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The Application of ICP-MS to High Matrix Samples such as those Found in the Ceramics Industry

By

Mark R. Landon

A Doctoral Thesis

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

September 2006

Abstract

Although the benefits of ICP-MS are well documented, the determination of analytes at low levels in high concentrations of matrix elements has proved difficult. As ICP-MS is a 'flow into' instrument the deposition of salts throughout the system is a common cause of significant loss of signal. The application of desolvation of aluminosilicate samples, to aid in the production of more robust plasma conditions, was investigated to increase the efficiency of the ICP in processing the sample. The performance of the ICP-MS was monitored with different cone arrangements and by running the skimmer cones at elevated temperatures.

An alternative to modification of the instrument is to employ chemical modification of the sample and hence the separation of Au and Pt from an aluminosilicate matrix via the use of solid phase extraction (SPE) columns were investigated as a means of dealing with high levels of dissolved solids. DVB based SPE columns were found to give high retentions of Au and Pt when chelated with ammonium pyrrolidinediethylcarbamate (APDC).

A second alternative that avoided digestion of the aluminosilicate matrices, was to carry out the analysis using laser ablation (LA). LA-ICP-MS is becoming increasingly used for trace elemental analysis but as yet no universal calibration method is available. The general problems associated with matrix matched standards are inherent as the ablation mechanism and plasma conditions can differ dramatically with very small changes in matrix composition. Hence the addition of chromophores was employed to increase the absorption of the laser energy. The use of vanillic, nicotinic and pyrazinoic acid were used to improve the ablation of pressed powder discs at the laser wavelength of 213 nm. Synthetic aluminosilicate discs and standard additions were both employed for the calibration and determination of Ti.

Keywords: ICP-MS, Laser Ablation, Separation, Pressed Powders, Chelation, Interface Modification, Solid Phase Extraction.
Aim

The determination of trace elements is extremely important with regards to refractory matrices like ceramics and high performance industrial materials. If a ceramic material is placed under stress the impurities can cause weaknesses and lead to fracturing and failure. Refractory matrices are problematic for ICP-MS because it is a ‘flow into’ technique and is therefore more prone to matrix interferences than other elemental techniques. The conventional approach of dilution is not always appropriate as the levels of impurities can be extremely low compared to those of the matrix elements. Thus this kind of analysis is one of the unsolved problem areas for the ICP-MS technique.

The aim of this project was to investigate possible solutions to trace metal analysis of refractory matrices by ICP-MS. The problem was approached from 3 different angles:

1. Instrument modification to deter sample deposition on the mass spectrometer interface and to produce optimum conditions for efficient analysis.
2. Chemical separation of particular elements of interest from the matrix.
3. Solid sample analysis by LA-ICP-MS to reduce sample preparation and the effects of plasma loading.
Acknowledgements

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I would also like to thank Thermo Electron for the provision of the VG PQ ExCell instrument and LGC for the loan of the laser ablation system.

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<td>AC</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>ADTC</td>
<td>Ammonium Diethyldithiocarbamate</td>
</tr>
<tr>
<td>ADTP</td>
<td>Ammonium Diethyldithiophosphoric Acid</td>
</tr>
<tr>
<td>AES</td>
<td>Atomic Emission Spectrometry</td>
</tr>
<tr>
<td>APDC</td>
<td>Ammonium Pyrrolidinedithiocarbamate</td>
</tr>
<tr>
<td>BBO</td>
<td><em>Beta</em> Barium Borate</td>
</tr>
<tr>
<td>BC</td>
<td>Ball Clay</td>
</tr>
<tr>
<td>CB</td>
<td>Calcined Bauxite</td>
</tr>
<tr>
<td>CN</td>
<td>Cyano</td>
</tr>
<tr>
<td>CRM</td>
<td>Certified Reference Material</td>
</tr>
<tr>
<td>DDTC</td>
<td>Diethyl Dithio Carbamate</td>
</tr>
<tr>
<td>DDTP</td>
<td>Diethyl Dithio Phosphate</td>
</tr>
<tr>
<td>DL</td>
<td>Detection Limits</td>
</tr>
<tr>
<td>DVB</td>
<td>Divinyl Benzene</td>
</tr>
<tr>
<td>ESA</td>
<td>Electrostatic Analyser</td>
</tr>
<tr>
<td>ETAAS</td>
<td>Electrothermal Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>ETV</td>
<td>Electrothermal Vaporisation</td>
</tr>
<tr>
<td>FAAS</td>
<td>Flame Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>FI</td>
<td>Flow Injection</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>HG</td>
<td>Hydride Generation</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>IP</td>
<td>Ionisation Potential</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>KD*P</td>
<td>Potassium Dideuterium Phosphate</td>
</tr>
<tr>
<td>KEtX</td>
<td>Potassium Ethyl Xanthate</td>
</tr>
<tr>
<td>LA</td>
<td>Laser Ablation</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low Density Polyethylene</td>
</tr>
<tr>
<td>MALDI</td>
<td>Matrix Assisted Laser Desorption Ionisation</td>
</tr>
<tr>
<td>MIBK</td>
<td>Methyl Isobutyl Ketone</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>Nd:YAG</td>
<td>Neodymium Yttrium Aluminum Garnet</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>ODMBAC</td>
<td>Octadecyl Dimethyl Benzyl Ammonium Chloride</td>
</tr>
<tr>
<td>OES</td>
<td>Optical Emission Spectrometry</td>
</tr>
<tr>
<td>PGE</td>
<td>Platinum Group Elements</td>
</tr>
<tr>
<td>PONPE-10</td>
<td>Polyoxyethylene(10)-p-isononylphenyl</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PTMEG</td>
<td>Polytetramethylene Ether Glycol</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl Alcohol</td>
</tr>
<tr>
<td>REE</td>
<td>Rare Earth Elements</td>
</tr>
<tr>
<td>RSD</td>
<td>Relative Standard Deviation</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SFC</td>
<td>Supercritical Fluid Chromatography</td>
</tr>
<tr>
<td>SPE</td>
<td>Solid Phase Extraction</td>
</tr>
<tr>
<td>SPMD</td>
<td>Surface Pressed Mixture Disc</td>
</tr>
<tr>
<td>SPSD</td>
<td>Surface Pressed Sample Disc</td>
</tr>
<tr>
<td>TCF</td>
<td>Thiol Cotton Fibre</td>
</tr>
<tr>
<td>TMD</td>
<td>Total Mixed Disc</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>ToF</td>
<td>Time of Flight</td>
</tr>
<tr>
<td>TRA</td>
<td>Time Resolved Analysis</td>
</tr>
<tr>
<td>TXRF</td>
<td>Total Reflection X-Ray Fluorescence</td>
</tr>
<tr>
<td>USN</td>
<td>Ultrasonic Nebuliser</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
</tr>
</tbody>
</table>
Chapter One

Inductively Coupled Plasma Mass Spectrometry
1. **Inductively Coupled Plasma Mass Spectrometry**

1.1. **Introduction**

Over the last 25 years, since the first reported coupling of an inductively coupled plasma (ICP) to a mass spectrometer (MS),¹ ICP-MS has become an extremely powerful tool for elemental analysis. ICP-MS has been used extensively for a vast range of samples including geological, environmental and biological. ICP-MS has the advantages of a large dynamic range (8 orders of magnitude) and high sensitivity (1 pg mL⁻¹ for many elements).² As well as quantitative analysis, ICP-MS is also capable of isotopic determinations of many elements, making it a very useful tool for many applications.

1.2. **ICP-MS Instrumentation**

A typical arrangement for a quadrupole based ICP-MS instrument is demonstrated in Fig. 1.1. Dependent on the manufacturer, the layout of the instrument can alter significantly. An extensive array of differing designs of nebulisers, spray chambers, torches, cones etc. are available for specific applications. Each segment of the instrument will be explained in greater detail in the following sections.

![Figure 1.1. Schematic diagram of a quadrupole based ICP-MS setup for solution nebulisation.](image-url)
1.2.1. Sample Introduction

As one of the most important aspects of ICP-MS is the efficiency of ion production, the transportation of samples to the plasma is of utmost importance. Although gases and solids can both be analysed by hyphenated techniques like gas chromatography (GC), laser ablation (LA) and electrothermal vapourisation (ETV), liquid nebulisation still remains the most common method of transportation of samples to the plasma. This is mainly due to the ease with which calibration and sample handling can be performed, giving excellent accuracy and precision.

1.2.1.1. Gas Sampling

The most common form of gaseous introduction of samples into the plasma is through hydride generation (HG). HG only works for certain elements including As, Bi, Ge, Pb, Sb, Se, Sn and Te as these efficiently form volatile hydrides. By forming the volatile hydrides many polyatomic and matrix interferences are reduced or removed.

More recently developments have seen the introduction of gas chromatography (GC) and supercritical fluid chromatography (SFC) used as a separation/sampling method with ICP-MS as a detector. As ICP-MS can process gases very easily the mobile phase in GC links easily to the torch injector. Similarly when SFC is linked to an ICP the mobile phase alters from a supercritical state to a gas prior to entry into the torch. For both techniques, the interface between the chromatograph and the ICP must be heated to avoid condensation of analytes. Both GC and SFC have been successfully linked to ICP-MS and used for the separation and determination of organometallics. They have been found to be extremely useful for the speciation of elements such as Pb, Sn, Hg, Cr, As and Se.

1.2.1.2. Liquid Sampling

The transportation of liquids to the plasma is the most commonly used method of sample introduction for ICP-MS. The general setup involves a nebuliser and spray
chamber arrangement. The liquid sample is either pumped (typically by a peristaltic pump) to the nebuliser or drawn to the nebuliser by the gas flowing through (natural uptake or aspiration). There is a wide range of nebulisers\textsuperscript{16} from various manufacturers, although the most commonly used nebuliser is a glass concentric nebuliser. The concentric nebuliser works by the liquid sample travelling down a central channel, as it reaches the end a coaxial gas flow produces an aerosol. The nebulised solution is now present in droplets of up to 100 $\mu$m and the transmitted fraction must be reduced to less than 10 $\mu$m with the use of a spray chamber. Many variations in spray chamber designs are available including bead, cyclonic and double pass. Their purpose is to remove large particles from the nebulised aerosol. The large particles are removed by centrifugal forces causing impact on the spray chamber walls or by an impact bead.

\textbf{1.2.1.3. Solid Sampling}

Laser ablation (LA) has become the main technique used for analysis of solids with ICP-MS detection.\textsuperscript{17, 18} LA has now become widely recognised as a versatile sampling technique. The sampling abilities range from conducting and non-conducting inorganic and organic compounds as solid or powders. Other methods of solid sample introduction are electrothermal vapourisation (ETV),\textsuperscript{19-33} arc/spark ablation\textsuperscript{18, 34, 35} and slurry nebulisation.\textsuperscript{19, 23, 25, 32, 36} With ETV-ICP-MS one of the major limitations is the sample size which must be 10 mg or less,\textsuperscript{16} so to get a representative sample a large amount of sample preparation is required hence removing the benefits of the time reduction associated with direct solid sampling.

Arc/spark ablation requires the sample of interest to be conducting, if this is not the case a coating of a conducting material, such as powdered copper or graphite must be employed. Similar to ETV, this requires more sample preparation time and diminishes the benefits of direct sample analysis. Also by the addition of these powders, possible interferences/contamination can occur and the additional cost of high purity powders is incurred.
As samples are not always a ‘true’ solid but often come in powdered form, a convenient way of dealing with such materials is by forming a slurry. Slurries can be nebulised directly into an ICP-MS instrument with a high solids nebuliser. It has been found that to obtain accurate results a few modifications need to be made to the system and to the sample preparation. A small particle size ($\phi 2 - 3 \mu m$) and lower nebuliser flow rates are required (~0.4 mL min$^{-1}$) with all obstructions i.e. impact bead, removed from the spray chamber, a larger injector needs to be employed in the torch (~3 mm).

The major problem associated with solid sampling is calibration. Making matrix matched samples which mimic the real samples has proved limiting to these techniques. Also a poorer accuracy and precision over solution nebulisation is obtained.

1.2.2. Torch and Plasma

The torch itself consists of three concentric tubes giving three separately controlled Ar flows. The flows are named the injector, auxiliary and coolant flows, and have values of 0.4 – 1 mL min$^{-1}$, 0.5 – 1 mL min$^{-1}$ and 12 – 14 mL min$^{-1}$ respectively.$^{37}$ The injector is connected to the sample introduction system and carries the sample (in Ar) into the core of the plasma. The torch is usually made from quartz although demountable injectors have been made from alumina or platinum to reduce background levels of Si and to handle HF.

The definition of a plasma is ‘an electrically neutral, highly ionised gas composed of ions, electrons, and neutral particles’. A plasma is produced by introducing high energy electrons (from a Tesla coil) into a stream of Ar at the end of the torch. Around the end of the torch a copper induction coil (2 – 3 turns) applies a magnetic and induced electric field which accelerates the electrons and the plasma is formed. The plasma is then self-sustaining as electrons ionise Ar atoms releasing further electrons, as long as the magnetic field is sufficient and the gas flows are not altered significantly.
The plasma is present at atmospheric pressure and possesses a temperature of around $10,000 \text{ K}$ with the central channel around $6500 - 7000 \text{ K}$. As the nebulised sample enters the central channel a residency time of several milliseconds causes rapid vaporisation, atomisation and ionisation of the analytes.

1.2.3. **Interface Region**

The interface region is where the ions get extracted from the plasma and transported to the mass analyser through a series of stages which reduce the pressure. The tip of the plasma is situated on an orifice ($\varnothing \sim 1 \text{ mm}$) of a sample cone, usually made of Ni, but can possess a Pt tip or be made of Al$^{17}$ for certain applications. Ions and neutral species present in the central channel of the plasma are extracted through the orifice and immediately undergoes supersonic expansion in the expansion chamber. The rapid expansion of the sample causes a shock wave behind the sample cone and encompasses the so-called zone of silence. From this region another cone, called the skimmer cone, extracts ions and neutrals forming a gas jet. The sample is then guided and focussed to the analyser through a series of ion optics.

Some instruments have an additional section within the ion optics called a collision or reaction cell. Dependent on the manufacturer this can consist of either a quadrupole, hexapole or an octapole. These cells can be filled with varying gases causing gas phase reactions, and with tuning of the voltages applied to the poles, certain elements/compounds can be discriminated or altered to reduce spectral interferences.

1.2.4. **Mass Analysers**

1.2.4.1. **Quadrupole Mass Analysers**

Quadrupole mass analysers are the most commonly used in mass spectrometry. The instrument consists of four parallel cylindrical rods. To opposite pairs of rods, rf and dc voltages are applied. The voltage on the rods is increased, whilst keeping the ratio constant. At any specific time an ion with a certain $m/z$ value will
either have a stable trajectory and will reach the detector or have an unstable trajectory and hit one of the rods and be neutralised. The quadrupole acts as a tuneable mass filter and has the advantage of high scan speeds with the spectrums being obtained in less than 100 ms.

1.2.4.2. Double Focussing Mass Analysers

The double focussing mass analyser consists of two sectors: the magnetic analyser and the electrostatic analyser (ESA). The two sectors can be arranged with either sector situated first, and are known as the forward Nier-Johnson arrangement in which the ESA is present first (Fig. 1.2. (a)) and the reverse Nier-Johnson geometry with the magnetic sector first (Fig. 1.2. (b)). The latter is most commonly used in conjunction with ICP-MS as it has displayed better performance over the forward Nier-Johnson geometry instruments. 38

The magnetic analyser consists on a curved flight tube situated between the poles of an electromagnet. As ions enter the magnet from the plasma, separation occurs due to their momenta (dependent on energy and mass of the ion). As the ion energy spread from a plasma can vary by up to 6 eV,38 ions of the same mass may not be focussed to the same point. These ions are then focussed using the ESA, consisting of two curved plates with a voltage applied between them. The kinetic energy of the ions then determines the trajectory through the ESA, so at a particular voltage ions with the same energies will be focussed towards the exit slit.

The forward Nier-Johnson arrangement is also commonly used in multi-collector ICP-MS (MC-ICP-MS). The MC-ICP-MS geometry incorporates the ESA followed by the magnetic sector (Fig. 1.2. (a)). By focussing the ions via the electrostatic sector, the ions are then separated by their trajectories in the magnetic sector. The ion beams are then measured using a series of Faraday cup detectors. The MC-ICP-MS systems are generally used for accurate isotope ratio measurements.
1.2.4.3. Time-Of-Flight Mass Analysers

As the name implies, the ToF mass analyser works by measuring the time taken for a particular ion of known energy to travel a known distance within a field free drift tube, typically about 1 m in length. Flight times are in the order of microseconds with different species being detected nanoseconds apart. As all the ions entering the drift tube possess the same kinetic energies, the velocities vary inversely with their mass, with lighter ions travelling faster than larger ions.

ToF instruments have the advantage of being able to scan up to 30 000 spectra per second. Due to this fast scan rate the measurement of transient signals is possible and hence the ability to link and record data from chromatographic techniques, LA, ETV and HG.

1.2.5. Detectors

The most commonly used detector in atomic mass spectrometry is the electron multiplier. The detector comes in two forms known as the discrete dynode (Fig. 1.3.) and the continuous dynode (Fig. 1.4.) electron multipliers. The discrete dynode detector possesses a series of dynodes coated with Cu/Be. As an ion
Inductively Coupled Plasma Mass Spectrometry

strikes the first dynode, electrons are released from the surface atoms, called secondary electron emission. These then hit further dynodes held at higher voltages, causing an increase in electron flow creating a measurable electron flow. The signal can then be amplified and recorded by the instrumental software. Discrete dynode detectors consist of 12 – 24 dynodes, giving an increased total surface area compared to the continuous dynode detector.

The continuous dynode detector works on the same principals as the discrete dynode detector, with secondary electron emission. Instead of multiple dynodes the continuous dynode possesses a trumpet like shape made from Pb doped glass. A potential of 1.8 – 2 kV is applied along the length of the transducer causing the secondary electron emission and hence the amplification of electrons.

Figure 1.3. Schematic of a discrete dynode detector.

Figure 1.4. Schematic of a continuous dynode detector.
Another type of detector used is the Faraday cup collector. This incorporates a collector electrode which is struck by the ion. A Faraday cage around the electrode prohibits any escape of reflected ions or secondary electrons. Positive ions hit the collector electrode and are neutralised by electrons from ground, the potential drop across a resistor is measured and amplified. As Faraday cups are relatively easy to calibrate and have a relatively good linearity and uniform response, they are mainly used in multi-collector instruments for isotope ratios.

1.3. INTERFERENCES IN ICP-MS

In ICP-MS, interferences have generally been classified into two categories: these being spectral and non-spectral interferences. Spectral interferences appear when elemental or molecular ions possess the same nominal mass-to-charge (m/z) ratio as the analyte of interest. These interferences are additive and hence enhance the recorded signal. The non-spectral interferences are commonly called matrix effects as they arise from matrix-induced changes to the signal intensity. This usually results in suppression in signal intensity, although certain substances can cause an enhancement to certain elements.

1.3.1. Spectral Interferences

When using ICP-MS, especially a quadrupole based instrument, a common problem encountered is overlapping of certain elemental isotopes by other elements/molecules with similar m/z values. With a resolution of around 0.5 amu for quadrupole instruments, overlapping isotopes cannot always be differentiated from each other, unlike the double focussing mass spectrometers.

Spectral interferences generally fall into one of three categories: isobaric, polyatomic and doubly charged species.40

Isobaric interferences occur when two elements possess isotopes with the same nominal mass. To overcome this problem alternative isotopes can be monitored, if available, and the signal corrected mathematically.
Polyatomic or molecular ion interferences are created by the combination of elements from the solvent, sample matrix or atmospheric/plasma gases. The vast majority of these occur below $m/z$ 82, as they contain combinations of Ar or the atmospheric gases. By comparison, polyatomic ions of metals as oxide/hydroxide ions can be found across the whole spectra.

The third type of spectral interference is the doubly charged ion ($M^{2+}$). The double charge occurs if an element possesses a relatively low second ionisation potential. Some of the most common examples are Ba, Sr and the rare earth elements (REEs). As the ions are measured using the $m/z$ ratios, doubly charged species appear at half the isotopic mass.

By careful selection of sample matrix/instrument conditions the interferences can be reduced or removed, although this is often out of the analyst’s hands. General methods of interference attenuation are explained below.

1.3.1.1. Matrix Removal

In liquid samples, the solvent is the dominant species in the sample and is the main cause of oxide, hydride and hydroxide polyatomic interferences. If the matrix is removed a reduction in polyatomic ions is often observed.

To remove the matrix, methods such as desolvation, HG and ETV have been employed. The most common desolvation systems consist of a heated spray chamber or tube followed either by a condenser or a semi permeable membrane. For aqueous samples a temperature of ~150 °C is commonly employed with the condenser held around 0 °C. At 150 °C an aqueous sample evaporates readily within 100 ms, in this time, 90 % of the particle diameter change occurs. The ‘dried’ sample and produced water vapour are transported to the condenser where the condensate is removed through a drain point or removed through diffusion across the membrane into a counter flow of gas in a membrane system.

Desolvation has been shown to reduce these polyatomics in particular the oxide/hydroxides and to increase the sensitivity of certain elements. There have
also been drawbacks found when using desolvation, as the systems tend to be inefficient at coping with samples of high dissolved solids and also cases of contamination have been reported.

Another technique for reducing the load on the plasma is through HG. This has been used for elements such as As, Sb, Sn, Se, Bi and Pb as they readily form volatile hydrides. HG works by an acid-borohydride reaction with forms volatile hydrides with are then transported to the plasma. As with desolvation the elements are removed from the matrix and hence a preconcentration effect is observed as well as a reduction in interferences.

1.3.1.2. Collision/Reaction Cells

Collision/reaction cells have been employed in ICP-MS to move either the interferent or the analyte of interest to another m/z. The alteration can either be via forming a polyatomic with the analyte of interest or by removal of an atom from a polyatomic interference. Certain gases have been used to perform charge transfer and remove the charge from the interference onto the collision/reaction cells gas.

The collision/reaction cells are constructed from a quadrupole, hexapole or octapole (dependent on manufacturer) ion guide situated within the interface region of the ICP-MS. To the cell a low pressure of a reactive gas is applied which promotes gas phase reactions to remove interferences.

Various gases have been employed for different purposes and to remove particular interferences (Table 1.1.). The gases are chosen in accordance with their reactivity towards certain elements and/or interferences. Ammonia and hydrogen\textsuperscript{41} have been employed to remove $^{38}\text{ArH}^+$ to free up the measurement of $^{39}\text{K}$. The analysis was capable due to the K possessing a low reactivity with these gases compared to the interferent.

Oxygen\textsuperscript{42-44} has also been used but instead of breaking up the polyatomic interference, $\text{O}_2$ has formed the oxide of the analyte of interest (hence moved to
m/z of +16). Oxygen has also been applied to the removal of $^{129}$Xe$^+$ interference for the determination of $^{129}$I$^+$. By removal of the charge on the Xe, the neutralised atom will be discriminated within the mass analyser and rejected, hence will not reach the detector.

Table 1.1. General gas phase reactions occurring in the collision/reaction cell (X and Z are general atoms/molecules and G represents gas atoms/molecules).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>General Formula</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensation</td>
<td>$XO^+ + GO \rightarrow XO_2^+ + G$</td>
<td>$CeO^+ + O_2 \rightarrow CeO_2^+$</td>
</tr>
<tr>
<td>Association</td>
<td>$X^+ + G \rightarrow X^*G^+$</td>
<td>$Ar^+ + He \rightarrow Ar^*He^+$</td>
</tr>
<tr>
<td>Collisional Dissociation</td>
<td>$XZ^+ + G \rightarrow X^+ + Z + G$</td>
<td>$Ar_2^+ + He \rightarrow Ar + Ar^+ + He$</td>
</tr>
<tr>
<td>Proton Transfer</td>
<td>$XH^+ + G \rightarrow GH^+ + X$</td>
<td>$ArH^+ + H_2 \rightarrow H_3^+ + Ar$</td>
</tr>
<tr>
<td>Charge Transfer</td>
<td>$X^+ + G \rightarrow G^+ + X$</td>
<td>$Ar^+ + H_2 \rightarrow H_2^+ + Ar$</td>
</tr>
<tr>
<td>Hydrogen Atom Transfer</td>
<td>$X^+ + GH \rightarrow XH^+ + G$</td>
<td>$Ar^+ + H_2 \rightarrow ArH^+ + H$</td>
</tr>
</tbody>
</table>

1.3.1.3. Cool Plasma

Cool/cold plasmas have been employed as a method for the reduction of spectral interferences. By reducing the forward power of the plasma from $>1000$ W down to $600 - 900$ W, and reducing the injector flow rate, the plasma possesses a cooler sampling zone and hence the ionic species produced alters dramatically.

The mass spectrum becomes simpler as there are less Ar based interferences, although metal oxide/hydroxides increase due to the lower energy within the plasma.

