homogenisation in the ball mixer. In this case, 50 \(\mu\)L of NIST 983 spike solution was added gravimetrically, the concentration of which varied depending upon the sample. This concentration varied in
order to yield the optimum spiking ratio of 1 and was therefore dependent upon the concentration of analyte within the sample. This is why a regular external calibration is often required before ID-MS analysis to help determine the quantity of isotopic spike to add. The compositions of all the discs can be viewed in Table 32.

Table 32 Composition of various discs used in the LA-ICP-ID-MS process.

<table>
<thead>
<tr>
<th>Disc description</th>
<th>Mass of NIST 983 isotopic spike (g)</th>
<th>Mass of sample (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass of vanillic acid (g)</td>
<td>140 µg g⁻¹</td>
</tr>
<tr>
<td>Blank</td>
<td>0.40000</td>
<td>-</td>
</tr>
<tr>
<td>Soil sample</td>
<td>0.16146</td>
<td>-</td>
</tr>
<tr>
<td>Sediment sample</td>
<td>0.16200</td>
<td>-</td>
</tr>
<tr>
<td>Peach leaves</td>
<td>0.16258</td>
<td>-</td>
</tr>
<tr>
<td>Sediment sample</td>
<td>0.16157</td>
<td>0.04980</td>
</tr>
<tr>
<td>Peach leaves</td>
<td>0.16054</td>
<td>0.05269</td>
</tr>
<tr>
<td>Sediment sample</td>
<td>0.16073</td>
<td>-</td>
</tr>
</tbody>
</table>

A one hour drying period at 60 °C was used prior to the homogenisation period in the ball mixer before subsequent pressing into discs using the method previously described in chapter four.

Aqueous Standard Preparation

For both the online additions approach and the pressed powder approach, isotopic spike solutions were prepared from NIST 983 (NIST, Gaithersburg, USA). The concentration of the spike solution was varied in order to achieve a measured ratio close to 1. For the online additions approach a Cd spike solution was prepared from a Technolab stock solution (Fisher Scientific, Loughborough, UK).

For the pressed powder approach a solution of NIST 981 was prepared, and used in the homogeneity testing of the spiking method as previously discussed. The certified isotopic composition of both reference materials is given in Table 33.
Table 33 The certified isotopic composition of NIST 983 and NIST 981.

<table>
<thead>
<tr>
<th>Reference Material</th>
<th>$^{206}$Pb</th>
<th>$^{207}$Pb</th>
<th>$^{208}$Pb</th>
<th>$^{209}$Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST 983</td>
<td>0.0342 ± 0.0020</td>
<td>92.1497 ± 0.0041</td>
<td>6.5611 ± 0.0025</td>
<td>1.2550 ± 0.0022</td>
</tr>
<tr>
<td>NIST 981</td>
<td>1.4255 ± 0.0012</td>
<td>24.1442 ± 0.0057</td>
<td>22.0833 ± 0.0027</td>
<td>52.3470 ± 0.0086</td>
</tr>
</tbody>
</table>

Online Additions Procedure

Devices to Combine Two Aerosol Streams

As already discussed isotope dilution is a definitive quantification strategy; however, in order to obtain the benefits offered by this quantification strategy it is vital that equilibrium exists between the sample and the spike. This is often a limiting step for many isotope dilution strategies, and even for strategies based upon regular internal standardisation. In the case of the online additions approach attaining this equilibrium between sample and spike is difficult since they are present in two different aerosol streams; hence efficient mixing of these two aerosol streams is vital.

In previous work a simple Y-piece was used to combine the two aerosol streams; however in the proposed isotope dilution strategy the degree of mixing offered by this Y-piece was thought to be insufficient to produce equilibrium between sample and spike. Hence, various devices were tested to determine the most efficient way of combining the two aerosol streams, and compared to the simple Y-piece already used. One device was based upon a coaxial combination, whereas two further devices employed a cyclonic arrangement incorporating the nebuliser and spray chamber. These devices can be seen in Figure 49, Figure 50 and Figure 51. Further details of the most successful device can be viewed in the appendices.
Figure 49 A photograph of the coaxial device designed to mix two aerosol streams.

Figure 50 A photograph of a cyclonic device designed to mix two aerosol streams.
Figure 51 A photograph of an improved cyclonic device designed to mix two aerosol streams.

Calibration

Pb (204, 206, 207 and 208) isotopes were first monitored to determine the mass flow ratio, meaning that in this case Pb was acting as an internal standard element. The multiple cycle capability of the instrument was utilised, enabling switching to other masses, such as $^{111}$Cd/$^{106}$Cd, to determine analyte concentration. In this scenario, there was a minimum 3 second difference between measuring the mass flow ratio and measuring the sample ratio as the instrument switches between cycles and the magnet field equilibrates.

These isotopes were first monitored during ablation of the NIST 612 Trace Elements in Glass. 5% HNO$_3$ was nebulised throughout this monitoring period. The HNO$_3$ was then replaced by the spike solution containing NIST 983 at a concentration of 20.001 ng g$^{-1}$, so that simultaneous ablation of the sample and nebulisation of the spike solution occurred. This concentration was required to give optimum spiking levels (a $^{208}$Pb/$^{206}$Pb ratio close to 1). Finally, ablation ceased and the isotopes were monitored whilst nebulisation of the spike solution occurred. Helium was passed through the ablation cell throughout the whole measurement process.
Since the Pb concentration within the NIST 612 CRM was known prior to analysis, LA-ICP-ID-MS was performed to yield the mass flow ratio. This mass flow ratio, calculated for Pb, was then applied to the quantification of Cd.

**Pressed Powder Approach Procedure**

The strategy was simpler for the pressed powder approach since the mass flow ratio was determined gravimetrically via gravimetric addition of the spike solution to the powdered mixture prior to pressing.

The $^{208}\text{Pb}^{206}\text{Pb}$ ratio was measured whilst ablating a line pattern, approximately 5 mm long, across the surface of the discs. The process was performed for a disc containing only 60% sample and 40% vanillic acid, and for a disc of the same composition except with the addition of an isotopic spike solution. This data allowed determination of the Pb concentration within the samples, according to equation 21.
Results and Discussion

Online Additions Approach

Combining Aerosol Stream

As discussed previously it is vital that equilibrium occurs between the spike solution introduced via solution nebulisation and the sample introduced via LA. For this reason a quick test was performed to determine the best method of mixing the two aerosol streams. The precision of the measured isotope ratio $^{208}\text{Pb}/^{206}\text{Pb}$ was used as an indication as to the effectiveness of the devices.

Poor measurement precision was obtained for the Y-piece and the coaxial device. Interestingly, utilisation of the coaxial device also led to a reduction in sensitivity which was attributed to the large dead volume of the outer chamber. It was thought that this device would prove more successful if redesigned with a smaller outer chamber. The first cyclonic chamber, in which the LA aerosol stream and the nebulised solution aerosol stream are introduced perpendicularly led to improved measurement precision in comparison to the Y-piece and the coaxial device, but it was observed that the signal intensity from the LA component of the total aerosol stream was much reduced. This was attributed to a conflict in gas flows within the chamber.

The benefits of improved measurement precision, and high sensitivity for both components of the aerosol, were offered by the improved design of the cyclonic chamber. In this design, the LA aerosol stream and the nebulised solution aerosol stream were introduced on the same plane. This device was selected for the remainder of the project, and utilised in all calibrations based upon the online additions approach.
Chapter Five

Calibration

Table 34 Calculation of mass flow ratio between two sample introduction sources e.g. a laser ablation system and nebuliser arrangement. The mass flow ratio was calculated by online isotope dilution.

<table>
<thead>
<tr>
<th>Isotope label</th>
<th>m1</th>
<th>m2</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z</td>
<td>206</td>
<td>208</td>
</tr>
<tr>
<td>Sample % abundance SRM612</td>
<td>24.2637</td>
<td>52.3730</td>
</tr>
<tr>
<td>Spike % abundance SRM983</td>
<td>92.1497</td>
<td>1.2550</td>
</tr>
<tr>
<td>Sample abundance SRM612</td>
<td>0.242637</td>
<td>0.52373</td>
</tr>
<tr>
<td>Spike abundance SRM983</td>
<td>0.921497</td>
<td>0.01255</td>
</tr>
<tr>
<td>Pb spike concentration (fraction)</td>
<td></td>
<td>2.00E-08</td>
</tr>
<tr>
<td>Pb sample concentration (fraction)</td>
<td></td>
<td>3.86E-05</td>
</tr>
<tr>
<td>Measured isotope ratio 207/206</td>
<td></td>
<td>0.3023</td>
</tr>
<tr>
<td>Measured isotope ratio 208/206</td>
<td></td>
<td>0.6085</td>
</tr>
<tr>
<td>Calculated elemental mass flow ratio</td>
<td></td>
<td>0.6864</td>
</tr>
<tr>
<td>Calculated mass flow ratio (spike/sample)</td>
<td></td>
<td>1320</td>
</tr>
</tbody>
</table>

This determination yields a mass flow ratio of 1320, meaning that in this scenario there is 1320 times more mass flux from the nebuliser introducing the spike solution, than from the laser ablation system introducing the sample. Although this value is a lot less than that obtained in chapter three (a mass flow ratio of 14,261 was obtained) this is as to be expected due to variation in solution nebulisation and ICP parameters. For example a 20 µL min⁻¹ nebuliser was employed rather than a 100 µL min⁻¹ nebuliser as employed in chapter three.

As discussed, the mass flow ratio calculated above can be used in the determination of analyte concentration. The results obtained, using the mass flow ratio calculated from LA-ICP-MS of Pb, for the determination of Cd can be seen in Table 35.
Table 35 Calculation of analyte concentration by online isotope dilution. Utilises the mass flow ratio calculated previously from ID-MS of Pb.

<table>
<thead>
<tr>
<th>Isotope label</th>
<th>m/l</th>
<th>m/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z</td>
<td>106</td>
<td>111</td>
</tr>
<tr>
<td>Sample % abundance SRM612</td>
<td>1.25</td>
<td>12.80</td>
</tr>
<tr>
<td>Spike % abundance Technospike</td>
<td>79.103</td>
<td>2.6</td>
</tr>
<tr>
<td>Sample abundance SRM612</td>
<td>0.01250</td>
<td>0.12800</td>
</tr>
<tr>
<td>Spike abundance Technospike</td>
<td>0.79100</td>
<td>0.02600</td>
</tr>
<tr>
<td>Cd spike concentration (fraction)</td>
<td>5.00E-09</td>
<td></td>
</tr>
<tr>
<td>Measured isotope ratio 111/106</td>
<td>0.6329</td>
<td></td>
</tr>
<tr>
<td>Certified Cd concentration 1 (µg g⁻¹)¹⁸</td>
<td>27.63 ± 1.09</td>
<td></td>
</tr>
<tr>
<td>Certified Cd concentration 2 (µg g⁻¹)¹⁸</td>
<td>28.92 ± 1.76</td>
<td></td>
</tr>
<tr>
<td>Calculated Cd concentration (µg g⁻¹)</td>
<td>26.24 ± 1.51</td>
<td></td>
</tr>
<tr>
<td>Recovery certified concentration 1 (%)</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>Recovery certified concentration 2 (%)</td>
<td>91</td>
<td></td>
</tr>
</tbody>
</table>

Using this strategy, recoveries of 95 and 91% of the certified values¹⁸ were obtained. As per the non ID-MS online additions approach utilised in chapter three, the major limitation for quantitative analysis was relative fractionation between Pb and Cd. To minimise the effect of fractionation it is vital to select an internal standard that behaves in exactly the same manner as the analyte.

It should be noted that the uncertainty associated with the calculated Cd concentration is based upon the expanded uncertainty of the entire measurement process. This was calculated using a spreadsheet produced by LGC. A detailed breakdown of this expanded uncertainty is beyond the scope of this work, but it is fair to say that measurement precision of the isotopic ratios was a major contribution.

Pressed Powder Approach

Homogeneity Testing

It was possible to add 50 µL of isotopic spike solution, and achieve a homogeneity adequate for the ID-MS process, providing homogenisation in a ball mixer was employed. This can be seen graphically in Figure 52 and numerically in Table 36.
Chapter Five

Figure 52 A chart to show the homogenous distribution of Pb, added to pure vanillic acid in the form of a 50 µL spike solution. Analysis is over a 12 mm line across the disc surface. The disc was spiked to produce a final Pb concentration of 5 ppm.

Table 36 A table to show the mean signal intensity of various Pb isotopes, the associated standard deviation and % RSD, shown as an indication of the homogeneity of the Pb distribution. The achievable isotope ratio precision is also listed.

<table>
<thead>
<tr>
<th>Pb</th>
<th>Pb 206</th>
<th>Pb 207</th>
<th>Pb 208</th>
<th>207/206</th>
<th>208/206</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean signal intensity (V)</td>
<td>0.53</td>
<td>0.49</td>
<td>1.17</td>
<td>0.92</td>
<td>2.20</td>
</tr>
<tr>
<td>Standard deviation (V)</td>
<td>0.019428</td>
<td>0.017915</td>
<td>0.042839</td>
<td>0.002548</td>
<td>0.006521</td>
</tr>
<tr>
<td>RSD %</td>
<td>3.66%</td>
<td>3.66%</td>
<td>3.67%</td>
<td>0.28%</td>
<td>0.30%</td>
</tr>
</tbody>
</table>

Calibration

The Pb concentrations calculated using the LA-ICP-ID-MS pressed powder approach, and their agreement with the certified Pb concentrations are shown numerically in Table 37.

It can be seen that the success of the quantification varied according to the CRM used. It was thought that the homogeneity and particle size distribution of the CRMs was a major factor.
Table 37 A table to show the certified and calculated Pb concentrations for three CRMs, using the pressed powder approach.

<table>
<thead>
<tr>
<th>Certified Reference Material</th>
<th>Certified value with associated uncertainty (µg g⁻¹)</th>
<th>Calculated value with associated uncertainty (µg g⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GBW 07401 Soil</td>
<td>98.00 ± 16.66</td>
<td>83.39 ± 4.17</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>81.03 ± 4.05</td>
<td>83</td>
</tr>
<tr>
<td>GBW 07311 Sediment</td>
<td>636.00 ± 69.96</td>
<td>605 ± 30</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>611 ± 31</td>
<td>96</td>
</tr>
<tr>
<td>NIST 1547 Peach Leaves</td>
<td>0.870 ± 0.030</td>
<td>0.892 ± 0.04</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.875 ± 0.04</td>
<td>101</td>
</tr>
</tbody>
</table>

Analysis of GBW 07401 yielded recoveries of 83 and 85%. However, there is a large degree of overlap of the associated uncertainties for the calculated and certified values. This indicates that the determination of Pb has been successful in this case. However, the poor “quality” of the CRM, as indicated by the large uncertainty in the Pb concentration, has made the determination appear more successful than is probably the case.

Analysis of GBW 07311 CRM yielded recoveries of 95 and 96%, which is much superior to the recoveries obtained during analysis of GBW 07401. In this case the “quality” of the CRM may have been slightly better, as indicated by the smaller uncertainty on the certified Pb concentration (±11% for GBW 07311, in comparison to ±17% for GBW 07401).

Analysis of NIST 1547 Peach Leaves proved very successful when using this approach, yielding recoveries of 101 and 102%. This analysis demonstrates the capability of the strategy for analyte determinations at sub ppb levels. The fact that this particular analysis was so successful would suggest that the quality of the sample/CRM with respect to particle size and homogeneity is exceptionally important. Prior to analysis it was observed that the NIST 1547 CRM was of a much finer particle size distribution, and visually appeared to be more homogenous. This was reflected in the quality of disc produced, which appeared to have a smoother, less granular finish. Ultimately, this is reflected in the quality of the analytical data obtained upon analysis.
The dependency of the quality of analytical data on the particle size and homogeneity of the samples would suggest that the sample preparation steps are of major importance. For this strategy to be applicable to a wide variety of 'real sample' an improved milling process may be necessary. This milling would need to reduce the particle size of the sample to an acceptable value, and also facilitate homogenisation of the sample and vanillic acid binder.
Chapter Conclusion

Two ICP-ID-MS strategies have been investigated in conjunction with LA sampling. The online additions strategy, in which the isotopic spike solution is introduced into the ICP via solution nebulisation yielded a Cd concentration in agreement with the certified concentration. Recoveries of 91 and 95% of the certified concentrations were obtained. These recoveries are an improvement of the Cd recoveries yielded in chapter three of 71 and 75%. This result has demonstrated the capability of this strategy for trace element determination in solid samples. The downside of this strategy is that it is dependent upon prior knowledge of the sample. As per the online additions strategy discussed in chapter three, an internal standard element of known concentration within the sample, is required to determine the relative mass flow rates of the two sample introduction sources. The fact that a mass flow ratio is determined from ID-MS of one element, and applied to the quantification of another element, removes a fundamental advantage of ID-MS methodology, in that the effects of relative fractionation between the internal standard element and the analyte are re-introduced.

The pressed powder approach, in which the isotopic spikes were mixed with the powdered samples prior to homogenisation and pressing, showed excellent capabilities. For the best quality CRM, NIST 1547, recoveries of 101 and 102% of the certified Pb concentration were obtained. The major advantage of this approach is that no prior knowledge of the sample is necessary (notwithstanding that an approximation of analyte concentration will help determine the optimum spike levels) – analysis relies on ID-MS performed on only the analyte, and not an internal standard element. This is of major relevance when LA is employed as a sample introduction source, since fractionation is eliminated by the ratio measurement of the isotope diluted sample.

One limitation of the pressed powder technique is the degree of homogenisation between analyte and isotopic spike that it is possible to achieve, particularly when a binder is employed since it is notoriously difficult to mix two powders. The use of a mixer mill has been shown to produce discs of adequate homogeneity for the LA-ICP-ID-MS procedure. To reduce the detrimental effects of heterogeneity between the spike and analyte it is vital that as large a sampling area as possible is employed, to average out these heterogeneities. This can be achieved using long sampling lines or rasters.
(which ultimately leads to an increased analysis time) and by selecting the largest laser beam spot size. By employing vanillic acid as a binder in this work, a larger spot size than would typically be available due to a reduction in energy densities, has been made available. This can be attributed to the lower energy densities required for efficient ablation of the sample materials, when vanillic acid is employed.

This work has determined that the addition of an isotopic spike solution to a powdered sample pressed with an absorbing chromophore matrix, before subsequent LA-ICP-MS, is the method of choice for direct determination of trace elements in powdered samples.
References


Chapter 6

Thesis Conclusions and Further Work
Online Additions

Chapter three demonstrated the online additions of aqueous standards for the calibration of LA-ICP-MS. Although the strategy devised was ultimately to be employed for quantification of analyte concentration in the absence of matrix matched calibration standards, it was realised early on that the method allowed a detailed investigation of fundamental processes occurring within the ICP. Measuring the relative elemental sensitivity allowed investigation of element specific matrix effects caused by mass loading effects upon introduction of the LA aerosol. It was demonstrated that these matrix effects, linked to sample loading, plasma robustness and particle size distribution, were more severe when utilising a dry aerosol rather than a wet aerosol. Hence, the major outcome of the chapter was the recommendation that desolvation of the aqueous aerosol was not performed for bulk analysis applications i.e. a wet plasma is preferred over a dry plasma.

Ideally, in order to validate the relationship between plasma based matrix effects and the particle size distribution of the LA aerosol, an online measurement of the particle size distribution post particle separator should be performed. This was not performed since the instrumentation required was simply not available. Such a measurement would ensure that the particle separator was removing material from the LA aerosol stream in a particle size discriminate manner, and that changes in particle size distribution were indeed responsible for the observed variation in plasma based matrix effects.

As a calibration strategy, online addition of aqueous standards allows ‘fit for purpose’ analytical data to be obtained for many applications. For instance, the method was validated by bulk analysis of glass, polyethylene and metal alloy CRMs. The downside of the online additions approach is the lengthy analysis time per sample (although for some applications a single point calibration may suffice, after performing the complete method to determine the mass flow ratio), and the fact that prior knowledge of the sample is required to determine the relative mass flow rates of the two sample introduction sources, and to select an appropriate internal standard element. The feasibility of a single point calibration, following determination of the mass flow ratio, requires further investigation. This single point calibration may then enable the online
additions technique to be applied to spatial determinations, and not be restricted to bulk analysis as is currently the case.

The online additions strategy was modified to allow the powerful quantification technique of isotope dilution to be utilised. The isotopic spike solution was introduced to the plasma online via solution nebulisation. Although, this method yielded a recovery of over 90% for Cd in NIST 612, when the mass flow ratio was calculated from LA-ICP-ID-MS of Pb, it was felt that ultimately, the major benefits of utilising an ID strategy were removed. Namely, the detrimental effects of elemental fractionation were present, and the fact that prior knowledge of the sample was required.

**Absorption Coefficient Modified Pressed Powders**

The analysis of absorption coefficient pressed powders in chapter four enabled a fundamental insight into absorption related ablation processes. This work has demonstrated the benefits of utilising an active, vanillic acid binder, which was shown to offer increased sensitivity and a less sample matrix dependent ablation process. The benefits offered by vanillic acid have great implications for quantification. An improvement in the analytical data obtained by external calibration has been demonstrated for sample matrices that do not exactly match in terms of physicochemical properties or composition. This improvement was attributed to the vanillic acid binder standardising the ablation process and therefore stabilising the mass flux to the ICP.

Throughout chapter four, the increase in observed sensitivity upon employing an absorbing binder was attributed to the generation of smaller particles at the ablation site. Such particles are transported to, and processed by the ICP, resulting in enhanced sensitivity, improved precision and a reduction in plasma based fractionation. Again, the generation of smaller particles at the ablation site, requires validation via an online measurement of particle size distribution.

In the pressed powder approach no benefit was observed upon simultaneous nebulisation of water to yield a wet plasma. This was expected, since the limiting step in this approach was the difference in sample and standard matrix, resulting in variations in ablation yields during the ablation process, and not the vaporisation and ionisation
processes occurring within the plasma. That is to say that plasma processes were secondary to the primary ablation processes in this technique.

As a calibration strategy, analytical data was obtained that would be 'fit for purpose' for many applications, even when internal standardisation was not utilised. However, a recommendation from this work is that if an internal standard element is available then it should be used, since ultimately this will offer the best accuracies and precisions. Although the addition of isotopic spike solutions has been investigated in chapter five, an investigation into the obtainable data quality upon introduction of elemental spike solutions to pressed powders is recommended.

Again, the strategy was modified to allow the quantification tool of ID-MS to be utilised. However, in this case the true benefits of ID-MS were maintained since no real prior knowledge of the sample is required, and importantly the detrimental effects of elemental fractionation are eliminated during the isotope ratio measurement of the isotopically diluted sample.
Appendices
Device for Mixing Two Sample Introduction Sources

Figure 53 A schematic of the improved cyclonic design to mix the aerosol generated by LA, with the aerosol generated by solution nebulisation. The direction, and plane, of introduction and exit, of the aerosols and waste solution are shown. Not to scale.
Figure 54 A schematic of the improved cyclonic design to mix the aerosol generated by LA, with the aerosol generated by solution nebulisation. The direction, and plane, of introduction and exit, of the aerosols and waste solution are shown. Not to scale. Dimensions in mm.
Figure 55 A schematic of the improved cyclonic design to mix the aerosol generated by LA, with the aerosol generated by solution nebulisation. The direction, and plane, of introduction and exit, of the aerosols and waste solution are shown. Not to scale. Dimensions in mm.
Professional Development

Professional Development
Publications


Helen J. Reid, Abdul A. Bashammakh, Phillip Goodall, Mark R. Landon, Ciaran O’ Connor and Barry L. Sharp, Determination of $^{127}$I and $^{129}$I in Milk by Collision/Reaction Cell ICP-MS, *The Analyst*, Submitted March 2007
Oral Presentations

Laser Ablation Sampling – Still Much to Learn
Ciaran O’Connor, Barry L. Sharp
May 2004
LGC
Teddington, Middlesex, UK

Laser Ablation Sampling – Still Much to Learn
Ciaran O’Connor, Barry L. Sharp
July 2004
12th Biennial National Atomic Spectroscopy Symposium
Plymouth University, Plymouth, Devonshire, UK

‘Solutions’ for Calibration of LA-ICP-MS
Barry L. Sharp, Ciaran O’Connor
September 2004
9th International Conference on Plasma Source Mass Spectrometry
University of Durham, Durham, County Durham, UK

‘Solutions’ for Calibration of LA-ICP-MS
Ciaran O’Connor, Barry L. Sharp
January 2005
2005 European Winter Conference
University of Budapest, Budapest, Hungary

LA-ICP-MS and ‘Solutions’ for Calibration
Ciaran O’Connor
March 2005
Masters Program - Atomic Spectroscopy Short Course
Department of Chemistry, Loughborough University, Loughborough, Leicestershire, UK
Absorption Coefficient Modified Pressed Powders for Calibration of LA-ICP-MS
Ciaran O’ Connor, Mark R. Landon, Barry L. Sharp
July 2006
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Glasgow University, Glasgow, UK