When cool/cold plasmas are employed the mass spectra of a 0.1 % v/v nitric acid solution alters from being dominated by $Ar^+$, $ArH^+$ and $O^+$ to having $NO^+$, $H_3O^+$, $H_2O^+$ and $O^+$ as the major peaks. This demonstrates the alteration in molecular species formed within the plasma. By using cool/cold plasma analysis of elements such as Ca, K and Fe$^{45, 46}$ is possible by reduction of the isobaric interferences.

Although cool/cold plasmas reduce some peaks, the formation of $NO^+$ can cause alternative problems for certain elements. These problems are not so much linked
with isobaric overlaps, but due to the removal of energy by the ionisation of the dominant species in preference to the element of interest.\textsuperscript{47} This is common when the analyte of interest possesses a higher first ionisation potential (IP) than that of the interferent i.e. $\text{Zn}^+ \text{IP} = 9.4 \text{ eV}$ and $\text{NO}^+ \text{IP} = 9.27 \text{ eV}$.

1.3.1.4. Increased Resolution

In a mass spectrum obtained from an ICP with a quadrupole mass analyser, two ions of the same $m/z$ may not truly possess the same actual mass. The difference between two isobars can be extremely small and therefore needs a greater resolution to separate than a quadrupole will allow. The main advantage of using a double focusing mass spectrometer is the ability to increase the resolution and separate isobars into their respective peaks.

The mass difference between two monoatomic ions is generally less than between a monoatomic and a polyatomic ion, for example $^{40}\text{Ca}^+ = 39.962\,590\,7 \text{ u}$ and $^{40}\text{Ar}^+ = 39.962\,383\,8 \text{ u}$ with a difference of 0.000 208 u compared to $^{39}\text{K}^+ = 38.963\,708\,0 \text{ u}$ and $^{38}\text{Ar}^+\text{H}^+ = 38.970\,557\,0 \text{ u}$ differing by 0.006 849 u. For the instrumental separation of $^{40}\text{Ca}^+$ and $^{40}\text{Ar}^+$ a resolution of 193 000 is required, with $^{39}\text{K}^+$ and $^{38}\text{Ar}^+\text{H}^+$ needing only 5700. This is beyond the realm of the quadrupole based instruments which possess a resolution of up to 150.\textsuperscript{48} Sector field instruments possess the ability to alter the resolution, although by increasing the resolution a decrease in sensitivity is incurred. A change of resolution from 400 to 3000 results in a 90 \% decrease in initial sensitivity, with only 2 \% of the initial response remaining when this is raised to 12 000.\textsuperscript{49}

1.3.1.5. Mixed Gas Plasma

The most commonly used gas to form plasmas is Ar, which gives rise to the Ar based interferences. By the addition of alternative gases such as N$_2$, O$_2$, He and H$_2$ into the plasma, the physical characteristics and analytical performance is altered and hence changes the analyte sensitivity, quantity and composition of polyatomic interferences. The alternate gases can be introduced into the torch through any of the channels.
When $N_2$ was added to the outer flow of the torch the formation of oxides, hydroxides and argon based interferences was found to be reduced. Generally enhanced analyte signals were also observed with a few exceptions, namely Si due to the $N_2^+$ dimer.\(^{50}\)

### 1.3.2. Non-Spectral Interferences

As mentioned, non-spectral interferences arise from species in the sample matrix and by the ICP instrumentation. Sample transportation, ionisation, ion extraction and ion focussing are amongst the factors which influence the extent of the matrix effects. The most severe matrix effects are observed when matrix elements have low IP and are heavier than the element of interest.

The sample matrix has an effect on the plasma temperature and hence the atomisation, vaporisation and ionisation of the analyte of interest.\(^{51}\)

High levels of dissolved solids in samples can lead to deposition within the ICP-MS. Solid material has been found to accumulate and can cause blockages throughout the injector of the torch and cone orifices as well as coating the ion lenses. To some extent, slight deposition can be advantageous as cone conditioning is advised. This is when a steady state occurs and deposition equals the rate of removal from the cones.\(^{52}\)

For accurate calibration of samples containing high levels of matrix elements the need for accurate matrix matching of calibration standards is essential.

Another cause of interference is observed when the ions are sampled through the cones and are focused. When the ions are moved closer together repulsion occurs, particularly in the "space charge" region behind the skimmer cone. The effect is seen to a greater extent on lighter ions as they move more easily away from the ion beam.

In most cases the matrix elements can cause a suppression of the signal by
1. Inductively Coupled Plasma Mass Spectrometry

increasing the load on the plasma and lowering the ionisation efficiency of the element of interest. However, the use of some organic compounds can cause an enhancement to the signal for certain elements.\textsuperscript{53-56} The use of alcohols (methanol, ethanol and 1-propanol),\textsuperscript{54-56} amines (ethylenediamine and triethylenediamine)\textsuperscript{53} and organic acids (lactic, acetic, gluconic, tartaric and citric acids)\textsuperscript{56} have all been added to improve the signal for certain elements.

The addition of small amounts of methanol or acetone has been observed to either enhance or suppress the analyte signals depending on the volatility and concentration of the compound and the mass and ionisation potential of the elements. Acetone was found to suppress the signal for certain elements to a larger extent due to the greater volatility.

1.3.2.1. Reduced Plasma Load

As mentioned in 1.3.1.1., desolvation can remove the solvent from the plasma and aid with removal of spectral interferences. Desolvation has also shown the removal of non-spectral interferences by reducing the load on the plasma. As less sample solvent is reaching the plasma, improved detection limits are often observed due to a higher ionisation temperature which affects the electron number density. Dependent on the matrix elements, a greater efficiency of analyte processing can be achieved. Reduced solvent has been seen to cause alternative problems especially when levels of dissolved solids have been high and with contamination occurring from the desolvation arrangement.\textsuperscript{57}

1.3.2.2. Instrumental Adjustments

The effect of the matrix can be reduced by the correct choices of nebuliser, spray chamber, torch, cones and settings applied to the ion lenses and mass analyser. The gas flow rates, nebuliser and spray chamber need to be matched with the sample, as the viscosity and surface tension influence the nebulisation efficiency and hence the particle size of the aerosol. The particle size has a major effect on the efficiency of the ionisation process within the plasma. If the aerosol contains a
large distribution of sizes, a single droplet can cause fluctuations in the plasma effecting the localised temperature and ionisation efficiency.

The cones are an important component to take into consideration as deposition is common on and around the orifices. Some instruments possess the choice of cones specially designed for higher level matrices. Thermo Elemental® have the “Xi” and “Xt” cones for environmental samples which dramatically differ in geometry from the standard cones, and are said to be less prone to deposition.

If high levels of dissolved solids are present the choice of a larger injector in the torch may be employed. The injector, commonly of 1 mm diameter, can be altered to a 2 mm or higher injector, and with different gas flows has been demonstrated to resist deposition to a greater extent.

1.3.2.3. Internal Standardisation

Internal standardisation has become one of the most common and effective ways of dealing with non-spectral interferences. Internal standardisation differs from the other methods mentioned as it does not try to solve the matrix effects but tries to compensate for the problem. By adding an element of known concentration to all samples and standards, the matrix effects on the internal standard, theoretically should be equal to those on the analyte of interest and be consistent throughout the samples/standards. Internal standardisation also aids in greater precision and accuracy when performing analysis.

1.3.2.4. Separation

Probably one of the most common means of dealing with samples with high matrix content is through separation of the analytes of interest. Separation also gives the advantage of preconcentration and the possible ability to choose an appropriate solvent which will not cause interferences and can be easily matched by the calibration standards.
Many methods of separation have been employed, these include; liquid-liquid or solvent extraction, chelating resins, ion exchange, co-precipitation and many more. These methods will be described in more detail with respect to Au and the PGEs in section 1.4.

1.4. SEPARATION AND PRECONCENTRATION OF THE PRECIOUS METALS

Due to the recent increased use of precious metals, determination of Au and the platinum group elements (PGEs) has become an extremely important area of research. As the use of catalysts increases the search for new sources of Pt and other PGEs become more important. As well as new sources the effect on the environment and human health need to be taken into account.

Environmental, geological and biological samples can contain extremely low levels of Au and the PGEs compared to the matrix components and hence often require an enrichment process as well as separation. Solvent and solid phase extraction, fire assay and co-precipitation have all been used for the selective separation and preconcentration of gold and the PGEs. Other methods for preconcentration of gold and the PGEs are via electrodeposition. The selection of a suitable approach to the separation and preconcentration is widely dependent on the method of analysis. Many of the techniques mentioned can be employed in an on-line or off-line basis depending on the level of preconcentration required. The advantages of on-line systems are the possibility of automation gaining increased precision and accuracy. With on-line systems, as they are generally a closed system, risk of contamination is reduced.\textsuperscript{58,59}

1.4.1. Ion Exchange

Chlorocomplexes of Au and the PGEs exhibit high affinities towards strong basic ion exchange resins. Amberlite\textsuperscript{®} XAD\textsuperscript{50-53} and Dowex\textsuperscript{®} 1 series\textsuperscript{64, 65} resins are commercially available anion exchange resins which have been found to retain precious metals. These types of anion exchange resins have proved to function well especially in conjunction with acidic halide solutions.
Speciation work performed by Nischwitz et al.\textsuperscript{66} used ion exchange chromatography linked to an ICP-MS for the determination of Pt species. A Dionex\textsuperscript{®} IonPac AG11 anion exchange column was employed to separate \([\text{PtCl}_4]^{2-}\) and \([\text{PtCl}_6]^{2-}\) from road dust leachate samples.

1.4.2. Chelating Resins

The most common form of enrichment for Au and the PGEs is the use of chelating resins. These are chosen as the high specificity of the resin to Au and the PGEs causes fewer problems associated with interferences from matrix elements present at much greater concentrations. A vast array of sorbents are widely available and many have been synthesised and investigated.

The sorbents for the retention of Au and the PGEs can differ dramatically although common base materials are available, these include silica gel anchored chelating groups,\textsuperscript{67-72} polymer anchored chelating groups,\textsuperscript{73-86} activated carbon (AC)\textsuperscript{87-92} and cotton\textsuperscript{93-96} or synthetic\textsuperscript{97-99} fibres.

Probably the most common form of preconcentration/separation of the PGEs and Au uses silica based chelating resins. These synthesised sorbents, retain by chelating metals directly to the sorbent, the standard non-selective silica based sorbents usually require a chelating agent to aid the retention of the metals. The advantage of using chelating groups is the high specificity towards Au and the PGEs. For this reason many of the chelating groups chosen contain sulfur. Substances like silica bonded thiourea derivatives\textsuperscript{70, 71, 72} and mercaptothiazoles,\textsuperscript{73, 74} have been used on and off-line for the retention of Au, Ag, Pt and Pd.

Au(III) is considered a soft Lewis acid due to the oxidation state and therefore is able to form complexes with soft ligands like tertiary phosphines and thiols as well as hard ligands such as fluorine and nitrogen-donors. Au has an extensive chemistry with particular affinity for cyanide and sulfur containing compounds, especially when two atoms are present, such as in dialkylsulfides and dithiolates like dithiocarbamates.
1. Inductively Coupled Plasma Mass Spectrometry

The more commercially available silica based sorbents generally need chelating agents added to the solution prior to addition on the column. As with the anchored chelating agents, these free chelating agents generally contain sulfur for greater specificity. O,O-diethyl dithiophosphate,⁶⁷, ⁷² dimethylglyoxime⁷⁵ and N(1-ethoxycarbonylpentadecyl)-trimethyl ammonium bromide⁶⁸, ⁶⁹ have all been employed to form chelates for extraction on C18 modified silica gel.

One advantage for the use of polymer anchored chelating resins is the ability for addition of a wide range of sorbents. A large range of polymers are used for the bonding materials with some examples being divinyl benzene (DVB),⁷⁹, ⁸⁰ polymethacrylic ester,⁷⁷ poly(vinyl pyridine),⁸² poly(vinyl chloride)⁸⁴ and cellulose.⁸¹ These can be used individually or can be combined to form copolymer backbones.

The groups added to the polymer can vary dramatically, although the use of amines,⁷⁹-⁸¹, ⁸⁴, ¹⁰⁰ amides,⁸⁶ pyridine derivatives⁷⁸, ⁸⁵ and sulfur containing compounds⁷⁷, ⁸² are common.

As with many of the procedures for the preconcentration of Au and the PGEs the extraction from HCl solutions was possible via the chloro complexes. Jermakowicz-Bartkowiak and Kolarz⁷⁹ found the use of aminoguanidyl groups gave good extraction, not only from acidic solutions but also from alkali solutions giving a capacity of 68 and 23 mg g⁻¹ sorption respectively.

Dithizone is a well known ligand capable of coordinating with transition metals as well as PGEs. Dithizone has been employed on a number of occasions for the enrichment of Au, Pt and Pd.⁷⁷, ⁸², ⁸³ Retentions of the metal were found to be high from aqua regia and were efficiently eluted by thiourea and nitric acid.

Activated carbon (AC) sorbents are generally used during the leaching of Au and the PGEs from geological samples. The sorbents are prepared from many carbon based products including charcoal, coal and anthracite. The leaching of Au is commonly performed into chloride,⁸⁷-⁹⁰ cyanate,⁹¹ thiocyanide⁹³ or thiourea⁹² solutions. Thio solutions are often used as an alternative to cyanide for leaching of Au due to the lower hazard associated with the compounds, whilst still
possessing greater selectivity towards Au and PGEs than chloride solutions. AC is commonly used throughout the mining industry as a means of monitoring the amount of Au and PGEs present in ore samples. During the leaching a number of competing processes are occurring; the leaching from the ore of Au and PGEs, preg-robbing at the ore surface and the adsorption onto the AC. These processes are often slow and can take up to a week for complete adsorption to occur. A problem associated with the adsorption of the Au onto the AC from the thio containing solutions is the decomposition of the compounds producing elemental sulfur. Although, with the addition of cysteine as a reducing agent, stabilisation of the thio compounds has been observed.

The fibres used for the preconcentration of Au and the PGEs can be separated into two categories, natural and synthetic fibres. The natural fibres are commonly prepared from cotton and treated with sulfuric acid to produce thiol groups. The thiol cotton fibres (TCF) have been observed to efficiently enrich water samples containing Au and the PGEs. Although the retention of most matrix elements, metal ions, and organic compounds was very low and did not interfere with the process, the selectivity of the TCF was relatively low. Many elements other than Au and the PGEs were found to also be retained to varying degrees. Pt(II), Pd(II), and Au(III) were found to be adsorbed preferentially over Se(IV), Te(IV), As(III), Hg(II), Sb(III), Bi(III), Sn(II), Ag(I), Cu(II), In(III), Pb(II), Cd(II), Zn(II), Co(II), Ni(II) and Tl(I) from a HCl medium. The metals were then easily eluted from the fibres with aqua regia and heating. TCF was also found to be reusable with no effect seen in adsorption rate of trace metals, although the saturation quantity was considerably decreased.

The synthetic fibres were produced from polymer based backbones with S, N and O functional groups present. The use of polyacrylonitrile fibres were used to produce poly(acrylp-aminobenzenesulfonamide-paminobenzenesulfonylamine), poly(acryldinitrophenylamidrazonedinitroacrylyphenylhydrazine), and polyacrylaminoimidazole chelating fibres, which proved selective for Au(III), Hg(III) and Pd(IV). The polyacrylonitrile fibres possess a 100 fold greater effective surface area than the spherical resin equivalent. These polymer based fibres were found to be more selective than
the TCF and resistant to very high levels of possible interferent elements from the matrices like Al, Fe, Ca, Mg, Ni, Mn, Cu and Zn.

1.4.3. Liquid-Liquid or Solvent Extraction

Liquid-liquid or solvent extraction is widely used for the separation and preconcentration of Au and the PGEs due to the simplicity of the sample preparation. This advantage is offset by a longer sample preparation process as well as problems associated with the possible formation of emulsions.

In general the solvent extraction of Au and the PGEs is performed in one of two ways. The first is to form the complex ion, whose nature depends on the solution, with the second to use chelating agents.

1.4.3.1. Liquid-Liquid or Solvent Extraction of Au and PGE Complex Ions

In a high chloride matrix, complex ions such as $[\text{AuCl}_4]^-$, $[\text{PdCl}_4]^{2-}$ and $[\text{PtCl}_6]^{2-}$ are readily formed. Methyl isobutyl ketone (MIBK) has become a popular choice for the extraction of these complex ions. Other solvents have also shown their ability to extract Au and PGEs complex ions, these generally possess ether linkages, such as diethyl ether, isopropyl ether and polyurethane ether foams.

Due to soft metals such as Au and Pt possessing an affinity for binding to sulfur containing ligands, thio-crown ethers have also been examined.

The use of impregnated filters has also been found to be a suitable method for selectively removing $\text{HAuBr}_4$, $\text{H}_2\text{Pt(SCN)}_6$ and $\text{H}_2\text{Pd(SCN)}_4$ from acidic halide solutions. Immobilised polytetramethylene ether glycol (PTMEG) in the pores of a polytetrafluoroethylene (PTFE) filter was used to retain the protonated complexes. With the use of either KBr or ammonium hydroxide solutions the complex ions were formed and eluted.

Another method reported for the removal of the complex ion via liquid-liquid extraction is known as salting-out. The technique involves a water miscible organic solvent and the formation of a phase separation upon the addition of an
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electrolyte. This occurs due to the decreased solubility of the organic layer in the water containing the electrolyte. This gives the ability for ion-pair complexes and highly charged species to be extracted into the organic layer. Chung and Tabata\textsuperscript{106} employed this phenomenon to extract Au into a layer of 2-propanol using NaCl as the electrolyte. The Au was present in the form of [AuCl\textsubscript{4}]\textsuperscript{-} in the aqueous solution, but was thought to transfer into the 2-propanol layer by forming an ion-pair with either Na\textsuperscript{+} or H\textsuperscript{+}. Au was found to be the only precious metal capable of being extracted quantitatively into 2-propanol via the salting-out process and was possible from solutions of 4 M NaCl and below. With NaCl concentrations of <4 M, the extraction percentage of Au was found to be up to 99%.

1.4.3.2. Liquid-Liquid or Solvent Extraction of Au and PGE Complexes

A wide range of chelating agents able to form complexes with Au and the precious metals has been amassed. Diethyl dithio phosphate (DDTP),\textsuperscript{107-109} diethyl dithio carbamate (DDTC)\textsuperscript{110} and octadecyl dimethyl benzyl ammonium chloride (ODMBAC)\textsuperscript{111} are amongst many studied for different samples and under various conditions.

The Au-DDTP complex has been selectively extracted into xylene, heptane, MIBK and Triton X-114 with the latter employed for cloud point extraction. Cloud point extraction is more commonly employed in separation and purification of hydrophobic and hydrophilic biological species, than the preconcentration of metals. The method involved the addition of HCl and DDTP to complex the Au and then Triton X-114 was added and heating applied producing a two phase system. Then centrifugation of the sample aided the separation of the two phases, with the surfactant rich phase settling to the bottom of the centrifuge tube due to the greater density. The metal chelate was situated in the surfactant rich phase due to a greater affinity than for the aqueous phase. On cooling, the phase became viscous and the aqueous layer was removed by decanting. A small amount of methanol in nitric acid was used to decrease the viscosity of the surfactant rich phase to aid transfer and nebulisation for FAAS\textsuperscript{107, 108} and ICP-MS\textsuperscript{109} determination of Au.
1.4.4. Co-Precipitation

Reductive co-precipitation has been used as an enrichment method for the determination of Au and PGEs in biological,\textsuperscript{112} alloys,\textsuperscript{113} geological,\textsuperscript{114-116} waters\textsuperscript{117} and environmental\textsuperscript{118} samples. A range of suitable carriers for Au and PGEs have been employed including Hg\textsuperscript{112}, Ni-DDTC\textsuperscript{117}, Te\textsuperscript{114-116,118} and Pd.\textsuperscript{113}

When Hg was used as the collector and formic acid as reducing agent, the main advantage was that the reaction by-products, namely H$_2$O and CO$_2$, were of low hazard and did not interfere with any reaction mechanisms. The Hg was then evaporated from the system leaving the Au and Pd for analysis by total reflection X-ray fluorescence (TXRF).\textsuperscript{112}

Hg was found to be suitable for Au and Pd as the reduced elements were found to possess a far greater solubility in Hg than Pt and the other PGEs.\textsuperscript{112} Although the practicalities of the method were offset due to using Hg and the lengthy time needed to perform the procedure.

A common method for the determination of PGEs is using Te as the co-precipitant. Te has been used on digested samples, after sodium peroxide fusion or after NiS fire assay. The sodium peroxide and NiS beads were dissolved and SnCl$_2$ added with the Te to act as the reducing agent, before filtering and dissolving ready for ICP-MS detection.\textsuperscript{114-116}

Itagaki \textit{et al.}\textsuperscript{113} used Pd with ascorbic acid as the reducing agent to investigate Au and Ag in high purity metals and alloys. The precipitate was removed by filtration and redissolved in \textit{aqua regia} before electrothermal atomic absorption spectrometry (ETAAS) analysis. The Pd was found to be an efficient releasing agent producing an increased signal for Au and Ag.

ETAAS was also employed for the determination of Au using Ni-DDTC as the co-precipitant.\textsuperscript{117} Ni-DDTC was found to be a very selective co-precipitant for Au and does not possess the hazardous characteristics of other collectors, like Hg and Te.
1.4.5. Electrodeposition

Electrodeposition has demonstrated the ability to perform preconcentration/separation of Au at extremely low levels when using ETAAS.\textsuperscript{119} In electrodeposition, the graphite tube was incorporated into a potentiostatic electrolysis system as the working electrode. A two stage electrodeposition was performed with elemental Pd pre-coating the graphite tube prior to the sample addition.\textsuperscript{120} Gold was separated from the matrix via a secondary electrodeposition onto the Pd coated graphite tube. When electrodeposition was performed, the sensitivity was found to be 50 times higher compared to direct sampling.

1.4.6. Other Methods

In recent years a lot of interest has been focussed on the use of industrial wastes, agricultural by-products and biological materials for the retention of the precious metals.\textsuperscript{121} Bacteria,\textsuperscript{122, 123} fungal cultures,\textsuperscript{124, 125} eggshell membrane\textsuperscript{126} and chitosan derivatives\textsuperscript{127} have all been studied as biosorbents. Au has been found to be retained effectively by many of the biosorbents with either bioaccumulation or biosorption occurring. Ion-exchange, adsorption, complexation and precipitation on the cell walls are all possible processes for the enrichment of Au on the biomass sorbents. Investigations have found that with immobilisation of the cells onto glass or silica gels enables regeneration and greater mechanical stability. Many of the biosorbent possesses are extremely complex and the mechanisms are still not fully understood.

Many of the biosorbents were found to use the loss of chloride ions from [AuCl\textsubscript{4}\textsuperscript{-}] to leave the Au(III) atom to combine freely with microbial cells. Extremely high abilities for the accumulation of Au were found for bacteria such as Escherichia coli and Pseudomonas maltrophilia.\textsuperscript{123} These bacteria strains were found to be more efficient at Au retention than actinomycetes, fungi and yeasts which were also investigated.

The use of chitosan derivatives was implemented by Arrascue \textit{et al.}\textsuperscript{127} and found to be efficient at removal of Au from dilute acidic solutions. The separation of the
Au was attributed to the chitosan becoming protonated under the acidic conditions. The protonated amine groups gave a site for sorption of anionic Au species to form ion pairs. This was observed as raising the pH caused a dramatic decrease in sorption capacity. The grafting of thiourea to the chitosan was found to cause far less pH dependence of the retention.

1.5. SUMMARY

Although ICP-MS has become a routinely employed technique for trace elemental analysis, the main limitation is many samples still cause extensive problems throughout the instrument and with the data attained. Numerous methods have been established to deter or remove interferences commonly associated with the sample matrix and the instrumentation. There is no single approach suitable for the removal of every detrimental effect and a combination of processes are often employed to perform the most accurate analyses.

Alteration of instrument parameters/arrangement alone is often insufficient to perform accurate analysis due to deposition of matrix elements. One of the most commonly employed sample preparation techniques for the removal of problems associated with the matrix is separation of the analytes of interest from the detrimental elements/compounds. Various techniques have been applied for matrix separation; with the main drawbacks incorporating contamination of the samples and loss of analyte of interest, as well as many involve the use of organic solvents and their disposal.

The combination of matrix separation to reduce the concentration of matrix element/compounds and the application of instrumental conditions to deter deposition is essential during any analysis with ICP-MS, especially when the matrix elements/compounds are of a refractory nature.
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Chapter Two

Laser Ablation
2. LASER ABLATION (LA)

2.1. INTRODUCTION

Laser ablation has become an increasingly powerful technique for elemental analysis. When coupled to ICP-atomic emission spectrometry (AES) or ICP-mass spectrometry (MS) it has proved to be a powerful tool for the analysis of a vast range of solid materials including geological, environmental, polymer, pharmaceutical and biological samples.

The direct analysis of solid samples is of immense interest as the time for sample preparation is reduced due to minimal manipulation. By performing less sample preparation, the handling of the samples is also reduced along with the risk of contamination and analyte losses. The reduction of interferences related to sample solvents is also achieved, hence producing a large decrease in oxide formation and other polyatomic interferences.

In LA, material is ablated from the surface of a solid sample using a short-pulsed, high-power laser beam. Photons from the laser interact with the solid and sputter/vaporise the material. Laser energy is also used in thermal heating of the sample. The ablated material contains electrons, ions and neutral particulate, forming a plume above the surface of the ablation site. The vaporised/ablated matter is then carried to the plasma from the ablation cell by a continuous flow of gas, usually He or Ar. A schematic diagram of a typical laser ablation system is demonstrated in Fig. 2.1.

LA has advantages over other solid sampling methods like electrothermal vaporisation (ETV) and arc/spark ablation, as a diverse range of samples can be analysed. Unlike other solid sampling methods, LA has the ability to sample from conducting and non-conducting, inorganic or organic solids or powders.
2.2. **PRINCIPLE OF LASER EMISSION**

The term LASER is an acronym for “light amplification by stimulated emission of radiation”. As the full phrase implies, the process of laser formation is based on the induced or stimulated emission of radiation. The stimulation is produced either by a light source (optical pumping) or an electrical source (electrical pumping).

2.2.1. **Solid State Lasers**

Solid state lasers are generally pumped optically, using a high-voltage flash tube to emit an intense burst of light. The lamp is commonly cylindrical with a diameter of a few millimeters and a length of a few centimeters, and concentrated on the active material. The lamp is filled with Xe, Ne or Kr (at low pressure) or Hg (at high pressure).
At a specific energy level, some atoms in the lasing medium emit photons. At first the photons are emitted in all directions. Photons from one atom stimulate emission of photons from other atoms and the light intensity is rapidly amplified. Mirrors at each end reflect the photons back and forth, continuing this process of stimulated emission and amplification. The photons then leave through a partially reflecting mirror situated at one end of the lasing medium.

2.2.2. Excimer and Gas Lasers

A gaseous lasing medium is usually pumped electrically. Excitation of the gas occurs by collisions between atoms and free electrons from an electrical discharge. The relaxation of the excited atom/molecule emits the laser lines.

2.3. LASER INSTRUMENTATION

2.3.1. Types of Lasers

Many different types of laser exist with solid state lasers the most commonly employed for LA-ICP-MS applications. Dependent of the lasing medium, monochromatic pulses of energy are produced which can range from the ultraviolet (UV) through the visible, to the infrared (IR).

2.3.1.1. Ruby Lasers

As the name implies, a crystal of ruby is formed into a cylindrical shape and is employed as the solid state lasing medium. Ruby consists of an aluminium oxide crystal in which some of the aluminium atoms have been replaced with ~0.05% chromium (III) ions. Chromium gives ruby its characteristic red colour and is responsible for the lasing behavior of the crystal. Chromium atoms absorb green and blue light and emit or reflect only red light. Due to the emission of red light, ruby lasers emit at a wavelength of 694.3 nm.

Ruby lasers possess a relatively good thermal stability although they operate at low repetition rates, making the reproducibility of shots poor.
2. Laser Ablation

2.3.1.2. **Nd:YAG Lasers**

Another example of a solid state laser is the neodymium-yttrium-aluminum-garnet (Nd:YAG) laser. The Nd:YAG laser has become the most widely used laser source for laser ablation. The lasing medium consists of Nd\(^{3+}\) (0.1 – 1%) doped yttrium-aluminum-garnet (Y\(_3\)Al\(_5\)O\(_{12}\)) rod of a few millimetres in diameter.

The fundamental wavelength for a Nd:YAG laser is 1064 nm. With the introduction of potassium dideuterium phosphate (KD\(^*\)P) crystals into the beam path, the ability to generate the second, third and fourth harmonics is possible at room temperature. These KD\(^*\)P crystals alter the emitted wavelength from 1064 nm to 532, 355 and 266 nm respectively for the second, third and fourth harmonic.

Recently a large amount of interest has been focused into sum frequency generation, in which two harmonics are summed producing lower wavelengths. The fifth harmonic is produced by passing the fundamental and the fourth harmonics through a beta barium borate (BBO) non-linear crystal. The fifth harmonic produces laser radiation at a wavelength of 213 nm. Shorter wavelengths are now commercially available with Nd:YAG laser systems producing shorter wavelengths of 193 nm.

2.3.1.3. **Excimer Lasers**

Excimer is derived from the terms *excited* and *dimers*. With the use of reactive gases, such as chlorine and fluorine, mixed with inert gases such as argon, krypton or xenon excited dimers can be produced when electrically stimulated. An excimer is a short lived molecule which only exists in its excited state. The relaxation to the ground state emits radiation and leads to repulsion of the individual atoms. Amongst the dimers of noble gas-halides, six are lasing: ArF (193 nm), KrCl (282 nm) KrF (248 nm), XeBr (282 nm), XeCl (308 nm) and XeF (351 nm). From these six dimers ArF, KrF, XeCl and XeF have shown promise as gas phase lasing media due to the efficient oscillating capabilities.
The laser vessel is filled with \(\sim 4 - 5\) mbar of halogen gas, \(20 - 100\) mbar of noble gas and pressurised to \(2 - 4\) bar with a buffer gas (usually He or Ne). Via electrical excitation the noble gas mixture produces excited noble gases as well as noble gas ions. Both these species will then readily form excited noble gas halides.

### 2.3.2. Laser Wavelengths

The choice of the laser wavelength is an important parameter dependent on the sample for analysis. No single wavelength is suitable for all applications and extensive discussion has occurred about the most suitable. More efficient ablation is produced by matching the wavelength to the sample. Factors affecting the ablation process include the optical penetration depth of the sample along with the photon energy required to break bonds in the sample.

In general the use of shorter wavelengths is advantageous as they offer higher photon energies, enabling more bonds to be broken in the surface of the sample. Many studies have been performed into comparisons between the main laser wavelengths of 1064, 532, 266, 213, 193 and 157 nm.\(^1-10\)

### 2.3.3. Laser Mode and Duration

Pulsed lasers can function in two ways with free running or Q-switched mode. Free running mode produces relatively long pulse widths of \(10 - 100\) \(\mu s\) of relatively low temperature. These long pulses are produced as the laser beam is emitted as soon as the threshold conditions for laser emission are reached. The ablated material produced in free running mode is generally large particulate matter.

Q-switched mode produces far shorter pulses of \(5 - 15\) ns duration of greater power. Q-switch mode involves an electro-optic switch placed in the laser path. The shutter is positioned to prevent the laser action and hence increases the
population inversion beyond the normal threshold level. As the switch is rapidly opened the population inversion is far greater than the threshold.

Using Q-switched mode the ablated material is thought to possess a larger percentage of vapourised matter although it has been suggested to unite to form larger clusters. Although ablation yields are lower by two to three orders of magnitude, the actual signal strength at the detector is only reduced by one order of magnitude. This implies the smaller particulate production of ablation in Q-switched mode produces better transport efficiency and higher ionisation efficiency in the plasma.

The majority of previous work on LA-ICP-MS has employed nanosecond pulsed lasers. More recent work has investigated the effect of picosecond and femtosecond laser pulses for LA with some distinct advantages of the shorter laser pulses.\textsuperscript{11-18}

Femtosecond LA has become useful due to the interactions of the laser beam with the surface of the sample. When a laser pulse interacts with the surface of a sample a free electron gas is formed through rapid heating. This heat is gradually dissipated to the sample lattice. Ablation of matter occurs due to thermal melting and evaporation as well as explosive evaporation. The heating of the electron gas takes around 100 fs with the cooling of the electron gas occurring in a few ps. Diffusion of the heat to the matrix occurs after \textasciitilde10 ps with thermal melting and ablation around 100 ps.\textsuperscript{11-13, 15, 17, 18} Picosecond lasers have the advantage of pulsing faster than the thermal heating of the sample. This means the ablation has occurred before the heating of the matrix, making the choice of wavelength virtually irrelevant. The cons of ps lasers are the cost of the equipment and poorer LOD due to less ablated material.

\textbf{2.3.4. Ablation Chamber}

The basic criteria for an ablation chamber are the promotion of transport efficiency, low memory effects, the ability to accommodate a wide variety of sample
sizes/geometries, provisions for laser alignment, focussing/viewing and the ability to alter the sample position.

The volume of the ablation cell can vary widely with internal volumes of 0.25 – 100 cm$^3$. The ablation cell is flushed with an inert gas, usually He or Ar to carry the ablated matter to the plasma. Different ablation cells volumes have been found to only slightly affect the signal intensity. The volume of the ablation cell however, does have a major effect on the signal-to-background ratios.

The ablation cell possesses a window to allow the entry of the laser energy to be focussed on the surface of the sample. It is essential the material used for the window is transparent to the wavelength of the laser with fused silica employed for use with UV lasers. The window is commonly at a slight angle to the incident laser beam to prevent reflection of light back into the laser system.

2.3.5. Particle Size and Transport System

To transport the ablated matter to the plasma for analysis a carrier gas is employed. Ar and He are the most commonly used carrier gases with the latter providing many advantages, including improved ablation, transport efficiency and a reduction in background.

Ar, He and Ne have been investigated with respect to the influence on particle size production and the transport efficiency to the plasma. Lasers at 193 and 266 nm were employed with all three carrier gases.

The findings displayed ablation in a He environment caused smaller particles to be produced. As smaller particles were produced the transport efficiency and the atomisation/ionisation efficiency of the plasma were increased. This was demonstrated with a gain in signal intensities.

The carrier gas was also an important factor in relation to condensation and coagulation of particles within the laser induced plasma directly above the ablation site. Helium possesses a higher thermal conductivity than that of Ar and hence
2. Laser Ablation

dissipates the energy required to form coagulates far more rapidly. The most reproducible results were obtained by the use of pure He in the ablation cell mixed with Ar prior to introduction to the torch.\textsuperscript{21} An increase in signal intensities was observed and attributed to greater transport efficiencies of the ablated elements and reduced backgrounds, lowering the DL by an order of magnitude.

The connective tubing used is vitally important for the efficient transportation of ablated material. Both the length and internal diameter affect the transfer from the ablation cell to the plasma.\textsuperscript{24} Larger diameter tubing possesses a greater ratio of gas volume to tubing wall area and hence reduces the number of particles lost through collision with the tube. With smaller bore tubing, a greater linear gas velocity is produced, which reduces the time to transport the particulate matter to the plasma. With the increased speed of the gas through the lines a reduction in gravitational settling and deposition in the tubes is observed. When choosing tubing for laser ablation a compromise must be reached between the two phenomena which is fit for purpose.

2.4. SAMPLE PREPARATION

One of the main benefits of LA-ICP-MS is the need for little or no sample preparation. LA is generally categorised into two types of sampling called microprobe or bulk analysis. If the sample of interest is homogenous, analysis can be performed directly. For inhomogenous samples pulverisation to a powder is needed prior to pressing into a disc/pellet, fusing into a glass or some other form of sample preparation.

2.4.1. Direct Solid Sampling

The ablation of solid samples directly is commonly used for spatial resolution or investigations into the fractionation of elements. The solids most commonly analysed by direct ablation are metals or alloys.

For direct analysis of metal samples the general consensus is to polish with fine sandpaper or diamond paste. The prepared surface is then washed with either
2. Laser Ablation

deionised water or acid. Certain samples need to be kept desiccated to deter surface reactions occurring with the atmosphere.

Use of spatial resolution has been employed in the analysis of teeth\textsuperscript{25-27} as well as of tree rings and leaves.\textsuperscript{28,29} The determination of the migration through a tooth by Hg from a filling was investigated by Hoffmann et al.\textsuperscript{25} A map was constructed to demonstrate the levels of Hg present throughout the tooth. The teeth were prepared by vertically halving with a diamond saw, then cleaning in deionised water in an ultrasonic bath\textsuperscript{25} or polishing with fine glass paper.\textsuperscript{27} The sample was then attached to a slide to hold the sample for laser analysis.

The samples involved in the analysis of tree rings were prepared by sanding wood sections and washing with HNO\textsubscript{3}.\textsuperscript{29

Oak leaves were prepared for analysis by washing in an ultrasonic bath with deionised water. The variation of element concentrations across the whole leaf and the main rib of the leaf were analysed. The analysis demonstrated three patterns in element variation: the element was enriched towards the top or towards the stalk of the leaf, or the elements were generally consistent throughout the leaf.\textsuperscript{28

The study of trace elements in automotive paints\textsuperscript{30} was performed directly with the only sample preparation being cutting the samples to fit in the ablation chamber. The use of elemental ratios was employed to differentiate between layers of paint.

2.4.2. Pressed Powders

As many samples and reference materials are present in powder form, some degree of sample preparation is necessary. Pressing into a disc or pellet has been widely used.\textsuperscript{6,31-39} As some powders are highly crystalline or highly elastic the addition of a binder is sometimes employed to increase mechanical stability.

The pressing of the powders is often performed on a standard laboratory press as used for KBr disc formation in IR spectroscopy. The pressures and time applied to
the powders can vary dramatically with the type of press utilised. The quantity of sample affects the thickness of the disc and is commonly between 0.2 – 0.5 g producing a disc of 1 – 5 mm thickness and 10 – 13 mm diameter (dependent on the die size of press).

The addition of binding substances is commonly performed by mixing with the sample prior to pressing to increase the mechanical stability of the discs. Many different binders have been employed including KBr, graphite, Ag powder, Al powder and cellulose. The sample and binder are commonly mixed in a ball-mill prior to the formation of a disc.

One distinct advantage of the pressed powders is the ability to add internal standards and this is often performed by addition into the binding substance. If the internal standard is in solid form, addition during the mixing process can be used. Often the internal standard is in aqueous form and is mixed with the binder, dried and mixed with the sample prior to pressing into a disc.

Tibi and Heumann employed polyvinyl alcohol (PVA) to act, not as a binder, but as a support to increase the mechanical stability of the disc. The process was performed by simultaneously adding PVA to a layer of sample already placed in the press.

2.4.3. Fusing Into Glass

Lithium borate fusion is a common method of sample preparation for analysis by X-ray fluorescence (XRF) and has also been used for LA-ICP-MS. The process involves mixing the sample and lithium tetraborate (Li₂B₄O₇) together and fusing in a Pt crucible at temperature in excess of 1000 °C. To ensure the homogeneity of the samples, the crucibles are rocked or shaken during the fusion process or inverted.

The addition of Fe₂O₃ to the lithium borate fusion process has been reported to enhance the signal. The addition of Fe₂O₃ improved the absorption of the laser photons at 266 nm and improved coupling between the laser and sample surface.
As the laser energy was absorbed by the sample more efficiently, the optical penetration depth of the laser was lower.\(^{51}\)

### 2.4.4. Fire Assay

Fire assay has been widely used in the mining industry for the quantitative determination of metals (commonly Au and the PGE's). The metals are separated from impurities before fusion into a button or bead. As beads or buttons are produced, LA can be applied directly to the sample.

Two forms of fire assay are commonly used: Pb and NiS. The general procedure is very similar for each method. For Pb fire assay the sample is crushed, ground and weighed before being heated and mixed with a flux containing litharge (Pb oxide), a reducing agent (e.g. flour) and compounds to form a slag (sodium carbonate, silica, borax). The litharge is reduced into metallic Pb, which quantitatively extracts the precious metals. The fused mix is then poured in a mould where the Pb containing the Au and PGE sinks to the bottom, while the undesired impurities are moved into the slag floating on the top. After cooling down and removal of the slag, the obtained bead is heated in an open furnace and cast into a bead for analysis.\(^{52}\)

A similar method is used incorporating nickel sulfide instead of the Pb (litharge). Nickel powder and purified sulfur are added to remove the precious metals prior to forming into a bead.\(^{53}\)

### 2.4.5. Other Methods of Sample Preparation

Certain samples need particular treatment and the sample preparation is extremely specialised. For instance, in the case of the analysis of a certified reference material of pig liver using LA, the sample was homogenised into a paste then placed between two glass slides and frozen. The ablation was performed in a cryogenically cooled ablation chamber. The cooling of the ablation cell was found to produce good results when the temperature was below -60 °C.\(^{54}\)
Klemm and Bombach\textsuperscript{55} employed a glue technique in which the powdered silicate sample was mixed with a methyl methacrylate resin dissolved in acetone. The sample was incorporated in the glue mixture and using circular motions spread into a circle of 4 – 8 mm diameter. The resin was then left to solidify at room temperature and analysed after 2 hours.

2.5. CALIBRATION TECHNIQUES FOR LA-ICP-MS

LA has become widely used for qualitative and semi-quantitative analysis. One of the major draw-backs of LA is the difficulty of finding a universal calibration technique for quantitative work. As the ablation characteristics of various solids differ widely, matrix-matched calibration standards are very hard to find for many sample types. For this reason quantitative analysis is not always possible to a suitable accuracy and precision.

2.5.1. Matrix-Matched Direct Solid Ablation

As with solution ICP-MS the use of matrix-matched external calibration is the most commonly employed technique for LA-ICP-MS. The need to matrix-match the standards to the samples is essential to reduce the effects of varying ablation rates (the amount of matter ablated per laser pulse). Although many solid reference materials are available, a total coverage of all samples is not feasible.

Many techniques have been employed to obtain matrix-matched standards, these include: pressing of powders with the addition of compounds, with and without binders;\textsuperscript{56,57} co-precipitation of standard solutions into a powdered matrix,\textsuperscript{58} drying and pressing; glass fusion;\textsuperscript{59} and co-precipitation gel techniques (also known as sintered compacts).\textsuperscript{60}

One of the easiest sample types to calibrate externally are metals. Many standards are available with similar properties to the samples, although careful selection needs to be performed to ensure any fractionation is the same/similar in both cases.
One such metal that has been investigated is brass.\textsuperscript{60, 61} As brass is a binary alloy, the major components of Cu and Zn were determined. A non-linear calibration plot was observed for Zn and attributed to the change in mass ablation rate, which in turn was related to the concentration of Zn. A larger percentage of Zn in the samples caused an increase in the ablated mass. The greater ablation mass was attributed to the lowering of the melting point of brass with increased levels of Zn. To achieve better calibration, the signal was normalised in two ways: Cu was used as an internal standard and, the ablated mass was calculated from the crater volume (measured by a white light interferometric microscope). The use of both methods produced a linear calibration curve.

Normalisation of the signal was applied to steel samples by Leach and Heiftje.\textsuperscript{62} Normalisation was performed to increase the single-shot measurement precision. The capabilities of a ToF mass spectrometer were employed to acquire the full spectrum which was subsequently summed to create a total value which theoretically should be proportional to the total ablated mass. Although a 2 fold improvement was obtained in the precision, it was concentration dependent and decreased with lower levels of analyte.

The evaluation of three different calibration techniques was performed by Craig et al.\textsuperscript{63} The analysis of natural calcium carbonate based matrices were performed with calibration by: 1. glass certified reference materials, 2. spiked calcium carbonate powder and, 3. calcium carbonate based geological reference materials. The study of In and Ca as internal standards was investigated to correct for discrepancies between samples and standards. The wetting of the calcium carbonate matrix material with an In solution before drying was used to add the spike. In was found to give an extremely erratic signal during ablation, with >50% variation in signal response showing major inhomogeneity within the pressed powders. With Ca employed as the internal standard and as a major component within the samples, short and long term signal reproducibility was achieved. $R^2$ values obtained from the synthetic pressed powder samples were found to be more scattered than for the glass standard. Fe and Mn gave both positive and negative values during calibration dependent on the sample. The random results were attributed to the pressed powders being sufficiently different.
in physical structure as well as chemistry to the natural materials. A negative bias was observed from the calibration using the certified glasses. The preferred calibration method was obtained from the use of certified geological samples, although the need for careful selection was deemed essential.

Bellotto and Miekeley\textsuperscript{58} also investigated calcium carbonate matrices with emphasis on mussel shells. Unlike the calibrations on calcium carbonate matrices performed by Craig \textit{et al.}\textsuperscript{63} the use of a binder was not employed. The internal standardisation was performed directly on the calcium carbonate matrix.

2.5.2. Dual Sample-Standard Introduction

The use of dual sample-standard introduction has been performed in two ways: 1. liquid nebulisation, mixed with the ablated aerosol,\textsuperscript{64-66} and 2. desolvation of a nebulised solution to produce a ‘dry’ aerosol.\textsuperscript{67, 68} The introduction of liquid samples removes one of the benefits of LA associated with the formation of polyatomics formed from the solvent employed.

The application of solution calibration has mainly been used for metals,\textsuperscript{64, 65, 68, 69} geological\textsuperscript{66, 67} and NIST glass samples. Liquid standards were employed for the semi-quantitative analysis of Fe in steel and Ba in a certified glass.\textsuperscript{70} The differences found between the measured and certified values were found to be less than 40\% for most elements determined. The ablated matter was found to possess a similar atomisation and ionisation efficiency in the plasma to the nebulised solution. A modified torch was employed to combine the wet nebulised aerosol and the dry laser aerosol. An annular adapter was attached prior to the torch to carry both the wet and dry aerosols to the injector.

For the analysis of high purity Cu the aqueous standards were prepared in a 250 mg L\textsuperscript{-1} Cu solution with varying levels of the analyte of interest.\textsuperscript{65} The spike concentrations of the nebulised standards were found to equate to 4000 times less than the concentration in the solid sample. For many of the determinations a higher percentage recovery was observed and attributed to fractionation during the laser ablation process. During the investigation a mixing gas adapter was
employed to combine the wet nebulised aerosol and the dry laser aerosol. The mixing chamber was situated directly after the spray chamber prior to entry into the torch.

The use of ultrasonic nebulisation (USN) was employed for addition of aqueous standards.\textsuperscript{50, 64} Instead of mixing the wet and dry aerosols prior to the torch, the wet aerosol was introduced as the carrier gas. The use of a single gas flow in which the nebulised standard solutions were produced prior to entry into the ablation chamber was investigated. The benefit of the introduction of the aerosol prior to the ablation cell is the nearly complete mixing of the wet and dry aerosols.\textsuperscript{64}

The introduction of nebulised standards directly into the ablation chamber has also been investigated.\textsuperscript{71} A microflow nebuliser was employed to add isotope enriched tracer at 7 μL min\textsuperscript{-1}. Uranium isotope ratios were measured in a NIST glass and Udoped apple leaves.

The use of dried aerosols as a calibration technique has been employed with desolvation of the nebulised standard solutions prior to addition to the dry laser aerosol. The addition of nebulised standards into the dry aerosol proves advantageous as matrix matched standards are unnecessary, although the response gained can differ dramatically from the ablated aerosol alone. If the nebulised solution is desolvated to form a ‘dry’ aerosol the response should mimic that of a laser produced aerosol more closely. However, the plasma formed in this case is referred to as being ‘dry’ and has a variable composition, depending upon the matrix of the target. In this case, different sample matrices will produce varied plasma loading.\textsuperscript{72}

The use of desolvation has demonstrated a 10 fold increase in signal intensity over liquid introduction.\textsuperscript{57} The increase was attributed to the reduced plasma load and the lower levels of polyatomics, like oxides. Although higher RSDs were obtained they were attributed to the poor stability of the desolvation nebuliser.
A form of standard additions was employed by Leach et al.\textsuperscript{68} with addition of liquid standards via flow injection. The liquid standards were added to a laser baseline with a USN desolvation unit. The accuracy of the analyses indicated the desolvated particles from the nebuliser behaved like those attained from the laser ablation system.

2.5.3. LA of Liquid Standards

The ablation of liquid standards for calibration of elements in NIST glasses was performed by Gunther et al.\textsuperscript{73} The use of an excimer laser system working at 193 nm was employed as the shorter wavelength reduced laser, matrix and fractionation effects. Na and Yb were employed as internal standards for the analysis of 96 different elements. No significant difference was found between determinations made with either of the internal standards. The particle size distribution of the liquid and solid ablated matter was measured to determine the similarities in the ablation behaviour and the individual contributions to the total ablation volume. Ablation of the aqueous standards was found to produce a far wider range of particles than the ablation of solids. 90\% of the ablated solution was found to be between 3 and 30 \( \mu \)m droplets and hence were completely atomised/ionised in the plasma. To stop evaporation into the Ar carrier gas stream, the solutions were covered by laboratory film. The laser was used to drill a hole through the film prior to ablation of the liquid.

Chromophores have been employed to modify the absorption characteristics of aqueous solutions.\textsuperscript{74, 75} The use of various chromophores were employed dependent on the wavelength of the laser. The chromophores improved the laser energy coupling between the laser and surface layers of the solution. Due to the threshold ablation fluence being reached in the surface layers of the solution a very fine aerosol was produced.

The main criteria for a chromophore are to absorb strongly at the desired wavelength, must not precipitate in contact with the analytes and must be non-toxic. The quantity of chromophore used was investigated and was found to be
dependent to the concentration of the analytes. The main advantage of ablating solutions is the continual renewal of the surface for each laser pulse.