Calibration of Laser Ablation Inductively Coupled Plasma Mass Spectrometry
Ciaran O’ Connor and Damon Green
November 2006
Perkin Elmer User Group
Perkin Elmer Facility, Seer Green, Buckinghamshire, UK

Absorption Coefficient Modified Pressed Powders for Calibration of LA-ICP-MS
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Glasgow University, Glasgow, UK

Poster Presentations
Laser Ablation Sampling – Still Much to Learn
Ciaran O’ Connor and Barry L. Sharp
July 2004
Analytical Research Forum
University of Central Lancashire, Preston, Lancashire, UK
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<td>Rob Hutchinson (New Wave Research)</td>
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On-line additions of aqueous standards for calibration of laser ablation inductively coupled plasma mass spectrometry: theory and comparison of wet and dry plasma conditions

Ciaran O'Connor,* Barry L. Sharp* and Peter Evans*

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This paper describes the theory of on-line additions of aqueous standards for calibration of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Establishment of a calibration curve enabled investigation of: fractionation, matrix effects, mass flow ratios, and the relative merits of wet and dry plasma conditions for laser ablation sampling. It was found that a wet plasma was much more tolerant of increased sample loading without reducing plasma robustness, leading to less severe and more constant mutual matrix effects. These findings indicate that the on-line addition of water is the preferred mode of operation for quantification by LA-ICP-MS. The analytical performance of the method was validated by the analysis of three certified reference materials: National Institute of Standards and Technology (NIST) 612 Trace Elements in Glass, European Reference Material (ERM) 681 Trace Elements in Polyethylene and British Chemical Standards (BCS) No. 387 Nimonic 901 Alloy. Analysis of NIST 612 was performed under both wet and dry plasma conditions, and the correlation with certified elemental concentrations was much better when a wet plasma was employed. Analyses of ERM 681 and BCS No. 387 were performed under wet plasma conditions, due to that method’s proven advantages. The differences between the found and certified elemental concentrations varied between 1-10% for the majority of elements, for all three certified reference materials.

Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has become the most versatile technique for the direct determination of trace elements in a wide variety of solid sample types. It has particular application for the determination of trace elements in sample types such as metals, rocks, polymers and ceramics, and avoids the risk of contamination associated with complex digestion procedures.

The limitations of LA-ICP-MS are well known: namely, elemental fractionation and a lack of certified reference materials (CRM's) for the majority of sample types. 'In house' synthetic standards can be prepared for this purpose, although their preparation is often time consuming and expensive, and they are frequently compromised by inhomogenous distribution of elemental composition. In the absence of solid calibration standards, aqueous calibration standards have been employed for quantification. Such aqueous standards can be ablated directly, with or without the presence of an organic chromophore to improve coupling between the laser and solution, or more commonly they are introduced on-line via a nebulizer and spray chamber in what is referred to as the "dual sample/standard approach".

Dual sample/standard calibration

The dual sample/standard approach, first proposed by Thompson et al., can provide quantitative data in the absence of solid calibration standards. In this calibration approach, the aerosol generated by laser ablation of the target is combined with the aerosol generated by solution nebulization of an aqueous calibration standard.

The limitation of this approach is the different sample and standard matrices that result in differing atomisation and ionisation characteristics within the ICP. Namely, ablated particles have larger mean diameters and size distributions than those particles produced by solvent evaporation from a wet aerosol. Consequently, these particles are vapourised along an extended region of the ICP, leading to wider ion density distributions along the central channel for LA in comparison with solution nebulisation.

The dual sample/standard approach, using a wet or a dry plasma, requires internal standardisation to compensate for the different mass transport rates of the two sample introduction sources. Consequently, an element of known concentration and homogeneous distribution must be present in the sample. However, this may not be as restrictive as at first may seem, since a matrix element of known concentration (from stoichiometry, or previous analysis) is often available.

In its simplest form, dual sample/standard introduction produces a wet plasma, leading to the possibility of spectral interferences such as oxides and hydroxides derived from the use of water as a solvent. In this paper the term "wet" refers to

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a plasma in which the liquid phase aerosol and vapour phase water are present, i.e., the classical wet plasma produced in solution analysis. Normally, desolvation of the standard aerosol is employed so that it more closely matches the sample aerosol.\textsuperscript{3-15} However, the plasma formed in this case is referred to as being “dry”, and has a variable composition depending upon the matrix of the ablation target; hence, a variable sample matrix will produce varied sample loading. In contrast, a wet plasma produces more standardised conditions with a single dominant plasma species, i.e., water; thus, water dominates the plasma loading and only small perturbations are caused by the sample matrix leading to reduced matrix effects.

Whereas the absence of oxides and hydroxides may be necessary for the accurate determination of isotopic ratios, the standardised plasma conditions offered by employing a wet plasma may be of greater benefit for routine analysis by LA-ICP-MS. Koch et al.\textsuperscript{16} observed that the $^{65}\text{Cu}/^{64}\text{Zn}$ ratio from brass using LA-ICP-MS with dry plasma conditions differed from the ratios obtained using wet plasma conditions. This was also confirmed by Boullyga et al.,\textsuperscript{17} who reported that the $^{65}\text{Cu}/^{64}\text{Zn}$ ratio obtained by LA-ICP-MS using wet plasma conditions was closer to the ratio obtained with a traditional digest and solution based nebulization than when using dry plasma conditions. These differences can probably be attributed to differential fractionation within the ICP, between dry and wet plasma conditions, due to different atomisation and ionisation conditions.

This work develops the theory of the on-line dual sample/standards technique and provides a comparison between the use of wet or dry plasma conditions. A strategy was devised using on-line, multi-point aqueous calibration, allowing the investigation of fractionation, matrix effects and characterisation of a mass flow ratio representing the ratio of mass transport between the two sources.

Theory of on-line additions. In this paper the terms used are as follows.

Nomenclature

\begin{align*}
I &= \text{Intensity or ion count rate} \\
C &= \text{Concentration} \\
C_{10} &= \text{X-axis intercept at } I = 0 \\
S &= \text{Sensitivity} \\
A &= \text{Mass flow rate} \\
\text{Superscript} \\
S &= \text{Solid or sample} \\
L &= \text{Liquid standard} \\
S+L &= \text{Solid in the presence of the aqueous standard aerosol} \\
\text{Subscript} \\
i &= \text{Internal standard} \\
A &= \text{Analyte} \\
\end{align*}

Generally the calibration function for an ICP-MS instrument is written as:

$$I = CS \tag{1}$$

The sensitivity (S) factor can be split into two terms: a true instrumental sensitivity term, i.e., the response of the ICP-MS instrument per unit mass (strictly speaking molar quantities should be used since these directly represent the number of atoms sampled) of a specified element, and a mass flow rate term representing the flux of sample or standard. Thus, for an analyte in the sample substrate, eqn. (1) becomes:

$$I_A^S = m_A^S C_A^S S_A^S \tag{2}$$

Dimensional analysis of eqn. (2) is instructive in understanding the meanings of the individual terms, thus:

$$\frac{\text{counts}}{s} = \frac{g^2}{s} \times \frac{g}{s^3} \times \frac{\text{counts}}{g_A} \tag{2b}$$

Note how the cancellation of dimensions is between, rather than within, terms, indicating the inherent separation of sample and analyte quantities.

For on-line additions the overall intensity is the sum of the intensity contributions from the sample and from the standard, in accordance with a standard additions type calibration. Hence:

$$I_A = m_A^L S_A^L C_A^L + m_A^S S_A^{S+L} C_A^S \tag{3}$$

Note that two sensitivity terms are present, one, $S_A^L$, representing the sensitivity of the aqueous calibration curve, and the other, $S_A^{S+L}$, representing the sensitivity of the on-line additions calibration curve, i.e., the sensitivity of the combined solid sample and aqueous standard. Plotting $I_A$ against $C_A^S$ yields a graph as shown in Fig. 1, with slope of $m_A^L S_A^L$ and intercept of $m_A^S S_A^{S+L} C_A^S$.

Extrapolation of the on-line addition curve to $I_A = 0$, and rearrangement of eqn. (3), yields the concentration of the analyte in the sample as:

$$C_A^S = \frac{m_A^S}{m_A^L} \times \frac{S_A^{S+L}}{S_A^L} \times C_A^{I_A} \tag{4}$$

![Fig. 1](https://via.placeholder.com/150)

**Fig. 1** A representation of the curves obtained by aqueous calibration and on-line additions calibration. In this simple scenario there are no mutual matrix effects, as indicated by the parallel curves, hence $S_A^L = S_A^{S+L}$. 

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<th>( C ) = Concentration</th>
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<th>( S ) = Sensitivity</th>
<th>( A ) = Mass flow rate</th>
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<td>( S+L ) = Solid in the presence of the aqueous standard aerosol</td>
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</table>

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Convergence indicates that mutual matrix effects are occurring. Solution nebulization with desolvation to produce a dry standard standards introduced by standard solution nebulization to produce a wet standard aerosol; and aerosol.

Characteristics.

Instrumentation

A commercially available UP-213 Laser Ablation System (New Wave Research Inc., Huntingdon, Cambridgeshire, UK) operating in the deep UV (213 nm) was employed using He as a carrier gas due to its improved ablation and transport characteristics. The two different experimental setups employed: (A) aqueous calibration standard aerosols by solution nebulization to produce a wet standard aerosol; and (B) introducing the standard aerosol by solution nebulization with desolvation to produce a dry standard aerosol. The sample aerosol from the LA system was combined with the standard aerosol from a PFA-100 µL Fixed Capillary Nebulizer (Elemental Scientific Inc., Omaha, Nebraska, USA) and custom made cyclonic spray chamber, using a polypropylene 'Y'-piece (Fisher Scientific, Loughborough, Leicestershire, UK). With this arrangement a wet plasma resulted. When a dry plasma was required, the nebulizer and spray chamber were replaced with a MCN-6000 sample introduction system (CETAC Technologies, Omaha, Nebraska, USA) for desolvation of the standard aerosol. The two 1 mL Tygon™, sample introduction lines were combined, using a polypropylene 'Y'-piece, 1 mL before the ICP torch. A further cyclonic mixing vessel was placed immediately before the ICP torch. This was placed in the Peltier chamber of the PQ ExCell and was cooled to 5 °C as in the standard operating mode. The gas flow, carrying the combined sample and standard aerosol, was introduced tangentially into this vessel to facilitate further mixing.

A VG PQ ExCell ICP-MS instrument (Thermo Electron Corporation, Winsford, Cheshire, UK) was used throughout the investigation. Optimisation of the torch-box position, lens voltages, and nebulizer gas flow was performed before analysis, with respect to the 115In signal intensity obtained upon nebulization of a 1 µg L⁻¹ solution. A He gas flow of 0.5 L min⁻¹ was found to give optimum sensitivity and a good peak shape upon single shot ablation of NIST 612, and importantly had no detrimental effect on the signal intensity obtained upon solution nebulization when the two sample introduction sources were combined. All optimisation was performed at 1350 W. Table 1 lists the experimental parameters employed. The laser conditions were chosen to represent those typically used in bulk analysis by LA-ICP-MS.

Sample preparation

Solid samples. NIST 612 (National Institute of Standards and Technology, Gaithersburg, Maryland, USA) Trace Elements in Glass was used when performing investigations into laser and plasma variables, due to its certification for a wide variety of trace elements. For method validation, NIST 612 Trace Elements in Glass, European Reference Material (ERM) 681 Trace Elements in Polyethylene and British Chemical Standards (BCS) No. 387 Nimonic 901 Alloy (42% nickel, 36% iron, 12% chromium, 6% molybdenum and 3% titanium) were analysed. No sample preparation was performed on these materials, excepting the chemical cleaning of the sample surface with 1% HNO₃ (Romil Pure Chemistry, Cambridge, Cambridgeshire, UK).

Aqueous standard preparation. Aqueous calibration standards, in a 1% HNO₃ matrix, were prepared by serial dilution of elemental stock solutions (Fisher Scientific, Loughborough, Leicestershire, UK) using 18.2 MΩ cm⁻¹ purity water (Elga Lab Water, High Wycombe, Buckinghamshire, UK). These standards contained the following elements: Ti, Cr, Mn, Co, Cu, Sr, Ag, Cd, Ba, Ce, Ti, Pb and U at concentrations 0, 0.1, 2, 5 and 10 µg L⁻¹.