Poly(sodium 4-styrene-sulfonate) and nitric acid were found to absorb at 193 nm with 2-thiobarbituric acid and 1,10-phenanthroline absorbing at 266 nm, and m-hydroxybenzoic acid was used with a 248 nm excimer laser. The calibration strategy was applied successfully to a NIST glass as well as a low density polyethylene (LDPE).

2.6. APPLICATIONS

As LA-ICP-MS is advancing, the fields in which it is used are expanding. Many areas of analysis are well established already, with others showing a great deal of promise. Some of the main sectors of applications of LA-ICP-MS are presented below.

2.6.1. Geology

Many of the greatest successes have occurred in the geological sciences, where the advantages of spatial resolution and trace element determination have aided the increased use of LA-ICP-MS. Another area of research has focussed on geochronology using isotope ratio measurements of U, Th and Pb especially of zircons.\textsuperscript{17, 57, 76-78} Many different forms of analysis have been performed including the use of various laser wavelengths,\textsuperscript{57} ns and fs lasers\textsuperscript{17} and soft ablation techniques.\textsuperscript{76} Freon gas has also been added to the carrier gas to aid the transportation of U.\textsuperscript{77}

Another technique commonly employed for geological analysis is X-ray fluorescence (XRF). LA-ICP-MS has been suggested as a complimentary technique to XRF\textsuperscript{48, 79} as the same sample can be analysed with both techniques. Repeated ablations were found not to influence subsequent measurements by XRF.
2.6.2. Forensic Analysis

LA-ICP-MS has been applied to the fingerprinting of gemstones due to its quasi non-destructive attributes. LA has shown the ability to determine more than 40 elements from a spot size of 120 µm to a depth of 1 µm.

Application of LA-ICP-MS to the elemental fingerprinting of cannabis crops for determination of the geological origin has been performed. The use of elemental fingerprinting has also been applied to the detection of art forgeries. Scrapings of paint were removed for elemental analysis for dating purposes.

Micro debris from crime scenes can also be analysed by LA-ICP-MS and matched by the elemental composition to debris found on a potential perpetrators clothing.

2.6.3. Material Sciences

LA-ICP-MS has become widely used in the material sciences field as its ability to obtain low level trace analysis rapidly has made it useful for testing raw materials and end products within a manufacturing process. The distinct advantage of LA over solution ICP-MS is the relatively rapid sample preparation, reduced risk of contamination and lack of hazardous chemicals being used.

2.6.4. Biological Sciences

A relatively new field of applications of LA-ICP-MS is in the biomedical sector. The investigation of metal binding properties of proteins or the P and S concentrations have all been investigated by LA-ICP-MS. One of the main limitations of the technique is from contamination by reagents used in the biomedical sample preparation, as high purity chemicals are not always employed. The need for internal standardisation is also needed if quantitative analysis is required.
The determination of Ni in tissue has been performed looking at the spatial elemental profiling around metal implants. Nickel wire was inserted into rats with the nickel migration studied against time through the tissue using LA-ICP-MS.\textsuperscript{87}

### 2.7. LIMITATIONS OF LASER ABLATION

As mentioned, calibration has always been one of the major hurdles to overcome when using LA. The need to find or produce matrix-matched standards to obtain consistent calibration results is of utmost importance. The ablation characteristics of solids can vary dramatically producing the need for to match ablation yields otherwise large variations of signal are observed.

One of the major limitations in LA-ICP-MS is the fractionation of elements. Fractionation can occur either during the ablation process, the transportation process or within the plasma. Four categories have been determined in which various forms of fractionation fall into: 1. intrinsic fractionation, 2. crater influence, 3. transportation process, and, 4. fractionation and matrix effects in the plasma.

As fractionation is element dependent, attempts have been made to correlate the degree of fractionation to elemental properties such as melting/boiling points, vapour pressure, atomic or ionic radius and charge.\textsuperscript{88,89}

Studies of the ablative and transport fractionation of NIST glass, mammalian teeth and copper were investigated and related to the oxide melting points.\textsuperscript{90,91} For the NIST glass sample an inverse logarithmic relationship was observed with the inflection point occurring when the oxide melting point fell between 1000 – 1500 °C. Elements with oxide melting points >1500 °C were found to generally agree with certified values, with oxide melting points <1000 °C the fractionation was >20%.

Chen\textsuperscript{92} associated the sum of the first and second ionisation enthalpies to the fractionation. The ablation of elements with lower sums of ionisation enthalpies proved easier than those of elements with higher ionisation energies. Continued
ablation was found to cause an enrichment of the high ionisation energy elements in the ablation crater.

Fractionation within geological\textsuperscript{32} and soil/sediment samples\textsuperscript{45} have been investigated with respect to Mg and Ba compounds of different chemical forms. The concentrations of Sr, Ba, Y and Rb were found to be low by a factor of 2 – 3 when using a spiked internal standard of Ni or Ag. The measurement of low concentrations was corrected for by employing Sr, Ba, Y or Rb as the internal standard for the other elements.

The use of a Nd:YAG laser operating at 1064 and 266 nm was employed for analysis of geological samples. The use of either wavelength was found to be insufficient in overcoming the matrix effects and hence fractionation was observed. The highest response of Mg was observed when MgSO\textsubscript{4} was employed followed by MgF\textsubscript{2} and MgO. This correlated with the melting points of 1127, 1263 and 2826 °C respectively.\textsuperscript{7, 32}

One of the most extensive materials for studies relating to fractionation is brass. The fractionation between Zn and Cu is well known and documented in LA-ICP-MS.\textsuperscript{16, 60, 61, 93} The influence of the laser properties on the fractionation was investigated by Borisov et al.\textsuperscript{60} using different laser systems: 20 and 30 ns (248 nm) KrF excimer, 3 ns and 35 ps (266, 532 and 1064 nm) Nd:YAG. Zn/Cu fractionation was found to depend extensively on the laser irradiance with large variations dependent on the laser pulse duration. The 30 ns, 248 nm laser showed that thermal vapourisation was the dominant process at low irradiance regions, with higher irradiance the ratio neared stoichiometry although still remained Zn rich. As Zn is more easily vapourised than Cu, a low Zn:Cu ratio implied non-thermal processes were occurring during the 35 ps laser ablation. Results showed both non-thermal and thermal mechanisms were observed during the use of the 3 ns LA. A reduction in fractionation was gained with the use of high laser irradiances during the 3 ns and 35 ps LA. Fractionation was shown to be influenced by the laser wavelength with more significant fractionation with ns lasers than ps lasers, especially at low irradiances. A shorter laser wavelength also yielded better stoichiometry. A shorter pulse length is thought to cause less
energy to be lost through thermal dissipation. This implies more laser energy is transferred to ablate matter and not lost through heating of the sample. As ps lasers cause less fractionation than ns lasers due to the shorter pulse length the use of fs lasers should produce accurate calibration. The comparison between fractionation of Zn and Cu with nanosecond and femtosecond laser systems was studied by Margetic et al.\textsuperscript{15,16} Linear calibration was obtained with the best results using high laser energy and lower pressure Ar carrier gas. In general the correlation coefficients were better when a fs laser was used under the same conditions as the ns laser system.

As mentioned, shorter wavelengths have been reported to cause less fractionation, Gunther and Heinrich\textsuperscript{22} found using a 193 nm excimer laser caused less fractionation than a Nd:YAG 266 nm laser which produced a time dependent fractionation. It was uncertain to the cause of the lower fractionation although it was attributed to either the higher photon energy or the different beam homogeneity and focussing conditions.

The laser wavelength was found to be only part of the cause of the fractionation problem. The signal intensity of a 157 nm F\textsubscript{2} laser and a Nd:YAG 213 nm were found to be similar for a NIST glass sample and this was attributed to the optical penetration depth being essentially the same for both wavelengths. However the 157 nm laser did provide an improvement in fractionation for transparent calcite samples.\textsuperscript{7}

Another factor to affect the degree of fractionation is the crater geometry, depth and aspect ratio when employing a single spot ablation process. The geometry was found to alter from flat bottomed to cone shaped with increased laser pulses. As the crater developed, shallow depths increased the signal for volatile elements, whereas deeper penetration saw the signal for refractory elements increase.\textsuperscript{88} The deposited material around the ablation spot was examined under Scanning Electron Microscopy (SEM) and demonstrated that vapour deposition caused the settling of material.
The aspect ratio of the crater was found to cause significant fractionation especially for some elements like Zn and Pb. When the depth:diameter ratio was >6, the analyte response was reduced to <50%. The use of large diameter craters was found to reduce elemental fractionation and cause a sustained signal response for a longer period of time. The exact mechanism of fractionation caused by the crater is still unclear, one theory is the plasma formed by the ablation is confined inside a deep crater and affects the sampling process. Also the actual irradiance decreases with sampling depth caused by the changes in effective area exposed to the laser beam.

Fractionation has also been attributed to the transportation process and involves the selective vapour condensation on the tubing walls or selective nucleation of species on different sized particles. Chemical composition and particle morphology effects the transport efficiency and particle size production. The use of a coiled transport tube was found to effect the particle size distribution and the fractionation. Large particles were thought to occur from ablation of the liquid layer produced at the ablation point. The composition of the liquid melt differs dramatically compared to the overall bulk. Cu, Ni, Ag, Y, Ti and Pb all show fractionation at lower irradiances ($10^8$ W/cm²) although at higher irradiances the ratios become closer to the real values.

The ICP also contributes to the fractionation, which is concerned with the particle size distribution affecting the ionisation efficiency. Figg et al. found when large particles were removed no fractionation of U, Be, Rb and Ce was observed, suggesting the incomplete ionisation of the larger particles in the plasma. Kuhn et al. also demonstrated the incomplete processing of silicate particles greater than 150 nm in diameter.

As with all forms of instrumental analysis LA-ICP-MS suffers from matrix effects causing alterations in the plasma. During solution nebulised ICP-MS the major component entering the plasma is the solvent (usually water), when a dry aerosol is used the major sample component is the dominant specie. Dependent on the major components the plasma conditions alter dramatically. The effect of Ca, Sr, Li, Na, K, Mg and Al were investigated with respect to plasma temperature and
electronic number density. Matrix elements with a second ionisation potential less than the first ionisation potential of Ar caused major matrix effects. The addition of He as the carrier gas reduced these matrix effects dramatically.98-100

2.8. FUTURE DEVELOPMENTS

The progression of LA-ICP-MS is towards the ideal situation of a single laser shot producing trace element determinations equal to or better than those obtained by solution ICP-MS, with comparable accuracy and precision. The ideal situation would be to generate the smallest crater possible with 100% transportation of the ablated matter. Each particle must be atomised and ionised efficiently by the plasma, then detected. This scenario must be independent of the matrix and hence allow the quantitative determination of elements by non-matrix matched standards.

The matrix dependency is one of the main problems associated with the calibration of LA-ICP-MS. The reduction of this dependency is paramount to the production of consistently sized particulate. Under these conditions fractionation of elements would also be reduced allowing greater accuracy of isotope ratios to be obtained. This has been somewhat achieved with the use of fs laser ablation.

The transportation of the ablated matter to the plasma is extremely important and must be kept as high as possible. The introduction of an on-line system for measuring transported aerosol mass and size distribution would be advantageous.

Advancements are also still needed within the ICP-MS itself, with complete atomisation and ionisation extremely important. The transportation of the ions to the detector could be increased to aid the determination of lower levels of elements.
2.9. REFERENCES


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2. Laser Ablation


2. Laser Ablation


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2. Laser Ablation


Chapter Three

Interface Modification
3. **INTERFACE MODIFICATION**

Many geological samples contain trace and ultra trace levels of analytes with the vast majority of the matrix either alumina (Al$_2$O$_3$) or silica (SiO$_2$). Both these compounds are classed as refractory compounds as they both possess high melting points (alumina = 2045 °C and silica = 1710 °C). Aluminum also possesses a relatively low ionisation potential (IP) of 5.99 eV causing problems when analysing elements with higher IP's. The most common method for analysing geological samples is by utilizing microwave assisted acid digestion. As these compounds are in high concentrations within the microwave digested sample, they can cause a large suppression in the sensitivity. As mentioned in section 1.3.2.3. instrument modification is a common way to eliminate potential matrix effects. This chapter documents work performed to modify the sample introduction and interface region of the ICP-MS with the aim of reducing deposition of refractory matrices, throughout the ICP.

3.1. **INSTRUMENTATION**

3.1.1. **ICP-MS**

A VG PQ ExCell ICP-MS instrument (Thermo Elemental, Winsford, Cheshire, UK) was employed throughout this work. The instrument was situated in a general purpose laboratory without air filtration or conditioning equipment. A Conikal concentric glass nebuliser (Glass Expansion, Hawthorn, Victoria, Australia) and standard silica torch (Thermo Elemental, Winsford, Cheshire, UK) were used throughout this work.

An impact bead spray chamber cooled to 5 °C in a Peltier cooler and standard nickel sample (1 mm Ø orifice) and skimmer (0.7 mm Ø orifice) cones (Thermo Elemental, Winsford, Cheshire, UK) were used unless otherwise stated.

Daily tuning was performed on the ion optics, torch position and nebuliser gas flows to optimise the signal of m/z 115 (In) for a 1 ng mL$^{-1}$ tune solution.
Sensitivity for $m/z$ 115 was typically 60,000 – 120,000 counts $s^{-1} ng^{-1} mL$ with a relative standard deviation not exceeding 1.5%. The oxide ratio was monitored using $^{140}Ce^{16}O/^{140}Ce$ and did not exceed 0.02. Common operating parameters for the ICP-MS are present in Table 3.1.

A 10 µg mL$^{-1}$ Ba, Be, Ce, Co, In, Li, Mg, Pb, Rh, Ti, U and Y multi-element standard solution (CLMS-Tune-1, SPEX Certiprep, Metuchen, NJ, USA) was used to prepare the tune solution in 2% nitric acid. Aristar grade 70% nitric acid (Fisher Scientific, Loughborouh, Leicestershire, UK) and 18.2 MΩ cm$^{-1}$ deionised water (Elga Ltd., High Wycombe, Buckinghamshire, UK) was used throughout.

**Table 3.1. Instrument operating instructions.**

**ICP parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rf power/W</td>
<td>1350</td>
</tr>
<tr>
<td>Reflected power/W</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Nebuliser gas flow/L min$^{-1}$</td>
<td>1.00 – 1.10</td>
</tr>
<tr>
<td>Auxiliary gas flow/L min$^{-1}$</td>
<td>0.8</td>
</tr>
<tr>
<td>Plasma gas flow/L min$^{-1}$</td>
<td>12.6</td>
</tr>
<tr>
<td>Lens voltage/V</td>
<td>Tuned daily to optimum $^{115}In$ sensitivity</td>
</tr>
</tbody>
</table>

**Analyser parameters**

- **Acquisition mode**: Peak hopping
- **Replicates**: 3
- **Points per peak**: 1

**3.1.2. Cones**

For the interface modification experiments a standard sample cone and an Xi sample cone were employed with varying designs of nickel skimmer cones. Both sample cones (Fig. 3.1. (a) and (b)) possessed a 1 mm Ø orifice. All three skimmer cones (Fig 3.1. (c) – (d)) possessed a 0.7 mm Ø orifice. The Xi and PS6R (Fig. 3.1. (d) and (e) respectively) cones both used the same copper adapter to fit the VG PQ ExCell ICP-MS. The PS6R skimmer cone was an experimental design.
and was supplied by the instrument manufacturer. The drilled cone was a modified standard skimmer which had holes laser drilled into the tip area around the orifice. A New Wave UP-266 nm laser was employed drilling holes of ~100 μm. All sample and skimmer cones were constructed from nickel.

Figure 3.1. (a) Standard sample cone, (b) Xi sample cone, (c) Standard skimmer cone, (d) Xi skimmer cone and, (e) PS6R skimmer cone.
The insulation material employed was a silicone impregnated sheet (RS, Corby, Northamptonshire, UK) which was cut to fit the application. The insulation was applied to the cones as stated in Fig. 3.2. Position A insulates between the cone or cone adapter and the water cooling system (as illustrated in Fig. 3.3.), with position B between the cone adapter and cone tip (only available for the Xi and PS6R).

![Figure 3.2. Diagram demonstrating the insulating positions for different cone designs: (a) Standard/drilled skimmer cone and, (b) Xi/PS6R skimmer cone.](image)

![Figure 3.3. Schematic diagram of an ICP-MS interface.](image)
3.2. ADDITIONAL APPARATUS

3.2.1. Cyclonic Spray Chamber Desolvation Setup

Fig. 3.4. demonstrates the dimensions of the cyclonic spray chamber and condenser used for initial desolvation trials. The spray chamber was immersed in a water bath of temperatures 50 – 70 °C with the condenser in a cooling bath at ~5 °C (Fig. 3.5.). The coiled condenser made from 6 mm i.d. glass tubing, promotes mixing as well as providing a greater surface area for condensation in a more compact design. The cyclonic spray chamber possessed an internal volume of 32 mL.

Figure 3.4. (a) Cyclonic spray chamber, frontal and side views and, (b) Coiled condenser.
3.2.2. Double Pass Spray Chamber Desolvation Setup

Fig. 3.6. shows the dimensions of the double pass spray chamber\(^1\) and the water condenser. The double pass spray chamber possessed an internal volume of 60 mL.

The double pass spray chamber setup differed from the cyclonic spray chamber (section 3.3.1.) due to the double pass spray chamber possessing a longer
residency time of the nebulised spray and hence a greater time for desolvation. The chilled water was also pumped around the condenser and hence more efficient cooling was achieved. With the ridges present more surface area was gained producing greater condensing potential. The setup of the double pass spray chamber and water condenser is shown in Fig. 3.7.

Figure 3.7. Schematic diagram of the desolvation system using a double pass spray chamber and a more efficient condenser.

3.3. SAMPLE PREPARATION

3.3.1. Microwave Digestion of Aluminosilicates

A CEM Mars 5 microwave (CEM Microwave Technology Ltd., Milton Keynes, Buckinghamshire, UK) was utilised with XP-1500 reaction vessels for the digestion of refractory matrices.

0.25 g of silicon (IV) oxide (99.5%), 0.25 g of aluminium oxide (99.7%) (both Alfa Aesar, Royston, Hertfordshire, UK), 5 mL 40% hydrofluoric acid and 5 mL 70% nitric acid (both Analar grade, BDH, Poole, Dorset, UK) were placed in the reaction
vessel and subjected to the following conditions: 15 minute increase in temperature to 210 °C and held for 1 minute, then a 5 minute rise to 230 °C and held for 30 minutes, with a cooling time of 30 minutes. The vessels were then opened and a 30 mL aliquot of saturated orthoboric acid solution was added to each sample. The vessels were then reassembled and subjected to the following conditions: 10 minute increase in temperature to 210 °C and held for 5 minutes with a cooling time of 30 minutes. On cooling the vessel contents were transferred to a 100 mL volumetric flask and filled to the line with deionised water.

3.3.1.1. Spiked Microwave Digestion

A 10 μg L⁻¹ In standard solution was prepared in an aluminosilicate matrix (section 3.2.1.) using 1000 mg L⁻¹ In (Alfa Aesar, Royston, Hertfordshire, UK).

3.3.2. Open Vessel Digestion of Aluminosilicates

0.5 g of silicon (IV) oxide and 0.5 g of aluminium oxide were placed into a platinum crucible and moistened with deionised water. 5 mL of 70% nitric acid and 10 mL of 40% hydrofluoric acid (both Analar grade, BDH, Poole, Dorset, UK) were added and evaporated to dryness on a sand bath. The residue was wetted with deionised water and 5 mL of concentrated nitric acid was added and heated to dryness. The sample was then fused with 0.4 g of orthoboric acid (BDH, Poole, Dorset, UK) and 1 g of sodium carbonate on a bunsen burner. After cooling, the crucible was half filled with deionised water, then 7 mL of nitric acid was added and the crucible filled with deionised water. The crucible was then heated until dissolution took place, topping up with deionised water as needed. The solution was then placed into a 50 mL volumetric flask and filled with deionised water.

3.3.2.1 Spiked Open Vessel Digestion

A 10 μg L⁻¹ In standard solution was prepared in a aluminosilicate matrix (section 3.2.2.) using 1000 mg L⁻¹ In (Alfa Aesar, Royston, Hertfordshire, UK).
3.3.3. Production of Synthetic Environmental Matrix

A synthetic sea water sample containing 10 μg L⁻¹ In, 1000 mg L⁻¹ sodium and 100 mg L⁻¹ calcium were prepared in a 2% nitric acid matrix, using 1000 mg L⁻¹ In (Alfa Aesar, Royston, Hertfordshire, UK), 2542 mg L⁻¹ NaCl, 277 mg L⁻¹ CaCl₂ and 70% nitric acid (all Fisher Scientific, Loughborough, Leicestershire, UK).

3.4. DESOLVATION RESULTS AND DISCUSSION

Initial trials with the ICP-MS in standard mode, showed the ¹¹⁵In spiked microwave digested aluminosilicate matrix gave a large reduction in sensitivity over a relatively short period of time (~85% signal intensity decrease over 2 hours continuous run time, as observed in Fig. 3.8.). The ¹¹⁵In signal dropped from 284 932 counts s⁻¹ to 43 972 counts s⁻¹ with a maximum response occurring after 12 minutes of continuous sample up-take time, causing a 7% increase in signal giving 305 453 counts s⁻¹. The increase in signal was thought to occur due to the cone conditioning.

![Figure 3.8. ¹¹⁵In sensitivity loss over time using the standard setup.](image-url)
On removal of the sample and skimmer cones, deposits were readily seen on both the front and rear of the sample cone, but mostly in and around the orifice of the skimmer cone. The sample cone deposit was a white solid which under examination with scanning electron microscopy (SEM) indicated the major constituents to be aluminium and oxygen, hence the formation or incomplete atomisation/ionisation of Al₂O₃ was a distinct possibility (Fig. 3.9.). At the base of the raised area of the sample cone there were signs of the formation of fused silica, which contained air bubbles. Also seen were large deposited fragments which caused localised deposition on and around the grains, implying the incomplete atomisation and ionisation of the sample.

The skimmer cone exhibited a large amount of deposit on and around the tip of the cone. The deposit around the tip was brown with gradual lightening of the colour down from the tip (Fig. 3.10. (b) and Fig. 3.11.). Under SEM examination the deposit on the skimmer was found to consist of mainly silicon and oxygen. The colouration was thought to be caused by entrainment of carbon into the silica deposit. The deposit on the skimmer was the likely cause of the dramatic change in ¹¹⁵In sensitivity as partial blockage of the orifice occurred (Fig. 3.10. (b)). The skimmer employed (Fig. 3.10. (a)) for the study was not new but had endured vast usage prior to these experiments. As physical abrasion was performed in order to remove the deposit, producing a clean cone, the risk of damaging the tip of the cone was inherent so the trials were performed on older used cones.
3. Interface Modification

To reduce or stop the build up of silicon based compounds on and around the skimmer cone orifice, which was attributed to the incomplete vapourisation in the plasma and/or condensation on the cool metal, more robust plasma conditions were needed. By reducing the plasma load through desolvation the plasma possesses a higher temperature and hence is more efficient at processing samples. This would imply the majority of silicon and aluminium would be completely vaporised and not deposited on the cones.

The cyclonic spray chamber desolvation arrangement (section 3.3.1.) employed a cyclonic spray chamber immersed in a water bath where the temperature was raised from 50 – 70 °C in 5 °C increments with the sensitivity of $^{115}$In monitored every 6 minutes. The results are shown in Fig 3.12. with the standard deviation of 5 replicates indicated by error bars. For the cyclonic spray chamber desolvation arrangement, maximum sensitivity for $^{115}$In was achieved at a spray chamber temperature of 60 °C. Observations made with this setup showed condensation on the silicone delivery tube between the spray chamber and the condenser with

Figure 3.10. Photo of the skimmer cone: (a) Prior to use and, (b) With deposit.

Figure 3.11. Side view of the skimmer with deposit around tip.
relatively little condensation in the condenser. These problems were attributed to the flow rate through the spray chamber being too rapid thus not giving the aerosol sufficient time to become totally dry.

![Graph](image_url)

**Figure 3.12.** The variation in $^{115}\text{In}$ signal intensity with changes in the cyclonic spray chamber temperature.

To overcome this problem, a double pass spray chamber (Fig. 3.6. (a)) was employed, as the residence time of the aerosol in the spray chamber is far greater and gives the potential for more solvent to be removed from the aerosol particles through evaporation. The setup as described in section 3.3.2. was used and gave the results shown in Fig. 3.13. with the standard deviation of 5 replicates indicated by error bars.
Figure 3.13. The variation in $^{115}\text{In}$ signal intensity with changes in the double pass spray chamber temperature.

The results show that 55 °C is the temperature for greatest sensitivity using the setup described in section 3.3.2. The condenser (Fig. 3.6. (b)) was also seen to be far more efficient than the coiled condenser described in Fig. 3.4. (b), as the vapour was visibly condensing in the condenser. A problem encountered with this setup was condensation build up in the delivery tube between the spray chamber and the condenser. After some time a droplet formed and blocked the tube. This caused fluctuations in the pressure and an erratic signal. The blockage was cleared by stopping the nebuliser gas flow long enough for the droplet to drain away before restarting.

The double pass desolvation setup was then used over the same time period as the standard setup described earlier. The results achieved are demonstrated in Fig. 3.14. The most noticeable advantage of using the desolvation system is the large increase in sensitivity observed at the beginning of the experiment. With the standard setup, the starting signal was $\sim 280,000$ counts s$^{-1}$ compared to the desolvation system giving $\sim 720,000$ counts s$^{-1}$ for $^{115}\text{In}$. As with the standard setup, a short period of cone conditioning was observed with an increase in $^{115}\text{In}$ sensitivity followed by a rapid decrease in sensitivity with a plateau at just over 1 hour of continuous sampling of the aluminosilicate matrix.
Possibly the most interesting observation is demonstrated in Fig. 3.14., where a comparison between the standard and desolvation setups is displayed. Although the two setups were very different in construction, they both plateaued after approximately the same length of time (slightly over an hour) and the level of the plateau was similar (~50 000 counts s\(^{-1}\)).

On closer inspection under a microscope it was observed that the deposition pattern was far more evenly spread using the desolvation setup. This demonstrated that a smaller particle size was created. This differed from the standard setup which was far more uneven in the deposition pattern. Deposition was also observed on the extraction lens situated behind the skimmer cone, causing problems with ion transmission under desolvation conditions.

![Graph showing comparison of standard and desolvation setups](image)

**Figure 3.14.** Comparison of the degradation of the \(^{115}\)In signal between the standard and desolvation setups.
3.5. CONE TRIALS RESULTS AND DISCUSSION

3.5.1. Microwave Digested Aluminosilicates

As Au is most commonly found and investigated in geological samples a digestion process was performed on aluminosilicate material (section 3.2.1.). The digest was spiked with $^{115}$In and the signal intensity monitored over time. As the matrix had shown problems in the past with deposition, the experiment was not taken to complete cone blockage. One hour of run time was decided upon as this gave an insight into the length of time needed to condition the cone and to monitor the rate of loss of signal. This also removed problems associated with the coating of the ion optics with deposit as problems were encountered with raised voltage settings and stability of subsequent analyses. Combinations of sample and skimmer cones were employed with the skimmer cones being insulated on occasions. The sample cones were not extensively studied as previously the deposition of the skimmer cone orifice showed far greater blockage, attributed to the lower temperature of the skimmer cones.

The Xi skimmer cone was found to give approximately $1/10^{th}$ of the sensitivity of the standard skimmer cone with hard extraction ($>-600$ V) of the ions, as used with the standard and PS6R skimmer cones. A far greater initial sensitivity was gained from the Xi cones by using a softer extraction voltage of around -200 V. The reasons for this observation are not yet understood.

Fig. 3.15. shows the results obtained from the use of the standard sample cone and the skimmer cones with no insulation applied. As can be clearly seen the drilled cone had the best performance with the greatest initial sensitivity as well as the loss in sensitivity of 24% over the 54 minutes compared to 53, 52 and 76% loss of signal for the PS6R, standard and Xi skimmer cones respectively. This implies the drilled cone was blocking to a far lower extent than the other cones. This could be attributed to the holes producing dead volumes of gas, causing a static gas cushion on the tip of the cone around the orifice. The gas layer would direct the sample matter either into the orifice or away from the orifice and not allow it to come into contact with the cone. Also by removing material from the tip
of the cone a lower heat transfer capability occurs, so the tip of the cone will run at a higher temperature, this will also aid the expansion of the gases in the holes.

![Graph](image)

**Figure 3.15.** $^{115}$In signal reduction caused by deposition of the aluminosilicate digest using the standard sample cone and different skimmer cones.

When insulation was applied to the skimmer cones many alterations in the loss of sensitivity were seen. For the standard and drilled cones the insulation was applied at position A (Fig. 3.2.) around the base of the cone between the cone and the water cooled mounting plate. As the Xi and PS6R cones needed an adapter to be compatible with the PQ ExCell, the addition of extra insulation between the adapter and the cone (position B, Fig. 3.2.) itself was possible.

As can be observed in Fig. 3.16, insulating the standard skimmer cone at position A, dramatically improved the perpetuity of the signal with only a 36% decrease in signal compared to the 53% with no insulation. The PS6R cone when insulated at position A and B, and the Xi cone when insulated at position A, gave similar losses of signal 55 and 75% respectively to the results obtained with no insulation. By insulating the drilled cone the performance was drastically reduced with a vast increase in loss of signal. The most spurious results were obtained by the PS6R cone when insulated at position B only. This gave an increase of almost double
the initial sensitivity after 42 minutes. The rise was thought to be due to cone conditioning, although unlike the other cones which condition in ∼12 minutes, the PS6R take a longer period.

![Graph](image-url)

**Figure 3.16.** $^{115}$In signal change caused by deposition of the aluminosilicate digest using the standard sample cone and different insulated skimmer cones (positions indicated on graph).

As the sample cone showed little or no deposition in these and previous experiments a few comparisons were investigated using the Xi sample cone. The results obtained were fairly similar to those found in the previous trials (see Fig 3.17. A slight improvement was seen with the Xi sample cone and the Xi skimmer cone combination giving only a 62% decrease in sensitivity compared to 75% when insulated and 76% when used with the standard sample cone. As with the standard cone, the Xi and the PS6R cone insulated at position A and B, showed similar results to those obtained previously. Once more, the same phenomenon was observed from the PS6R cone which gave over a 7 times increase in the initial sensitivity after 36 minutes. Again the rise was attributed to the conditioning of the PS6R skimmer cone needing a longer period for cone conditioning.

There are two effects that occur through blocking of the orifice in respect to matter transportation through the skimmer cone. The first is: as the cone blocks, fewer
ions can go through the orifice to reach the detector and hence a reduction in sensitivity will be observed. The second involves the lowering of the expansion chamber pressure due to a smaller orifice size. This could cause an increase in efficiency of the extraction as the reduced pressure will produce less ion scattering and hence higher transmission.

![Graph](image)

**Figure 3.17.** $^{115}$In signal change caused by deposition of the aluminosilicate digest using the Xi sample cone and different skimmer cones.

Uncertainties about the effect of the insulation will have to be investigated further to come to a decisive conclusion. One explanation relates to the alteration in the sample to skimmer cone distance. To confirm that this is a factor, a spacer (e.g. made from Cu) with the capability for efficient heat transfer would need to be used in the place of the insulation.

During the cone cleaning process, physical abrasion was necessary to remove the deposited material. During cleaning, the deposit was seen to be made up of polymorphs of silicate. These distinct layers were attributed to different crystalline structures resulting from the variation in temperature as the deposit insulated the front surface of the cone. Difficulties were encountered when cleaning the drilled
cone as the abrasive cleaning caused the holes to collapse and hence there was a loss in the quantity of holes and the uniformity of coverage.

3.5.2. Open Vessel Digested Aluminosilicates

As seen in previous experiments, the interface region of the ICP-MS was found to be problematic with respect to samples of high dissolved solids. The cones were prone to deposition and partial blocking of the orifice was common, this in turn giving rise to a significant reduction in the sensitivity of the instrument over a relatively short period of time. With respect to aluminosilicate digests, the deposition on the skimmer cone was found to compare mainly silicon and oxygen under SEM examination, while the sampler cone was seen to have slight aluminium and oxygen deposits around the orifice, but to a far lesser extent. As the microwave digestion method was a closed system, both the aluminium and the silicon were both present in the digest. By using a more traditional method of open vessel digestion (section 3.2.2.), the silicon was fumed off as the SiF$_4$ molecule hence removing the more problematic element, according to previous experiments. The In spiked open vessel digest (sections 3.2.2.1.) was then run through the instrument continually with the $^{115}$In signal monitored every six minutes.

As can be seen in Fig. 3.18. the reduction in sensitivity was extremely rapid. Over the 66 minutes of run time the initial signal had decreased by 82%, from 200 882 to 35 720 counts s$^{-1}$ for $^{115}$In. On inspection of the cones this was seen to be due to the blocking of the orifice. There were large amounts of white deposit around and in the orifice of the cone. Under closer inspection with a microscope the white deposit was seen to be made up of small fragments which appeared to have grown as further deposition occurred. The solid was also seen to be reacting with the moisture in the air. This was assumed to be due to the interface region being under vacuum whilst the instrument was in operation and hence if the deposit was aluminium, in the presence of atmospheric oxygen/moisture, the formation of the oxide/hydroxide would occur.
3. Interface Modification

Figure 3.18. $^{115}$In response for the open vessel aluminosilicate digest.

3.5.3. Environmental Matrix Results

Another example of a sample with high levels of dissolved solids is sea water. A synthetic 10 fold dilution was prepared as described in section 3.2.3. The solution contained 1000 mg L$^{-1}$ Na, 100 mg L$^{-1}$ Ca and 10 µg L$^{-1}$ In, with $^{115}$In used for monitoring the change in signal intensity. As the orifice was expected to become blocked, the expansion pressure was also measured to give an indication of the extent of deposition. To deter deposition, the cones were also insulated from the water cooled interface using the silicon impregnated washer. This meant that the cones were running at an elevated temperature to discourage the deposition from occurring. The expansion region is differentially pumped to reduce the pressure, aiding the extraction of the ions from the plasma, and producing a step down in pressure to the detector region. The expansion pressure was also monitored as the pressure would be expected to decrease as the skimmer orifice became blocked. Figs. 3.19. (a) – (f) show the results obtained for the $^{115}$In signal intensity and the expansion pressure for the standard, Xi and PS6R skimmer cones, both in the normal configuration and insulated, in all cases a clean standard sampler was employed.
Figure 3.19. $^{115}$In signal intensity and expansion pressure readings for trials involving the synthetic sea water matrix using: (a) Standards skimmer cone; (b) Insulated standard skimmer cone (continued).
Figure 3.19. $^{115}$In signal intensity and expansion pressure readings for trials involving the synthetic sea water matrix using: (c) Xi skimmer cone; (d) Insulated Xi skimmer cone (continued).
As can be seen from Figs. 3.19. (a) – (f) the expansion pressure has decreased along with the $^{115}\text{In}$ signal as expected. This indicates the blocking of the cone orifices has occurred. Figs. 3.19. (a) – (d) show the decrease in expansion...
pressure is fairly linear, whereas Figs. 3.19. (e) and (f) seem to be decreasing more exponentially, and hence mimicking the $^{115}$In signal intensity.

The deposition patterns for the various cones were seen to differ between cone style and were independent of the insulation. The standard and PS6R cones were seen to be covered in a relatively even coating of deposit. The Xi cones appeared to have varying deposit at different regions of the skimmer cone as demonstrated in Fig. 3.20.

![Figure 3.20](image)

**Figure 3.20.** Position and character of environmental matrix deposition on Xi skimmer cone: (a) Large mass partially/totally blocking orifice and covering tip of cone, (b) Grains which appear to have grown in situ, (c) Layer of even depth deposit and, (d) Thin layer of deposit extending approximately half way down the inside walls.

Insulating the standard cones seemed to have had no great effect on the deposition or the signal loss. The PS6R and the Xi cones both showed a marked decrease in loss of signal when the cones were insulated. This phenomenon could have been due to the cones running hotter than the standard cones as they were insulated in two places, between the base of the adapter and the interface, and between the adapter and the cone itself, whereas the standard cone was only insulated between the base and the interface region, as this was the only place available for insulating. The PS6R and Xi cones are also both far thinner towards the tip than the standard cone and hence the dissipation of heat will be less and cause the tip to increase in temperature.

On removal of the cones from the instrument for examination the deposit was observed to effervesce. This again was attributed to the interface region being under vacuum whilst the instrument was in operation and in the presence of atmospheric oxygen/moisture, the formation of the oxide/hydroxide of elemental
sodium or calcium would occur. The deposit was easily washed from the skimmer cone with deionised water.

3.6. SUMMARY

The determination of $^{115}$In in an aluminosilicate matrix caused extensive problems throughout the interface region of the ICP-MS. As ICP-MS is a flow into instrument rather than a flow-by instrument as with ICP-AES, the sample which enters via the nebuliser continues into the instrument. This caused deposition and blocking of the sample and skimmer cones, which in turn leads to major loss of signal intensity.

The use of a double pass spray chamber in the desolvation setup was preferential to the cyclonic spray chamber arrangement due to the increased residency time associated with the nebulised aerosol. The double pass spray chamber combined with the water cooled condenser gave a far greater efficiency of solvent removal.

The use of desolvation with the standard cone arrangement caused a 2.5 fold increase in initial sensitivity over the standard instrument arrangement for $^{115}$In. Although an initial increase in $^{115}$In sensitivity was observed the degradation of the signal was far more prominent with the desolvation setup than the standard setup. Both arrangements gave a slight increase in signal over the first 12 minutes followed by a rapid decrease in sensitivity over the next hour. Both arrangements then plateaued around the 50 000 counts s$^{-1}$ for $^{115}$In.

When the standard sampler was employed with different skimmer cones, the drilled skimmer cone presented the most favourable results with the lowest loss of signal intensity over an hour of continuous run time, giving only a 24% decrease. The drilled skimmer cone also gave the highest initial sensitivity. The other skimmer cones employed gave between 52 to 76% decrease in signal. The insulation of the Xi and PS6R skimmer cones returned similar results to those obtained with no insulation applied. The insulated standard skimmer cone showed a decrease in deposition with only a 36% loss in signal, 17% better than when no insulation was applied.
3. Interface Modification

When the Xi sampler was employed only the Xi skimmer cone arrangement showed a significant increase in efficiency. The decrease in $^{115}$In signal intensity dropped from 75% to 63% from the initial values.

When the microwave digested aluminosilicate sample was used, a large deposition on and round the orifice of the skimmer was observed, causing the reduction in signal. Under SEM examination this was discovered to be made of mainly Si and O. For this reason the use of an open vessel digestion process was employed as the Si was fumed from the Pt crucible as SiF$_4$. After the addition of HF however, the removal of the Si from the sample solution actually proved worse than the microwave digest with an 82% loss in sensitivity over a period of an hour.

The aluminosilicate samples from both digestion methods caused a large deposit on the cones, especially the skimmer. As these matrices are extremely refractory and resilient to the common cleaning solutions, physical abrasion was needed to remove the deposit. Continued cleaning would cause an increased risk of damage to the cone tip and drastically shorten the lifetime of the cone.

The environmental matrix sample showed similar deposition to the aluminosilicate samples. The major difference occurred with the signal plateauing between 2 – 3 hours of continuous running.

Insulating the cones generally had little or no effect on the constancy of the signal and was attributed to the inability to affect the temperature sufficiently to deter deposition.
3.7. REFERENCES

Chapter Four

Preconcentration/
Separation of Au and Pt
4. **PRECONCENTRATION/SEPARATION OF Au AND Pt**

When the determination of ultra trace elements present in complex matrices is accomplished, problems occur due to matrix effects and hence detection limits (LOD) are affected. Dilution is often not a viable option to reduce the effect of the matrix as the concentration of the analyte of interest may drop below the LOD of the ICP-MS. Thus, the aim of the present chapter is to develop a procedure for the preconcentration/separation of Au and Pt from a microwave digested aluminosilicate sample, to be analysed by ICP-MS. By separation of the analytes from the main constituent of the sample, matrix effects are reduced and LOD may improve to a recordable level.

4.1. **INSTRUMENTATION**

4.1.1. **ICP-MS**

A VG PQ ExCell instrument was configured as described in section 3.1.1. The Conikal concentric nebuliser, impact bead spray chamber, standard silica torch and standard nickel sample/skimmer cones were all employed throughout the work.

Tuning of the torch position and ion lenses was performed daily as reported in section 3.1.1.

4.2. **SAMPLE PREPARATION**

4.2.1. **HF/HNO₃ Microwave Digestion of Aluminosilicates**

The microwave digestion process performed on the aluminosilicate samples was followed as in section 3.2.1. with the addition of 0.1 mL of 1 mg L⁻¹ Au solution (SPEX Certiprep, Metuchen, NJ, USA) to the initial reaction. 0.1 mL of 1 mg L⁻¹ Pt solution (Aldrich, Milwaukee, WI, USA) were also applied to the initial reaction when stated.
4.2.2. **HF/HNO₃/HCl Microwave Digestion of Aluminosilicates**

The microwave digestion process performed on the aluminosilicate samples was followed as in section 3.2.1. with the addition of 5 mL 35% hydrochloric acid (Analar grade, BDH, Poole, Dorset, UK) and 0.1 mL of 1 mg L⁻¹ Au and Pt solution to the initial reaction vessel.

4.3. **ADDITIONAL APPARATUS**

4.3.1. **Solid Phase Extraction (SPE) Columns**

4.3.1.1. **Bakerbond SPE Columns**

The Bakerbond SPE columns used were produced by JT Baker (Phillipsburg, NJ, USA). The columns were constructed from polypropylene with 20 μm polyethylene frits surrounding the sorbent bed. The sorbents were silica gel based bonded phase (CN, CH, C2, C8 and C18), of 40 μm in diameter with 60 Å pore size. The columns possessed a 3 mL volume.

4.3.1.2. **Bond Elut SPE Columns**

The Bond Elut CN solid phase extraction columns employed were produced by Varian (Palo Alto, CA, USA). The sorbent was silica gel based CN bonded phase of 40 μm in diameter with 60 Å pore size. The columns possessed a 3 mL volume.

4.3.1.3. **Alltech SPE Columns**

The solid phase extraction columns used were produced by Alltech (Deerfield, IL, USA). The sorbents were silica gel based CN bonded phase and divinyl benzene (DVB) of 40 μm in diameter with 60 Å pore size positioned between 20 μm polyethylene frits. The columns possessed a 1 mL volume with 25 mg of sorbent.
4.3.1.4. *Phenomenex SPE Columns*

The strata-X and strata-XC solid phase extraction columns used were produced by Phenomenex (Torrance, CA, USA). The strata-X sorbent has a surface modified styrene divinyl benzene phase (Fig. 4.1. (a)) with the strata-XC sorbent a styrene divinyl benzene modified with strong cation exchanger (Fig. 4.1. (b)) of 33 μm diameter spheres with 85 Å pore size. The columns possessed a 1 mL volume with 30 mg of sorbent.

![Chemical structures](a) strata-X and (b) strata-XC.

4.3.2. **Activation of SPE Columns**

For SPE columns with a 3 mL capacity, 3 mL of methanol followed by 3 mL of deionised water was applied at flow rates of 2 mL min⁻¹.

For the 1 mL SPE columns, 1 mL of 50:50 methanol:water followed by 3 mL of deionised water at 2 mL min⁻¹.
4. Preconcentration/Separation of Au and Pt

4.3.3. Sample Addition to SPE Columns

5 mL (unless otherwise stated) of Au/Pt spiked aluminosilicate microwave digest (section 4.2.1 and 4.2.2.) were passed through the SPE column (specific column stated in text) and collected.

These samples as well as a sample of the unspiked digest, which had not been put through a column, were tested using ICP-MS looking at the $^{197}$Au and $^{195}$Pt response when stated.

4.4. PRECONCENTRATION OF Au AND Pt USING SPE

4.4.1. Direct Preconcentration of Au From Sample Digests

Initial experiments involved the retention of Au from the HF/HNO$_3$ aluminosilicate digest by various SPE columns. Trials involved the determination of Au in the post column eluent and monitoring with ICP-MS for $^{197}$Au. A blank (unspiked digest) and three replicates of spiked HF/HNO$_3$ digest were performed on each of the following columns with CH, C2, C8, C18 and CN (all Bakerbond) bonded phases. With the monitoring of $^{197}$Au in the eluent the non-retained Au was compared to an Au spiked aluminosilicate standard which had not been applied to a column. No manipulation was performed on the HF/HNO$_3$ aluminosilicate digest prior to application to the column. The samples were drawn through the columns under negative pressure with the aid of a peristaltic pump. Throughout the trials a wash solution of 5% HCl was employed between sample analysis. As these preliminary trials possessed uncertainty associated with the extent of Au retention, elution was not performed on the SPE columns.

All the alkyl bonded phases showed poor retention of Au (Table 4.1.), ranging from 5 – 18%. The CN SPE columns showed the greatest retention with 65% of the Au retained. The CN SPE columns were thought to show a greater affinity for Au over the alkyl bonded phases as cyanide compounds of Au are stable and easily formed. Although the CN is not free in the columns some affinity for Au was thought to be occurring.
As the greatest potential for retention of Au was found using the CN columns, further investigation was performed. The other alkyl bonded phased SPE columns were omitted due the poor retentions shown towards Au direct from the solution.

To discount the overloading of the columns by Au an aliquot of digest was diluted by half with deionised water. Again the unretained Au was compared to the test solution. An average retention of 46% Au was monitored from the three replicate samples. As the retention is approximately 20% less than the previous experiment the likelihood of the column being overloaded seems unlikely. Although the variability in the repeatability of retention was attributed to one of two factors: the pump speed and/or the instability of the Au specie at the digest pH (~0.2).

Due to back pressure resulting from the packaging material of the SPE columns, consistent flow rates were difficult to maintain. Fairly erratic retentions occurred with no real pattern when the flow rate was altered between 1.3 – 3.5 mL min⁻¹, as can be observed in Fig. 4.2. As the pump speed increased an elevated back pressure was observed causing the actual flow rate to become non-consistent with the dial speed. As the peristaltic pump reached 80 – 100% of the maximum speed, little or no alteration was observed in flow rate.
4. Preconcentration/Separation of Au and Pt

Figure 4.2. The effect of sample flow rate on the retention of Au on a CN SPE column.

The greatest Au retention attained occurred when the samples were processed at a flow rate of 3 mL min\(^{-1}\) through the column.

The Au in solution was thought to be in the form of either \([\text{AuCl}_4]^-\), \(\text{AuCl}_3\), \(\text{AuF}_3\) or as the oxide \((\text{Au}_2\text{O}_3)\). The oxides of Au were discounted as they are unstable and easily reduced to the metal, so is unlikely to be present in the samples.\(^1\)

As the CN SPE columns retain neutral species, the retained Au was thought to be as a neutral compound or present as an ion pair. The chloro compounds/ions are very common in the chemistry of Au and with the addition of the analyte spike, a small quantity of aqua regia was added to the system. The Au is present within the standard solution as chloroaauric acid (HAuCl\(_4\)). For the retention of the \([\text{AuCl}_4]^-\) neutralisation must occur either by forming an ion pair with a cation of either Al, Si or H or via the loss of a chlorine atom to produce \(\text{AuCl}_3\). \(\text{AuCl}_3\) and \(\text{AuF}_3\) are both neutral compounds of Au and so theoretically could be retained directly on the CN sorbent.
4.4.2. Effect of pH on Au Retention

The alteration of the pH of the HF/HNO₃ microwave digested aluminosilicate solutions was investigated with the pH changed from ~0.2 to 3, 5, 7, 9 and 11 with the addition of ammonium hydroxide. The flow rate of the sample was set to 3 mL min⁻¹. As the pH was increased towards neutral a white precipitate formed, likely to be caused by the formation of aluminium hydroxide. The formation of the precipitate caused extensive problems relating to the blocking of the CN SPE (Bakerbond) columns. These problems caused erratic results for the pH 7, 9 and 11 samples, with little or no signs of retention. The sample at pH 3 gave ~40% retention of Au. The greatest retention of 99% was found at pH 5 with nearly all the Au retained by the CN SPE columns.

As pH 5 demonstrated the greatest potential for retention of Au from the HF/HNO₃ aluminosilicate digest, smaller pH increments encompassing pH 5 were chosen. Again ammonium hydroxide was used to alter the pH of the digest to 4, 4.5, 5, 5.5 and 6. Each pH was analysed in triplicate with an unspiked digest acting as a blank. Bakerbond CN SPE columns were employed with a flow rate of 3 mL min⁻¹. The eluent was collected and compared to the original spiked digest.

The retentions differed dramatically compared to those obtained from the previous trial with only 13, 29, 35, 36 and 37% Au retention for the digests at pH 4, 4.5, 5, 5.5 and 6 respectively. The results were all significantly lower than the 99% Au retention achieved by the pH 5 digest sample in the previous trial.

The large variation between these results was accredited to the period of time between the digestion process, the preconcentration stage and the instrumental testing of the samples. The low results were attributed to the instability of the Au in the primarily nitric acid media. To test the theory a new digestion was prepared as in section 4.2.1. and altered as mentioned to pH 4, 4.5, 5, 5.5 and 6.

Although the retentions for Au were found to mimic the previous results the retentions where slightly higher with 19, 32, 35 and 41% for pHs 4, 4.5, 5 and 6. pH 5.5 was omitted as the Au standard in the aluminosilicate digest gave a
spuriously low result. As the results were seemingly reproducible with only a slight increase of Au retention from the freshly prepared digest, the degradation of the Au compound/ion was discounted as a major factor attributing to the erratically lower results.