On-line additions

The on-line additions involved simultaneous introduction of aqueous calibration standard aerosols by solution

\[ C_{f0} \text{, which is negative, is taken directly from the graph, and it remains to determine the mass flow ratio, } \frac{m_f}{m_i} \text{, since the sensitivity ratio, } \frac{C_f}{C_i}, \text{ can be calculated from the slopes of the two curves. It is this sensitivity ratio that can be used as a direct indicator of mutual matrix effects, i.e. two parallel curves indicate no mutual matrix effects, whereas any divergence or convergence indicates that mutual matrix effects are occurring.} \]

The mass flow ratio can be determined by performing on-line additions for an internal standard element; hence, eqn. (4) can be written as:

\[ \frac{m_f}{m_i} = \frac{C_f}{C_i} \times C_{f0} \]

Knowing \( C_f \), the mass flow ratio can be determined. For this to be useful in solving eqn. (4), it is necessary to assume that:

\[ \frac{m_f}{m_i} = \frac{m_L}{m_A} \]

That is, there is no elemental fractionation between the internal standard element and the analyte, since differing mass flow ratios are a direct measure of elemental fractionation.

Experimental

Instrumentation

Fig. 2 The two different experimental setups employed: (A) aqueous standards introduced by standard solution nebulization to produce a wet standard aerosol; and (B) introducing the standard aerosol by solution nebulization with desolvation to produce a dry standard aerosol.
nebulization, with or without desolvation, and a laser ablated sample aerosol. In order to allow the investigation of matrix effects and calculation of the mass flow ratio, multiple calibration standards were used. The whole calibration series was nebulized (with He passing through the ablation cell) to yield a standard calibration curve. Then, ablation of the sample commenced and the aqueous calibration series was repeated, so that simultaneous introduction of sample and standard occurred. This procedure yielded two curves, as shown in Fig. 1: one curve representing the contribution from the aqueous calibration standards only; and the other representing the contribution from the aqueous calibration standards in addition to the laser ablated sample aerosol. Comparison of the slope of the two curves enabled investigation of the occurrence of mutual matrix effects, as explained above. The mean and standard deviation of the sensitivity ratios obtained from various isotopes (n = 14) were used as an indication of the extent and consistency of matrix effects.

Data were acquired under different ablation and plasma conditions, including ablation crater diameter and plasma forward power. By increasing crater diameter and keeping the fluence constant, the ablated mass and consequently the sample loading of the plasma was increased. Further, since the fluence remained constant throughout the investigation, the ablation products should remain similar (particle size distribution etc.), leaving sample yield as the sole variable. Crater diameters of 15–110 μm were investigated. The effect of plasma robustness on matrix effects was investigated by performing on-line additions under varying ICP forward powers, within the range of 1100–1600 W. This investigation was performed using fixed carrier gas flows. Although forward power and injector flow are recognised as being interdependent variables, it was felt that in these experiments changing the Ar/He ratio and hence the transport properties of the delivery systems might introduce too many additional variables. All experiments were performed using both standard solution nebulization, and solution nebulization with desolvation to allow a comparison between wet and dry plasma conditions.

**Calibration procedure.** Once the optimum ablation and plasma conditions had been found, with respect to minimising matrix effects, the reference materials were analysed. First, using on-line simultaneous sample/standard introduction for an internal standard element, a mass flow ratio was calculated. Then, by performing on-line simultaneous sample/standard introduction for the analyte element and applying the mass flow ratio obtained from the internal standard element, \( C_A \) was calculated from eqn. (4).

For NIST 612 Trace Elements in Glass the analysis was performed under wet and dry plasma conditions and the quality of the data compared with the certified elemental concentrations. Analyses of ERM 681 Polyethylene and BCS No. 387 Nimonic 901 Alloy were performed using wet plasma conditions only.

For analysis using a dry plasma, an ICP forward power of 1500 W was used; whereas for a wet plasma 1300 W was applied. LA parameters were kept constant throughout the analysis: a fluence of 13 mJ cm\(^{-2}\), a frequency of 20 Hz, an ablation crater diameter of 80 μm and a sample translation rate of 10 μm s\(^{-1}\) were employed.

**Results and discussion**

**Variation in ablation crater diameter**

The on-line additions strategy was performed at differing ablated crater diameters, i.e., successively introducing more ablated mass into the ICP to increase the sample loading of the plasma. The data obtained are presented in Tables 2 and 3. Increasing the ablated crater diameter had the effect of increasing the relative sensitivity above unity and, importantly, the standard deviation in the sensitivity ratios obtained. This effect was much more pronounced under dry plasma conditions than under wet plasma conditions, as can be seen in Fig. 3.

The laser was run at constant fluence, leading to increased mass transport to the ICP with increasing ablated crater diameter; consequently, the sample loading of the plasma was increased. Under dry plasma conditions, with higher
conditions existed. The fact that the level of oxides remained constant upon introduction of the sample aerosol again in this reason, the molecular ion 38 U I ·O+ manifested itself as an increase in sensitivity ratios, and the standard deviation thereof, across the suite of elements studied. The degree of variation in the sensitivity ratios with increased sample loading was much more constant under wet plasma conditions. It appears that the presence of water buffered the plasma against the detrimental effects of sample loading on plasma robustness. Importantly, the data indicates that there was no significant change in the extent of oxide formation upon the introduction of the laser ablated aerosol. This is shown by the absence of any significant change in sensitivity upon introduction of the sample aerosol, especially for the oxide forming elements Ce and U. Oxide and hydroxide formation would be expected if less robust plasma conditions existed. The fact that the level of oxides remained constant upon introduction of the sample aerosol again indicates that the presence of water was beneficial in maintaining robust plasma conditions. The best way to detect changes in oxide formation is to monitor the 140Ce/140 Ce ratio; however, this was not possible in this case as the ablation of the NIST glass produces several interfering species at m/z 156. For this reason, the molecular ion 258 U60+ (m/z 254) was monitored as an indicator as to the extent of oxide formation. Under wet plasma conditions there was no increase in the degree of oxide formation for U upon introduction of the ablated aerosol, indicating there was no significant change in plasma robustness. This can be seen in Table 3, wherein the ratio %UO2%/UO2+L (representing the degree of UO2 formation for standard introduction only, divided by the degree of UO formation for simultaneous sample and standard introduction) does not deviate from unity under wet plasma conditions. Under dry plasma conditions this ratio is more erratic and deviations from unity were obtained, indicating that the dry plasma was more susceptible to changes in sample loading.

The more constant sensitivity ratios obtained under wet plasma conditions have implications when applying an internal standard element in a calibration by LA-ICP-MS. When using wet plasma conditions, it is more likely that data obtained from an internal standard element will be representative of a larger suite of elements. The mean sensitivity ratio at an ablation crater diameter of 110 µm did not quite follow the trend, but the change was small and is not likely to indicate a true reversal of slope.

Variation in plasma forward power

The on-line additions strategy was performed for varying ICP forward powers, with fixed LA parameters, to determine the effect of forward power on the severity of matrix effects for both wet and dry plasma conditions. The results can be seen in Tables 4 and 5.

As is shown in Fig. 4, under wet plasma conditions the standard deviation of the sensitivity ratios was almost constant with respect to changes in ICP forward power. For dry plasma conditions, the variation in sensitivity ratios was strongly related to the ICP forward power. This can be explained by differences in plasma robustness, i.e., a low ICP forward power and high sample load yielded a less robust plasma, leading to severe matrix effects. As stated above, under wet plasma conditions this effect was much less pronounced, confirming that the presence of water buffered against the detrimental effects of low plasma robustness. Again, the data indicated that the degree of oxide formation remained constant with varying ICP forward power, upon introduction of the laser ablated aerosol, when wet plasma conditions were employed. This is shown in Table 5, wherein the %UO2%/UO2+L is more constantly close to unity than under dry plasma conditions (notwithstanding that the smaller ratios obtained for the dry plasma will lead to greater statistical variation).

The fact that the presence of water alters the fundamental properties of the plasma, such as temperature and electron density, is well documented.21–30 However, the effects of water remain poorly understood, with experimental outcomes often depending upon the exact details of the sample introduction.

Table 2 Standard deviation and mean of sensitivity ratios obtained under varying ablated crater diameters, during the analysis of NIST 612

<table>
<thead>
<tr>
<th>Ablated crater diameter/µm</th>
<th>Wet Mean of sensitivity ratios</th>
<th>Dry Mean of sensitivity ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n = 14)</td>
<td>(n = 14)</td>
</tr>
<tr>
<td>15</td>
<td>Wet 0.005 0.012</td>
<td>Dry 1.030 1.041</td>
</tr>
<tr>
<td>30</td>
<td>Wet 0.009 0.024</td>
<td>Dry 1.038 1.023</td>
</tr>
<tr>
<td>55</td>
<td>Wet 0.022 0.036</td>
<td>Dry 1.065 1.119</td>
</tr>
<tr>
<td>80</td>
<td>Wet 0.029 0.072</td>
<td>Dry 1.144 1.139</td>
</tr>
<tr>
<td>110</td>
<td>Wet 0.040 0.106</td>
<td>Dry 1.008 1.296</td>
</tr>
</tbody>
</table>

Table 3 Degrees of UO2+ formation using a wet and dry plasma, with and without the presence of a laser ablated aerosol for varying ablated crater diameters. The ratio %UO2%/UO2+L thus represents any changes in the degree of oxide formation upon introduction of the ablated aerosol.

<table>
<thead>
<tr>
<th>Ablated crater diameter/µm</th>
<th>Wet plasma oxide analysis</th>
<th>Dry plasma oxide analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%UO2 %UO2+L %UO2%/UO2+L</td>
<td>%UO2 %UO2+L %UO2%/UO2+L</td>
</tr>
<tr>
<td>15</td>
<td>1.40 1.37 1.02</td>
<td>0.08 0.08 1.00</td>
</tr>
<tr>
<td>30</td>
<td>1.41 1.39 1.00</td>
<td>0.09 0.07 1.29</td>
</tr>
<tr>
<td>55</td>
<td>1.39 1.39 1.00</td>
<td>0.1 0.08 1.25</td>
</tr>
<tr>
<td>80</td>
<td>1.43 1.36 1.05</td>
<td>0.08 0.08 1.00</td>
</tr>
<tr>
<td>110</td>
<td>1.41 1.40 1.01</td>
<td>0.09 0.08 1.13</td>
</tr>
</tbody>
</table>
system and the total water flux and vapour:liquid ratio. It was beyond the scope of this investigation to quantify all of these parameters. Generally, plasma energy is consumed in the vaporisation and dissociation processes; however, this energy can be replaced by energy transfer from the outer regions of the plasma into the central channel, and the dissociation products (molecular hydrogen and oxygen) contribute to a local increase in thermal conductivity and heat transfer. The more robust conditions offered by employing a wet plasma have been observed in the present work. The wet plasma was more tolerant of variable sample loading and variable ICP forward powers, evidenced by more constant sensitivity ratios.

**Calibration**

Method validation was performed on NIST 612 Trace Elements in Glass, ERM 681 Trace Elements in Polyethylene and BCS No. 387 Nimonic 901 Alloy. The uncertainty quoted on all calculated concentrations is based upon the standard error (S_y/x) associated with the whole calibration curve and is a very robust estimate of the uncertainty associated with each result. Thus, the concentration uncertainties were calculated from the regression line for a signal intensity of ±S_y/x. This method ignores the uncertainties in the concentration values, which is justified in the case of the NIST 612 glass, since the relative

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**Fig. 3** Standard deviation (n = 14) of sensitivity ratios obtained with differing ablated crater diameter, during the analysis of NIST 612, under (a) dry and (b) wet plasma conditions.

**Fig. 4** Standard deviation (n = 14) of sensitivity ratios obtained with differing ICP forward power, during the analysis of NIST 612, under both (a) dry and (b) wet plasma conditions.
uncertainties are only 10% of the LA uncertainty values. It is less so in the case of ERM 681 Polyethylene.

**Table 4** Standard deviation and mean of sensitivity ratios obtained under varying ICP forward power, during the analysis of NIST 612

<table>
<thead>
<tr>
<th>ICP forward power/W</th>
<th>Standard deviation of sensitivity ratios (n = 14)</th>
<th>Mean of sensitivity ratios (n = 14)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet</td>
<td>Dry</td>
</tr>
<tr>
<td>1100</td>
<td>0.050</td>
<td>0.159</td>
</tr>
<tr>
<td>1200</td>
<td>0.038</td>
<td>0.080</td>
</tr>
<tr>
<td>1300</td>
<td>0.011</td>
<td>0.064</td>
</tr>
<tr>
<td>1400</td>
<td>0.030</td>
<td>0.053</td>
</tr>
<tr>
<td>1500</td>
<td>0.035</td>
<td>0.052</td>
</tr>
<tr>
<td>1600</td>
<td>0.031</td>
<td>0.066</td>
</tr>
</tbody>
</table>

**Table 5** Degrees of UO+ formation using a wet and dry plasma of varying forward power, with and without the presence of a laser ablated aerosol. The ratio %UO%/%UO2+L thus represents any changes in the degree of oxide formation upon introduction of the ablated aerosol

<table>
<thead>
<tr>
<th>ICP forward power/W</th>
<th>Wet plasma oxide analysis</th>
<th>Dry plasma oxide analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%UO</td>
<td>%UO2+L</td>
</tr>
<tr>
<td>1100</td>
<td>7.21</td>
<td>7.92</td>
</tr>
<tr>
<td>1200</td>
<td>1.95</td>
<td>1.71</td>
</tr>
<tr>
<td>1300</td>
<td>1.52</td>
<td>1.52</td>
</tr>
<tr>
<td>1400</td>
<td>1.41</td>
<td>1.53</td>
</tr>
<tr>
<td>1500</td>
<td>1.30</td>
<td>1.18</td>
</tr>
<tr>
<td>1600</td>
<td>1.42</td>
<td>1.30</td>
</tr>
</tbody>
</table>

The analysis proved a lot more successful when wet plasma conditions were used. Generally, the agreement between the calculated and certified concentrations was much closer under wet plasma conditions. Under wet plasma conditions, the majority of elements quantified were within 1–10% of the certified values. One exception was Ti, for which poorer data was obtained, but no explanation for this is available.

The matrix effects were less severe and less variable between elements when using a wet rather than a dry plasma: as a direct result, the mass flow ratios calculated were less elementally variable, indicating that they were subject to less plasma related fractionation. This simplifies the choice of an internal standard, since it is more likely that the chosen element will be representative of the set. For this reason, more accurate data can be obtained from the on-line additions approach when wet plasma conditions are employed. This is shown in Figs. 5 and 6, wherein a better correlation between the calculated elemental concentrations and certified elemental concentrations was obtained under wet plasma conditions, shown by a slope close to 1 when using a wet plasma and a slope well below 1 when using a dry plasma (R_Wet = 0.89 versus R_Dry = 0.60). However, the R_Wet value was distorted by the Ti outlier and would be closer to unity if this point was omitted.

**Analysis of ERM No. 681 Trace Elements in Polyethylene.** Analysis of ERM No. 681 Polyethylene was undertaken as an example of a typical polymer sample. For this analysis Cd was chosen as an internal standard element, due to it being in the middle of the mass range investigated. The data obtained are shown in Table 8.

The results for the mass flow ratios indicate that there was a much greater signal contribution from the aqueous calibration standards than from the laser ablated aerosol. This is highlighted by the large values calculated for the mass flow ratio, i.e., the ratio of flux between sample and standard. Values this large are indicative of the small amounts of ablated material transported to the ICP when employing such an LA system. This value means that an analyte concentration of tens of mg kg⁻¹ in the solid sample will correspond to a signal intensity equivalent to one μg L⁻¹ of analyte in the aqueous calibration standards. This may be disadvantageous in terms of absolute detection limit, but as shown here, limiting the plasma loading is beneficial for obtaining good quantitative data.

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all three analyses, the change in mass flow ratio must have been due to a large difference in the ablated mass transported to the plasma. The results indicate that much more polymer sample was transported, most likely due to increased coupling between the laser beam and the polymer.

Analysis of BCS No. 387 Nimonic 901 Alloy. Analysis of BCS No. 387 Nimonic 901 Alloy was undertaken as an example of a typical metal alloy sample. For this analysis Cu was chosen as an internal standard element. The data obtained are shown in Table 9.

When using Cu as an internal standard, the analysis proved successful in the quantification of Co and Pb, and good agreement with the certified concentration was obtained. The quantification of Mn was less successful. This was due to the fact that the certified concentration of Mn was very high in the reference material, producing a signal intensity above the linear range of the ICP-MS detector (especially when combined with the signal intensity from the aqueous calibration standards). This gave erroneous calibration data, leading to an inaccurate quantification. Mass flow ratios were similar to those obtained for the polymer sample, again indicating that there was an increased transport of metal sample to the plasma in comparison to the glass.

### Table 6

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Certified concentration with associated uncertainty/mg kg^-1</th>
<th>Mass flow ratio</th>
<th>Calculated concentration with associated uncertainty/mg kg^-1</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>^{48}Ti</td>
<td>50.1 ± 0.8</td>
<td>10982</td>
<td>63.3 ± 4.8</td>
<td>126</td>
</tr>
<tr>
<td>^{52}Cr</td>
<td>Not certified</td>
<td>—</td>
<td>36.4 ± 2.5</td>
<td>—</td>
</tr>
<tr>
<td>^{54}Mn</td>
<td>39.6 ± 0.8</td>
<td>14679</td>
<td>37.4 ± 1.9</td>
<td>94</td>
</tr>
<tr>
<td>^{59}Co</td>
<td>35.5 ± 1.2</td>
<td>14679</td>
<td>Internal standard</td>
<td>—</td>
</tr>
<tr>
<td>^{65}Cu</td>
<td>37.7 ± 0.9</td>
<td>16170</td>
<td>32.4 ± 2.6</td>
<td>86</td>
</tr>
<tr>
<td>^{68}Sr</td>
<td>78.4 ± 0.2</td>
<td>14679</td>
<td>7.31 ± 1.7</td>
<td>97</td>
</tr>
<tr>
<td>^{101}Ag</td>
<td>22 ± 0.3</td>
<td>13092</td>
<td>23.3 ± 3.5</td>
<td>106</td>
</tr>
<tr>
<td>^{111}Cd</td>
<td>Not certified</td>
<td>—</td>
<td>20.6 ± 0.9</td>
<td>—</td>
</tr>
<tr>
<td>^{137}Ba</td>
<td>41 ± not quoted</td>
<td>10744</td>
<td>33.4 ± 1.2</td>
<td>81</td>
</tr>
<tr>
<td>^{146}Ce</td>
<td>39 ± not quoted</td>
<td>13731</td>
<td>39.4 ± 2.6</td>
<td>101</td>
</tr>
<tr>
<td>^{206}Pb</td>
<td>15.7 ± 0.3</td>
<td>14386</td>
<td>15.2 ± 1.4</td>
<td>97</td>
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<tr>
<td>^{208}Pb</td>
<td>38.57 ± 0.2</td>
<td>13863</td>
<td>37.4 ± 1.6</td>
<td>97</td>
</tr>
<tr>
<td>^{232}U</td>
<td>37.38 ± 0.0</td>
<td>14042</td>
<td>37.0 ± 4.0</td>
<td>101</td>
</tr>
<tr>
<td>Mean</td>
<td>—</td>
<td>14294</td>
<td>—</td>
<td>98</td>
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</table>

### Table 7

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Certified concentration with associated uncertainty/mg kg^-1</th>
<th>Mass flow ratio</th>
<th>Calculated concentration with associated uncertainty/mg kg^-1</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>^{48}Ti</td>
<td>50.1 ± 0.8</td>
<td>21055</td>
<td>30.7 ± 3.0</td>
<td>61</td>
</tr>
<tr>
<td>^{52}Cr</td>
<td>Not certified</td>
<td>—</td>
<td>40.1 ± 3.2</td>
<td>—</td>
</tr>
<tr>
<td>^{54}Mn</td>
<td>39.6 ± 0.8</td>
<td>16193</td>
<td>34.4 ± 3.0</td>
<td>87</td>
</tr>
<tr>
<td>^{59}Co</td>
<td>35.5 ± 1.2</td>
<td>14074</td>
<td>Internal standard</td>
<td>—</td>
</tr>
<tr>
<td>^{65}Cu</td>
<td>37.7 ± 0.9</td>
<td>11999</td>
<td>44.2 ± 7.1</td>
<td>117</td>
</tr>
<tr>
<td>^{68}Sr</td>
<td>78.4 ± 0.2</td>
<td>21065</td>
<td>52.4 ± 4.8</td>
<td>67</td>
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<tr>
<td>^{101}Ag</td>
<td>22 ± 0.3</td>
<td>11248</td>
<td>27.5 ± 3.7</td>
<td>125</td>
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<tr>
<td>^{111}Cd</td>
<td>Not certified</td>
<td>—</td>
<td>30.0 ± 1.8</td>
<td>—</td>
</tr>
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<td>^{137}Ba</td>
<td>41 ± not quoted</td>
<td>19549</td>
<td>29.5 ± 3.0</td>
<td>72</td>
</tr>
<tr>
<td>^{146}Ce</td>
<td>39 ± not quoted</td>
<td>15618</td>
<td>35.1 ± 3.0</td>
<td>90</td>
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<tr>
<td>^{206}Pb</td>
<td>15.7 ± 0.3</td>
<td>9667</td>
<td>22.9 ± 1.6</td>
<td>146</td>
</tr>
<tr>
<td>^{208}Pb</td>
<td>38.57 ± 0.2</td>
<td>10258</td>
<td>30.7 ± 9.5</td>
<td>89</td>
</tr>
<tr>
<td>^{232}U</td>
<td>37.38 ± 0.0</td>
<td>9869</td>
<td>32.2 ± 12.3</td>
<td>83</td>
</tr>
<tr>
<td>Mean</td>
<td>—</td>
<td>11336</td>
<td>23.8 ± 6.3</td>
<td>64</td>
</tr>
</tbody>
</table>

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Conclusions

Although dry plasma conditions may be beneficial when performing isotope ratio measurements by LA-ICP-MS due to reduced oxides and hydroxides, it has been shown that a wet plasma is more advantageous for routine analysis. The findings indicate that the on-line addition of water is the preferred mode of operation for quantification by LA-ICP-MS. Employing a wet plasma produces more standardised plasma conditions and buffers against the detrimental effects of sample loading and reduced plasma robustness. Furthermore, the exclusion of a desolvation system results in faster analysis time (due to reduced sample uptake, wash-in and wash-out times) and less expense (due to reduced analysis time, energy and gas requirements).

The theory presented in this paper has enabled differentiation between "sensitivity" and mass flow. The calculation of a mass flow ratio is useful not only for calibration, but also as a measure of the relative flux between two sample introduction
sources. The mass flow ratios reported indicate the very small amounts of material that are transported to the plasma from the ablation site when compared with the quantities introduced by a standard nebulizer and spray chamber. It has been shown that different samples can yield highly different mass flow ratios, related to the optical and physico-chemical properties of the sample. Differences in the mass flow ratios between elements are a direct indication of the occurrence and extent of elemental fractionation.

This paper has shown that on-line additions of aqueous calibration standards without desolvation can produce rapid and ‘fit for purpose’ quantitative data in the absence of a CRM. The ability of this method to make such determinations has gained particular relevance with the introduction of the Restriction of the use of certain Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment (WEEE) Directives.

The practical aspects of multi-point, on-line additions calibration may make it more useful for method development than practical analysis, (as a precursor to a single point calibration by normal internal standardisation), especially since it requires a large sample area of homogenous analyte and internal standard distribution and typically a ten minute time for sample analysis. For example, the method could be performed on a CRM to investigate fractionation and matrix effects, aiding the choice of internal standard (if a choice is
available), before subsequent single point calibration on the real sample.

Acknowledgements

This work was performed with financial backing from the Valid Analytical Measurements Program (VAM). The authors would like to express their gratitude to Thermo Electron Corporation (Winsford, Cheshire, UK) for provision of the VG PQ ExCell ICP-MS instrument and LGC (Teddington, Middlesex, UK) for provision of the UP-213 LA system.

References


Table 8 Data for ERM 681 Trace Elements in Polyethylene showing the certified elemental concentration, calculated mass flow ratio, and calculated elemental concentration using Cd as an internal standard, performed under wet plasma conditions with constant LA parameters

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Certified concentration with associated uncertainty/mg kg⁻¹</th>
<th>Mass flow ratio</th>
<th>Calculated concentration with associated uncertainty/mg kg⁻¹</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁵⁵Cr</td>
<td>17.7 ± 0.6</td>
<td>4974</td>
<td>17.5 ± 3.5</td>
<td>99</td>
</tr>
<tr>
<td>¹¹ⁱCd</td>
<td>21.7 ± 0.7</td>
<td>4910</td>
<td>Internal standard</td>
<td>—</td>
</tr>
<tr>
<td>²⁰⁸Pb</td>
<td>13.8 ± 0.7</td>
<td>4813</td>
<td>14.1 ± 0.48</td>
<td>102</td>
</tr>
<tr>
<td>²⁰⁹Pb</td>
<td>13.8 ± 0.7</td>
<td>4869</td>
<td>13.9 ± 0.43</td>
<td>101</td>
</tr>
<tr>
<td>Mean</td>
<td>—</td>
<td>4892</td>
<td>—</td>
<td>101</td>
</tr>
</tbody>
</table>

Table 9 Data for BCS 387 Nimonic 901 Alloy showing the certified elemental concentration, calculated mass flow ratio and calculated elemental concentration using Cu as an internal standard and performed under wet plasma conditions with constant LA parameters

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Certified concentration with associated uncertainty/mg kg⁻¹</th>
<th>Mass flow ratio</th>
<th>Calculated concentration with associated uncertainty/mg kg⁻¹</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁵⁵Mn</td>
<td>200 ± not quoted</td>
<td>4575</td>
<td>193 ± 4</td>
<td>77</td>
</tr>
<tr>
<td>⁵⁵Co</td>
<td>200 ± not quoted</td>
<td>4703</td>
<td>198 ± 7</td>
<td>99</td>
</tr>
<tr>
<td>⁴⁰Ca</td>
<td>76 ± not quoted</td>
<td>4660</td>
<td>Internal standard</td>
<td>—</td>
</tr>
<tr>
<td>²⁰⁸Pb</td>
<td>0.8 ± not quoted</td>
<td>5107</td>
<td>0.73 ± 0.23</td>
<td>91</td>
</tr>
<tr>
<td>²⁰⁹Pb</td>
<td>0.8 ± not quoted</td>
<td>4933</td>
<td>0.75 ± 0.19</td>
<td>95</td>
</tr>
<tr>
<td>Mean</td>
<td>—</td>
<td>4796</td>
<td>—</td>
<td>91</td>
</tr>
</tbody>
</table>
Absorption coefficient modified pressed powders for calibration of laser ablation inductively coupled plasma mass spectrometry†

Ciaran O'Connor, Mark R. Landon and Barry L. Sharp*

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Powdered samples have been pressed, utilising a standard KBr infrared (IR) press, to produce mechanically stable 13 mm discs. Three 'absorbing', organic based binders have been employed in this work, vanillic acid, pyrazinoic acid and nicotinic acid, chosen because of their high optical absorbance at the wavelength of the incident laser energy (213 nm). Poly(vinyl alcohol) (PVA) was employed as an example of a 'non-absorbing' binder and because its use has been described previously in the literature. Discs of various sample/binder compositions were prepared and their absorption properties characterised by diffuse reflectance spectroscopy. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to investigate the effect of different sample/binder compositions on signal sensitivity, whilst surface profilometry was performed on the resulting tracks to provide an estimate of the ablation depth achieved by the laser beam. It was found that discs prepared with vanillic acid had the highest optical absorbance at the wavelength of the laser system employed, resulting in a lower ablation depth and improved signal sensitivity, probably through the formation of smaller particles during the ablation process.

Analysis of certified reference materials (CRMs) was performed using simple external calibration standards of similar and dissimilar CRMs. It was found that discs produced using a 40% vanillic acid binder, with a 60% sample composition gave superior quality analytical data when compared with the use of 40% PVA binder or no binder at all. These findings indicate the potential for fit-for-purpose quality analytical data to be obtained unless employing external calibration standards, without internal standardisation and without exact matrix matching. These data also provide further evidence that standardisation of ablation conditions and mass flux to the plasma are prerequisites for robust calibration, particularly in the absence of a suitable internal standard element.

Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has become the most versatile technique for the direct determination of trace elements in a wide variety of solid sample types. It has particular application for the determination of trace elements in sample types, such as metals, rocks, polymers and ceramics, and avoids the risk of contamination associated with complex digestion procedures.

The limitations of LA-ICP-MS are well known, namely elemental fractionation and a lack of certified reference materials (CRMs) for the majority of sample types. 'In house' solid synthetic standards are often prepared to allow external calibration; however, with such external standards it is especially important that the standard matches the sample in terms of matrix composition, since even a small difference in composition can lead to vastly different rates of ablation.

There are two common approaches to solid standard preparation. The first approach is fusion to form a glass bead or disc.1–9 The second approach is to press a powdered sample into a disc.2–4,7,10–21 These studies have shown that since the ablation yield can vary by as much as 50% between discs, poor analytical data is obtained unless the calibration standards are prepared to exactly match the sample, or an internal standard element is used to correct for these large differences in ablation yield.

A major advantage of standard preparation of this type is that it facilitates the addition of internal standard elements, isotope spikes, or matrix modifiers. The use of matrix modifiers has been demonstrated by Boue-Bigne et al.22 to improve the analytical data obtained from the direct ablation of liquid calibration standards. The absorption coefficients of the standards were modified by the addition of organic chromophores so that they more closely matched those of the sample.

Matrix modification to improve the ablation efficiency has been achieved by addition of metal oxides in order to enhance the absorbance characteristics of the target.23–25 Weis et al.25 reported an extensive investigation into the addition of Fe2O3 as a matrix modifier to modify the absorption coefficient of lithium metaborate discs. It was found that the addition of Fe2O3 led to a greater absorption of the incident laser energy, leading to a shorter optical penetration depth and a subsequent reduction in the size of particles produced by the
ablation process. Lee et al.\textsuperscript{21} found that the addition of Triton-X to samples pressed into discs led to increased sensitivity and suggested that this might be due to improved absorption of the laser energy.

Much work has been performed relating LA parameters to the particle size distribution of the generated aerosol and the effect upon figures of merit for ICP-MS. The parameters that have been investigated include fluence, pulse duration, wavelength, carrier gas and absorption properties of the sample.\textsuperscript{25-39} However, it is important to understand that the particle size distribution created by the ablation process is not indicative of what reaches the ICP, since particles can change shape by processes such as vaporisation, condensation and agglomeration with other particles.\textsuperscript{40} The processes involved in the formation of particles from ablated matter are complex and remain poorly understood; however, recent models provided by Hergenroder,\textsuperscript{41-43} have helped to clarify this complexity and provide explanations for the different particle size fractions encountered.

This paper reports a detailed investigation into the benefits of the addition of organic chromophores, simultaneously acting as binders, to powdered samples before subsequent pressing into discs. The organic chromophores chosen for this investigation, vanillic acid, pyrazinoic acid and nicotinic acid, are common matrix assisted laser desorption ionisation (MALDI) matrices and were chosen due to their high absorbance at 213 nm, the wavelength of the laser ablation system employed. The other binder investigated in this work, poly(vinyl alcohol) (PVA), was chosen since it and other high molecular weight alcohols and polymers have been reported to act as effective sample binders.\textsuperscript{16,44-48} Further, PVA is relatively non-absorbing in comparison to the ‘absorbing’ binders at the laser wavelength. The molecular structures of all four binders are shown in Fig. 1, whilst Table 1 lists their $\lambda_{\text{max}}$ values and associated molar absorptivities.\textsuperscript{49}

![The molecular structures of the four binders investigated in this work.](image)

The addition of chromophores should improve the coupling between the laser beam energy and the sample, leading to an improved efficiency of ablation and the formation of smaller particles at the ablation site. The smaller particles are more efficiently transported to and more fully processed by the plasma, leading to enhanced sensitivity and a reduction in elemental fractionation. It was anticipated that by incorporating the chromophores into the discs a more sample independent ablation process would result, offering the possibility of improved analytical data when using external calibration standards. This is of particular importance when no suitable internal standard is available.

### Experimental

#### Solid sample preparation

The powdered sample, in this case a CRM, and the powdered binder, PVA (Fisher Scientific, Loughborough, Leicestershire, UK), vanillic acid, pyrazinoic acid or nicotinic acid (Alfa Aesar, Heysham, Lancashire, UK), were weighed out to yield a combined total mass of 0.40 g.

Two methods were employed for mixing the two powders. The first was to simply combine the powders in a pestle and mortar and grind for a period of 10 min until a homogenous looking mixture was achieved. The second approach involved the use of an MM 200 mixer mill (Retsch, Leeds, Yorkshire, UK) to obtain a more homogenous mixture. In this case, the mixture was weighed out directly into a 25 ml polystyrene sample vial with two, 9 mm polyamide beads. The mixture was homogenised for a period of 15 min at a frequency of 30 Hz.

0.25 g of the resulting mixtures of sample and binder were transferred to a standard infrared (IR) press using 13 mm dyes (Specac, Orpington, Kent, UK) and pressed into a disc using 10 t of pressure for approximately 5 min. The resulting discs had a diameter of 13 mm and a thickness of 1.2 mm.

This method of pressing produced discs of good mechanical stability and of good surface finish, as can be seen in Fig. 2, especially as the ratio of binder to sample was increased. Early trials with PVA suggested that particle sizes of $<50 \mu m$ were required for good ablation performance. The particle sizes used in this investigation were much smaller than this and were mostly in the 1–10 $\mu m$ range, which is the range

![Digital photograph of a disc produced using vanillic acid as a binder and employing the mixer mill as a sample/binder mixing method.](image)

### Table 1

$\lambda_{\text{max}}$ values and molar absorptivities for various binders used in this investigation\textsuperscript{49}

<table>
<thead>
<tr>
<th>Binder</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>Molar absorptivity, $\epsilon_{\text{max}}$/L mol$^{-1}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanillic acid</td>
<td>217</td>
<td>22900</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>217</td>
<td>8610</td>
</tr>
<tr>
<td>Pyrazinoic acid</td>
<td>208</td>
<td>7960</td>
</tr>
</tbody>
</table>


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Table 2  Experimental parameters for all instrumentation employed in this investigation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser ablation system</td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>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>Fluence</td>
<td>2 J cm⁻²</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>20 Hz</td>
</tr>
<tr>
<td>Sampling strategy</td>
<td>Raster</td>
</tr>
<tr>
<td>Spot diameter</td>
<td>110 µm</td>
</tr>
<tr>
<td>Sample translation rate</td>
<td>10 µm s⁻¹</td>
</tr>
<tr>
<td>He carrier gas flow</td>
<td>0.80 L min⁻¹</td>
</tr>
<tr>
<td>Ar make up flow</td>
<td>1.00 L min⁻¹</td>
</tr>
<tr>
<td>Binders</td>
<td>Poly(vinyl alcohol) (PVA)</td>
</tr>
<tr>
<td></td>
<td>Nicotinic acid</td>
</tr>
<tr>
<td></td>
<td>Pyrazinoic acid</td>
</tr>
<tr>
<td>Samples</td>
<td>JMEP 14 Sediment CRM</td>
</tr>
<tr>
<td></td>
<td>GBW 07311 Sediment CRM</td>
</tr>
<tr>
<td></td>
<td>GBW 07401 Soil CRM</td>
</tr>
<tr>
<td></td>
<td>NIST 8435 trace elements in powdered milk CRM</td>
</tr>
<tr>
<td>ICP-MS</td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>PQ ExCell</td>
</tr>
<tr>
<td>Auxiliary gas flow</td>
<td>0.80 L min⁻¹</td>
</tr>
<tr>
<td>Cooling gas flow</td>
<td>12.0 L min⁻¹</td>
</tr>
<tr>
<td>Plasma RF power</td>
<td>1400 W</td>
</tr>
<tr>
<td>Isotopes monitored</td>
<td>11B, 13C, 14N, 26Al, 27Al, 28Si, 40Ca, 44Ca, 52Cr, 54Mn, 55Mn, 59Co, 65Zn, 66Zn, 137Ba, 138La, 141Pm, 140Eu, 207Tl, 208Pb, 218U</td>
</tr>
<tr>
<td>Acquisition mode</td>
<td>Peak hopping</td>
</tr>
<tr>
<td>Detector mode</td>
<td>Dual range</td>
</tr>
<tr>
<td>Channels per peak</td>
<td>1</td>
</tr>
<tr>
<td>Dwell time</td>
<td>100 ms</td>
</tr>
<tr>
<td>No. of sweeps</td>
<td>100</td>
</tr>
<tr>
<td>No. of replicates</td>
<td>50</td>
</tr>
<tr>
<td>Solution nebulisation</td>
<td></td>
</tr>
<tr>
<td>Nebuliser</td>
<td>PFA-100 µL fixed capillary</td>
</tr>
<tr>
<td>Spray chamber</td>
<td>Custom made cyclonic</td>
</tr>
<tr>
<td>Diffuse reflectance</td>
<td></td>
</tr>
<tr>
<td>Spectrometer</td>
<td>USB 2000</td>
</tr>
<tr>
<td>Light source</td>
<td>DH 2000</td>
</tr>
<tr>
<td>Reflectance probe</td>
<td>R400-7-SR-BX</td>
</tr>
<tr>
<td>Probe holder</td>
<td>RPH-1 probe holder</td>
</tr>
<tr>
<td>Integration time</td>
<td>1 s</td>
</tr>
<tr>
<td>Spectra average</td>
<td>5</td>
</tr>
<tr>
<td>Reflectance standard</td>
<td>WS-1 diffuse reflectance standard (PTFE)</td>
</tr>
<tr>
<td>Replicates</td>
<td>5</td>
</tr>
<tr>
<td>Surface profiling</td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>RM 600 laser stylus</td>
</tr>
<tr>
<td>No. of points</td>
<td>800</td>
</tr>
<tr>
<td>Spacing</td>
<td>2 µm</td>
</tr>
<tr>
<td>Vertical range</td>
<td>±300 µm</td>
</tr>
<tr>
<td>No. scans per sample</td>
<td>5</td>
</tr>
</tbody>
</table>

produced by the mixer mill (values taken from manufacturer's specification for mixing of soft powders).

**Instrumentation**

Table 2 lists experimental parameters for all the instrumentation used throughout this investigation.

A commercially available UP-213 laser ablation system (New Wave Research Inc., Huntingdon, Cambridgeshire, UK) operating in the deep UV (213 nm) was employed using He as a carrier gas due to its improved ablation and transport characteristics. The He carrier gas was combined with an auxiliary Ar gas flow 1 m before the torch using a simple polypropylene Y-piece (Fisher Scientific, Loughborough, Leicestershire, UK). A further tangential mixing vessel was placed in the Peltier chamber of the ICP-MS to facilitate further mixing of the two gas lines. All gas lines used were constructed from 1 m lengths of 6 mm od Tygon tubing (Fisher Scientific, Loughborough, Leicestershire, UK).

The LA system was coupled to a VG PQ ExCell ICP-MS instrument (Thermo Electron Corporation, Winsford, Cheshire, UK). Optimisation of the torch-box position, lens voltages, auxiliary Ar gas flow and LA carrier gas flow was performed before analysis, with respect to the signal intensity obtained upon ablation of NIST 612 Trace Elements in Glass CRM. The LA parameters employed were used to reproduce the typical conditions encountered in bulk analysis by LA-ICP-MS.

Calibration experiments were performed both under 'dry' and 'wet' plasma conditions and the quality of analytical data compared to determine whether the more standardised plasma conditions offered by employing a 'wet' plasma led to an improvement in data quality, as has been previously reported. In this paper the term "wet" refers to a plasma in which the liquid phase aerosol and vapour phase water are present, i.e., the classical wet plasma produced in solution analysis. This was achieved by combining the aerosol produced by solution nebulisation of 18.2 MQ cm⁻¹ purity water (Elga Lab Water, High Wycombe, Buckinghamshire, UK) using a PFA-100 µL fixed capillary nebuliser (Elemental Scientific Inc., Omaha, Nebraska, USA) and a custom-made cyclonic spray chamber, with the LA aerosol using the polypropylene Y-piece (Fisher Scientific, Loughborough, Leicestershire, UK). Fig. 3 shows the experimental arrangement employed.

Diffuse reflectance analysis was performed on the discs to characterise their absorption properties. For the purpose of this investigation it was the reflectance of the discs at 213 nm that was of particular relevance since this coincided with the wavelength of the LA system employed. An Ocean Optics (Dunedin, Florida, USA) USB 2000 photodiode array spectrometer operated in diffuse reflectance mode was employed.

Surface profiling of the craters produced was performed using a custom made system employing a Rodenstock RM 600 laser stylus (Munich, Germany). This is a non-contact laser
styrus that uses dynamic focusing of the laser beam and the focus error signal to determine surface topography.

Homogeneity trials

In order to perform bulk analysis by LA-ICP-MS it is vital that the analyte is homogenously distributed throughout the sample. This is of particular importance when a binder is used, whether it is absorbing or not. For this reason an investigation into the homogeneity of the elemental distribution was performed, utilising the Transient Rapid Analysis (TRA) function of the ICP-MS. A dry plasma was used for this investigation.

Using the setup described in Fig. 3 and the parameters listed in Table 2, the distributions of elements within discs produced by mixing in a pestle and mortar and discs produced by mixing in an MM 200 mixer mill were compared. For this investigation, three discs were analysed, consisting of GBW 07311 Sediment CRM and a vanillic acid binder. Their composition and mixing method is shown Table 3.

$^{13}$C was used as an internal standard element to correct for differences in rates of ablation during the ablation of each track. The elemental distribution across the discs was monitored and the %RSD of the ratio of analyte signal intensity to $^{13}$C signal intensity was determined and used as an indication of homogeneity. The %RSD was determined over a range of 9 mm in the middle of the laser ablated track, i.e., between the 3 mm and 12 mm points on the graphs produced.

Effect of varying disc composition

Discs of varying composition were produced to determine the effects of different types and compositions of binders and samples. Three different ‘absorbing binders’ were chosen for this investigation due to their high absorptivity around the wavelength of the incident laser beam as shown in Table 1. $^{1}$Vanillic acid, nicotinic acid and pyrazinoic acid. PVA was chosen as an example of a ‘non-absorbing’ binder. GBW 07311 Sediment CRM was chosen as a sample in this particular investigation, since it is well characterised for a range of analytes. A series of discs with increasing CRM composition, i.e., 0, 10, 20, 40, 60, 80 and 100%, was produced for each combination of sample and binder.

LA-ICP-MS analysis

These discs were analysed by LA-ICP-MS, using the parameters described in Table 2 and the setup shown in Fig. 3, to determine the effects of differing binder type and binder composition on signal sensitivity and stability and to establish the optimum disc composition. In each case the laser beam was focused upon the disc surface. Response curves were plotted for all the isotopes monitored.

It should be noted that although the concentration of C was around 50% in the discs, the ablated mass produced by the UP-213 LA system was so small that no significant deposition was observed upon the cones, even in bulk analysis mode. For this reason no O$_2$ addition to the plasma was required.

Diffuse reflectance analysis

Diffuse reflectance analysis was performed, employing the parameters described in Table 2, on the same series of discs used for the LA-ICP-MS investigation, to determine the effect of differing binder type and binder composition on the absorption properties of the discs. The mean % reflectance at 213 nm was determined for each disc using five replicates. All reflectance measurements were made relative to a PTFE diffuse reflectance standard, as stated in Table 2.

The absorption properties of the pure binders were characterised by determining the mean % reflectance of ‘100% blank’ discs with respect to the PTFE standard.

Surface profilometry

Surface profilometry was performed on the discs produced from 100% of each of the binders to determine the maximum ablated crater depth, produced using the same LA parameters as described in Table 2. This crater depth was used as an indication of the effective ablation depth achieved by the laser. It is recognised that optical absorbance was not the sole parameter affecting the data obtained in this investigation and that the different physicochemical properties of the binders also affected the outcomes. However, the particle sizes of the binders used to press the discs were all similar and the press has been shown to produce discs of consistent density and hardness, so it was reasonable to assume that absorbance was the major factor determining the depth of the craters ablated.

Calibration

To determine whether the presence of the organic chromophore offered any advantage when performing quantitative analysis by LA-ICP-MS, two simple calibration strategies based upon external calibration with and without internal standardisation were devised.

Nomenclature

$I =$ Signal intensity or ion count rate (counts s$^{-1}$)
$C =$ Concentration (mg kg$^{-1}$)

Superscript

$A =$ Analyte
$IS =$ Internal standard element

Subscript

$S =$ Sample
$Std =$ Standard.

The concentration of analyte within the sample disc is determined from eqn (1)

$$C^S = I^S/I^A_{Std}/C^A_{Std}$$

(1)

Table 3 Composition and production method of discs used in homogeneity trials. GBW 07311 Sediment CRM was used as a sample

<table>
<thead>
<tr>
<th>Disc no.</th>
<th>Mixing method employed</th>
<th>Binder type</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disc 1</td>
<td>—</td>
<td>—</td>
<td>100% CRM</td>
</tr>
<tr>
<td>Disc 2</td>
<td>Pestle and mortar</td>
<td>Vanillic acid</td>
<td>40% binder 60% CRM</td>
</tr>
<tr>
<td>Disc 3</td>
<td>Ball mixer</td>
<td>Vanillic acid</td>
<td>40% binder 60% CRM</td>
</tr>
</tbody>
</table>


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If an element of known concentration is available within the sample and standard, than internal standardisation can be utilised, yielding eqn (2).

$$C_s = \frac{I_s}{I_s} \times \frac{I_s}{I_s}$$

(2)

Calibration was performed using sample and standard discs produced from 100% CRMs and from sample and standard discs produced from 60% CRM and 40% PVA or vanillic acid binder. Different combinations of discs were used as sample and external standard and the quality of data compared to determine the effects of the presence of the vanillic acid organic chromophore, in particular whether utilising vanillic acid offered an improvement in data quality over PVA or pure pressed sample/standard. These investigations were performed under both wet and dry plasma conditions to determine whether the use of wet plasma conditions offers any advantage with respect to standardising plasma conditions, as was observed in previous work.52

Another set of calibrations was performed involving the use of a sample and a standard that were totally different in terms of their matrix composition. NIST 8435 Whole Milk Powder CRM was employed as either sample or standard with the other soil and sediment CRMs used previously. Again vanillic acid and PVA were used as a binder. This type of calibration was performed solely to verify the advantages offered by employing an absorbing binder. It is recognised that this deliberate ‘mismatching’ of sample and standard would not be employed for the analysis of a real sample. This series of calibrations were performed utilising ‘dry’ plasma conditions only.

It should be noted that for analysis of a ‘real’ sample, an internal standard element would normally be employed to correct for differences in ablation rates between the sample and the standard. In this investigation, the relative data quality between calibration sets, without internal standardisation, was more important than the absolute data quality with internal standardisation in showing the differences between the binders. However, since CRMs have been used as both samples and standards, then an internal standard element was available. For this reason, data utilising 65Cu as an internal standard element is also presented and is useful in providing a comparison of the data quality obtainable with this method.

Results and discussion

Homogeneity trials

The elemental distributions across the discs produced using the ball mixer were much more homogenous when compared with those produced using a simple pestle and mortar. This can be seen in Fig. 4 and is numerically indicated by the much smaller %RSDs obtained for those discs as highlighted in Table 4. Importantly, discs produced from 100% CRM, with no subsequent homogenising stage, also showed poor homogeneity, indicating the importance of using a homogenising mixer mill even when no binder is employed, since the CRMs may not be as homogenous as is often assumed.

It is vital that the distribution of analyte within the discs is homogenous in order to obtain accurate and precise data. Table 4 shows the RSDs (%) of the (analyte signal intensity/13C signal intensity) ratio for discs 1–3. Discs 2 and 3 were prepared using a 60% CRM and 40% vanillic acid binder mixture.

<table>
<thead>
<tr>
<th>Type</th>
<th>199La</th>
<th>208Pb</th>
<th>238U</th>
<th>Mean RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disc 1 100% CRM</td>
<td>44</td>
<td>27</td>
<td>127</td>
<td>66</td>
</tr>
<tr>
<td>Disc 2 pestle and mortar</td>
<td>39</td>
<td>29</td>
<td>117</td>
<td>62</td>
</tr>
<tr>
<td>Disc 3 Retsch MM 200</td>
<td>26</td>
<td>13</td>
<td>26</td>
<td>22</td>
</tr>
</tbody>
</table>

Fig. 4 LA-ICP-MS analysis to determine the elemental distribution across discs: (1) produced from 100% sample, (2) 60% CRM and 40% vanillic acid binder mixed using a simple pestle and mortar and (3) 60% CRM and 40% vanillic acid binder mixed using a MM 200 mill. CRM was GBW 07311 Sediment.
Fig. 5 LA-ICP-MS data for discs produced using GBW 07311 Sediment as a sample and different binders of varying composition.

Table 5 Reflectance data at 213 nm for discs produced from 100% of all the binders used in the investigation of discs produced from 100% GBW 07311 Sediment

<table>
<thead>
<tr>
<th>Disc</th>
<th>Mean reflectance (%)</th>
<th>Standard deviation (%)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanillic acid</td>
<td>1.37</td>
<td>0.30</td>
<td>22.70</td>
</tr>
<tr>
<td>Pyrazinoic acid</td>
<td>2.40</td>
<td>0.33</td>
<td>8.68</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>5.26</td>
<td>0.40</td>
<td>7.57</td>
</tr>
<tr>
<td>GBW 07311 Sediment</td>
<td>8.48</td>
<td>0.40</td>
<td>4.72</td>
</tr>
<tr>
<td>PVA</td>
<td>11.19</td>
<td>0.96</td>
<td>8.58</td>
</tr>
</tbody>
</table>

Quantitative data. Using the ‘absorbing binders’ it is also necessary to ensure that the sample and binder have been adequately mixed, prior to pressing to facilitate an efficient coupling of the laser beam energy and the sample surface. It has been shown in this investigation that the use of a mixer mill is essential to provide a sufficient degree of mixing between sample and binder. All further discs employed in this investigation were therefore prepared using the mixer mill method rather than the pestle and mortar, which produced an inadequate degree of mixing.

Effect of varying disc composition

LA-ICP-MS analysis. The use of vanillic acid as a binder led to increased sensitivity in comparison with the other binders investigated, as indicated by the steep climb and the high optimum of the curve in Fig. 5 (although Fig. 5 uses $^{238}$U as the analyte, all the analytes investigated, see the list in Table 2, gave the same result). Vanillic acid was followed by pyrazinoic acid and nicotinic acid in terms of overall sensitivity.

This order correlated with the molar absorptivities of the compounds quoted in Table 1, in which vanillic acid is shown to possess a greater molar absorbivity when compared with pyrazinoic and nicotinic acids. Importantly, all three ‘absorbing binders’ showed a gain in sensitivity when compared with the use of ‘non-absorbing’ PVA.

The absorbing binders, vanillic acid, nicotinic acid and pyrazinoic acid, yielded distinct curves with optima around 60–80% CRM composition. Significantly, analysis of the series of discs produced using PVA yielded a straight line ($R^2 = 0.9994$), as is found for a regular external calibration, rather than a curve, indicating the absence of any optical absorbance effect.

Diffuse reflectance analysis. The diffuse reflectance data obtained are shown in Fig. 6. The occurrence of the distinct curves can be related to the optical properties of the binders employed. When an ‘absorbing binder’ was employed, as the concentration of sample and consequently analyte was increased, there was a subsequent decrease in the absorbance of the sample surface (indicated by an increase in % reflectance) due to a reduction in absorbing binder concentration. There is a crossover point for the curves obtained from the analysis of pyrazinoic and nicotinic acid; as yet no explanation can be given, although it was observed that after pressing a pink tinge was often present on the surface of discs produced from pyrazinoic acid, indicating the occurrence of some unusual surface effects. Importantly, the data for PVA showed a slight decrease in reflectance as the sample concentration was increased, due to the fact that in this case the sample, GBW 07311 Sediment, had a greater absorptivity than the binder, PVA.

The diffuse reflectance data followed the same trend as the quoted molar absorptivities, see Table 5, of the compounds and the LA-ICP-MS data described previously. Vanillic acid offered the greatest absorbance of the laser energy, followed by pyrazinoic and nicotinic acids. As expected, PVA has been shown to possess the lowest optical absorbance at the lasing
condensation of vaporised material. Nevertheless, a highly absorbing substrate results in a thinner melt layer and lower penetration depth, which in turn produces an aerosol with smaller particle sizes and importantly an absence of larger particles that are not efficiently transported and processed by the plasma. The generation of smaller particles during the ablation process is likely to reduce elemental fractionation occurring within the ICP, which may be caused by selective volatilisation from the surface of large particles that are not fully vaporised. Therefore, the use of these absorbing binders should contribute to minimising the detrimental effects of elemental fractionation on quantitative analysis by LA-ICP-MS, as well as providing the more obvious benefits offered by increased sensitivity.

Surface profiling. Surface profiling of the laser ablated tracks showed that, as expected, ablation produced shallower craters in more absorbing matrices. These data are shown in Table 6. The depth of the craters produced correlated with the LA-ICP-MS and diffuse reflectance data already reported, in that the shallower craters were produced in the most absorbing substrate, the vanillic acid. The deepest craters were produced in the least absorbing substrate, the PVA, as expected. The crater depths indicate directly the depth of penetration of the laser beam before its intensity falls below the threshold intensity for ablation. Nicotinic acid and pyrazinoic acid gave similar, relatively shallow crater depths, indicating that they offer a similar optical penetration depth.

It would have been interesting to characterise the shape and maximum depth of the craters produced in discs containing sample rather than just the binders. However, access to the surface profiling instrumentation was restricted and it was felt that it was most important to characterise the craters produced in the four binders used.

Although the greatest volume/mass of substrate was removed for the non-absorbing binder, the highest analytical sensitivity was obtained from the smallest crater volumes. The increased sensitivity offered by using an 'absorbing binder', such as vanillic acid, was almost certainly due to the production of smaller sized particles at the ablation site. Such smaller particles were more efficiently transported to and processed by the ICP. Recent studies have shown that small particles are not necessarily produced directly from the laser-solid interaction, but more likely through secondary processes, namely by condensation of vapourised material. Nevertheless, a

<table>
<thead>
<tr>
<th>Disc</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Mean</th>
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<th>RSD (%)</th>
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<td>4.8</td>
</tr>
<tr>
<td>Nicotinic acid</td>
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<td>86</td>
<td>91</td>
<td>105</td>
<td>108</td>
<td>97</td>
<td>9.4</td>
<td>9.7</td>
</tr>
<tr>
<td>Pyrazinoic acid</td>
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<td>PVA</td>
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<td>127</td>
<td>109</td>
<td>135</td>
<td>17.3</td>
<td>12.9</td>
</tr>
</tbody>
</table>

Table 6 Maximum crater depth measurements for discs produced from each of the four binders, obtained using surface profilometry.

The data obtained under 'dry' plasma conditions are shown in Table 7. The recoveries were consistently closer to 100% when vanillic acid was used as a binder, compared with the use of a less absorbing binder or no binder at all. This outcome was true for all the elements studied with no outliers. When employing the vanillic acid, all external cross-calibrations resulted in recoveries well within ±10%. This was due to the chromophore dominating the ablation process rather than the sample. Unlike simple dilution of the sample, this 'active substrate' dilution/matrix matching enhanced sensitivity rather than reduced it. Vanillic acid yielded a signal response that was three times greater than when PVA was used.

External cross-calibration using discs of 100% CRM resulted in a broad range of recoveries (47–199%), indicating that the differences in sample matrix had large effects on the quality of data obtained. It is well documented that even small changes in sample matrix can lead to large variations in the recovery data shown in Table 7. The recoveries were consistently closer to 100% when vanillic acid was used as a binder.
Table 8  Analytical data showing the mean and RSD (%) recoveries using different combinations of discs as sample and standard. The data were obtained under 'wet' plasma conditions. The term 'n = ' represents the number of analytes quantified per calibration. IMEP 14 and GBW 07311 are sediments whilst GBW 07401 is a soil.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard</th>
<th>Mean</th>
<th>RSD</th>
<th>Mean</th>
<th>RSD</th>
<th>Mean</th>
<th>RSD</th>
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</tr>
</thead>
<tbody>
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<td>183</td>
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<td>6</td>
</tr>
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<td>GBW 07401</td>
<td>GBW 07311</td>
<td>23</td>
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<td>125</td>
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<td>15</td>
</tr>
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<td>GBW 07311</td>
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<td>15</td>
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<tr>
<td>RSD (%)</td>
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<td>41</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
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</tr>
</tbody>
</table>

Table 9  Analytical data showing the mean and RSD (%) recoveries using different combinations of discs as sample and standard. In this case the sample and standard were deliberately chosen to differ in terms of their matrix composition. IMEP 14 and GBW 07311 are sediments, GBW 07401 is a soil, whilst NIST 8435 is a powdered milk. The data were obtained under 'dry' plasma conditions. The term 'n = ' represents the number of analytes quantified per calibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard</th>
<th>Mean</th>
<th>RSD</th>
<th>Mean</th>
<th>RSD</th>
<th>Mean</th>
<th>RSD</th>
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<td>80</td>
<td>45</td>
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</tbody>
</table>

Ablation rates and hence the poor quality data obtained by this type of cross-calibration were hardly surprising.

When the non-absorbing PVA was employed as a binder, the quality of the data declined even further and a larger range of recoveries was obtained (47-219%). This can probably be attributed to the dilution of the sample, resulting in reduced sensitivity, since unlike vanillic acid, PVA does not offer an increase in target absorbance. This reduction in sensitivity meant that many analytes in the discs were at levels closer to their detection limits where the quality of analytical data was poorer.

The fact that an absorbing binder such as vanillic acid does offer an advantage over the use of a non-absorbing binder, such as PVA, was confirmed by the repeat of the analyses under wet plasma conditions. Table 8 shows that the calculated recoveries were much closer to 100% when vanillic acid was used rather than PVA or no binder at all.

The quality of the analytical data obtained under wet and dry plasma conditions showed no significant differences. The recoveries were perhaps slightly better under wet plasma conditions, but the differences were not large enough to confirm the merits of employing a wet plasma for this type of calibration. Unlike in previous work, the determining factor in this investigation was the difference in sample and standard matrix, resulting in variations in ablation yields.

Table 10  Analytical data, using $^{64}$Cu as an internal standard element, showing the mean and RSD (%) recoveries using different combinations of discs as sample and standard. The data were obtained under 'dry' plasma conditions. The term 'n = ' represents the number of analytes quantified per calibration. IMEP 14 and GBW 07311 are sediments whilst GBW 07401 is a soil.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard</th>
<th>Mean</th>
<th>RSD</th>
<th>Mean</th>
<th>RSD</th>
<th>Mean</th>
<th>RSD</th>
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<td>14</td>
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</tbody>
</table>

Table 11 Analytical data, using $^{65}$Cu as an internal standard element, showing the mean and RSD (%) recoveries using different combinations of discs as sample and standard. In this case the sample and standard have been deliberately chosen to differ in terms of their matrix composition. IMEP 14 and GBW 07311 are sediments, GBW 07401 is a soil, whilst NIST 8435 is a powdered milk. The data were obtained under ‘dry’ plasma conditions. The term ‘n’ represents the number of analytes quantified per calibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard</th>
<th>Recovery data 100% CRM (%)</th>
<th>Recovery data 40% PVA (%)</th>
<th>Recovery data 40% vanillic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>RSD</td>
<td>Mean</td>
<td>RSD</td>
</tr>
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<tr>
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</tr>
</tbody>
</table>

during the ablation process and not during the vapourisation and ionisation processes occurring within the plasma, i.e., plasma processes were secondary to the primary ablation processes. Here, by using a standardised and strongly absorbing matrix, the total plasma loading did not vary as much between samples and standards as when a dried nebuliser derived aerosol is used to calibrate the response from a laser ablated solid substrate (water is needed in this case to produce a single dominant plasma species).

The advantages of employing an absorbing binder are emphasised in Table 9, which shows the analytical data obtained by using a sample and standard that differed greatly in terms of matrix composition. Once again the vanillic acid binder yielded a considerable improvement in data over that obtained from the use of discs produced from 100% CRM and those produced using PVA as a binder.

Table 10 and Table 11 show the data obtained when $^{65}$Cu was employed as an internal standard element. There was a vast improvement in the quality of the analytical data from the calibrations performed using discs produced from 100% CRM and those produced from 40% PVA. This improvement is expected since the use of $^{65}$Cu as an internal standard element corrects for differences in ablation rates between sample and standard, which would have been significant when utilising 100% CRM or the PVA due to differences in target matrix. The quality of data did not improve for discs produced using vanillic acid since the standardised target matrix offered by these discs meant that rates of ablation were similar between sample and standard and hence internal standard correction was not required.

**Conclusion**

This work has shown that by utilising a binder that absorbs strongly at the lasing wavelength of 213 nm, such as vanillic acid, rather than a non-absorbing binder such as PVA, excellent quality analytical data was obtained without the use of internal standardisation. By adding vanillic acid to the powdered sample of interest, an approximately three-fold gain in sensitivity was achieved over the use of PVA, leading to lower limits of detection and an improvement in quantitation. Importantly, the chromophores employed were successful as binders and produced discs of greater mechanical stability than was obtained by pressing the sample alone.

The data suggest that the mechanism for the increase in sensitivity was through the formation of smaller particles during the ablation process. Diffuse reflectance data showed that a greater absorptivity at the lasing wavelength was obtained by utilising vanillic acid as a binder. A greater absorption of the laser energy by the sample surface leads to a shorter effective penetration depth, as was shown by the surface profilometry. This allows a greater energy density to be achieved in the target, leading to the formation of smaller particles. Such particles are more efficiently transported to and processed by the ICP, leading to an improvement in sensitivity and a reduction in plasma based elemental fractionation.

Employing vanillic acid as a binder introduces a degree of matrix matching between sample and standard but, more importantly, standardises the absorptivity of the matrix. This in turn leads to a standardisation of ablation conditions and mass flux to the plasma, which are prerequisites for robust calibration. Unlike the use of a traditional, non-absorbing binder, which simply dilutes the sample, this matrix matching is accompanied by an increase in sensitivity. The result is a substantial improvement in the quality of data obtained when using external calibration for LA-ICP-MS.

The use of absorbing chromophore binders has been shown to offer a robust calibration method for the quantitative analysis of powdered samples using simple external calibration. The data produced would be fit-for-purpose in many practical analytical applications. The technique is simple and employs commonly available laboratory reagents and equipment.

**Acknowledgements**

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Metrology Department, Loughborough University, for the surface profiling.

References