As a discrepancy was apparent within the results compared to earlier trials, investigations into the retention of Au standards in a 5% HCl matrix were performed. The pH of a 1 \( \mu \text{g L}^{-1} \) Au standard solution in 5% HCl was altered using ammonium hydroxide to approximate pH values of 3, 5, and 7 from the original solution at pH 0.4. Bakerbond CN SPE columns were used with a flow rate of 3 mL min\(^{-1}\).

The results demonstrated in Table 4.2. show the Au was mainly removed from the sample where no manipulation was performed to the pH (at pH 0.4). The retention of the Au from the 5% HCl matrix was 0.993 \( \mu \text{g L}^{-1} \) which equates to 99% retention. The closer the pH was adjusted towards neutral the lower the retention became with 63 and 58% retentions for pH 2.5 and 5.5 respectively. The neutral solution gave extremely spurious results with large relative standard deviations (RSDs) of the counts s\(^{-1}\), implying a problem with the analysis, hence will be omitted from discussion. The discrepancy was attributed to the increased levels of ammonia present in the sample at pH 7 causing fluctuations in the plasma, creating instability.

<table>
<thead>
<tr>
<th>Sample pH</th>
<th>Matrix</th>
<th>Au Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>5% HCl</td>
<td>99.3</td>
</tr>
<tr>
<td>2.5</td>
<td>5% HCl</td>
<td>62.7</td>
</tr>
<tr>
<td>5.5</td>
<td>5% HCl</td>
<td>57.9</td>
</tr>
<tr>
<td>7</td>
<td>5% HCl</td>
<td>&lt; LOD</td>
</tr>
</tbody>
</table>

As the retained Au would need to be washed to remove any aluminosilicate matrix which remained within the dead volume of the sorbent bed, a brief trial with HCl as
the wash solution was investigated. 5 mL aliquots of 5% HCl were chosen as the wash solution, as Au was retained efficiently from the same solution in the previous trials. The percentage Au elution by the wash solution was calculated from the amount of Au retained on the columns at the different pHs. The results show a considerable difference in the amount of Au eluted between varying pHs. For pHs of 0.4, 2.5 and 5.5 the amount of Au eluted by the 5% HCl wash solution returned results of 17, 44 and 38% respectively. As the wash solution was the same matrix as used in the sample at pH 0.4, the elution of the Au was unexpected. This could imply the Au is not bound strongly to the CN phase but is only weakly attached to the surface.

As relatively high quantities of Au were being retained, elution with ammonium hydroxide was employed, as previous experiments demonstrated by increasing the pH, low retentions were observed. Three CN SPE columns (Bakerbond) were prepared and 5 mL of 1 mg L\(^{-1}\) Au in 5% HCl were retained on each at 3 mL min\(^{-1}\). The columns were then eluted with varying concentrations of ammonium hydroxide solution. 0.01, 0.1 and 1 M ammonium hydroxide solutions were prepared with 5 mL applied to the columns.

The retention of Au on the CN columns was very good with two columns retaining 97% and the final column retaining 96%. The elutions with ammonium hydroxide proved far less promising giving elutions of 58 and 64% for 0.01 and 0.1 M ammonium hydroxide respectively. 1 M ammonium hydroxide solution gave rather low and random results, which is thought to occur due to the high levels of ammonia causing the plasma to become erratic and unstable.

Other solvents for the removal of retained Au were also investigated; methionine and methanol were employed. The methionine was employed as Au has a well known affinity for sulfur containing compounds, the methanol was chosen due to it possessing a high partition coefficient for neutral, non-polar compounds. The methionine was prepared in a 5 molar excess compared to Au. 100% methanol was also employed as an eluent. 10 mL of eluent was employed at a flow rate of 3 mL min\(^{-1}\).
When methanol was used to remove the Au only 0.6 μg L$^{-1}$ of Au was found in the eluent equating to only 3% of the retained Au on the Bakerbond double pass column. The trials into methionine proved more promising with 46 μg L$^{-1}$ of Au being recorded which equated to 63% of Au retained on the Bakerbond single pass column.

Trials into the reproducibility between different manufacturers CN columns were performed. Two CN columns from different companies (Bakerbond and Bondelut) were compared to see the consistency between columns, as the specifications implied the same particle size and CN coverage.

Quite a difference in Au retention was found between the BondElut and Bakerbond columns. The BondElut retained 34% with the Bakerbond retaining 73%. This demonstrates a large variation between different manufacturers columns on the retention of Au.

As previous experiments were performed involving the HF/HNO$_3$ aluminosilicate digest as well as the HCl standards, comparisons between the retention of Au were performed. As some of the previous results had displayed a problem associated with the reproducibility, 5 mL of conc. HCl was added to the HF/HNO$_3$ digest in an attempt to form a stable Au compound or ion to create a greater consistency between trials. Pump flow rates were also altered for the different matrices and the sample volume was altered. The pump flows were altered to 1.5, 3 and 4.5 mL min$^{-1}$ for the 5% HCl, HF/HNO$_3$ microwave digest and the HCl spiked HF/HNO$_3$ digest. 5 mL of sample was added to CN (Bakerbond) SPE columns from each matrix with 1 and 10 mL aliquots of the HCl spiked HF/HNO$_3$ digest also employed. The results are shown in Table 4.3.
4. Preconcentration/Separation of Au and Pt

Table 4.3. Au retention from various matrices at different flow rates.

<table>
<thead>
<tr>
<th>Sample Matrix</th>
<th>Sample Volume (mL)</th>
<th>Flow Rate (mL min⁻¹)</th>
<th>Au Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% HCl</td>
<td>5</td>
<td>1.5</td>
<td>26</td>
</tr>
<tr>
<td>5% HCl</td>
<td>5</td>
<td>3</td>
<td>18</td>
</tr>
<tr>
<td>5% HCl</td>
<td>5</td>
<td>4.5</td>
<td>38</td>
</tr>
<tr>
<td>HF/HNO₃ Digest</td>
<td>5</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>HF/HNO₃ Digest</td>
<td>5</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>HF/HNO₃ Digest</td>
<td>5</td>
<td>4.5</td>
<td>0</td>
</tr>
<tr>
<td>HCl Spiked HF/HNO₃ Digest</td>
<td>1</td>
<td>1.5</td>
<td>61</td>
</tr>
<tr>
<td>HCl Spiked HF/HNO₃ Digest</td>
<td>1</td>
<td>3</td>
<td>49</td>
</tr>
<tr>
<td>HCl Spiked HF/HNO₃ Digest</td>
<td>1</td>
<td>4.5</td>
<td>60</td>
</tr>
<tr>
<td>HCl Spiked HF/HNO₃ Digest</td>
<td>5</td>
<td>1.5</td>
<td>12</td>
</tr>
<tr>
<td>HCl Spiked HF/HNO₃ Digest</td>
<td>5</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>HCl Spiked HF/HNO₃ Digest</td>
<td>5</td>
<td>4.5</td>
<td>17</td>
</tr>
<tr>
<td>HCl Spiked HF/HNO₃ Digest</td>
<td>10</td>
<td>1.5</td>
<td>20</td>
</tr>
<tr>
<td>HCl Spiked HF/HNO₃ Digest</td>
<td>10</td>
<td>3</td>
<td>21</td>
</tr>
<tr>
<td>HCl Spiked HF/HNO₃ Digest</td>
<td>10</td>
<td>4.5</td>
<td>10</td>
</tr>
</tbody>
</table>

The results demonstrated relatively high differences between retention and pump flow rates, although the retentions are generally low for all the matrices. The main difference observed was between the HCl spiked HF/HNO₃ aluminosilicate digest using different quantity aliquots. The samples where 1 mL of the spiked matrix was used showed far better retention than those when 5 and 10 mL of sample was employed. 1 mL of HCl spiked HF/HNO₃ digest gave 50 – 60% retention with 5 and 10 mL aliquots giving far less with 10 – 20% retention of Au.

As the samples were analysed there was a noticeable increase in the RSD associated with the digest samples, particularly the HCl spiked digest (final set to be analysed). This rise in instability was attributed to the deposition on the cones by the aluminosilicate material. In general the RSD worsened with prolonged analysis and deposition was observed on both the sampler and skimmer cones.
The deposition mimicked that seen during the desolvation experiments in Chapter 3.

4.4.3. Preconcentration of Au and Pt After Chelation

The retention of Au on the CN SPE columns gave inconsistent results from all of the matrices with no manipulation of the sample solution or by altering the pump flow and pH. As reported in Chapter 1.4.1., chelating agents have been applied to Au solutions with retention on modified silica gels.\(^2\)\(^-\)\(^6\) As Au has a high affinity for sulfur a range of chelating agents containing two sulfur atoms were chosen for the investigation. The compounds shown in Fig. 4.3. were ammonium diethylidithiocarbamate (ADTC), ammonium pyrrolidinedithiocarbamate (APDC), ammonium diethylidithiophosphoric acid (ADTP) and potassium ethyl xanthate (KEtX).

\[(a) \text{Ammonium pyrrolidinedithiocarbamate (APDC)}\]
\[(b) \text{Ammonium diethylidithiophosphoric acid (ADTP)}\]
\[(c) \text{Potassium ethyl xanthate (KEtX)}\]
\[(d) \text{Ammonium diethylidithiocarbamate (ADTC)}\]

Figure 4.3. Structure of chelating agents used for the retention of Au and Pt.

Theoretically these chelates would form a square planar arrangement with Au (III) and form a complex cation.\(^1\) For Pt(II) and Pd(II) four membered neutral chelate rings are formed.\(^7\)

The retention of Au on CN and C18 SPE columns was investigated using a 5 molar excess of chelating agents in relation to Au. The pH of the HF/HNO\(_3\) digest
was altered to 3.6, 5 and 7.4 prior to the chelate addition. A digest sample without addition of a chelating agent was also used as a blank. Au retention was calculated on the unretained Au in the post column solution. Elution was not performed as the level of Au retention was unknown.

In general all the samples with chelating agents gave similar or greater retentions of Au than the sample without (Table 4.4.). A couple of exceptions were observed with the addition of ADTP at pH 5 and 7 on both columns and with KEtX at pH 0.2 on a C18 column, gave significantly lower retentions.

When the pH of the digests remained unchanged (~0.2) the retentions on the CN columns were found to be greater in comparison to the C18 columns, for all the chelating agents employed. The difference in Au retention was 10 – 20% lower for the C18 columns that the CN. The retention of Au from the sample with no chelate was found to be relatively equal with 75 and 77% for the CN and C18 columns respectively. This phenomenon was also observed for all the pH 7.4 samples and in most cases for the pH 3.6 samples.

For the samples at pH 5 the opposite was true with all the samples employing a C18 column giving better retention of Au.

With the addition of no chelating agent to the digest, the greatest retentions of Au were seen at pH 5 with 97 and 82% for the C18 and CN SPE columns respectively. At pH 0.2, 3 and 7.4 the Au retentions were fairly similar for both columns with ~76, ~65 and ~82% respectively.

KEtX was found to give high retentions using the C18 column with the pH 5 digest as well as the CN column with the pH 3.6 digest producing 97 and 90% retentions respectively.

ADTP proved to be the least effective chelating agent for the retention of Au especially at higher pHs. The greatest retentions were observed at pH 0.2 with a CN column and pH 3.6 with a C18 column, where retentions of 89% were reached.
For all pHs analysed (0.2, 3.6, 5.0 and 7.4), ADTC was found to give between 80 and 90% retention of Au on the CN SPE columns. When the C18 SPE columns were employed the greatest retention of Au was found from the solution of pH 5.0 with 93.8%. At all other tested pHs the retention of Au was found to be <72%.

APDC showed the greatest potential as retentions of >95% were obtained on both the columns at pH 3.6 and 5. At pH 5, 99 and 98% Au retentions were observed for the C18 and CN columns respectively.

Table 4.4. Results of Au retention on CN and C18 SPE columns at varying pH.
(Key: 90 – 95% retention, 95 – 100% retention)

<table>
<thead>
<tr>
<th>pH</th>
<th>Chelating agent</th>
<th>CN column retention of Au (%)</th>
<th>C18 column retention of Au (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>No chelate</td>
<td>75.3</td>
<td>76.8</td>
</tr>
<tr>
<td>0.2</td>
<td>KetX</td>
<td>82.7</td>
<td>24.1</td>
</tr>
<tr>
<td>0.2</td>
<td>ADTP</td>
<td>88.7</td>
<td>78.0</td>
</tr>
<tr>
<td>0.2</td>
<td>ADTC</td>
<td>83.4</td>
<td>62.7</td>
</tr>
<tr>
<td>0.2</td>
<td>APDC</td>
<td>86.8</td>
<td>69.0</td>
</tr>
<tr>
<td>3.6</td>
<td>No chelate</td>
<td>66.8</td>
<td>63.8</td>
</tr>
<tr>
<td>3.6</td>
<td>KetX</td>
<td>90.1</td>
<td>76.9</td>
</tr>
<tr>
<td>3.6</td>
<td>ADTP</td>
<td>79.0</td>
<td>88.8</td>
</tr>
<tr>
<td>3.6</td>
<td>ADTC</td>
<td>81.1</td>
<td>63.8</td>
</tr>
<tr>
<td>3.6</td>
<td>APDC</td>
<td>98.8</td>
<td>96.8</td>
</tr>
<tr>
<td>5.0</td>
<td>No chelate</td>
<td>81.7</td>
<td>97.2</td>
</tr>
<tr>
<td>5.0</td>
<td>KetX</td>
<td>80.4</td>
<td>97.1</td>
</tr>
<tr>
<td>5.0</td>
<td>ADTP</td>
<td>25.6</td>
<td>64.6</td>
</tr>
<tr>
<td>5.0</td>
<td>ADTC</td>
<td>89.3</td>
<td>93.8</td>
</tr>
<tr>
<td>5.0</td>
<td>APDC</td>
<td>98.3</td>
<td>99.3</td>
</tr>
<tr>
<td>7.4</td>
<td>No chelate</td>
<td>79.3</td>
<td>85.0</td>
</tr>
<tr>
<td>7.4</td>
<td>KetX</td>
<td>87.5</td>
<td>56.0</td>
</tr>
<tr>
<td>7.4</td>
<td>ADTP</td>
<td>30.5</td>
<td>22.5</td>
</tr>
<tr>
<td>7.4</td>
<td>ADTC</td>
<td>88.4</td>
<td>71.9</td>
</tr>
<tr>
<td>7.4</td>
<td>APDC</td>
<td>82.8</td>
<td>71.5</td>
</tr>
</tbody>
</table>
As the addition of APDC gave high retentions for both the C18 and CN columns when the pH of the digest was altered to 3.6 and 5, further investigations were performed into the pH dependency of the retention of Au. HF/HNO₃ digest samples were pH altered to smaller increments of 3.5, 3.9, 4.5, 5.0, 5.5 and 6.0. The results for the experiment (Table 4.5.) are significantly lower than for the previous experiment where pH 3.5 and 5 were employed. In comparison to the equivalent pH 3.5 solutions, both columns retained about 20% less Au with the pH 5 digests giving as high as 40% reduction in Au retention.

In general the C18 columns were equal or better at retaining Au than the CN SPE columns. At lower pH (3.5, 4 and 4.5) the reproducibility was slightly higher on the CN columns. As the pH of the digest was increased (5, 5.5 and 6) the reproducibility was found to be greater for the C18 columns. Also at higher pH the retentions were far greater, reaching >95% for the pH 5.5 and 6 digests.

Table 4.5. Reproducibility of C18 and CN SPE columns under different pH conditions using APDC as a chelating agent.

<table>
<thead>
<tr>
<th>pH</th>
<th>Column Type/Replicate No.</th>
<th>Au Retention (%)</th>
<th>Column Type/Replicate No.</th>
<th>Au Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>C18/1</td>
<td>77</td>
<td>CN/1</td>
<td>83</td>
</tr>
<tr>
<td>3.5</td>
<td>C18/2</td>
<td>84</td>
<td>CN/2</td>
<td>84</td>
</tr>
<tr>
<td>4.0</td>
<td>C18/1</td>
<td>86</td>
<td>CN/1</td>
<td>90</td>
</tr>
<tr>
<td>4.0</td>
<td>C18/2</td>
<td>91</td>
<td>CN/2</td>
<td>91</td>
</tr>
<tr>
<td>4.5</td>
<td>C18/1</td>
<td>85</td>
<td>CN/1</td>
<td>78</td>
</tr>
<tr>
<td>4.5</td>
<td>C18/2</td>
<td>89</td>
<td>CN/2</td>
<td>78</td>
</tr>
<tr>
<td>5.0</td>
<td>C18/1</td>
<td>80</td>
<td>CN/1</td>
<td>54</td>
</tr>
<tr>
<td>5.0</td>
<td>C18/2</td>
<td>83</td>
<td>CN/2</td>
<td>62</td>
</tr>
<tr>
<td>5.5</td>
<td>C18/1</td>
<td>99</td>
<td>CN/1</td>
<td>95</td>
</tr>
<tr>
<td>5.5</td>
<td>C18/2</td>
<td>98</td>
<td>CN/2</td>
<td>89</td>
</tr>
<tr>
<td>6.0</td>
<td>C18/1</td>
<td>95</td>
<td>CN/1</td>
<td>98</td>
</tr>
<tr>
<td>6.0</td>
<td>C18/2</td>
<td>96</td>
<td>CN/2</td>
<td>96</td>
</tr>
</tbody>
</table>

As the C18 columns gave good retention for Au, Pt was added to the HF/HNO₃/HCl digest in order to ascertain the feasibility for retention of other
precious metals. The HF/HNO$_3$/HCl digest was prepared with a 1 mg L$^{-1}$ Pt spike together with the Au. C18 (Alltech) columns were employed with DVB (Alltech), strata-X and strata-XC (both Phenomenex). Instead of drawing the solution through the columns with the aid of a peristaltic pump as with previous assays (see Figure 4.4. (a)), syringe adapters (Phenomenex) were employed which fitted into the top of the SPE columns and pushed the sample through under pressure (Fig. 4.4. (b)).

![SPE Column Arrangements](image)

**Figure 4.4.** SPE column arrangements: (a) peristaltic pump (-ve pressure) and, (b) syringe arrangement (+ve pressure).

The syringe adapters possessed the advantage of better control over the flow rate as the flow was regulated manually. The application of greater pressure to the syringes increased the flow, so reduced flow rate caused by blockage of the sorbent bed was not an issue. A slower flow was adopted of 2 mL min$^{-1}$ on the columns as recommended by the manufacturers.

The application of a larger excess of APDC was also decided upon to promote the formation of the metal chelates. The concentration of chelate was increased until the production of a precipitate was observed. At levels of 0.075% w/v APDC a white precipitate formed then dissolved over a short period of time (<10 s). At higher concentrations the precipitate remained visible.

As can be seen from Table 4.6., high retentions of Au were observed from all the columns. Pt was retained on the DVB, strata-X and strata-XC to very high levels.
of >95%. The C18 SPE column showed slightly worse retention for Au with 94.6%, although for Pt the retention was significantly lower at only 85%.

**Table 4.6. Au and Pt retentions on various SPE columns using APDC as a chelating agent.**

<table>
<thead>
<tr>
<th>SPE Column</th>
<th>Pt Retention (%)</th>
<th>Au Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>strata-XC</td>
<td>95.8</td>
<td>95.7</td>
</tr>
<tr>
<td>strata-X</td>
<td>97.2</td>
<td>97.2</td>
</tr>
<tr>
<td>DVB</td>
<td>96.1</td>
<td>97.4</td>
</tr>
<tr>
<td>C18</td>
<td>85.0</td>
<td>94.6</td>
</tr>
</tbody>
</table>

Further investigations were performed into the reproducibility of the Au and Pt retentions on the DVB columns with the addition of APDC to the HF/HNO₃/HCl aluminosilicate digest. During the conditioning stage a 1 mL aliquot of 5% w/w HCl was added to the column. This was added after the methanol and water conditioning stages. A possible cause of Au and Pt loss was inefficient retention at the solvent front as it progresses through the sorbent bed. In an attempt to reduce the difference between the conditioning solvents and the sample matrix the acid solution was added. As the acids were present in the same concentrations as in the aluminosilicate digests and of similar pH, the extra conditioning would minimise any effect caused by the solvent front on the retentions.

Further investigations into the DVB columns were performed with the extra conditioning stage of the columns. Pt and Au retentions from the HF/HNO₃/HCl digest with the addition on APDC were monitored on 4 DVB columns. A 1 mL aliquot of deionised water was added to wash the matrix from the dead volume of the column and methanol was employed for elution. The retentions were found to be extremely high and consistent for Pt and Au. Table 4.7. shows the retentions of each column.
Table 4.7. Reproducibility of Au and Pt retentions on DVB columns from the HF/HNO₃/HCl digest with APDC as the chelating agent.

<table>
<thead>
<tr>
<th>Column Type/Replicate No.</th>
<th>Pt Retention (%)</th>
<th>Au Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVB/1</td>
<td>99.1</td>
<td>99.6</td>
</tr>
<tr>
<td>DVB/2</td>
<td>99.3</td>
<td>99.8</td>
</tr>
<tr>
<td>DVB/3</td>
<td>99.3</td>
<td>99.8</td>
</tr>
<tr>
<td>DVB/4</td>
<td>99.3</td>
<td>99.8</td>
</tr>
</tbody>
</table>

The results demonstrate over 99% of Pt and Au is retained from the HF/HNO₃/HCl digest by the DVB columns. The columns were washed with 1 mL of H₂O to remove any aluminosilicate solution which remained in the dead volume of the column. The counts s⁻¹ for Au in the wash solutions were very low and ranged from 28 – 31 compared to a deionised water blank at 14 counts s⁻¹. Pt gave slightly higher counts in the wash solutions ranging from 62 – 162, the deionised value was 17 counts s⁻¹. The results implied very little elution was occurring during the washing of the columns with deionised water. This implies the method employing the DVB SPE columns conditioned with methanol/water, then HCl/HNO₃ followed by the HF/HCl/HNO₃ microwave digest showed high retention and reproducibility for Au and Pt for an aluminosilicate matrix.

As APDC was added to chelate the Au and Pt, the elution of the metals from the column would therefore contain a proportion of chelate. The concentration of the metals would directly affect the amount of chelate in the eluent and cause changes in sensitivity due to the increased carbon content. As methanol was thought to be a possible eluent for the chelates, dilution would be necessary as 100% methanol is incompatible with the plasma causing extreme fluctuations in the plasma conditions causing instability.

A series of calibration standards were prepared in 5% HCl/HNO₃, 10% methanol, and 10% methanol/0.019% APDC (equivalent concentration to APDC added) of 0, 100, 400 and 1000 pg mL⁻¹ Au and Pt.
Fig. 4.5. (a) – (c) demonstrates a dramatic decrease in sensitivity of both Au and Pt. The slope of Au decreased from 23.791 to 6.4224 by altering the matrix from 5% HCl/HNO₃ to 10% methanol. The decrease translates to almost a 75% loss in signal. The $R^2$ value for the best fit line also decreased significantly from 0.9998 to 0.9957 for the 5% HCl/HNO₃ and 10% methanol respectively.

The addition of APDC to the 10% methanol solution produced a similar sensitivity to that observed from the 10% methanol. The APDC seemed to affect the Au signal to a greater extent than Pt. The sensitivity of Pt was almost unaffected by the addition of APDC with only a slight increase observed.

Au was found to exhibit decreased sensitivity with the addition of APDC to the methanol solution. The decrease was thought to be due to increased plasma load associated with the extra carbon content of the plasma, lowering the ionisation efficiency.

**Figure 4.5.** Calibration graphs for Au and Pt in: (a) 5% HNO₃/HCl (■ Au, ♦ Pt) (continued).
4. Preconcentration/Separation of Au and Pt

Figure 4.5. Calibration graphs for Au and Pt in: (b) 10% methanol: and (c) 10% methanol/0.075% APDC (■ Au, ♦ Pt).

As the sensitivity of Au and Pt was dramatically reduced by the addition of large amounts of carbon (primarily from the methanol) a poorer LOD would be observed. Due to the volatility of methanol the ability to evaporate to dry matter then redissolve into a suitable matrix was investigated. The 5% HCl/HNO₃ matrix was chosen as it gave good sensitivity and consistency for both metals. The advantage of extra preconcentration was also inherent.
A fast and reproducible method for the separation of Au and Pt from an aluminosilicate microwave digestion process has been displayed. The initial problems associated with inconsistency of retentions were overcome by the alteration of the digestion procedure to incorporate HCl. The addition of excess Cl⁻ was thought to stabilise the Au and Pt into the chloride compound/complex.

The removal of Au and Pt as the APDC chelates onto a commercially available DVB SPE column was found to be both quick and consistent.

Retentions of >95% were obtained for Au and Pt for DVB, modified DVB (strata-X) and modified DVB with cationic exchangers (strata-XC). Modification to the activation process of the DVB column was also found to increase the retention slightly giving >99% retention of Au and Pt.

As the digestion procedure produced a strongly acidic solution no manipulation of pH was necessary to produce the greatest retentions. The simple addition of an aliquot of APDC solution was adequate to achieve very high retentions for Au and Pt.

The application of deionised water to the column was sufficient to remove any residual aluminosilicate digest from the dead volume of the column whilst not affecting the retained Au and Pt.

Methanol was showing promise as a suitable eluent for the removal of the retained chelates, although problems with the amount of carbon reaching the plasma would need to be further addressed. Two possible solutions to removing methanol, is *via* desolvation, leaving a dry plasma, or by 'blowing down' the methanol solution to dryness then redissolving in a more suitable matrix.

Many SPE columns were employed throughout the investigation with only DVB based columns showing consistently high retentions for Au. The CN SPE columns were found to possess a very inconsistent repeatability, with the C18 bonded
phase performing only slightly better. The mixed mode SPE columns (Strata-XC) performance was equal to the DVB based columns implying no advantage was obtained from the cation exchangers.
4.6. REFERENCES


(2) V. L. Dressler, D. Pozebon and A. J. Curtius, Determination of Ag, Te, U and Au in waters and in biological samples by FI-TCP-MS following on-line preconcentration, *Analytica Chimica Acta*, 2001, 438, 235-244.

(3) J. Hajkova, V. Kanicky and V. Otruba, Preconcentration and separation of gold on modified silica gel, *Collection of Czechoslovak Chemical Communications*, 2000, 65, 1848-1864.


Chapter Five

Laser Ablation of
Pressed Powder Discs
5. **LASER ABLATION OF PRESSED POWDER DISCS**

ICP-MS has become an extremely powerful tool for the analysis of trace metals in liquid samples. The use of LA in conjunction with ICP-MS has given the opportunity for the benefits of ICP-MS to be applied to solid samples. Direct solid sampling and LA in particular has its own distinct advantages over solution analysis with a far lower sample preparation time incurred and the relatively low amount of sample handling, reducing the risk of contamination. Of the solid sampling techniques coupled with ICP-MS, LA has become the most commonly employed due to its quasi non-destructive nature and the ability to sample from a vast array of sample types as well as a relatively low sample quantity required. LA works by focusing a laser beam onto the surface of the sample to produce small particulate. The ablated matter is then carried in a gas stream to the torch and then into the plasma. Unlike other methods employed for solid sampling ICP-MS, LA is relatively universal, with the capabilities encompassing conducting and non-conducting, organic and inorganic solids.

A plethora of sample preparation methods are employed for LA-ICP-MS, dependent on the sample form. Many raw materials, certified reference materials and 'real' samples are in powdered form and so are easily pressed into a disc. Although pressed powder sample preparation is commonly performed with pure sample, occasionally binders are needed to aid the mechanical stability of the discs. Pressed powder sample preparation is relatively quick due to the lack of heating/cooling time incurred when using other common LA sample preparation methods. The simplicity of preparation as well as the ease of addition of internal standards or isotope spikes makes pressed powder sample preparation an extremely useful tool for LA-ICP-MS.

LA has been found to be a relatively universal sampling method the coupling between the laser and the sample is not always efficient as the laser wavelength may not be absorbed sufficiently. To aid the ablation process, chromophores or absorbing compounds have been added to improve the absorption of the laser energy by the sample.
5. Laser Ablation of Pressed Powder Discs

One of the main drawbacks with LA is associated with the calibration strategy and the ability to find matrix matched reference materials. The idea of producing matrix independent standards is of immense importance to the advancement of the technique. This chapter investigates the addition of chromophores to pressed powder discs for LA. The effect of altering the absorption characteristics of the discs is documented for different support media.

5.1. INSTRUMENTATION

5.1.1. ICP-MS

A VG PQ ExCell ICP-MS instrument (Thermo Elemental, Winsford, Cheshire, UK) was employed throughout this work. The instrument was situated in a general purpose laboratory without air filtration or conditioning equipment.

Standard nickel sample (1 mm Ø orifice) and skimmer (0.7 mm Ø orifice) cones (Thermo Elemental, Winsford, Cheshire, UK) were used. Common operating parameters for the ICP-MS are present in Table 5.1.

Table 5.1. ICP-MS operating parameters.

<table>
<thead>
<tr>
<th>ICP parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rf power/W</td>
<td>1350</td>
</tr>
<tr>
<td>Reflected power/W</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Auxiliary gas flow/L min⁻¹</td>
<td>0.8</td>
</tr>
<tr>
<td>Plasma gas flow/L min⁻¹</td>
<td>12.0</td>
</tr>
<tr>
<td>External Ar gas flow/L min⁻¹</td>
<td>0.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Analyser parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Acquisition mode</td>
<td>Peak hopping</td>
</tr>
<tr>
<td>Replicates</td>
<td>3</td>
</tr>
<tr>
<td>Channels per peak</td>
<td>1</td>
</tr>
<tr>
<td>Dwell time/ms</td>
<td>100</td>
</tr>
<tr>
<td>No. of sweeps</td>
<td>100</td>
</tr>
</tbody>
</table>
5. Laser Ablation of Pressed Powder Discs

5.1.2. Laser

A UP-213 laser ablation system (New Wave Research Inc., Huntingdon, Cambridgeshire, UK) operating at 213 nm (UV) was employed. Helium was employed as a carrier gas for the ablated matter for the improved ablation and transport characteristics. Common operating parameters for the LA equipment are present in Table 5.2.

Table 5.2. LA system operating parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Solid state Nd:YAG, UP-213</td>
</tr>
<tr>
<td>Wavelength/nm</td>
<td>213</td>
</tr>
<tr>
<td>Pulse duration/ns</td>
<td>4</td>
</tr>
<tr>
<td>Fluence/mJ cm⁻²</td>
<td>13 (unless otherwise stated)</td>
</tr>
<tr>
<td>Repetition rate/Hz</td>
<td>10 (unless otherwise stated)</td>
</tr>
<tr>
<td>Sampling strategy</td>
<td>Line</td>
</tr>
<tr>
<td>Spot diameter/µm</td>
<td>100</td>
</tr>
<tr>
<td>Translation rate/µm s⁻¹</td>
<td>20</td>
</tr>
<tr>
<td>He gas flow/L min⁻¹</td>
<td>0.4</td>
</tr>
</tbody>
</table>

5.1.3. Connective Tubing and Transportation

The laser ablation setup is shown in Fig. 5.1. and employed 6 mm i.d. Tygon® tubing throughout. A 1 m section connected the laser ablation system to the ‘Y’-piece, with another 1 m section connecting the ‘Y’-piece and the cyclonic mixing device. The ‘Y’-piece was polypropylene with a 60° angle (Fisher Scientific, Loughborough, Leicestershire, UK). Ar was added at the ‘Y’-piece and mixed with the He carrier gas/ablated material in a custom made cyclonic mixing device situated in the Peltier cooler (5 °C). The mixing chamber was situated directly prior to the torch (Fig. 5.1.).
5.1.4. Reflectance Spectrometer

Reflectance data was obtained using a Perkin Elmer Lambda Bio 40 UV/Vis Spectrometer. The reflectance was recorded from 1100 nm to 250 nm.

5.2. SAMPLE PREPARATION

5.2.1. Samples

Two certified reference materials were used in this study: BCS-CRM 348 Ball Clay and BCS-CRM 394 Calcined Bauxite (both Bureau of Analysed Samples Ltd., Middlesbrough, Cleveland, UK). A candidate reference material 006 Automotive Catalyst was also employed (LGC, Teddington, Middlesex, UK). The support materials utilised were polyvinylalcohol (PVA) powder (Acros Organics, Geel, Belgium), vanillic acid, nicotinic acid and pyrazinoic acid (all Alfa Aesar, Heysham, Lancashire, UK).

A laboratory test sieve (Endecotts Ltd., London, UK) was employed to reduce the particle size of the PVA to <50, 50-250 and >250 μm. The sieve were constructed from brass and caused a decolouration of the PVA fractions even with extensive cleaning. The contamination was not of particular concern as quantitation was not performed using PVA as a disc binder.
5. Laser Ablation of Pressed Powder Discs

5.2.2. Pressed Powder Disc Formation

Grinding and mixing of the support material and sample was performed in a pestle and mortar for 10 minutes. 0.2 g of support material, sample or mixture was placed in a standard laboratory IR KBr press (Specac Ltd., Orpington, Kent, UK) under 10 metric tonnes pressure for 10 minutes. The discs produced were 13 mm in diameter and approximately 1.2 mm thick.

5.3. RESULTS AND DISCUSSION

5.3.1. LA of Polyvinylalcohol Pressed Powder Discs

PVA has been used as a support for the improvement of mechanical stability of a pressed powdered sample.\textsuperscript{1,2} Initial trials investigated the influence on ablation of the particle size of PVA ablation. The PVA was separated into three fractions of \(<50, 50–250\) and \(>250\) \(\mu\)m and pressed into discs as mentioned in section 5.2.2. Under microscope inspection, the disc composed of particles \(<50\) \(\mu\)m produced a far smoother surface with better packing of the particles causing less spaces. The disc made with particles of \(>250\) \(\mu\)m possessed a much rougher surface with larger crevices between the particles. This affected the ablation dramatically with the \(>250\) \(\mu\)m disc producing local melting rather than ablation. The melting was thought to be due to the lack of heat transfer away from the ablation site due to the lower amount of contact between particles in the sample. With the smaller particle size, ablation was observed to occur rather than melting. Minimal melting was observed as the heat was dissipating away from the ablation site more efficiently between the smaller particles.

5.3.2. Absorption Modification of Pressed Powder Discs

The modification of samples to increase the absorption of the laser wavelength has been performed for liquid calibration standards,\textsuperscript{3,4} fused lithium borate glasses\textsuperscript{5,6} and for pressed powder discs.\textsuperscript{7} In these cases, the chromophores were
present in addition to a binder and of relatively low concentration compared to the main matrix.

To aid the ablation process, the use of chromophores were investigated. Matrix assisted laser desorption ionisation (MALDI) employs substrates as binders, which also aid the removal of analytes from the sample surface. Vanillic acid and nicotinic acid (see Fig. 5.2.) are two well known substrates used for the analysis of proteins in MALDI as they are both known to absorb strongly at 266 and 213 nm (Table 5.3.).

![Structure of: (a) vanillic acid and, (b) nicotinic acid](image)

**Figure 5.2.** Structure of: (a) vanillic acid and, (b) nicotinic acid.

**Table 5.3.** Absorption coefficients for commonly used MALDI matrices.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$ (L mol cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nicotinic acid</td>
<td>262</td>
<td>2750</td>
</tr>
<tr>
<td></td>
<td>217</td>
<td>8610</td>
</tr>
<tr>
<td>Vanillic acid</td>
<td>259</td>
<td>11900</td>
</tr>
<tr>
<td></td>
<td>217</td>
<td>22900</td>
</tr>
</tbody>
</table>

5.3.2.1. **Automotive Catalyst**

Automotive catalyst samples were prepared in three different forms using vanillic and nicotinic acid as the chromophore/binder, as demonstrated in Fig 5.3. Although (a) and (b) possess the same ablation surface comprised of a chromophore/sample mixture, form (b) would use less sample which is advantageous if sample quantity is limited, or expensive reference materials are employed or the use of isotope dilution calibration methods are used. In form (c) the vanillic and nicotinic acid is acting solely as a support medium for the pure
sample. As the ablation is only of the sample, the benefits of using substances which absorb at the laser wavelength are removed.

\[ \text{(a) Total Mixed Disc (TMD)} \]
\[ \text{(b) Surface Pressed Mixture Disc (SPMD)} \]
\[ \text{(c) Surface Pressed Sample Disc (SPSD)} \]

**Figure 5.3.** Various forms of pressed powder discs: (a) support and sample mixed prior to pressing; (b) support and sample mixed prior to pressing onto a disc of pure support; (c) pure sample pressed onto the surface of a pure support disc (* support, \( \Delta \) sample).

During the pressing process different methods for the formation of SPMD and SPSD were attempted. When the discs were prepared in two parts by forming the support disc then adding the sample or sample/support mixture, difficulties were encountered with the expansion of the disc when removed from the constraints of the die. When the disc was added to the die for the second pressing process, the edges needed to be broken slightly to enable reinsertion.

A method for the formation of SPMD and SPSD was performed using a single pressing process, hence removing the problems associated with the damage to the discs. After addition of the support material to the die the plunger was used to flatten the disc for the addition of the sample/mixture. Pressing was then performed producing a two layer disc with no fracturing of the ablation surface.

Brief visual investigations into the ablation characteristics of all three forms of discs were initially performed. Both TMD and SPMD were found to ablate well, giving smooth craters. The SPSD was found to ablate but gave more uneven craters as ablation was more dependent on the coupling between the laser and
the sample. As the ablation surface of SPSD is the same as for a disc of 100% sample, no further investigation was performed. The SPSD would be a convenient disc preparation method if a limited quantity of sample is available. A series of discs were prepared with varying quantities of automotive catalyst sample ranging from 0 to 100% (20% intervals) using vanillic and nicotinic acid as binding materials. For each disc a total of 0.2 g of material was employed, for the surface pressed mixture discs, the support was 0.1 g and the mixture of sample/support was 0.1 g. The automotive catalyst was found to press sufficiently well in its 100% form to produce a mechanically stable disc.

As the automotive catalyst was only certified for Pd the isotopes at 105 (22.33% abundance), 106 (27.33%) and 108 (26.46%) were chosen to monitor the isotope ratios. The total mixture disc (Fig. 5.3. (a)) and the surface pressed mixture disc (Fig. 5.3. (b)) were both employed for the study.

As the ablation surface was the same for TMD and SPMD, containing a mixture of binder and sample, different ablations conditions were applied. For the TMD, the laser parameters were 100 μm spot size with 40% power at 10 Hz, giving a fluence of ~0.08 mJ cm⁻². The SPMD were subjected to 25 μm spot size, 100% power at 10 Hz producing a fluence of ~17 mJ cm⁻².

The isotope ratios where calculated for the three Pd isotopes measured using Equation 5.1.

**Equation 5.1. Isotope ratio calculation.**

\[
I = \left( \frac{S^{105\text{Pd}}}{A^{105\text{Pd}}} \right) \div \left( \frac{S^{106\text{Pd}}}{A^{106\text{Pd}}} \right)
\]

\(I = \text{Isotope Ratio}; \ S = \text{Signal Intensity}; \ A = \text{Abundance}\)

If the signal intensities were comparable to the abundances the isotope ratio will equal 1. The isotope ratios are tabulated in Table 5.4., almost all the results obtained were the same for both support materials under the two conditions. The accuracy was fairly good, with good precision of the Pd isotope ratios. The
exception was the 100% support disc which gave poor ratios due to extremely low levels of Pd recorded (<1500 counts s\(^{-1}\) for \(^{106}\)Pd).

Table 5.4. Isotope ratios for Pd for the total mixed discs (TMD) and surface pressed mixture discs (SPMD).

<table>
<thead>
<tr>
<th>Sample (% w/w)</th>
<th>Support</th>
<th>(^{108})Pd: (^{106})Pd</th>
<th>(^{108})Pd: (^{106})Pd</th>
<th>(^{108})Pd: (^{106})Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TMD</td>
<td>SPMD</td>
<td>TMD</td>
<td>SPMD</td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vanillic acid</td>
<td>0.4</td>
<td>0.3</td>
<td>2.2</td>
<td>2.6</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>0.4</td>
<td>0.3</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vanillic acid</td>
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<td>1.0</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vanillic acid</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2</td>
<td>1.2</td>
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<td>Nicotinic acid</td>
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<td>1.0</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>60</td>
<td></td>
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</tr>
<tr>
<td>Vanillic acid</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Vanillic acid</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2</td>
<td>1.3</td>
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<tr>
<td>Nicotinic acid</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>100</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Vanillic acid</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The most interesting results were observed when the signal intensities were compared to the disc composition. Fig. 5.4. (a) and (b) show the vanillic acid discs under the two conditions. The optimum composition was found to be 60 – 80% automotive catalyst at the larger spot size and 80% at 25 μm spot size.

For the two different laser spot sizes the signal maxima differed from 60% for the 100 μm laser spot size and 80% for the 25 μm laser spot size. The use of the larger spot area produced from the 100 μm laser spot, enabled more chromophore to absorb a greater amount of the beams radiation, enabling a lower sample quantity to be required as more efficient ablation occurs.
Figure 5.4. Effect of disc composition on the signal intensity for Pd using vanillic acid and laser spot size of (a) 100 μm and (b) 25 μm.

The production of a signal maximum from an optimal mixture of binder/sample was attributed to two opposing phenomena. As the catalyst composition increases the greater amount of sample should produce a higher signal. Although as the sample concentration increases the absorption characteristics of the discs will be lower.
and the chromophore will aid the ablation process to a lower extent. Therefore the ablation efficiency will be worse with higher sample composition, producing fewer small particles and hence a lower recorded signal. As the two contrasting phenomena are competing an optimal composition is reached giving a signal maxima.

The discs consisting of nicotinic acid and automotive catalyst did not produce an optimum composition. The Pd signal intensity (Fig. 5.5. (a) and (b)) was found to be relatively linear with the maximum signal intensity when the pure sample was used.

![Figure 5.5](image-url)  
**Figure 5.5.** Effect of disc composition on the signal intensity for Pd using nicotinic acid and laser spot size of: (a) 100 μm (continued).
The reason no optimum mixture was observed with the nicotinic acid was attributed to the nicotinic acid possessing a lower absorption coefficient than that of vanillic acid at 213 nm. Hence the addition of the nicotinic acid seemed insufficient to alter the adsorption characteristics already present from the sample to a great enough extent to form an optimum mixture.

Visual observations of the ablated discs are presented in Table 5.5. (a) and (b) for the different chromophores and ablation conditions. When the pure binder/chromophore was employed the crater was observed to be very shallow due to the optical penetration depth being low. The laser energy was absorbed efficiently by the upper layers of chromophore/sample and produced a mechanically stable crater of shallow depth.
Table 5.5. (a) Characteristics of the ablation craters with varying compositions using vanillic acid as the binder.

<table>
<thead>
<tr>
<th>Spot Size (µm)</th>
<th>Sample (%)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0</td>
<td>Very curved edges, quite shallow crater</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>More defined than 0% sample disc, sharper edges, deeper</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>Slightly deeper, much more defined than 20% sample disc</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>Very defined, lightly curved edges, poor depth uniformity</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>As 60% sample disc with better depth uniformity</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Only scratched the surface</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>Very curved edges, quite shallow crater</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>Fairly defined crater, same depth as 0% sample disc</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>Deeper than 20% sample disc, very smooth and uniform</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>Deeper and narrower than 40% sample disc</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>Shallower than 60% sample disc, messier edges/crater</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Only slightly scratched the surface</td>
</tr>
</tbody>
</table>

Table 5.5. (b) Characteristics of the ablation craters with varying compositions using nicotinic acid as the binder.

<table>
<thead>
<tr>
<th>Spot Size (µm)</th>
<th>Sample (%)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0</td>
<td>Shallow smooth crater with curved edges</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>Deeper than 0% sample disc, jagged edges/uneven depth</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>As 20% sample disc, better depth uniformity</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>Sharper edges to crater, not as deep as 40% sample disc</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>Well defined crater, same depth as 60% sample disc</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Rough edges, uneven depth profile</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>Shallow smooth crater with curved edges</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>Smoother crater compared to 0% sample disc</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>Deeper than 20% sample disc, smooth sides/base to crater</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>Thinner crater/more rounded edges than 40% sample disc</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>Only scratched surface, very shallow and smooth crater</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Rough edges of crater, more depth than 80% sample disc</td>
</tr>
</tbody>
</table>

Since the use of nicotinic acid as the binder seemed to produce an unexpected low result at 80% sample, a rerun was performed under the two different ablation conditions. As the automotive catalyst was not certified, there was uncertainty about the homogeneity of the composition. To investigate the homogeneity of the Pd distribution, $^{195}$Pt and $^{196}$Pt were also monitored. Fig 5.5. (a) and (b) show the same spurious result at 80% sample composition was present in the graphs. The
erroneous result could be due to insufficient mixing to produce a homogenous disc or due to actual inhomogeneity in the reference material.

![Graph](image)

**Figure 5.6.** Effect of disc composition on the signal intensity for Pd and Pt using nicotinic acid and laser spot size of: (a) 100 μm; (b) 25 μm.
5.3.2.2. **Ball Clay and Calcined Bauxite**

A new range of discs were prepared using the BCS-CRM 348 ball clay and the BCS-CRM 394 calcined bauxite. The discs were prepared using vanillic acid and nicotinic acid as well as another MALDI chromatophore, pyrazinoic acid (Fig. 5.7.).

The discs were prepared with 0, 20, 40, 60, 80 and 100% sample. As the samples were both certified reference materials, concentration values for Ti and Zr were both available, the isotopes of $^{47}$Ti, $^{49}$Ti, $^{90}$Zr and $^{91}$Zr were monitored.

![Figure 5.7. Structure of pyrazine-2-carboxylic acid (pyrazinoic acid).](image)

For the ball clay/vanillic acid discs, an optimum composition was found to be with 60% sample (Fig. 5.9 (a)). With the nicotinic acid (Fig. 5.9 (b)) and pyrazinoic acid (Fig. 5.9 (c)) discs a relatively linear response was observed with the highest
signal response attained from the 100% sample disc. This mimicked the trend from earlier trials using the automotive catalyst with the vanillic and nicotinic acids as binders. The lack of an optimal mixture from the nicotinic and pyrazinoic acid discs was attributed to the absorption coefficients being lower than that of vanillic acid and not absorbing substantially enough to affect the actual coupling of the laser to the sample surface.

Figure 5.9. Signal intensities of discs containing varying compositions of ball clay and: (a) vanillic acid (continued).
Figure 5.9. Signal intensities of discs containing varying compositions of ball clay and: (b) nicotinic acid and, (c) pyrazinoic acid.

For the discs of calcined bauxite, the graphs for all three chromophores displayed
an optimum sample composition of 80% sample (Figs. 5.10 (a) – (c)). As all the chromophores produced the same optimum mixture, this implies the calcined bauxite sample was less absorbing at 213 nm than the ball clay. This is demonstrated by all the chromophores possessing sufficiently high absorption coefficients to affect the laser coupling aiding the ablation efficiency causing the highest counts.

Figure 5.10. Signal intensities of discs containing varying compositions of calcined bauxite and:
(a) vanillic acid (continued).
Figure 5.10. Signal intensities of discs containing varying compositions of calcined bauxite and:

(a) vanillic acid; (b) nicotinic acid (continued).

Figure 5.10. Signal intensities of discs containing varying compositions of calcined bauxite and:

(b) nicotinic acid and, (c) pyrazinoic acid.
The ratios of Ti and Zr were compared (Table 5.6.) to establish the homogeneity of the discs. The Zr isotope ratios for the higher sample composition discs were closer to the actual value of 1. Although the Ti isotope ratios were not very accurate and were consistently below the actual value the precision was fairly consistent for all the chromophores and sample compositions. When the Ti:Zr ratios were examined the values were extremely erratic and did not appear to follow any trend.

Table 5.6. Ti and Zr isotope ratios for the ball clay (BC) and the calcined bauxite (CB) sample discs.

<table>
<thead>
<tr>
<th>Sample (%)</th>
<th>Vanillic acid</th>
<th>Nicotinic acid</th>
<th>Pyrazinoic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{47}$Ti:$^{49}$Ti</td>
<td>$^{90}$Zr:$^{91}$Zr</td>
<td>$^{47}$Ti:$^{49}$Ti</td>
</tr>
<tr>
<td>0</td>
<td>B C</td>
<td>5.05</td>
<td>2.19</td>
</tr>
<tr>
<td>20</td>
<td>B C</td>
<td>0.84</td>
<td>1.07</td>
</tr>
<tr>
<td>40</td>
<td>B C</td>
<td>0.87</td>
<td>0.86</td>
</tr>
<tr>
<td>60</td>
<td>B C</td>
<td>0.86</td>
<td>0.86</td>
</tr>
<tr>
<td>80</td>
<td>B C</td>
<td>0.87</td>
<td>0.83</td>
</tr>
<tr>
<td>100</td>
<td>B C</td>
<td>0.87</td>
<td>0.85</td>
</tr>
</tbody>
</table>

In an attempt to improve the isotope ratios and further test the homogeneity of the discs the dwell time of the analysis was reduced to 50 ms with 100 runs in time resolved analysis (TRA) mode. The ball clay/vanillic acid sample discs were analysed as the ablation characteristics of the samples seemed superior to the other disc combinations. The Ti isotope ratios were found to mimic the previous trial (Table 5.7.), with the recorded values slightly lower than the true value although relatively consistent across the different compositions (excluding the pure chromophore disc due to extremely low counts). With the Zr isotope ratios, the lower sample composition discs possessed poorer accuracy than those of higher sample composition. Again the bi-elemental isotope ratios between Ti and Zr were erratic. The lowest RSD's were found with 60% sample composition indicating more precise isotope ratios. The trend was also observed with the raw counts for the element signal intensities giving the lowest RSD's when the 60% sample composition was employed (Fig.5.11.).
Table 5.7. TRA analysis of ball clay/vanillic acid discs.

<table>
<thead>
<tr>
<th>Sample (%)</th>
<th>Mean</th>
<th>SD</th>
<th>RSD (%)</th>
<th>Mean</th>
<th>SD</th>
<th>RSD (%)</th>
<th>Mean</th>
<th>SD</th>
<th>RSD (%)</th>
<th>Mean</th>
<th>SD</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.52</td>
<td>2.03</td>
<td>80.3</td>
<td>3.25</td>
<td>9.37</td>
<td>140.86</td>
<td>7.77</td>
<td>10.94</td>
<td>161.03</td>
<td>8.52</td>
<td>13.72</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.87</td>
<td>0.18</td>
<td>20.7</td>
<td>0.73</td>
<td>0.25</td>
<td>34.74</td>
<td>1.52</td>
<td>0.85</td>
<td>3.51</td>
<td>4.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.88</td>
<td>0.08</td>
<td>9.35</td>
<td>0.88</td>
<td>0.19</td>
<td>22.13</td>
<td>3.37</td>
<td>0.56</td>
<td>2.05</td>
<td>11.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.89</td>
<td>0.06</td>
<td>6.36</td>
<td>0.92</td>
<td>0.12</td>
<td>12.96</td>
<td>3.61</td>
<td>0.41</td>
<td>1.82</td>
<td>12.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.89</td>
<td>0.05</td>
<td>5.5</td>
<td>0.97</td>
<td>0.09</td>
<td>8.95</td>
<td>3.71</td>
<td>0.54</td>
<td>2.32</td>
<td>13.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.91</td>
<td>0.03</td>
<td>3.78</td>
<td>0.98</td>
<td>0.08</td>
<td>8.03</td>
<td>2.89</td>
<td>0.62</td>
<td>2.53</td>
<td>10.79</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.11. Relative standard deviations of the mean counts s⁻¹ of Ti and Zr for different sample composition discs.

Using TRA over 200 runs (~45 s in total analysis time) the signal was monitored and plotted in an attempt to observe any trends. The 0% sample disc was as
expected with generally low counts with erratic jumps, with the 20% sample disc showing a generally stable signal for Ti and Zr (Fig. 5.12. (a)). The discs of higher sample composition were found to be less consistent with larger variation in signal. For the 40 and 60% sample discs (Figs. 5.12. (b) and (c)) an initial rise in signal for Zr and Ti was observed before stabilising approximately half way through the run. For the 80 and 100% sample discs (Figs. 5.12. (d) and (e)) the signal started relatively consistently and increased gradually towards the end of the run. The cause of the fluctuations in the signal were attributed to three factors: 1. inhomogeneity of the elements within the disc, 2. different mechanical stability across the disc, or 3. fluctuations in the laser power/fluence. The fluctuations in the laser seems unlikely as the period of time of the signal changes is substantial up to 20 s. The inhomogeneity of the disc causing the variation in signal is also questionable as the 100% sample disc shows differences in signal continuity. As the ball clay is a CRM the sample should in theory, be homogeneous. This leaves the most likely cause of the fluctuation in signal attributed to inconsistent mechanical stability cause during the pressing process.

Figure 5.12. TRA analysis of vanillic acid discs with: (a) 20% ball clay (continued).
Figure 5.12. TRA analysis of vanillic acid discs with: (b) 40% ball clay; (c) 60% ball clay (continued).
5.3.3. Reflectance Spectrometry of Varying Composition Discs

Reflectance analysis was performed on the discs to assess the effect of the percentage binder addition on the absorption characteristics. The data in Figs. 5.13. (a) – (c) shows the reflectance data from 250 – 1100 nm for the ball clay
samples employed with each of the three binders. These spectra clearly show a
dramatic change in reflectance with the varying compositions of the discs.

All three chromophores show little absorption in the near IR and visible region of
the spectra, although absorb strongly in the UV region. The 100% ball clay
sample absorbs fairly evenly throughout the near IR, visible and UV spectra with
ranging from ~35% reflectance at 1100 nm to ~15% reflectance at 250 nm. From
all the compositions the 0% sample absorbed strongest in the UV with the 100%
ball clay absorbing least. The other composition discs were fairly evenly
distributed between the two extremities in composition order.

For all the chromophores a similar pattern was observed for the series of
compositions with reverse order of the lines in the UV compared to that in the
visible and near IR region. The crossover points for the signals varied according
to the chromophore employed with 290, 335 and 355 nm for the nicotinic, vanillic
and pyrazinoic acids respectively.

Although the reflectance spectrometer used was unable to monitor efficiently at
213 nm the data in Figs. 5.13. (a) – (c) indicates the effectiveness of the
chromophores in the UV region around this wavelength. According to the Table
5.3. the absorption coefficients around 213 nm is equal or better than that at 266
nm and Figs. 5.13. (a) – (c) clearly show the chromophores absorb greatly at this
wavelength.
Figure 5.13. Reflectance data for varying compositions of ball clay mixed with: (a) vanillic acid: (b) nicotinic acid: (continued).
5. Laser Ablation of Pressed Powder Discs

5.3.4. Calibration Strategies of Pressed Powder Discs

5.3.4.1. Synthetic Matrix-Matched Standards

When performing experiments with LA, the difficulty of producing matrix matched standards for use with calibration is a major limitation. As the composition of the ball clay was known, synthetic standards using silica and alumina were prepared. The compounds were present in the ball clay at levels of 51.1 and 31.6% respectively translating to 0.06 and 0.04 g per disc. As 1.2 g of ball clay was added to the 60% sample discs with 0.8 g of binder the addition of only silica and alumina would have produced a disc of ~55% sample composition. As the optimum sensitivity was found at 60 – 80% is was decided to form the 1.2 g of synthetic sample from the equivalent weight ratio of silica:alumina (1:0.6) present in the ball clay.

The results displayed in Fig. 5.14. show the calibration graph obtained from the ablation of the synthetic ball clay standards, with the standard deviation of 10 replicates indicated by error bars. The actual value of Ti in the ball clay sample

![Graph of data](image-url)
equated to 3890 mg kg\(^{-1}\). Using the synthetic ball clay standards to analyse the ball clay sample, values of 2926 ± 267 and 2938 ± 264 mg kg\(^{-1}\) for the Ti isotopes at 47 and 49 respectively, which both equated to 76% of the actual value. The R\(^2\) values for the lines were fairly poor (0.9823 and 0.9827 for \(^{47}\)Ti and \(^{49}\)Ti respectively) and could be attributed to the possibility of the titania spikes being of such small amounts, complete homogeneity during mixing was not reached.

![Figure 5.14. Calibration graph of the synthetic ball clay samples.](image)

### 5.3.4.2. Standard Additions

A common form of calibration used for solution work is standard additions, in which known aliquots of the element of interest are added to the original solution. Standard additions was performed on the ball clay samples by the addition of known amounts of solid titania and pressed into discs using vanillic acid as the binder. Fig. 5.15. shows the calibration graph and standard deviation of 10 replicate analyses, for the monitored Ti isotopes at 46, 47, 49 and 50.
5. Laser Ablation of Pressed Powder Discs

Figure 5.15. Standard additions calibration graph for ball clay.

Again fairly poor $R^2$ values were obtained although the results were closer to the actual value than when using the synthetic ball clay standards (Table 5.8.). The closest result to the actual was achieved using the isotope at 46 giving 103% of the actual value.

Table 5.8. Calculated values for total Ti content using different Ti isotopes using standard additions on ball clay/vanillic acid discs.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$^{46}\text{Ti}$</th>
<th>$^{47}\text{Ti}$</th>
<th>$^{49}\text{Ti}$</th>
<th>$^{50}\text{Ti}$</th>
<th>Certified value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated value (mg kg$^{-1}$)</td>
<td>3975 ± 359</td>
<td>4779 ± 385</td>
<td>3145 ± 318</td>
<td>3241 ± 315</td>
<td>3870*</td>
</tr>
<tr>
<td>% of certified value</td>
<td>103</td>
<td>123</td>
<td>81</td>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>

5.4. SUMMARY

The application of reflectance spectroscopy to determine the absorption characteristics of sample discs for LA, has provided a valuable insight into the efficiency of ablation. The sample discs showed a distinct difference in reflectance, relating to the composition of sample and binder. The difference observed throughout the composition range altered dramatically according to the
wavelength, with the discs absorbing more strongly at 1100 nm when a greater quantity of sample was employed and the discs performing inversely at 250 nm.

The use of chromophores aided the ablation process causing smoother craters and for the vanillic acid discs an optimum composition of sample/binder gave a maximum signal intensity was found for all samples investigated. Although a dilution of the sample was occurring the vanillic acid was sufficiently absorbing at the laser wavelength to increase the ablation efficiency beyond that of the pure sample.

The same was only seen for the nicotinic and pyrazinoic acid when the calcined bauxite was employed. When the automotive catalyst and the ball clay discs were ablated a relatively linear signal response was observed against sample/binder composition. These binders possessed lower absorption coefficients than that of vanillic acid and so were unable to effect the laser wavelength absorption of the disc sufficiently to reach an optimum mixture and so the pure sample disc returned the highest signal. Table 5.9. indicates the optimum sample compositions for all sample/binder combinations performed.

**Table 5.9.** Optimum sample/binder compositions for different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binder</th>
<th>Optimum Sample Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive Catalyst</td>
<td>Vanillic Acid</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Nicotinic Acid</td>
<td>100</td>
</tr>
<tr>
<td>Ball Clay</td>
<td>Vanillic Acid</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Nicotinic Acid</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Pyrazinoic Acid</td>
<td>100</td>
</tr>
<tr>
<td>Calcined Bauxite</td>
<td>Vanillic Acid</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Nicotinic Acid</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Pyrazinoic Acid</td>
<td>80</td>
</tr>
</tbody>
</table>

Two different calibration methods were attempted for the determination of Ti in the ball clay/vanillic acid samples. The use of standard additions and the production of synthetic ball clay standards were investigated. As expected the standard additions approach proved to give closer results to the actual values for Ti. This is expected as the mechanical stability of the discs, the laser interactions/ablation and matrix effects will be very similar between the sample disc and the spiked
discs, as the bulk properties of the discs are almost identical when employing standard additions. With the synthetic standards the chemical form of the SiO$_2$ and Al$_2$O$_3$ may be different to the sample and also failed to take into account other minor elements present within the sample.
5.5. REFERENCES


Chapter Six

Conclusions and Further Work
6. **CONCLUSIONS AND FURTHER WORK**

6.1. **INTERFACE MODIFICATION**

The problems associated with the determination of low level elements in high concentrations of matrix elements were addressed with the modification of the sample introduction system and via alteration of the interface region. The use of synthetic environmental samples consisting of aluminosilicate and sodium/calcium chloride were employed to study the degree, position and extent of deposition within the instrument.

In order to process the sample in the plasma more efficiently, desolvation was employed to reduce plasma load for the aluminosilicate matrix. The presence of lower levels of solvent caused more robust plasma conditions increasing the degree of atomisation and ionisation. This was indicated by a higher initial sensitivity over standard solution nebulisation, although a part of this increase in sensitivity would have been due to increased mass flux to the plasma. Desolvation, however, did not stop the deposition of the aluminosilicate matrix onto the sample and skimmer cones, causing extensive build-up and blockage around the skimmer orifice giving a large reduction in recorded signal over a short period of time.

The deposition on the sample and skimmer cones was examined using SEM and was found to mainly contain aluminium and oxygen on the sample cone and silicon and oxygen on the skimmer cone. The deposition was attributed to either the incomplete atomisation of the alumina or silica in the plasma or by the condensation of the compounds as they reached a cooler part of the plasma/interface. The order of deposition was thought to be due to the melting points of the compounds. As the sample cone is situated next to the plasma and will be at a higher temperature than the skimmer cone, alumina was deposited as it possesses a higher melting point than silica.
The effect of various cone alterations and combinations was investigated to observe any trends associated with cone geometries and running temperature. The skimmer cone which produced the smallest drop in sensitivity was found to be the drilled cone. The drilled cone was a standard skimmer with holes laser drilled in the surface of the tip, in an attempt to produce a layer of static gas to replace the metal contact surface. The gas layer was anticipated to deter the condensation of compounds onto the metal surface due to redirection of the sample either through or away from the orifice. This would reduce the material build-up on and around the orifice and reduce blockage and subsequent loss of signal. Also with the removal of material from around the tip, the cone will possess a higher running temperature, deterring deposition through condensation onto the metal surface.

Instrumental setup differed for each of the different skimmer cones with the extraction lens voltage becoming extremely important to gaining high signal intensities. To gain the greatest initial sensitivity, the extraction lens voltage for the standard, drilled and PS6R skimmer cone was found to be -600 – -1000 V. When the Xi skimmer was employed in this range of extraction lens voltages, the recorded signal was ~10% that of the standard skimmer cone. The $^{115}\text{In}$ signal was increased from ~10% to ~40% when using the Xi skimmer by lowering the extraction voltage to ~200 V (soft extraction).

The use of the standard sample cone in conjunction with the different skimmer cones resulted in large differences in the initial signal as well as the losses in sensitivity with time. The drilled skimmer cone was found to give 2 – 3 times less decrease in the $^{115}\text{In}$ signal over the standard, Xi and PS6R skimmer cones during an hour of continuous running. The drilled cone also started at the highest initial $^{115}\text{In}$ signal.

The effect of insulating the skimmer cones from the water cooling system was investigated. By running the cones at elevated temperatures the amount of condensation onto the surface would be reduced and cause less blockage. The loss of signal with an hour of continuous running, using the standard skimmer was reduced by nearly 20%. The results obtained for the insulated PS6R (A+B) and Xi
(A) skimmer cones mimicked those gained when no insulation was applied. The insulated drilled skimmer cone performed less efficiently than previous trials causing a far greater loss of signal to occur. Most of the cone combinations gave a slight increase in initial sensitivity after 5 – 10 mins, which then decreased fairly dramatically after that. The insulated PS6R (A) cone was found to differ from the other cones by offering a relatively constant performance for ~30 mins then increasing dramatically to nearly double the initial sensitivity. This phenomenon was attributed to the PS6R (A) cone taking longer to equilibrate causing a longer period of cone conditioning.

When the standard sample cone was changed for the Xi sample cone, very little difference in the longevity of the signal was observed for different skimmer cones. A slight improvement was seen for the Xi skimmer both in standard mode and when insulated. Again the PS6R cone was found to give a dramatic increase in signal of 7 times after ~35 mins.

During the aluminosilicate trials the cone cleaning process involved physical abrasion to remove the deposit. On inspection, different layers of polymorphs of silicate were present. The different structures of the silicate were most likely formed by insulating the layers of the deposit from the water cooling system and hence later layers would have been formed at elevated temperatures prior to solidification.

As the blockage of the skimmer orifice with Si was the main problem associated with the loss of signal, an alternative digestion process was employed. Digestion of the aluminosilicate material in an open Pt crucible allowed SiF₄ to be fumed from the solution. Unexpectedly the blockage of the skimmer orifice occurred with remarkable likeness to the previous experiments when employing the closed vessel aluminosilicate microwave digest, where Si was present in the sample.

The deposition pattern of the aluminosilicate onto the cone was different according to the position on the cone. Around the tip of the skimmer cone the deposit was heavy and encroached on/blocked the orifice. Down the sides of the cone, grains of deposit were present which appeared to have grown in situ. Along the inner
surface of the cone and the lower regions of the exterior a fine layer of deposit covered these areas.

With the use of a synthetic sea water sample, the expansion pressure and the signal were monitored and comparisons performed. The plots for both variables followed very similar patterns of degradation, with a rapid decrease in pressure as the orifice became blocked.

The insulated standard and the Xi skimmer cones both became totally blocked and hence returned no signal after \(\sim 400\) and \(\sim 350\) mins respectively of continuous running. All other skimmer cones generally plateaued at \(\sim 10\,000\) counts s\(^{-1}\) for \(^{115}\text{In}\). although as seen with the aluminosilicate digest trials the initial sensitivity was higher for the standard and PS6R than the Xi.

Although insulating the cones showed some degree of promise the temperature could not be raised enough to deter the environmental matrices from depositing on the surface of the cone. The non-linear character and speed in which the signal decreased, also made it impractical to use standards for drift correction. With improved insulation the signal loss may be slowed further and decrease the degree of deposition, although the risk of melting the cones could be incurred.

6.2. SEPARATION/PRECONCENTRATION OF Au AND Pt

As the modification of the interface region of the ICP-MS was found to be insufficient to cause any significant increase in signal stability, separation of the analytes of interest from the matrix was necessary. The effect of pH, flow rate and addition of chelates on a wide range of SPE columns was investigated for the retention of Au and Pt.

A large degree of variation was observed in the reproducibility of retention when employing a HF/HNO\(_3\) microwave digest. The retention on C18 and CN SPE columns varied dramatically, with both the reproducibility and repeatability being poor. Higher and more consistent retention was observed when HCl was added to
the digestion process, producing a more stable chloride matrix for the compound/complexes of Au and Pt.

The retention was vastly increased by the addition of chelating agents to the digest. Ammonium pyrrolidinedithiocarbamate (APDC) was found to aid the retention of both Au and Pt. The retention was found to be >99% for Au and Pt when DVB based SPE columns were employed.

Retention was high when the DVB SPE column was conditioned with methanol and water then a solution of HCl/HNO₃ was added prior to addition of the digest. The chelate was added straight to the aluminosilicate microwave digest prior to addition to the column. Au and Pt were washed with deionised water without elution from the SPE column.

Methanol showed promise as an eluent for the chelates although higher levels caused a vast decrease in sensitivity and created an unstable plasma causing a large variation in the signal. Further investigation into methanol as an eluent is required to fully clarify its suitability. To overcome the problems associated with elevated levels of carbon in the plasma, the methanol could be removed through heating or under vacuum and the residue redissolved in a stable matrix, such as aqua regia.

6.3. LA OF PRESSED POWDER DISCS

Although the use of SPE as a separation method was relatively quick to perform the problem associated with a laborious digestion procedure and danger from the chemicals is inherent. The limited number and cooling of the vessels between processes was lengthy and prolonged the digestion process significantly. The use of solid sampling techniques, such as laser ablation (LA), reduces the sample preparation time as often little or no sample preparation is required.

The main problem associated with solid sampling is the ability to obtain suitable solid calibration standards. Very few matrix matched calibration standards are commercially available in relation to the sample types, and hence the variation
between sample composition and standard composition, both chemically and physically may differ dramatically. Thus the addition of organic chromophores to different aluminosilicate samples was investigated with the aim of producing mechanically stable, matrix independent standards.

A range of common MALDI chromophores were investigated as suitable binders for the aluminosilicate samples: vanillic acid, nicotinic acid and pyrazinoic acid. The laser wavelength employed was 213 nm, and all the chromophores were known to absorb well at this wavelength.

With the aid of reflectance spectrometry, the absorbance characteristics of varying sample/binder composition discs were studied and found to produce a vast difference in the range of 250 - 1100 nm. As the sample composition was decreased the reflectance at 250 nm was increased, as opposed to the opposite occurring at 1100 nm.

When vanillic acid was employed as a binder, an optimum composition was reached at 60% sample for 006 Automotive Catalyst and BCS-CRM 348 Ball Clay with BCS-CRM 394 Calcined Bauxite giving highest signal at 80%. An optimum composition was expected as two opposing phenomena were occurring: as the sample composition increased more would be ablated giving a higher signal, and if the chromophore was aiding the ablation process, the higher binder composition would cause better coupling between the laser beam and the sample surface producing more efficient ablation.

The optimum composition for the BCS-CRM 394 Calcined Bauxite when nicotinic and pyrazinoic acid was employed was found to be 80% sample. For the 006 Automotive Catalyst and BCS-CRM 348 Ball Clay the optimum sample composition was 100%. This implied that these binders were unable to affect the ablation characteristics of the sample sufficiently to increase efficiency. Nicotinic and pyrazinoic acid both possessed lower absorbance coefficients than vanillic acid at 213 nm.
The production of a synthetic matrix matched calibration series and standard additions were both employed for the determination of Ti in BCS-CRM 348 Ball Clay with vanillic acid as the binder. The synthetic standard calibration strategy was found to produce 76% of the actual certified value from analysis of both $^{47}$Ti and $^{49}$Ti isotopes. The variation in analysed values was attributed to the forms of SiO$_2$ and Al$_2$O$_3$ in the sample and the synthetic standards being different. The standard additions approach was found to give closer results to the certified value. Four isotopes of Ti were analysed with all producing values nearer to the certified than when the synthetic calibration series was employed. For $^{46}$Ti a value of 3975 mg kg$^{-1}$ was obtained compared to the certified of 3870 mg kg$^{-1}$, which equates to 103% of the actual value.

Throughout the laser ablation trials the homogeneity of the discs was brought into question. The combining of the sample and binder involved manual mixing in a pestle and mortar, and this was thought to be insufficient to get a totally homogenous disc. With the use of a ball mill the mixing should be improved dramatically to efficiently combine the sample and binder.

One of the advantages of the pressed powder discs is the ability to add isotope spikes or internal standards to improve calibration. This would further the aim of improving the calibration strategy for laser ablation.
Appendices
Appendix 1 – Professional Development

University Lectures/Courses Attended

**October/November 2001**
- Induction, H. Gross and B. Vale
- How to get the best from your supervisor, M. Lansdale
- Research Issues, H. Gross
- Ethical Issues and research projects, R. Hooper
- Getting the message across and managing your time, H. Gross
- Fire and laboratory safety, B. L. Sharp and D. Wilson

**January 2002**
- Laser safety training, J. Tyrer.

**May 2002**
- Teaching skills for PGs and RAs, J. Darby and B. Kniveton.

**September 2002**

**March 2003**
- Wardens and Sub-Wardens training – Dealing with Confrontational Situations and Fire and Safety Training.

**May 2003**

**July 2003**
- "Sour Grapes", A. Buglass.
External activities

January 2002
Week training at CERAM laboratories in Stoke-on-Trent on the correct use of HF and the microwave digestion system.

April 2002
Three day visit to Micromass Ltd., Altrincham, to use Platform ICP-MS instrument for determination of I in milk sample.

August 2002
Visit to British Geological Survey, Keyworth to use laser ablation system for modification of the standard skimmer cone.

February 2003
Sample preparation at CERAM laboratories, Stoke-on-Trent.

March 2003
Visit to Corus, Scunthorpe.

July 2003
Sample preparation at CERAM laboratories, Stoke-on-Trent.
Non-Conference Oral Presentations Performed

*January 2002*
Oral presentation to CERAM to report progress on project.

*July 2002*
Oral presentation to CERAM to report progress on project.

*November 2002*
Oral presentation performed to prospective students entitled “Loughborough University Halls of Residence”.

*March 2003*
Oral presentation performed to MSc students titled “Application of ICP-MS to Samples with High Level Matrices”

*September 2003*
Oral presentation to CERAM to report progress on project.

*August 2004*
Oral presentation on work progression entitled “Improving the Performance of ICP-MS for Difficult Samples”. Presented to CERAM laboratory management staff.

*November 2004*
Oral presentation on work progression entitled “Improving the Performance of ICP-MS for Difficult Samples”. Presented to all CERAM laboratory staff.
Appendix 2 – Conference Contributions

Conferences Attended/Contributions

2\textsuperscript{nd} Analytical Research Forum, Kingston-upon-Thames, Surrey, 15\textsuperscript{th} – 17\textsuperscript{th} July 2002.

11\textsuperscript{th} Biennial National Atomic Spectroscopy Symposium, Loughborough, 8\textsuperscript{th} – 10\textsuperscript{th} July 2002.

3\textsuperscript{rd} Analytical Research Forum, Sunderland, Tyne and Wear, 21\textsuperscript{st} – 23\textsuperscript{rd} July 2003.

12\textsuperscript{th} Biennial National Atomic Spectroscopy Symposium, Plymouth, 12\textsuperscript{th} – 14\textsuperscript{th} July 2004.

9\textsuperscript{th} International Conference on Plasma Source Mass Spectrometry, Durham, Co. Durham, 12\textsuperscript{nd} – 17\textsuperscript{th} September 2004.

10\textsuperscript{th} European Winter Conference on Plasma Spectrochemistry, Budapest, Hungary, 29\textsuperscript{th} January – 2\textsuperscript{nd} February 2005.

\textbf{Oral Presentations:}

\textbf{M. R. Landon}, H. J. Reid and B. L. Sharp, “Interface Modification of ICP-MS to Improve the Performance of ICP-MS for Difficult Matrices”, 12\textsuperscript{th} Biennial National Atomic Spectroscopy Symposium, Plymouth, 12\textsuperscript{th} – 14\textsuperscript{th} July 2004.


\textbf{M. R. Landon} and B. L. Sharp, “Modified Pressed Powder Sample Preparation for LA-ICP-MS”, 10\textsuperscript{th} European Winter Conference on Plasma Spectrochemistry, Budapest, Hungary, 29\textsuperscript{th} January – 2\textsuperscript{nd} February 2005.
Appendices

Poster Presentation:

Publications: