Development and application of a calibration technique for laser ablation - ICP - MS

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DEVELOPMENT AND APPLICATION OF A CALIBRATION TECHNIQUE
FOR LASER ABLATION - ICP - MS.

By

Fabienne Boué-Bigne

A Doctoral Thesis

Submitted in partial fulfillment of the requirements for the award of
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20th August 2000

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Abstract

Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS) is a powerful analytical technique for the direct elemental analysis of solid samples, with spatial resolution down to a few microns. However, calibration remains the limiting factor in obtaining quantitative analysis by LA-ICP-MS for a wide range of sample types. No universal method exists as yet and the ones that are currently used tend to employ matrix-matched solid standards.

Matrix-matched solid standards are not available for many types of sample, such as polymers, biological materials, fluid inclusions, etc. The need for a universal method of calibration that involves standards that are easy to prepare and suitable for any type of sample is required. Additional to matrix-matching, internal standards are widely used in LA-ICP-MS for quantitative analyses. The internal standard compensates for the different ablation yields from the sample and the standard and for the laser shot-to-shot variation. Given that the use of an internal standard is required to obtain reliable results, the need for matrix-matching might be regarded as questionable.

This project has focused on the development and application of a new method of calibration for LA-ICP-MS. It involves the use of aqueous standards whose absorption characteristics are modified by the addition of a chromophore to the solution.

Additives were selected for ablation with KrF excimer, and Nd.YAG lasers. The influence of the additive concentration on the ablation yield was investigated for different laser energies. Response curves were obtained showing that as the additive concentration was increased, less energy was required to ablate the modified standard solutions efficiently. A general procedure was then defined for the preparation and use of the modified standard solutions for a given sample.

The new method of calibration was used for the quantitative analysis of different sample types: low density polyethylene (LDPE), polyketone (PK), polyethylene thin film as well as gels contained in the thin film, and stainless steel.
Investigations were carried out on the mechanism of ablation of the modified standard solutions. It appeared that the ablation proceeded by a three-step process leading ultimately to nebulisation of the bulk liquid.
I wish to express my thanks to my supervisors Dr B L. Sharp and Dr J.S. Crighton as well as Bridget Gibson, for the help they gave me throughout my research.

I would also like to thank Alan, Simon, and Dave for their help in keeping the instrument operational at Loughborough University, as well as Jill and Sonia for their help in the laboratory.

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Thanks very much to my friends and fellow colleagues in the lab Simi, Maggi, Shikha, Jo, Abdul, Stéphanie, Hussain, Colin, Javi and Neil who made of those three years an enjoyable time. Many thanks also to my family and friends in France for their support.
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Chapter 1:

Inductively Coupled Plasma
Mass Spectrometry
Chapter 1  Inductively Coupled Plasma-Mass Spectrometry

1. Introduction.

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) is a powerful analytical technique for determining quasi-simultaneously the presence of any elemental isotope of the Periodic Table, from 6 to 238 amu with the exception of the rare gases and the atmospheric gases. Qualitative, semi-quantitative, quantitative analyses and isotope ratio measurement are readily achievable. The limits of detection obtained with ICP-MS are comparable or better than those for furnace atomic absorption spectrometry with the additional advantages that all elements can be monitored in one run and individual isotopes are measured. The development of this analytical technique goes back to the mid seventies\(^1\), after the development of other atomic spectroscopies, such as atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray fluorescence (XRF) and neutron activation analysis (NAA). The motivation for the development of these techniques originated from the requirement to determine ever lower concentrations in a minimum of time.

2. The torch and the plasma.

2.1. Definition of a plasma

A plasma is any form of gaseous matter that contains an appreciable fraction (>1%) of electrons and ions in nearly equal numbers, in addition to atoms and neutral molecules.

2.2. Description of the ICP torch

The plasma is sustained in a torch which is composed of three concentric fused silica tubes in which the following gas streams, usually Ar, flow\(^1\):
the outer or coolant flow which protects the tube walls and acts as the main plasma support gas (10 to 15 l min$^{-1}$),

- the auxiliary plasma gas which keeps the hot plasma clear of the inner torch tube (0 to 1.5 l min$^{-1}$),

- the central gas flow or carrier flow which conveys the sample to the plasma, (~ 1 l min$^{-1}$). Introducing the sample through this channel, which is physically distinct from the outer tubes, does not interfere with the electrical processes that sustain the plasma

2.3. Formation and description of the plasma

A load coil of three turns of copper tube, cooled by a water flow, surrounds the end of the torch. It is linked to a generator that supplies a radio frequency (RF) current (27 MHz). This RF oscillation causes a magnetic field in the area at the top of the torch. A spark applied to the gas produces free electrons in the argon that interact with the magnetic field and are accelerated. This method of introducing energy to the electrons is called inductive coupling. These free electrons produce collisions, some of which lead to further ionisation; then the plasma is formed.$^{1,2,3}$ The plasma is sustained at atmospheric pressure.

The first function of the high temperature of the plasma is to desolvate the sample. This process occurs predominantly in the preheating zone (PHZ). The dry aerosol is then atomised, excited and ionised in the initial radiation zone (IRZ) and in the normal analytical zone (NAZ). Fig 1 shows the different zones of the ICP.
2.4. Mixed gas plasmas.

Various gases, including N\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}, etc., have been added to the Ar ICP to improve analytical performance. Different effects were observed. The addition of O\textsubscript{2} is now routinely used for the analysis of organic solutions\textsuperscript{4}. Its introduction in the central channel of the torch reduces the carbon deposition on the sampling cone.

The effect of the addition of N\textsubscript{2} has been widely studied\textsuperscript{4-9} N\textsubscript{2} has been added to the different streams of Ar. When added to the coolant flow, the plasma tends to shrink\textsuperscript{4} (the thermal pinch effect); the Ar-N\textsubscript{2} plasma then provides a hotter plasma with a more compact central channel than an all Ar plasma. The effects observed were an increase in analytical response, as well as the decrease of major interferences (ArO\textsuperscript{+}, ArOH\textsuperscript{+}, Ar\textsubscript{2}\textsuperscript{+}, ClO\textsuperscript{+} and ArCl\textsuperscript{+})\textsuperscript{4} When added to the nebuliser flow, the signal to background ratio (S/B)
was improved\(^9\) for \(^{76}\text{Se}\) and \(^{78}\text{Se}\). When added to the plasma flow, the analyte signal was increased\(^4\).

The addition of other gases such as \(\text{H}_2\), \(\text{He}\) and \(\text{Xe}\) showed various analytical improvements\(^4,8\). \(\text{H}_2\) showed a response enhancement; \(\text{He}\), a decrease in detection limits for both metallic elements and halides; \(\text{Xe}\), an attenuation of polyatomic interferences\(^4\).

Analytical benefits are obtained by the use of mixed gas plasmas. However, the results of the different studies need to be considered with care as different results are observed with different ICP-MS instruments\(^3\). Many other factors are also variable, such as the location of the introduction of the additive gas in the ICP torch, the nature of the gas, its volume, and the re-optimisation of the system after the introduction of the additive gas.

3. Sample and sample introduction.


The sample can be introduced into the ICP as a gas, an aerosol of fine droplets or solid particles. In order to be efficiently ionised, the particles introduced into the plasma should have a size smaller than approximately eight micrometers\(^1,10\).

3.2. Introduction of the sample

When the sample is a liquid, it is drawn by a peristaltic pump to a nebuliser where its interaction with an argon gas flow produces a spray. The spray passes through a spray chamber where droplets larger than eight \(\mu\text{m}\) diameter (and many less than this size) are removed before they enter the plasma\(^1\).
Many different types of pneumatic nebulisers are available:\textsuperscript{1}\textsuperscript{3}.

- the concentric nebuliser: for general purpose with limited salt tolerance,
- the cross-flow nebuliser, similar to the concentric nebuliser,
- the Babington type nebuliser: great tolerance for solutions with a high content of dissolved solid, problem of extensive memory effect.
- the V-groove and Cone Spray type nebuliser: similar characteristics to the Babington type without the memory effect.
- the micro-concentric nebuliser: small quantity of sample required (60 \(\mu l\) min\(^{-1}\)), good with high salt content or concentrated acid, including HF
- direct injection nebuliser: small quantity of sample required, no memory effect as it is used without a spray chamber.

Various designs of spray chamber are in common use. The ideal spray chamber has a minimum dead volume and is temperature controlled around 5\(^\circ\)C as this reduces the water input to the plasma\textsuperscript{1}.

For the direct analysis of solids, several methods of sample introduction exist\textsuperscript{1}

- electrothermal vaporisation,
- spark nebulisation, where a spark arcs between a copper anode and the sample cathode which is then eroded,
- slurry nebulisation where the solid sample is suspended in aqueous solution and nebulised through a Babington or a V-groove nebuliser,
- laser ablation

3.3. Ionisation and distribution in the plasma.

Most elements have first ionisation energies below 10 eV, while there are none whose second ionisation energies fall below 10 eV. Although there are a number of elements such as the rare earths, thorium and uranium that undergo some double ionisation, the
majority do not and doubly charged ions do not present serious problems. The temperature in the central channel is high enough to produce almost complete ionisation of many elements and a significant level for those of higher ionisation energy\(^1\). The sample atoms represent only \(10^{-6}\) or less of the total population of the plasma.

The distribution of ions in the plasma is the following\(^1\):

- as the first ionisation of argon requires a high energy (about 15 eV), the population of the corresponding ions, \(\text{Ar}^+\), is low, following the axis of the central channel, whereas on each side of the central channel, following the hotter induction region, a bigger population of argon ions is observed: this describes the plasma annulus.
- ions of the analyte elements appear in the central channel where the temperature is high enough to achieve ionisation.

Following the ionisation process, the orifice of the sampling cone has to be located along the axis so that the highest possible ion density might be extracted. The further it is from the load coil, the more the ion beam diffuses into the plasma annulus and ions may be lost as they will not reach the aperture of the sampling cone. Thus, the earlier the plasma is intercepted, the better it seems to be; but on the other hand, for a particle to be desolvated, volatilised, dissociated and ionised, depending particularly on its size, may require a relatively long time\(^1\). As it is necessary to avoid, as far as possible, the passage of unionised particles, the axial position of the extraction or sampling orifice must be carefully optimised.
4. The ion extraction interface.

4.1. Description of the interface.

After the torch, an interface brings gradually, in separate stages, the ion beam from atmospheric pressure to the ion focusing chamber where the pressure is about $10^{-4}$ mbar. This interface is composed of a mechanically pumped volume limited between two cones of metal of high conductivity:

- the sampling cone
- the skimmer cone

The sampling cone faces the torch, following the same axis. It is water-cooled and made of nickel or platinum, with a 1 mm diameter aperture at its tip. Most of the central channel of the plasma flows through the sampling orifice, most of the gas from the annulus passes over the sides of the cone. The pressure ratio across the orifice of the cone is roughly 1 bar / 1 mbar, which is sufficient for a supersonic jet to be formed inside this first stage. The jet structure is determined by shock waves called the barrel shock and the Mach disc. They are caused by collisions between fast atoms from the jet and the background gas. The central orifice of the skimmer cone is positioned inside the Mach disc to transmit as much of the sampled beam as possible into a second vacuum chamber. Approximately 1% of the gas that passes through the sampler traverses the skimmer. Furthermore, only the centreline gets through the skimmer, resulting in a spatial resolution of the plasma comparable to the skimmer diameter. As the extraction process takes about 3 μs, and the temperature is low at this stage, there is little opportunity for ion loss by recombination between ions and electrons or by chemical reaction.
A: torch and load coil, B: induction region, C. aerosol gas flow, D IRZ, E NAZ, F. sampler, G· skimmer, H: boundary layer of ICP gas deflected outside sampler, I. supersonic jet, J ion lens.


4.2. Ion kinetic energies.

During the extraction, the ions originate from a region in the plasma whose potential is positive with respect to the grounded sampling cone. This difference of potential may give rise to an electrical discharge (commonly called secondary discharge) between the plasma and the sampling orifice; it then generates multiply charged ions, induces high kinetic energies, a wide spread of kinetic energy in the extracted ion beam, as well as eroding the cone aperture. This discharge can be minimised by reducing the electrical field close to the sampling cone or reducing the potential of the plasma, but cannot be eliminated fully. As the ions enter the aperture, they are accelerated across the potential
difference and thus acquire extra kinetic energy that displaces the measured ion energies to higher values than would be obtained from the supersonic expansion alone. Once the sampled gas passes through the sampling orifice, collisions occur for the first few orifice diameters, after which the atoms continue to flow under essentially collisionless conditions. Most of these collisions occur between neutral Ar atoms, which are by far the most abundant, and other species, and there is little opportunity for ion loss by recombination with electrons.

5. Ion focusing.

5.1. Purpose.

After crossing the skimmer, the electric field established by the ion lenses collects ions and repels electrons. As the electrons are no longer there to keep the ions confined in a narrow beam, the ions tend to form a diffuse, expanding cloud. The function of the ion optics is to focus this cloud of ions into a narrow axial beam at the entrance of the mass analyser.

5.2. Description

The ion focusing system is composed of a series of electrostatic lenses. The pressure in this region is kept at $10^{-4}$ mbar by a diffusion or turbo-molecular pump. Before the lens stack, a gate valve can close the path into the high vacuum of the ion focusing region. This valve is located just after the skimmer and allows the removal of the sampler and the skimmer, for cleaning or replacement, without interfering with the pressure in the high vacuum region.

When a cation with charge $z$ enters a region of potential $V$, its kinetic energy becomes $z(V_{\text{initial}} - V)$. This ion will travel towards a region where the potential is below $V_{\text{initial}}$. 
with the velocity \( v = \left[ 2z \left( V_{\text{total}} - V \right) / m \right]^{1/2} \). This principle is applied in the ion focusing process\(^1\) where two cylinders of potentials, \( V_1 \) and \( V_2 \), are applied, one after the other. As \( V_1 \neq V_2 \), curved equipotential contours are created between them: this forms the lens. When an ion leaves the source at the centre, the curves of potential act symmetrically on it and it passes straight through the lenses. If the ion leaves the source away from the centre, the forces acting on it are unbalanced, and for \( V_1 \) and \( V_2 \) adjusted properly, the ion will be deflected closer to the axis. These lenses can be compared to optical lenses, but with the difference that the transmission and focal properties can be varied externally, by changing the voltages applied to the elements.

The focusing action of the curved equipotential surfaces improves ion transmission and therefore sensitivity. The lens system may incorporate a central disc to prevent photons from the plasma from reaching the detector. Alternatively, this disc may be located in the extraction region. Fig. 3 shows a schematic diagram of the extraction system and the ion focusing lens stack for a VG PQII ICP-MS instrument.

![Schematic diagram of the extraction system and the ion focusing lens stack for a VG PQII ICP-MS instrument.](image)

5.3. Problems.

Ions of different m/z require different ion optical conditions to be transmitted. The ion lens voltages are selected to maximise the ion signal for an ion in the middle of the mass range; this then corresponds to a compromised set of voltages.

The mutual repulsion of ions of the same charge (the space charge effect) limits the total number of ions that can be compressed into a beam of given size. The expansion produced makes it more difficult to collect all the ions leaving the skimmer; this is a major source of ion loss in ICP-MS. Furthermore, for a group of different ions, the light ones are more deflected outside the acceptance volume of the lens than the heavy ones. This leads to a lower sensitivity for light elements. This space charge effect is a major cause of matrix interferences in ICP-MS, above all when light elements are analysed in a heavy element matrix.

The central disc in the lens stack used as a photon stop is also a cause of loss of ions. 50–80% of the ions may be lost at this stage although careful design reduces this problem. An alternative way to prevent photons reaching the detector is to offset the entrance of the quadrupole from the plasma axis. A voltage is applied to the ion beam, which is then deviated to the axis of the quadrupole. Such a device results in a significant enhancement of the sensitivity of the instrument and a reduction in the background count.

6. Quadrupole mass spectrometer.

6.1. Purpose.

The quadrupole mass spectrometer provides the (m/z) separation of the extracted and focused ions prior to their detection. It uses the stability of the trajectories of the ions through the quadrupole rods.
6.2. Description of the quadrupole.

The quadrupole mass spectrometer consists of four straight metal rods which are parallel and equidistant from the axis. Opposite pairs are connected together. In order to obtain the separation:

- a DC voltage of amplitude $U$ is applied, positive for one pair, negative for the other pair;
- RF voltages of opposite sign and of amplitude $V$ are also applied to the pairs of rods.

Whether a particular ion strikes an electrode, and thus is eliminated from the beam before it reaches the detector, is a function of how long it takes that ion to reach a negative biased electrode. The dynamics of this process are governed by a number of factors including the instantaneous magnitude of the negative potential, the period of time during which the electrodes are held at a negative potential (e.g., the frequency of the waveform), as well as the position, the velocity and mass to charge ratio of the particle. The DC potential acts as a high pass filter where ions below some critical $m/q$ value will be filtered out of the beam, owing to the speed with which they can respond to defocusing action provided by the negative portion of the potential. The RF voltages act as a low mass pass filter, correcting the trajectories of light ions thus preventing them from striking the electrodes.

The ion beam enters along the axis into one end of the quadrupole structure, at velocities determined by their energy and mass. The RF and DC voltages are selected properly so that ions of a given $(m/z)$ ratio might have stable paths through the rods and will emerge from the other end; the other ions are deflected too much and strike the rods where they are neutralised and lost.

The mass spectrometer is maintained at $10^{-6}$ mbar by a diffusion or turbo pump in order to prevent collisions between the ions and neutral particles or stray ions and to prevent unwanted electrical discharges inside the rods. The typical operating pressures in ICP-MS instruments are limited largely by the electron multiplier rather than by the mass analyser.
6.3. Ion trajectories and stability diagram.

The ion trajectories\textsuperscript{1,11} are determined by the amplitude of the DC and RF voltages. U and V, by (m/z) and other parameters such as the dimension of the rods, the inscribed radius between rods. The stability diagram is a plot of the parameters $a$ and $q$, with $a$ a function of $U/(m/z)$ and $q$ a function of $V/(m/z)$. For most values of $a$ and $q$, the RF and DC fields displace the ions outside the rod boundaries, where they are lost. In this case, ions have unstable paths. Their paths are stable when their corresponding $(a, q)$ values fall within the pyramidal enclosure of the stability diagram.

\begin{align*}
a &= 4U/[(m/z)r^2w^2] \\
q &= 2V/[(m/z)r^2w^2]
\end{align*}


Scanning is carried out with a constant value of the ratio between the amplitudes of the DC and the RF voltages: $U/V$. For given values of U and V, a scan line is produced, whose slope is $U/V$ on the stability diagram, on which a given point corresponds to one particular value of (m/z). Thus, the ions of the given value (m/z) have a stable path through the rods if the values of $a$ and $q$ selected corresponds to the part of the scan line which is common to the stability diagram. In this way, the scan moves from one (m/z) to another, changing the values of U and V, keeping $U/V$ constant, to produce a mass spectrum.
6.4. Sensitivity and resolution

The degree of separation of $M$ from $M+1$ or $M-1$ depends on the slope of the scan line\(^1\). Fig. 4 shows that the greater the slope, the less the proportion of the stability region that is bounded by the scan line and the greater the separation of adjacent masses at $M$ and $M+1$ (that is the resolution). However, the number of ions transmitted depends roughly on the area of the stability diagram enclosed. A compromise has to be found between sensitivity and resolution.

Another concept of importance is the abundance sensitivity. It is a measure of the ability to discriminate a weak peak from a trace constituent at a (m/z) value adjacent to a major peak. Normally, quadrupole ICP-MS can achieve abundance sensitivity of $10^4$ for low mass and $10^6$ for high mass ions.

Quadrupoles perform best with ions having low kinetic energies ($< 20$ eV). Indeed, ions which have too high an energy pass through the rods too quickly and do not undergo enough RF cycles for resolution; the peaks resulting are then broad and/or split. To adjust the axial ion energy and ion transit time, an additional DC potential can be supplied to the four rods to either accelerate slow ions or retard fast ones. This potential is called “pole bias”. This DC bias is of the same magnitude and polarity for all four rods.

6.5. Scanning and data acquisition

For multi-element measurements\(^1\), the values of $U$ and $V$ can be changed rapidly, by computer control, between discrete values (peak hopping), or the quadrupole can be scanned continuously through the (m/z) region of interest (multi-channel scanning). This can be done repetitively and rapidly to average out some of the fluctuations in ion signal,
thereby improving precision. Multi-channel scanning and the peak jumping methods are complementary in the sense that:

- the first one records all the peaks in the selected (m/z) region and therefore provides a full record of the elemental composition of the sample,
- the second one spends a greater time on the selected peaks and is usually superior for repetitive determination of the same suite of elements.

7. Ion detection.

7.1. Channeltron electron multiplier tube.

The most common ion detectors used in ICP-MS are Channeltron electron multipliers\textsuperscript{12}. They consist of an open glass tube with a cone at its end and are coated with a lead oxide semiconducting material. Electrical connections are made to the semiconducting coating through metal strips. For detection of positive ions, the cone is biased at a high negative potential (~ -3 kV) and the back of the tube near the collector is held near ground When a positive ion leaves the mass analyser, it is attracted by this high negative voltage applied to the cone and hits its surface One or several secondary electrons are rejected as the result of an inelastic collision. Then, secondary electrons are accelerated by the potential gradient with more secondary electrons being generated by inelastic collisions on the tube walls. The result is a discrete pulse containing as many as $10^8$ electrons at the collector after one ion strikes the mouth of the detector.

The pressure required during the use of this detector is below $5.10^{-5}$ mbar, but it is possible to vent it to air, without damage, in order to dismantle the system for cleaning or other maintenance.

An electron multiplier tube has a limited lifetime that is determined by the total accumulated charge, its interior surfaces become exhausted and the detector has then to be replaced. An alternative is the discrete dynode multiplier that has an internal structure
similar to a photomultiplier tube. This device enables simultaneous pulse counting (low signal) and analogue current (high signal) mode of operation.

7.2. Signal measurement by pulse counting

The pulse of $\sim 10^8$ electrons, yielded by an ion at the collector, is sensed and shaped by a fast pre-amplifier. This signal goes to a digital discriminator and counting circuit which counts only pulses with amplitudes above a certain threshold level. This threshold level is chosen high enough to discriminate against low-amplitude pulses caused by spurious emission of electrons inside the tube. The usual background expected, despite the precautions taken, is 10–50 counts/s. It seems that the background tends to increase with the total ion signal, the process responsible for this is not precisely known. Modern instruments with off-set quadrupoles can achieve background counts as low as 0.1 cps.

8. Interferences.

The interferences that occur in ICP-MS broadly fall in two groups:

- spectroscopic interferences,
- non-spectroscopic interferences or matrix effects

8.1 Spectroscopic interferences.

Four distinct types are gathered under this group.

First of all, isobaric overlap which occurs when two different elements have isotopes corresponding to the same mass. In fact their mass may differ slightly, but a quadrupole cannot resolve this difference. Most elements in the periodic table have one or several
isotopes free from isobaric overlap, except In. Further, there are no isobaric interferences below 36 (m/z). To overcome isobaric interferences, an isotope of the element of interest, free of interference, can be selected. If this is not possible, a correction of the total analyte signal must be done for the contribution from the interfering mass. There are two ways to achieve this correction. A blank subtraction can be done when the sample has a known concentration of the interfering element or a calculation based on the known abundances of the interfering species can be performed. In principle, any isobaric overlap can be corrected, providing that another isotope of the interfering element is itself free from interference.

Another interference is from the formation of polyatomic ions, which result from the combination of two or more species. Ar, H and O are the dominant species present in the plasma, they can combine with each other or with elements from the analyte matrix. The matrix itself is a large source of elements which may yield recombinations. A large number of polyatomic ion peaks can occur, but they are only significant up to about 82 (m/z). This interference problem depends on many factors including extraction geometry, operating parameters for the plasma, nebuliser systems and most importantly on the nature of the acid and sample matrix. A possibility for minimising the formation of ArO⁺, ClO⁺ and Ar₂⁺, while keeping the maximum analyte sensitivity, is to chose the right value for the RF forward power and nebuliser gas flow rate. Many interferences are created by the formation of polyatomic ions that include O and H. These can be reduced by minimising the amount of water vapour reaching the plasma, e.g. using a micro-nebuliser with a desolvating membrane or a temperature regulated spray chamber. Cold plasma techniques avoid ionisation of Ar atoms. This allows an easier detection of elements that normally suffer Ar interferences in hot plasma condition. Limits of detection as low as a few ppt can be achieved for Na, K, Fe, Ca and Li. The cool plasma technique is only applicable to elements that are easily ionised and to samples with no real matrix. Additionally, sensitivity is lower relative to normal plasma conditions. The use of a collision cell or reaction cell is another approach to remove interfering species as this device separates analyte and potentially interfering...
polyatomic species prior to their entry into the mass filter\textsuperscript{14}. Alternatively, a technique that can introduce a "dry" sample, such as laser ablation or electrothermal vaporisation, will minimise this problem.

Some refractory oxides\textsuperscript{1} can interfere as the result of incomplete dissociation of the sample matrix or from recombination in the plasma tail. These oxides are found at +16, +32, +48 amu from the main peak (or +17 for hydroxides e.g. BaOH). The level of oxides expected can be predicted from the monoxide bond strength of the element concerned; the stronger is the bond, the greater the yield of MO\textsuperscript{+} is. The levels of oxides are estimated with respect to the elemental peak; a ratio MO\textsuperscript{+} / M\textsuperscript{+} no greater than 5\% is generally expected. For polyatomic ion formation, the RF forward power and nebuliser gas flow rate have a significant effect on the level of MO\textsuperscript{+} ions generated. As with most interference effects in ICP-MS, the extent of the problem depends on the sample matrix and the analyte level of interest; oxide ion interferences are generally at low levels but matrix oxide peaks may interfere with some trace analyses.

The presence of doubly charged ions\textsuperscript{1} is another source of interference. Indeed, most of the ions produced in the ICP are singly charged; only those which have a second ionisation energy lower than the first ionisation energy of the argon will undergo a second ionisation (the elements concerned are typically the alkaline earths, some transition metals and the rare earth elements). At normal operating conditions, the level of doubly charged ions is less than 1\%. The effect of this interference is a small loss of signal and therefore sensitivity loss for the singly charged species, but more importantly, it generates a number of isotopic overlaps. Fortunately, the number of elements affected is few. To avoid the problem, an alternative isotope of the element of interest is used, if available, if not, interference corrections are needed.
8.2. Non spectroscopic interferences.

The early ICP-MS instruments were not tolerant to solutions whose concentrations of dissolved material were greater than 500 μg ml\(^{-1}\). Indeed, high levels of total dissolved solids caused progressive blocking of the sample aperture, and as a consequence, the signal drifted over a short period of time. Modern instruments have sampling and skimmer cones with larger apertures and can accommodate concentrations up to about 2000 μg ml\(^{-1}\). Studies, done on solutions containing a high level of a refractory element, show that the signal loss is not simply due to a reduction of the number of ions entering in the ICP-MS system, but more likely a modification of the ion extraction process as a result of the diminution of the orifice diameter. A solution to this problem is to aspirate a solution of similar composition to the sample, during ~ 20 min, then the aperture diameter will be already reduced and will stay constant during the analysis of the sample.

Other sources of interferences are matrix effects. Although signal suppression is generally observed, presumably owing to space charge effects, enhancements have also been reported. Instrumental conditions can be adjusted to decrease the magnitude of these effects, or even eliminate them, but this is usually achieved to the detriment of sensitivity. Internal standardisation can also, to some extent, compensate for these effects. However, if the analytes of interest are spread over a large mass range, many internal standards would be required to compensate for the mass discrimination effect. An alternative way to minimise the matrix effects was found to be the addition of N\(_2\) to the Ar outer gas. The mass discrimination produced by 0.01 mol l\(^{-1}\) of Na was eliminated by this method. If possible, a dilution can be done to bring the matrix concentration to less than 500 ~ 1000 μg ml\(^{-1}\).

Good practice requires that all samples are scanned prior to quantitative determination to establish the nature of the matrix and the possible interference effects which are likely to occur. Then, the most effective remedy can be implemented.
Chapter 1  Inductively Coupled Plasma-Mass Spectrometry


The ICP-MS technique does not give absolute results but is a comparative technique. Thus, a calibration must be done in order to compare the measured counts from an unknown sample with those from a substance containing a known amount of the element of interest. The response of signal versus concentration is typically linear over 6 orders of magnitude when an ion detector in the pulse mode is used.

9.1 Qualitative analysis.

Qualitative analysis can be carried out over the complete mass range (4 - 240 m/z) in less than 60 s. The spectra obtained by scans or peak jumps can be examined for the presence or the absence of an analyte, and to identify possible sources of interference (employing the scan mode in order to collect all the information).

9.2 Semi-quantitative analysis

This is accomplished by establishing a sensitivity versus mass curve over the mass range of interest. The curve is generally defined using six to eight elements suitably spread across the mass range; the response for each element is corrected for isotopic abundance, concentration and degree of ionisation, a second order curve usually fits to the data. This curve has to be redefined prior to analysis as its shape is highly dependent on the instrument optimisation. This kind of analysis is useful to give approximate levels (+/- 20%) of the components in the sample.
9.3. Quantitative analysis.

There are several ways to achieve a quantitative analysis.

9.3.1. External calibration

This consists of recording the signals corresponding to standards containing the element of interest that cover the range of concentrations expected. The fitting of the calibration line is usually done by using least-squares regression analysis. As the stability of the calibration may not remain constant, corrections may be required. An external correction can be applied. The assumption is made that the signal change is linear with time and run order, then, an external drift correction is applied which monitors independently the individual behaviour of each element, as the signal change is different for each element.

An internal standard can be added to the blanks, standards and samples. It must reflect the other elements' behaviour. The internal standard should not suffer an isobaric overlap or polyatomic ion interference. The elements often added as internal standards are In and Rh; it can also be an element which is naturally in the sample and whose concentration has already been determined.

9.3.2. Standard additions.

This is performed by adding, to aliquots of the sample to be analysed, equal increments of a spike containing the element or elements of interest. This calibration consists of a number of spiked samples plus the unspiked original sample. In this method, the sample and the standards have the same matrix, as the dilutions induced by the increments are negligible. The graph “intensity of the isotope of interest versus the concentration of the
element added” gives the concentration of the unspiked sample at the intercept of the calibration line on the concentration axis

9 3.3. Isotope dilution.

This is another way to calculate the concentration of an element in the sample if it has at least two stable isotopes. The basis of the method is the measurement of the change in the ratio of the signal intensities for two selected isotopes, of an element of interest, after addition of a known quantity of a spike enriched in one of these isotopes
Chapter 1 References

Chapter 2:

Lasers
1. Introduction.

The principle of the action of the lasers is based on the induced, or stimulated, emission of radiation. The term LASER is an acronym for “light amplification by stimulated emission of radiation”. Many different types of lasers exist such as solid-state lasers, gas lasers, dye lasers, semi-conductor lasers, metal vapour lasers and others. A solid-state laser and a gas laser were used for this research project.


Unlike ordinary light sources, the laser is an oscillator. The basic structure of a laser consists of an amplifying medium, with an inverted population, between two mirrors that confine light at a resonant frequency.

In order to invert populations of atomic levels, the atoms must be excited by depositing energy into the medium to decrease the number of atoms in the lower level and increase the number of atoms in the upper level. This process is called pumping.

To obtain an oscillator from an amplifier, it is necessary to introduce a suitable positive feedback. In the laser, this is done by inserting the active medium between two mirrors. The electromagnetic wave bounces back and forth along the direction normal to the mirrors, being amplified at each transit through the active material.

If one of the mirrors is partially transparent, the light emitted through it will constitute the output beam.

3.1. Definition.

A solid-state laser is one in which the laser material is a crystal or glass that has a sharp fluorescent spectral line\(^2\). The lasing medium materials are transparent, heat resistant, hard crystals or glass containing transition metals or rare earth elements as active ions. The laser medium is shaped into a cylindrical rod whose ends are ground, polished. The rod ends are cut at Brewster angle\(^3\) in order to minimise prelasing and provide complete reflection within the laser rod.

Solid-state lasers are usually pumped optically\(^1\). The light emitted by a suitable lamp is concentrated on the active material. The lamp usually has a cylindrical shape, with a diameter of a few millimetres and a length of a few centimetres, and is filled with either a low-pressure (Xe, Ne or Kr) or high-pressure (Hg) gas. In a common configuration, the lamp is placed along one of the two focal axes of an elliptical cylinder. The active material, shaped like a rod with the same dimension as the lamp, is placed along the other focal axis. The inner surface of the elliptical cylinder being very reflective, a consistent fraction of the light emitted is concentrated on the active material.

When the medium is excited by an appropriate method, a population inversion is produced. Different schemes exist to obtain an inversion population where three or more energy levels of the lasing medium are used\(^1\). A two level system cannot lead to a population inversion as the upper level grows during the excitation process, the stimulated emission becomes more and more important, thus, in competition with the absorption, leading to equalisation for the populations of the two levels.

In the three energy level scheme\(^1\) (Fig 1), the atoms / molecules are excited from level 1 to level 3. Since this excitation will be followed by a very rapid decay to level 2, population inversion will be obtained between levels 1 and 2. The rapid decay from
level 3 and level 2 is the crucial point of this scheme as it not only generates a rapid population in level 2, but it also keeps level 3 practically empty, thus avoiding stimulated emissions that would compete with the excitation process.

In the four energy level process (Fig. 2), the atoms / molecules are excited from level 0 to level 3. They rapidly decay to level 2 and a population inversion is obtained between levels 1 and 2. Since the laser action will bring the atoms to level 1, this level must remain practically empty through a rapid decay to level 0. The lower level of laser transition in a four level laser (level 1) does not coincide with the ground state (as in the three-level laser) and is practically empty under equilibrium conditions.

![Diagram of three-level laser and four-level laser]

**Fig. 1:** Three-level laser  
**Fig. 2:** Four-level laser


3.2. The Nd:YAG laser.

The most practical solid-state laser which is currently used for material processing, machining and LA-ICP-MS analysis is the Nd:YAG laser. Its laser medium is made of Y$_3$Al$_5$O$_{12}$ (yttrium aluminium garnet) crystal containing 0.1 - 1% of Nd$^{3+}$. 
3.2.1 Energy levels.

A simplified energy level diagram of the Nd YAG crystal is shown in Fig 3.

The pump transitions $^4I_{9/2} \rightarrow (^4F_{5/2}, ^2H_{9/2})$ and $^4I_{9/2} \rightarrow (^4S_{3/2}, ^4F_{7/2})$ are in the red region of the spectrum, while the laser transition $^4F_{3/1} \rightarrow ^4I_{11/2}$ occurs in the near infrared ($\lambda = 1064$ nm). Since the lower laser level ($^4I_{11/2}$) lies well above the fundamental level ($^4I_{9/2}$), the Nd YAG laser operates to the four energy level scheme.

Fig. 3. Energy levels of a Nd YAG laser. Reproduced from "Analytical Laser Spectroscopy", a series of monographs on analytical chemistry and its applications, volume 50, Edited by N. Omenetto, Published by J. Wiley, 1979.

3.2.2 Modes of operation.

For laser ablation, the laser is generally operated in a pulsed mode. Solid-state lasers can be run following two modes."
• normal mode: the laser is simply pumped by the pulsed flash tube, and the radiation is allowed to emerge when the threshold conditions for laser operation are reached. In the normal mode, population inversion cannot greatly exceed the corresponding threshold value. Laser action starts as soon as the inversion reaches threshold value, thus using the inversion and preventing it from growing further. The resulting laser pulses have a width in the range of 100 μs to 1 ms.

• Q switch mode: the light path entering the resonator is obstructed by an electro-optic switch, such as a Pockels cell (active method). The effect of the "screen" is to prevent the laser action, thus letting the population inversion grow well beyond the normal threshold value. When the "screen" is suddenly removed, the laser will experience a population inversion much higher than the threshold, i.e., the gain is much higher than the losses. The technique is called Q-switching operation since the quality factor Q of the cavity is switched from a very high value (when the resonator is obstructed) to a negligible value corresponding to the cavity without the screen. The lasing operating is therefore delayed and the pulse is emitted at higher power and shorter duration, between 20 ns and 10 μs.

3.2.3. Wavelength selection.

The fundamental wavelength of a Nd:YAG laser is 1064 nm. Second and fourth harmonics are generated by the addition into the beam path of crystals. KD*P (potassium dideuterium phosphate) producing outputs at 532 and 266 nm. More recently, frequency quintupled output (213 nm) has been obtained by passing the fundamental, second and fourth harmonics through a temperature controlled type I β BaBO₄ (BBO) non-linear crystal. The fifth harmonic of the Nd:YAG laser was produced by the process of sum frequency mixing, the BBO crystal combining the fundamental and the fourth harmonic.
Chapter 2

Lasers

3.3 Conclusion

The efficiency of solid-state lasers is not high. The output of an ordinary laser is below 0.1% of the input and even that of the most efficient laser is no more than 40%. However, because of its good directivity, the laser light can be focused to a diameter equal to only a few times the wavelength using a short focal length lens. Additionally, the width of the laser pulse is variable, either by an external or an internal modulator, and can be as short as sub-picoseconds. Consequently, the power density of the light can reach very high values by the control of both the space and the time. Nd:YAG lasers are widely used for LA-ICP-MS analysis as they are simple to operate and relatively cheap. The possibility to use frequency quadrupling (266 nm) and, more recently, frequency quintupling (213 nm) make their use very attractive. Recently, there have been improvements in Nd:YAG laser systems. The overall size has been greatly reduced and their use for laser ablation has been facilitated by the application of computer control systems.


4.1. Definition.

The lasing material is a gas mixture. It is usually pumped electrically. The population of the upper level of the laser transition can occur only by collision of the atoms with the free electrons of the discharge. When excited by an electric discharge, the lasing material emits laser lines. Gas lasers can be classified by their medium as follows: neutral atomic lasers, ion lasers, molecular lasers, excimer lasers, etc. Excimer lasers are of particular interest as they are currently used for LA-ICP-MS analysis by some research groups and also for this project.
4.2. Excimer lasers.

4.2.1 Definition

The term “excimer” stands for “excited dimer”. In this type of laser, the lasing medium is a gas mixture which when excited forms excimer molecules. An excimer is a short-lived molecule which only exists in its excited state. Its relaxation to the ground state produces a light emission and leads to the separation of the individual atoms, due to their repulsive interaction in the ground state.

4.2.2 Gases and light emission.

A common type of excimer laser is based on excited states of a noble gas (A) halide (B) molecule (AB). Since atoms A and B are distinct, this is an exciplex (excited complex) laser, but is commonly called an excimer laser.

Amongst the rare gas - halides excimer existing, six of them are lasing: ArF (193 nm), KrF (248 nm), XeF (351 nm), KrCl (222 nm), XeCl (308 nm) and XeBr (282 nm). Of these, ArF, KrF, XeCl and XeF have been observed to oscillate rather efficiently, which is the principal reason for the great interest in these molecules for lasers. Fig 4 shows the schematic potential diagram of an excimer molecule.

The laser vessel is filled with a mixture typically consisting of 4-5 mbar pressure of halogen gas F₂ or HCl, a few tens to hundred mbar of the working noble gas Ar, Kr or Xe and then pressurised to a total pressure of 2-4 bar with either He or Ne buffer gas. The result of electrical excitation of predominantly rare gas mixtures is to produce both excited rare gas and rare gas ions. Both these products lead very rapidly to excited rare gas halides. The excimers are formed by several reactions, for example:

\[
\text{Ar}^* + \text{F}_2 \rightarrow \text{ArF}^* + \text{F}
\]

\[
\text{Ar}^* + \text{F}^* + \text{Ar} \rightarrow \text{ArF}^* + \text{Ar}
\]

\[
\text{Kr}^* + \text{F}_2 \rightarrow \text{KrF}^* + \text{F}^*
\]
\[ \text{Kr}^+ + \text{F} + \text{Ar} \rightarrow \text{KrF}^* + \text{Ar} \]

Since the density of the buffer gas is higher than that of the other rare gas, more ArF* excimers are formed. By a displacement reaction, Kr + ArF → KrF* + Ar, KrF* excimers can be efficiently produced. All these formation processes occur very rapidly in times typically of the order of $10^{-8}$s and are very efficient in populating the upper laser level in KrF* excimers. There are also quenching processes that depopulate this level by forming new products. The formation of the KrF* excimers therefore has to occur rapidly enough to allow a sufficient buildup of the laser field to compete with the quenching process.

![Schematic potential diagram of an excimer molecule (KrF)](image)

Fig 4. Schematic potential diagram of an excimer molecule (KrF). Reproduced from "Lumonics - Excimer 700 series lasers - Reference Manual", 1992
4.2.3. Excimer laser principles.

Excimer lasers convert electrical energy into pulses of laser light. This transformation involves four steps:

- The high voltage power supply (20 to 40 kV) charges the main energy storage capacitor through an inductor,
- on receipt of the trigger pulse, the thyratron switch closes and initiates the transfer of charge from the main capacitor to an array of secondary capacitors connected across the laser electrodes,
- once the voltage on the secondary capacitors has reached a sufficiently high value, the gas between the electrodes breaks down and a uniform electrical discharge is formed. This discharge forms the excimer molecules in the region between the electrodes,
- because the electrodes are incorporated within a two-mirror laser cavity, the excimer molecules give up their energy in the form of an intense pulse of ultraviolet light.

Fig 5 shows a typical electrical circuit of UV preionised electrical discharge laser.

For all gas mixtures and pressures, there is a range of operating voltages which produce a quiet, smooth discharge and give increasing pulse energy as the voltage increases\textsuperscript{9}. Fig 6 shows a typical plot of pulse energy versus discharge voltage.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{plot}
\caption{Typical plot of laser output energy versus discharge voltage for KrF mixture. Reproduced from "Lumonics - Excimer 700 series lasers - Reference Manual", 1992.}
\end{figure}

A key to successful laser operation is to ensure that the gases initially entering the laser vessel contain no impurities and that a minimum of impurities are introduced during the laser operation\textsuperscript{9}. The lifetime of an excimer gas mixture depends on many parameters such as the transition used (ArF, KrF, XeCl, etc), the number of laser pulses fired, the laser repetition rate, the cleanliness of the gas supply and the laser optics, the use of filters and cryogenic traps to remove impurity gases and to reduce the build up of dust, and the make of the laser.
The laser pulse can be triggered in different ways. This can be internal; the laser fires under the control of an internal rate generator at a selected repetition rate. An external trigger can be connected to the laser to control the frequency of the pulse or to synchronise it with another event.

4.3 Conclusion

While excimer lasers do not produce as high average powers as longer wavelength infrared lasers such as Nd:YAG and CO₂, in principle their shorter wavelength allows their beams to be focused to smaller spots thereby obtaining high intensities at the workpiece. Nearly all the applications of excimer lasers realised in industry make use of the unique manner in which these lasers interact with materials.

Their application in laser ablation-ICP analysis is increasing. The analysis of geological samples is commonly performed with the ArF transition at 193 nm, polymers were analysed at 193 nm, and finally, biological material at 248 nm and 308 nm. It was observed that the ArF transition gives the best performance regarding the efficiency and the resulting quality of the ablation.

The disadvantages of excimer lasers are their high price compared to the Nd:YAG lasers, and they involve the use of very high purity gases which are corrosive (i.e., F₂) and expensive.


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Chapter 3:

LA-ICP-MS systems
at Loughborough and BP Chemicals
Chapter 3

LA-ICP-MS systems at Loughborough and BP Chemicals

1. Introduction.

Experiments related to the development of the calibration strategy took place in two different laboratories (Loughborough University and BP Chemicals, Sunbury-on-Thames), the two instrumental systems are described below

2. Loughborough University system.

2.1 The laser

A Lumonics EX-742 excimer laser (Lumonics Ltd, Rugby, UK) was used to ablate the different targets (standards and samples). It was operated at the KrF transition (248 nm). The laser chamber was filled with the following mixture:

- 120 mbar 5% F₂ in He (Air Products, Weston Road, Crewe, CW1 6BT),
- 100 mbar Kr, CP Grade (99.995%) (BOC, 24 Dear Park Road, London SW19 3UF),
- 4080 mbar Ne, CP Grade (99.994%) (Air Products).

Under optimum conditions, the energy output should reach 550 mJ when the laser is operated at 35 kV and 25 Hz. The laser should then keep this optimum work condition for five days.

Initial attempts to use the laser were unsuccessful. After the laser was filled with a new gas mixture, the energy output decreased drastically within an hour, making the use of the laser impossible. Gas cylinders were changed to ensure the use of gases with the required purity. Different parts of the laser, such as the solenoid valves on the gas lines and the gas chamber were cleaned. The rear and front optics of the laser were realigned using a He-Ne laser. The gas scrubber, situated in the gas evacuation exhaust line, used to neutralise F₂ gas when a gas mixture was emptied from the laser, was replaced to ensure a good isolation of the laser chamber from the possible presence of oil vapour coming from the vacuum pump. These efforts only slightly
increased the energy output and did not improve the gas mixture lifetime. It was finally found that to increase the laser energy to 300 mJ, and more importantly, to increase the lifetime of the gas mixture to two working days, it was necessary to renew the gas lines that had become contaminated.

All control functions of the laser were performed from a hand held keypad that continuously displayed the pulse energy output, the pulse frequency and other relevant operating parameters of the laser. The reading of the laser energy was found to be out of calibration. The internal energy meter was recalibrated by reading the actual energy output measured with an external energy meter. The laser incorporated a “Stabilase” feature that automatically adjusted the voltage applied to the electrode in order to maintain the selected energy output.

2.2 The optical system

In some laser ablation experiments, a rim was observed around the crater formed after ablation. The existence of a voluminous friable mass raised above the irradiated polymer surface had already been noticed in studies using polymethylmethacrylate (PMMA). The presence of a rim was also observed when ablating alloys or ceramics. This was usually interpreted as consisting of molten material ejected out of the crater during ablation.

Mermet and Hemmerlin, however, proposed another explanation. They observed that at three wavelengths (1064, 532 and 266 nm), used to ablate poly(vinylidene fluoride) (PVDF), a more or less important rim was observed above the plane of the sample surface. The rim volume and height decreased by almost a factor of 20 from 1064 to 266 nm. However, as no crater was observed at 1064 nm, alternative interpretations other than the ejection of molten material had to be given. The concept of fluence threshold was then used to explain the formation of the rim around the crater. Under the fluence threshold, no craters appeared, but a modification of the surface of the sample was observed. This threshold value was dependent on the type of polymer.
involved (its absorbance characteristics), the laser wavelength and the pulse duration used

Mermet and Hemmerlin\textsuperscript{3} observed that the energy distribution of the beam of a Nd:YAG laser was not homogenous. Nd YAG lasers have a Gaussian beam. The use of harmonic generators results in energy loss and a slight distortion of the Gaussian profile of the beam. The beam surface is divided in two concentric parts corresponding to:

- a high energy core which made the ablation of the sample possible, provided that its fluence was above the threshold value,
- a lower energy area, surrounding the first one, under the fluence threshold, which created rims on the target as the result of thermal effects

Thus, the rim observed around the crater could be interpreted in terms of the energy distribution in the laser beam.

In order to eliminate the formation of swelling and to reach the most reproducible conditions for laser ablation, it was shown that the low energy portion of the beam could be rejected by masking\textsuperscript{3}. This was important because heating without ablation could allow local migration of elements, making the ablated material less representative of the sample bulk.

The use of an excimer laser led to similar problems, due to the very heterogeneous energy distribution in this type of laser beam\textsuperscript{4}. The beam quality of the KrF excimer laser operating at 248 nm was therefore improved in order to obtain optimal ablation conditions.

To achieve this improvement, an optical system, which comprised three main sections, was constructed:
• a 1m focal length plano-convex fused silica lens \( L_1 \) to focus down the initial laser beam and a mask \( M \) to select a section of it to provide a flat energy distribution. The long focal length lens was chosen to provide a large depth of focus, which minimises chromatic aberrations, the laser beam having 1 nm band pass. The mask was mounted on orthogonal \( x, y \) stages to allow selection of the section of the beam that provides a flat spatial power distribution. It was situated after the focal point, in order not to be ablated.

• a three element imaging objective \( L_2 \), to image the mask aperture onto the target. This lens combination was optimised to minimise aberrations and provide high quality imaging at a 15:1 reduction. The lenses were coated to minimise reflection losses at 248 nm.

• visual control of the ablation was possible with the aid of two systems. The first one combined a retractable mirror, a tube correction lens and an eyepiece, to provide a microscopic view of the target while the laser was off. The second one allowed observation of the ablation of the standard solutions from below the transparent ablation cell, using a mirror at 45° to reflect the image onto a closed circuit television camera.

Fig. 1 shows a schematic diagram of the optical system.

The beam of the excimer laser passed through several optical components, therefore the amount of energy reaching the target was smaller than the energy initially available at the exit of the laser. Considering that 1% of the energy is lost each time the laser beam passes through the face of an optical component, the total energy loss through this optical system could be estimated at 35% of the initial beam energy. An additional loss of the energy is occurring as only a portion of the laser beam is selected through the mask. For the experiments involving the excimer laser, the laser energy measured at the exit of the laser by an internal energy meter, was the one reported as it was easily monitored and therefore reproducible.
Chapter 3  LA-ICP-MS systems at Loughborough and BP Chemicals

Fig. 1: Optical system developed at Loughborough University.
Fig. 2a: Photograph of the ablation cell.

Fig. 2b: Schematic diagram of the ablation cell.
Fig 2c: Plan and end view of the bottom part of the ablation cell. (Dimensions in mm)
Fig. 2d: Plan and end view of the top part of the ablation cell  (Dimensions in mm)
2.3 The ablation cell

An ablation cell was constructed following the design of Arrowsmith and Hugues\(^4\). A special feature of this design was that it allowed sealing to the work piece by the means of a gas curtain rather than a solid seal. The internal volume of the cell was 14 cm\(^3\). The material used to make this cell was Perspex. A photograph of the cell and its schematic diagram are given in Figs 2a and 2b. A technical drawing of the cell is given in two parts in Figs 2c and 2d.

The gas used to transport the ablated material from the cell to the plasma source was argon. The connections between the cell and the plasma torch were made with Tygon tubing (6 mm OD).

The ablation cell consisted of two parts:

- an outer box which was gas tight and filled with plasma support gas (argon) at ~4 torr above atmospheric pressure to provide a pressure gradient along the transfer tube for transport of ablated material into ICP.
- a small ablation cell that enclosed the plume of ablated material but did not form a seal to the sample surface.

The inlet gas flow went into the cell through the outer box and entered through an annulus to form a symmetric gas sheath around the base of the cell. The inlet gas flow was then divided in two outlet gas flows:

- the carrier gas went through the small ablation cell where the ablated material was collected as a plume and transported through the tubing into the ICP.
- the second outlet gas flow was evacuated towards the periphery of the base of the cell, forming a gas curtain, and therefore, providing a gas seal. This prevented any air and other contamination from outside coming into the cell and being transported to the ICP-MS.

Optimal Ar flows were determined for efficient transport of the plume of ablated material out of the ablation cell. For this, two small glass crucibles containing concentrated hydrochloric acid and concentrated ammonia respectively were enclosed...
in the cell. A white smoke of ammonium chloride was formed in the cell. The Ar flows were optimised to transport this plume out of the cell with a minimum of turbulence. The values found for the Ar flows were as follows:

- 1 L\,\text{min}^{-1} for the inlet gas flow,
- 0.4 L\,\text{min}^{-1} for the waste outlet flow.

The resulting plume went straight up vertically above the sample container before bending towards the aperture on the sidewall of the cell.

The outlet flow transporting the ablated material was 0.6 L\,\text{min}^{-1}. An Ar make up flow of 0.4 L\,\text{min}^{-1} had to be added to it, before the torch, in order to obtain an optimal sample flow for the efficient extraction of the ions from the plasma. The two flows were combined by the mean of a Y connection, whose two arms were 30° apart, placed a few tens of centimetres before the plasma torch.

2.4 The ICP-MS instrument.

The instrument used was a prototype PQ1 instrument (V.G. Elemental, Winsford, Cheshire, UK). The plasma R.F. generator was a 27.12 crystal controlled supply (Plasma Therm Incorporation, Kresson, NJ, USA; model HFP 2500F) with an automatic impedance matching network. The ion extraction interface was the same as that used in a V.G. PlasmaQuad I. A modified version of the V.G. PlasmaQuad II ion lens stack was employed, in which lenses L3 and L4 were of reduced length. A quadrupole mass analyser (Micromass, Altrincham, Cheshire, UK, model 12-12S) having a mass range of 0-600 u was used as a mass filter. The detector was a Channeltron electron multiplier (Galileo Sturbridge, MA, USA; model 4870V) positioned at right angles to the central axis of the instrument. The plasma position, ion optics and gas flows were optimised daily to obtain a maximum and stable signal at \text{m/z} 115 for a modified standard solution, with 10 \mu g\,\text{g}^{-1} of In and 0.2 g\,\text{l}^{-1} of m-hydroxy-benzoic acid, ablated at 50 m\,\text{j} and 10 Hz. Table 1 gives the operating parameters of the ICP-MS instrument.
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LA-ICP-MS systems at Loughborough and BP Chemicals

Parameters of the plasma
RF power 1.25 kW
Reflected power < 0.5 W
Argon flow rates:
- coolant 12 l.min\(^{-1}\)
- auxiliary 1 l.min\(^{-1}\)
- carrier 1 l.min\(^{-1}\)

Potentials of electrostatic lenses
Extraction -212 V.
Collector -7.6 V.
L1 -7.8 V.
L2 -55.5 V.
L3 -4.9 V.
L4 -30.5 V.

Vacuum Pressures
Extraction phase 2 mbar
Focusing phase 10\(^{+}\) mbar
Separation phase 5*10\(^{-6}\) mbar

Data acquisition parameters
Points per peak 1
Dwell time 10 ms
Acquisition mode Time resolved analysis (peak jumping)

Table 1: Typical parameters for the PQ1 ICP-MS instrument when run with the laser.
3. BP system.

3.1 The laser.

The laser system was originally a Nd:YAG laser (V.G. Laserlab system), emitting at 1064 nm. The original Spectron SL402 (Spectron Laser System Ltd, Rugby, UK) laser was replaced with a Spectron SL282 system to make room for two doubling crystals in order to obtain emission in the visible (532 nm) and in the UV (266 nm) as well as the IR. The fundamental frequency (1064 nm) was doubled using a DCDA crystal (12x12x20 mm, controlled at 40°C) and then doubled again using a KD*P (12x12x20 mm, controlled at 40°C). The appropriate wavelength, i.e. 1064 nm, 532 nm or 266 nm, depending on which crystals were selected, was separated from the others using dichroic mirrors.

In the experiments that involved the Nd:YAG laser, the voltage applied to the electrodes was reported, instead of the energy output, as this was the laser parameter which was controlled during the experiments. No power meter was available to measure the energy output, but the energy value is proportional to $1/2CV^2$ (where $C$ is the capacitance and $V$ the voltage applied).

3.2 The optical system.

The laser beam was turned through 45 degrees by a beam splitter and focused onto the sample using a 100 mm focal length fused silica lens. With the laser beam focused onto the target, a 500 µm diameter crater was obtained. A circular mask could be inserted in the beam path to reduce the crater diameter to 60 µm.
3.3 The ablation cell.

The ablation cell was the standard VG Laserlab device. It was 55 mm in diameter, with a sloping quartz top window (50 mm high at its highest point and 40 mm high at the lowest point). The Ar outlet was 5 mm diameter; the gas was introduced tangentially through an inlet placed 40 mm above the base, on the 50 mm high edge. The base was made of PTFE.

3.4 The ICP-MS instrument.

Two ICP-MS instrument were used, coupled to the Nd:YAG laser: a V.G. Elemental PQII+ and a HP4500 plus. The plasma position, ion optics and gas flows were optimised daily to obtain a maximum and stable signal at m/z 90 for a modified standard solution, with 10 \( \mu \text{g.g}^{-1} \) of Zr and 1 mg.\( \text{l} \) of 2-thiobarbituric acid, ablated at 650 V and 10 Hz. Table 2 and 3 show the operating parameters for both ICP-MS instruments.
Parameters of the plasma

RF power 1.35 kW
Reflected power 20 W
Argon flow rates:
- coolant 13.75 l.min⁻¹
- auxiliary 0.9 l.min⁻¹
- carrier 1 l.min⁻¹

Potentials of electrostatic lenses

Extraction -107 V.
Collector -7.56 V.
L1 -8.09 V.
L2 -74.3 V.
L3 -6.84 V.
L4 -27.5 V.

Vacuum Pressures

Extraction phase 2 mbar
Focusing phase 10⁻⁴ mbar
Separation phase 2.4*10⁻⁶ mbar

Data acquisition parameters

Points per peak 1
Dwell time 10 ms
Acquisition mode Time resolved analysis (peak jumping)

Table 2: Typical parameters of the V.G. Elemental PQII+ ICP-MS instrument when run with the laser.
Parameters of the plasma
RF power 1.25 kW
Argon flow rates:
  - coolant 15 l.min⁻¹
  - auxiliary 1 l.min⁻¹
  - carrier 1.27 l.min⁻¹

Potentials of electrostatic lenses
Extract 1 -162 V.
Extract 2 -258 V.
Einzell 1,3 -190 V.
Einzell 2 3.5 V.
Omega Bias -30 V.
Omega (+) 2 V.
Omega (-) -2 V.
QP Focus 2 V.
Ion Def 13 V.

Vacuum Pressures
Extraction phase 2 mbar
Focusing phase 10⁻⁴ mbar
Separation phase 7.36*10⁻⁶ mbar

Data acquisition parameters
Points per peak 1
Dwell time 10 ms
Acquisition mode Time resolved analysis (peak jumping)

Table 3: Typical parameters of the HP4500 plus ICP-MS instrument when run with the laser.
4. Characteristics of Loughborough University and BP systems.

The characteristics and performances of both systems are gathered in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>Loughborough University</th>
<th>BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser wavelength (nm)</td>
<td>248</td>
<td>266</td>
</tr>
<tr>
<td>Laser energy</td>
<td>0 - 300 mJ</td>
<td>550 - 640 volts</td>
</tr>
<tr>
<td>Repetition rate (Hz)</td>
<td>1 - 25</td>
<td>1 - 15</td>
</tr>
<tr>
<td>Crater diameter at focus point of the laser (µm)</td>
<td>250</td>
<td>without mask: 500 with mask: 60</td>
</tr>
<tr>
<td>ICP-MS sensitivity (nebulisation)</td>
<td>4</td>
<td>VG PQII+</td>
</tr>
<tr>
<td>CPS x 10⁶ /ppm In</td>
<td>10 ~ 20</td>
<td>HP4500 plus</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
</tr>
</tbody>
</table>

Table 4: Characteristics and performances of the laser ablation ICP-MS systems used in Loughborough University and in BP Chemicals laboratories.
Chapter 4:

Calibration strategies in LA-ICP-MS
Chapter 4  

Calibration strategies in LA-ICP-MS

1. Introduction.

Certainly the most important aspect in LA-ICP-MS and still the limiting factor for quantitative analysis is calibration. Indeed, no universal method of calibration exists and the methods most commonly used involve the use of solid standards whose matrix is matched to the matrix of the sample.

The following review gathers studies on the different types of standards used for analysis by LA-ICP-MS. Three main sections group the form under which standards can be found.

- glasses,
- pressed pellets, synthetic minerals, synthetic polymers,
- liquid suspension and microwells

2. Current techniques of calibration for LA-ICP-MS.

2.1. Glasses.

The use of the National Institute of Standards and Technology (NIST) glass standards\(^1\) is very common for the optimisation of instrument sensitivity and to establish the response curve.

A series of home-made glass standards, providing concentration values for 45 elements, has been evaluated for quantitative analysis\(^2\). Calibration graphs were obtained by ablation of the glass standards (blank, 35, 75, 150 and 450 μg g\(^{-1}\)). For all standards, La was used as an internal standard. Excellent regression coefficients were obtained for the rare earth elements. The light elements, as well as the transition metals, often yielded a lower regression coefficient: Mg (r=0.8620), Cr (r=0.9652), Sc (r=0.988); this was believed to be due to interferences.

Moissette et al.\(^3\) used a glass standard material in a study on “calibration strategies for the elemental analysis of individual aqueous fluid inclusions by LA-ICP-MS”.

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They tried to determine if:

- synthetic fluid inclusions in Halite,
- microvolume aqueous solutions (microwells),
- NIST SRM 611 Glass,

would be suitable as calibration standards for the determination of elemental ratios in natural fluid inclusions by LA-ICP-MS.

By adopting a multiple calibration standard approach, it was possible to assess variation in ablation efficiency due to material state (liquid versus solid), transfer losses between chamber and plasma torch, and possible matrix effects. A dual gas flow sample introduction system was used to obtain matched plasma conditions. NIST SRM 611 Glass contains $\sim 500 \mu g g^{-1}$ of most elements except for Ca ($85,700 \mu g g^{-1}$) and Na ($140,000 \mu g g^{-1}$). This was used extensively to optimise the ICP-MS operating conditions and as a reference baseline for comparison with the synthetic fluid inclusions and microwells.

In order to allow rigorous comparison between the synthetic fluid inclusions, microwells and NIST SRM 611 Glass, a statistical $t$-test was carried out on the mean ratios for different combinations of the three calibration materials. This test measures the truth of a null hypothesis that there is "no significant difference between the means of two different samples". Except for Ba and Rb, the NIST SRM 611 Glass calibration showed good agreement with the synthetic fluid inclusions. This confirmed that glasses constitute suitable alternatives to synthetic fluid inclusions as calibrants for the analysis of natural fluid inclusions.

2.2 Fusion beads, pressed pellets, synthetic minerals, synthetic polymers.

A study of zeolites$^4$ was achieved by fusing the sample in a mixture of lithium carbonate and lithium metaborate; this produced a bead which could be continuously ablated with an IR laser.

Two calibration approaches were studied by Perkins et al.$^5$ for the quantitative determination of trace elements (Mn, Sr, Ba and Pb) in carbonates. Results obtained
with pressed powder pellets were compared with those obtained with fused glass discs. The pellets consisted of carbonates or oxide powders of the elements of interest mixed with CaCO₃. In₂O₃ powder was added to the mixture as an internal standard. After mixing and the addition of a binder, the pellets were pressed. Fused glass discs were synthesised by mixing together CaCO₃, MgO and solutions of the trace elements. The mixtures were fused and left to cool. Linear calibration curves were obtained with both types of solid standards. Correlation coefficients greater than 0.95 were obtained with the fused glass discs. The pellets gave poorer results than the discs. These were improved when the natural internal standard (⁴⁴Ca) was used as internal standard instead of In. This problem was related to the difficulty of producing homogeneous pellets. Certified Reference Materials were analysed using both standard types. Again, the results obtained were better with the fused glass discs than the pressed pellets. Accuracy was better than +/- 10%.

Other results reported by the same group used different pressed pellets to perform semi-quantitative determination of trace elements in carbonates. The pellets differed from the previous ones in the way the elements were added into the matrix. Standard solutions were added to CaCO₃ powder. The additions and the powder were mixed whilst wet, then dried, reground and finally pressed into pellets. The solid standards obtained were more homogeneous than those produced by powder additions to a powder matrix. Semi-quantitative analyses were performed. The results fell within +/- 10% of the accepted values across a wide concentration range (0.52 - 3741 ppm).

LA-ICP-MS has been used for the quantitative determination of trace elements to characterise annual growth rings of tree. The elements studied were Mg, Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cd, Ba, Tl, Pb, Bi and U.

As wood standards for calibration with laser sampling are not available, cellulose powder (Aldrich, Ca. 20 micron) was doped with standard solutions of the analytes. Cellulose, the major constituent of wood, is similar in its composition to most types of wood in its hydrogen and oxygen composition. However, typical carbon concentrations of woods are higher than the one for cellulose by about 5 mass%. Therefore, 5 mass% carbon powder was added to the standard reference materials as
internal standard. Pellets were formed. Using internal standardisation with $^{12}$C, the precision was typically better than 10% relative standard deviation. The limits of detection were limited by the purity of the cellulose.

In a study on the determination of elements in tree bark to obtain information about anthropogenic and geogenic sources of pollution, home made solid standards were prepared to analyse the bark sample by LA-ICP-MS. The lack of commercially available standards for the calibration of solid bark material was compensated by the preparation of bark pellets with different element concentration obtained from regions of the pine bark (outmost, middle and inner part). After grinding, homogenising the different barks and pressing them into pellets, their elemental concentrations were determined. This was done by sampling a small portion of each pellets which was then analysed by digestion and solution ICP-MS. The solid matrix-matched standards were then ready for use.

A semi-quantitative determination of trace elements in a wide range of polymers intended for food contact use was carried out by ICP-MS, following two methods of sample introduction. In the first one, the polymers were digested to give samples suitable for introduction into the plasma. A single indium internal standard was used. Limits of detection for the polymers were generally of the order of 1 µg g$^{-1}$.

In the second case, laser ablation was used. Owing to the paucity of suitable standard reference polymer materials, a series of in-house reference materials were prepared. Stearates were weighed out to give nominally 50 mg (as metal) of incorporated material per kg of polymer, then pre-blended with each polymer material by tumble-mixing to achieve an even distribution. The blend was transferred to the hopper of a compounding feeder and the strands of molten polymer produced were passed through a water bath to solidify. The solidified polymer was then pellitised. The homogeneity of the polymer pellets was observed. A RSD of 10% was found for five ablations of the polymer on different sites. The home made standards were used for the determination of the concentration of Co and Sb in a PET sample. The differences
between the results obtained and those obtained by digestion ICP-MS and NAA were within 15 %.

LA-ICP-MS was used for direct analysis of ceramic layers forming parts of solid oxide cells\(^{10}\). Here again, a great problem arises in the analysis of ceramics from the lack of matrix-matched certified reference materials that are needed for quantification. To overcome this problem, synthetic laboratory standards of the material of interest were prepared.

The standards consisted of a binder and 30 elements in standard solutions added to ultra high purity ceramic powder. After homogenising in an ultrasonic bath, drying and mixing in a vibrational ball mill, the mixture was pressed into pellets at 40 tonnes

Matrix elements were used for standardisation.

LA-ICP-MS is more seriously affected by inhomogeneities than ICP-MS of dissolved samples because only small amounts of material are analysed from small parts of the sample. Thus care must be taken during the preparation of the pellets.

The following results were obtained:

- the regression coefficients of the calibration curves were better than 0.995 \((n = 15)\),
- detection limits for most elements were in the range 0.1-2 \(\mu g \, g^{-1}\),
- results obtained by LA-ICP-MS were in satisfactory agreement with those of other methods,
- reproducibility was below 15 %, depending very much on the homogeneity of the samples

2.3. Liquid suspensions, dual gas flow, synthetic inclusions, nebulised solutions.

A new technique for sampling solids, laser ablation in a liquid medium \((LALM)\), was developed and evaluated\(^{11}\).

The solid sample, brass in this study, was placed in a liquid medium, in a flat bottomed beaker (Fig. 1).
Fig.1: Schematic diagram of the laser ablation assembly.
A: flat-bottomed beaker,
B: sample,
C: quartz (or stainless steel) rod for holding the sample, which can be rotated by the action of a stepping motor,
D: single lens of 150 mm focal length,
E: 45° prism

Introduction of the laser beam (λ=1064 nm) from the bottom of the beaker prevented the deleterious effects of surface waves, which stem from the shock of laser ablation. Both vapour and particles, produced by laser ablation, were trapped by the surrounding liquid and a suspension formed. The suspension was then nebulised.

This method of solid sampling offers several advantages:
- separation between the sampling and introduction processes,
- temporal separation as the necessity for high-speed scanning or a multichannel detection system can be avoided,
- spatial separation, as the laser can be positioned separately from the large excitation and detection instruments,
- solid standard materials become unnecessary as the direct introduction of a laser-generated suspension into the ICP is quantitatively achieved ~ nearly 100% trapping efficiency is obtained,
- loss of analyte on transport between the ablation cell and the plasma source is eliminated,
- fractional ablation (vaporisation) is absent,
- the suspension obtained consists of fine particles of around 1 \( \mu \text{m} \) or less and is stable over several hours
Unfortunately, the following disadvantages occur:

- the advantage of the spatial resolution in normal laser ablation is lost by the accumulated sampling in LALM,
- dilution effects by the liquid medium (LM),
- possibility of contamination by the LM,
- some limitations exist for the combination of LALM and the direct introduction of a suspension in the ICP because of the poor efficiency of the nebulisation process which is usually 1% efficient or less,
- aqueous sample introduction might cause solvent loading in the ICP and higher intensities of molecular oxide species

It was suggested that other types of sample introduction techniques, such as electrothermal vaporisation or glow discharge sputtering, should be more advantageous for trace element determinations by LALM.

In a study on the determination of rare earth elements in single mineral grains by Laser Ablation Microprobe-ICP-MS (LAMP-ICP-MS)\textsuperscript{12}, a dual gas flow sample introduction system was used, to permit calibration of the ICP-MS with aqueous standards (Fig 2). The flow from the ablation cell (0.6 l min\(^{-1}\)) was merged with the carrier gas from a conventional nebuliser/spay chamber (0.4 l min\(^{-1}\)), so that the plasma might run under “wet” conditions. The two gas flows were combined concentrically in a small glass mixer placed between the nebuliser and torch. This was termed the “dual gas flow system” or “solid-liquid calibration”
Additionally, in order to compensate for the poor precision in the analytical signal caused by variations in the mass of material ablated, an internal standard was used. The internal standard would normally be a minor isotope of a major elemental component, the concentration of which is either known from stoichiometry or determined by an independent analytical technique.

As the dual gas flow system allows simultaneous introduction of laser ablated solids and nebulised aqueous solutions, both forms of material are introduced into an identical bulk plasma environment. Thus, the ICP-MS can be tuned and directly calibrated using aqueous standards just as if solution nebulisation is being performed. The use of this dual gas flow system has the following benefits:

- no need for solid standards for direct calibration,
- no need for extrapolation of aqueous sensitivities to the different spectroscopic conditions of the dry plasma,
- the aqueous solutions offer homogeneous standards,
- a dry plasma would be preferred to reduce oxide formation; however, these oxides rarely exceed 4% of the parent isotope in a wet plasma,
- repeatability of the order of 10% relative is achieved with the use of an internal standard

Arrowsmith and Cromwell\(^\text{13}\) also studied the use of a dual gas flow system to obtain matched plasma conditions to perform semi-quantitative analysis. Matched plasma conditions for LA and solution nebulisation were obtained by simultaneous introduction of the two sample streams using an annular adaptor tube attached to the injector inlet of the ICP torch. The two streams were mixed in a short section before entering the plasma. Standards were therefore introduced by nebulisation and the ablated samples were introduced in the plasma with a blank solution being nebulised. They compared the element Relative Sensitivity Factors (RSF) obtained for laser ablation and for solution with conventional, single channel, sample introduction. The results showed obvious discrepancies for the unmatched ICP conditions. This may be attributed to the \(\sim10^{-4}\) g s\(^{-1}\) of water transported to the ICP by pneumatic nebulisation, compared to the \(\sim10^{-7}\) g s\(^{-1}\) particulates loading for LA. The high concentration of
water changes the plasma temperatures, T(e⁻) and T(ion), and the e⁻ and ion number densities. Hence, the RSFs for some elements can be strongly dependent upon ICP conditions.

Following this, RSFs were obtained under matched plasma conditions, using the mixed sample introduction technique. It was observed that there was a good agreement between the RSFs for the solid and aqueous standards, at the higher laser fluence applied.

The following benefits were claimed:

- no need to prepare matrix-matched standards; ease of standards preparation,
- the atomisation and ionisation efficiency of elements introduced into the plasma as aqueous solvated ions by nebulisation are similar to those for elements introduced as solid microparticles by ablation,
- the introduction of a stream of ablated material does not obviously influence the excitation properties of the matched plasma,

The only disadvantage reported was the high level of oxide formation compared with dry laser ablation.

Semi-quantitative analyses of glass and stainless steel were performed using this matched plasma technique. Differences between the measured and certified concentrations were +/- 40% for the metal and +/- 20% for the glass.

Some preliminary experiments indicated that these results could be improved using an ultrasonic nebuliser with desolvation to introduce the aqueous solution standard and blank streams, instead of the pneumatic nebuliser. The removal of water from the matched plasma has the beneficial effect of reducing the likelihood of analyte element-oxide ion interferences in the LA mass spectra.

A paper published by Krishna Prabhu et al described the development of a technique for the analysis of small volumes of solutions using laser vaporisation ICP-MS.

The vaporisation cell consisted of the usual LA cell with a small boat, containing the test solution. A graphite wheel, partially dipping into the solution, was rotated using a stepper motor. The film of solution, which adhered to the wheel, passed through the laser beam for ablation. The solution vapours were then swept away by a stream of argon, into the ICP.
A plot of the ion intensities of Pb and Cu in the test solution as a function of concentration (0.5-25 μg ml\(^{-1}\)) produced a straight line. Internal standards were used for each element; \(I_{\text{element}}/I_{\text{std}}\) remained virtually constant by choosing internal standards with masses comparable to those of the elements of interest. When higher concentrations were determined (100 - 1000 μg ml\(^{-1}\)), the laser intensity was reduced so that less material was injected into the plasma. It was possible to analyse solutions with concentrations at the 10 - 100 ng ml\(^{-1}\) level.

The usefulness of the laser vaporisation technique was checked by applying it, combined with the method of standard additions, to eight elements whose concentrations in the standard ranged from ppm to percentage levels. The experimental results were in fairly good agreement with the certified values. The advantages of this technique are:

- a large dynamic range of concentration can be analysed (5 ng ml\(^{-1}\)-mg.ml\(^{-1}\)),
- small sample volumes are required for an analysis (200 μl); indeed, 2 μl min\(^{-1}\) are introduced into the plasma,
- there is no collection of drain solution which is particularly attractive in the analysis of solutions containing radioactive elements,
- reduced oxide formation compared with the nebulisation technique,
- with only minor changes in the experimental set-up, the technique can handle both solids and solutions.

LA-ICP-MS is used to study fluid inclusions which are a geological record of the fluid inventory of the earth's crust. Their reliability in providing unequivocal information on the chemistry of the fluid has not been universally accepted. Indeed, as well as being extremely small, typically < 30 μm, it is rare to find a material that contains only one generation of inclusions. While multiple populations of inclusions offer an exciting insight into changes in fluid activity, their existence complicates bulk sample methods of analysis and adds to the uncertainty of data interpretation. To avoid such problems, considerable effort has been invested in the development of single inclusion techniques. This kind of analysis can be achieved with Laser Ablation Micro Probe-ICP-MS as it provides the requisite specifications: multi-element capability and a spot size of less than 5 μm.
Moissette tried to determine if synthetic fluid inclusions in halite and aqueous solutions (microwells) would be suitable as calibration standards for the determination of elemental ratios in natural fluid inclusions. The same experiment, performed for reference glass material, was described previously. A dual gas flow sample introduction was used.

The results showed that:

- synthetic fluid inclusions in halite and microwells gave excellent elemental ratio working curves,
- for most purposes, microwells containing aqueous solutions could replace synthetic fluid inclusions as working calibration standards for the elemental analysis of single fluid inclusions,
- theoretically, microwells have less long-term stability than the glass standards, but they approximate much more closely to the LA of the fluid inclusions and can be designed to cover a wider range of chemical compositions and elemental concentrations than the NIST glasses,
- synthetic fluid inclusions in halite simulate even more closely the laser response of natural fluid inclusions and, for the study of evaporated minerals, are the perfect match. Their disadvantage is that they cannot readily be used for the calibration of Na and Cl because of host matrix contamination.

In a study led by Shepherd and Chenery, a UV laser ($\lambda = 266$ nm) was used to carry out tests on 10-100 $\mu$m diameter aqueous inclusions in fluorite, quartz and halite, up to 60 $\mu$m beneath the surface. A key feature of their system was a novel high temperature ablation cell that substantially improved the efficiency and reproducibility of fluid release.

Calibration was carried out using a dual gas flow system that allowed use of standard solutions and NIST glasses for tuning the instrument and for obtaining RSFs.

As an alternative to synthetic fluid inclusions, a new calibration approach was described involving the encapsulation of microdroplets of standard solutions in epoxy resins to form “fluid inclusion analogues”.

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Elemental detection limits vary according to the mass of material released for analysis and are thus related to the volume and composition of each inclusion. Precision was estimated to be better than 30%.

The advantage over the synthetic inclusions in halite was that the epoxy inclusions permitted the determination of sodium, but a few problems were encountered such as the fact that the resins contained trace metal impurities, there was a progressive loss of water from the droplets over a period of several weeks and the epoxy resin has a low thermal stability and cannot be ablated at elevated temperature ($T > 100^\circ C$).

A calibration for the quantitative elemental analysis of single fluid inclusions of Sr and Rb in halite samples has been achieved with the use of microcapillary tubes. A set of artificial fluid inclusion standards were prepared by drawing small volumes (about 0.2 - 0.3 µl) of standard solution of known composition (1000, 500, 250 ppm of Sr and Rb) into 4 µl volume glass microcapillary tubes. The wall thickness and inner diameter of the microcapillary tubes was accurately known (+/-1%), permitting precise measurements of volume of “ablated fluid” per laser pulse. After the solution had been drawn into a tube by capillary action, the tube was sealed at both ends. The tubes were then placed horizontally in the ablation cell. The laser was fired continuously ($\lambda = 266$ nm) and gave a clean hole through the wall of the microcapillary tube. The liquid was then consumed by the ablation process. The average volume of fluid released, per laser pulse, was approximately 100 pl. Calibration curves were created by plotting signal intensity versus concentration. For the measurements of the different concentrations of Sr and Rb, the RSD % were in the range of 1.1 to 6.3 %. The precision of analysis for individual natural fluid inclusions ranged from 5 to 31 % for Sr and Rb. The concentration of Sr in halite samples calculated by this method was in agreement with earlier work.

Aqueous standards were used for calibration in an analysis of the elemental pattern of bones. It was expected that this study would help to explain how osteoporosis develops. In this case again, reference materials were not available. A new technique was reported that enables standards to be easily prepared, with the ability to mimic the matrix of the sample material. The technique was based on the use of aqueous...
standards with modified absorption characteristics. This modification was achieved using a suitable chromophore, a soluble styrene based polymer in this case. The resultant solution has similar UV absorption characteristics to the sample.

2.4. Dry atomic vapour for internal standardisation

A simple system has been reported that can produce constant amounts of metals in dry vapour form\textsuperscript{18}, independently of the LA unit, and introduce them into the sample carrier gas, prior to the ICP torch. The metallic vapours can be used as internal standards (IS) for quantitative analysis or as reference signals for laser and plasma diagnostic studies.

The central feature of the system was the \textit{internal standard vapour generator (ISVG)}. The IS vapour was generated by applying a current to metal filaments of the internal standard elements, which were in a glass bulb. Increasing the current heated the filaments close to their melting points with the result that atomic vapour was generated. Vapour was swept out of the ISVG by an Ar stream (0.2 ml min\textsuperscript{-1}) and merged with the Ar sample carrier gas (0.8 ml min\textsuperscript{-1}), exiting the LA cell prior to its entry into the ICP torch. The vapour was filtered and the filtrate examined by SEM-EDX to confirm an absence of particulates. The amount of metallic vapour added to the ablation cell stream was controlled by a bleeder valve in the exit line of the ISVG.

The advantages of this internal standardisation are:

- ease of operation,
- produces signal stability of < 1% RSD over 15 min. and < 5% over 60 min,
- negates the problems of oxide interferences, compared to wet-dry dual systems, by generating IS elements as dry atomic vapour,
- spectrometer parameters can be varied with greater precision compared to the usual methods involving ablated analyte signals or solution nebulisation,
- permits the study of the sources of signal noise and matrix effects under dry plasma conditions.
The potential disadvantage of this technique of internal standardisation is that it is not representative of the ablation event.

3. Conclusions.

The use of certified reference materials should ensure the use of standards with well defined elemental concentrations. Despite this apparent assurance of quality, the NIST glass offers an example of a CRM whose elemental concentration was the object of discussion. Additionally, the use of this type of standard provides a relatively narrow choice in the selection of the elements that the analyst may want to determine and the elements which are not desirable in the standard as they may cause interferences on some elements of interest. Another limitation in the use of these solid standards is the limited range of matrices in which they are available, reducing their use to the analysis of some particular sample types. In the case where many different types of samples have to be analysed, many different CRMs would be required.

An alternative to the commercial CRMs are home-made solid standards. The preparation of such standards is more a consequence of the lack of commercially available CRMs for certain matrices (barks, polymers, biological tissues, etc.) than the genuine desire to prepare home-made solid standards. This alternative solution presents a few difficulties and disadvantages. The raw material that is used to bind the standard and to match the desired sample matrix may not be easily found in a pure state. The elements of interest which are added to the standards have to be mixed thoroughly into the matrix to ensure a good homogenisation; the homogeneity of the standard may be incomplete and this procedure risks contamination of the standard from the mixing equipment. Overall, the preparation of home-made solid standards is a time consuming procedure which does not always result in quality standards.

Other methods of calibration for LA-ICP-MS analysis use standard solutions. These are introduced into the plasma either by nebulisation or by ablation. In the first case, the use of a dual flow introduction system allows the simultaneous introduction of the ablated solid sample and the nebulisation of a solution (either blank or standard) which
maintain the plasma in a “wet” condition. This method leads to the appearance of oxide species into the mass spectrometer due to the water loading of the plasma. The other methods which involve the use of standard solutions are the ones generally used by geoscientists for the determination of elemental ratios in fluid inclusions. These standards were described as “microwells” or “fluid inclusion analogues”, etc. They consist of a micro volume of standard solution enclosed in a solid (plastic tubes, covered wells, epoxy-resin) As a conventional standard solution does not significantly absorb UV radiation, the signal resulting from this ablation is extremely noisy.

The precision, obtained with these different calibration techniques, ranges from 40 to 10% depending on the homogeneity of the standards, the reproducibility of the successive laser shots, the transport efficiency of the ablated material from the ablation cell to the plasma and the use of an internal standard. Indeed, the use of an internal standard is essential to obtain reliable results as it compensates for the shot-to-shot variation in laser ablation and therefore, improves the precision of the measurement.

Given that the use of an internal standard is required for quantitative analysis, the need for matrix matching might be questioned. The development of a new method of calibration that would be applicable to any type of sample and that would involve the use of easy to prepare standards is required.
Chapter 4

References

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Chapter 5:

Ablation mechanism
1. Introduction.

A simple and convenient source of laser radiation in the ultraviolet (UV) region became available with the invention of the excimer laser in the 1970's. Most of the modelling work carried out on the processes that occur when UV laser radiation interacts with a solid surface can be found in the Physics literature. From the analytical point of view, such models are sometimes of little worth because of the considerable variety of sample materials. Despite a large amount of data having been accumulated on the subject, a quantitative understanding of the ablation process is not yet available.

The following sections report previous work carried out on parametric effects on laser ablation and then proceed to discuss theoretical models.

2. Observations.

2.1. Fluence threshold and etch rate

Dyer\(^1\) observed that, in essentially all UV laser-polymer ablation experiments, a threshold fluence \(F_T\) (energy per unit area per pulse) exists for significant material removal. This threshold typically lies in the range of a few tens to a few hundred mJ cm\(^{-2}\) per pulse, being dependent on the type of polymer involved, the laser wavelength and the pulse duration used.

Fluence thresholds were found for polyimide, corresponding to three different excimer laser wavelengths (193, 248 and 308 nm). The results obtained were as follows:

\[
\begin{align*}
F_t (193 \text{ nm}) & \quad 0.77 \text{ MW/cm}^2 \\
F_t (248 \text{ nm}) & \quad 0.98 \text{ MW/cm}^2 \\
F_t (308 \text{ nm}) & \quad 1.7 \text{ MW/cm}^2
\end{align*}
\]
The decrease in threshold fluence for the onset of etching with decreasing wavelength was also observed by Srinivasan.

The thresholds and etch rates in PMMA were compared at different temperatures, 90 K and 273 K:

- at $\lambda = 193$ nm, the threshold and the etching characteristics remained unaltered at the two temperatures,
- at $\lambda = 248$ nm, the threshold remained unaltered, but the etch rate at a given fluence at 90 K was only half of the value at 273 K.

Measurements of thermal energy loading of a polyimide target showed close agreement with a $\sim 100\%$ thermal coupling coefficient, below the threshold fluence; but above this, the thermal loading becomes approximately constant, due to transport of energy away from the surface by the ablated products.

Geertsen studied the ablation efficiency of metals by observing the material removed as a function of melting temperature, laser wavelength and laser energy. The experiments carried out were:

- investigation of ablated mass as a function of laser energy for the following wavelengths, 193, 266, 308 and 1064 nm (Fig. 1),
- investigation of ablated mass as a function of melting point, for the same wavelengths (Fig. 2),
- the different wavelengths used, were the first three harmonics of a Q-switched Nd:YAG: 1064, 532, 266 nm; and 308 and 193 nm from excimer laser.

In the first set of experiments, it was found that the ablation efficiency of a copper target, was more than one order of magnitude higher (20 times) for a UV laser than for an IR laser or even a visible laser, at 200 J.cm$^2$. Similar results were obtained for targets made of Mo, Ni and W, while the dependence on laser wavelength of the amount of material removed from a zinc target was less pronounced.
Fig.1: Ablation efficiency (mass ablated per one hundred shots) on a copper target in air buffer gas as a function of laser energy for four different lasers.


As the amount of sample material that can be accepted by an ICP-MS instrument is limited, this advantage of UV laser sampling might not be capable of being exploited to its full extent.

In the second set of experiments, a linear relationship between the ablated mass and the melting point temperature of the sample material was found for UV radiation. For IR radiation, the differences in ablated mass were considerably larger and no simple relation between the two variables existed. The results obtained for IR laser indicated an almost exponential decrease in the ablated mass as a function of melting temperature.
Fig. 2: Ablated mass versus fusion temperature of several targets in air buffer gas at different laser wavelengths at a laser energy of 85 mJ per laser pulse. This corresponds to a fluence of 90 J cm\(^{-2}\) for the excimer laser (A, XeCl 308 nm) and 425 J cm\(^{-2}\) for the Nd:YAG lasers (B, 532 nm; C, 1064 nm) \textit{Reproduced from C. Geertsen, A. Briand, F. Chartier, J.-L. Lacour, J.-M. Mermet, J. At. Anal. Spec., 1994, 9, 17.}

This indicates a fundamental difference in the physics involved in the ablation process and might have important analytical consequences since it drastically reduces matrix effects in the case of UV laser sampling.

Dyer studied the properties and ablation characteristics of vascular tissue in a liquid environment, conditions more closely corresponding to those under which the laser would be used in the clinical situation than the air sample case. A comparison of the ablation thresholds for sample in air and in liquid environment suggested that there was a small but significant increase in threshold for the latter condition. This was probably due to the impedance to expansion presented by the liquid environment. Additionally, the removal rate, at high fluence, was suppressed for samples in a liquid environment, compared with an air environment.
2.2 Penetration of radiation.

In all cases, the amount of laser energy that is coupled to the target is highly variable, depending on the laser power, wavelength, pulse duration, and the target's material and optical properties, as well as the surrounding medium.

According to Srinivasan, the penetration of radiation through a solid follows Beer's law:

\[ I_t = I_0 10^{-\alpha d} \]

In a weak absorber, such as poly(methyl methacrylate) (PMMA), a pulse of laser radiation of 193 nm wavelength would penetrate to a 6.5 \( \mu \)m depth before 95% of it would have been absorbed, whereas in a strong absorber, such as polyimide, the penetration depth, \( I_s \), would be only a few hundred nanometers.

If the fluence \( F \) of the laser beam exceeds a certain threshold value, \( F_T \), then a depth \( I \) of the material is ablated per pulse. Finally, the depth \( (I_s - I) \) has been exposed to the light but has not been removed. The next pulse will go through \( (I_s - I) \) and through the pristine material underlying it. By this fact, the first pulse is unique.

A study of the depth increment \( (I_s - I) \) by X-ray photoelectron spectroscopy (XPS) showed that polyimide - containing oxygen - had its surface depleted in oxygen; this change was attributed to loss of oxides of carbon. Wet reactions showed that there might have been a very thin (<50 Å) layer that had undergone oxidation by air, on the top of the altered layer.

Dyer et al. investigated the phenomenon of one-photon incubated absorption on polymers (low density polyethylene and polypropylene films), using an ArF excimer laser (\( \lambda = 193 \) nm). This incubated absorption can play an important role in determining the ablation properties of weakly absorbing polymers under excimer laser exposure. Low density polyethylene and polypropylene have a relatively low absorption coefficient at 193 nm; therefore, a high fluence (\(~ 400-500 \text{ mJ.cm}^{-2}\)) is required to achieve ablation with the first pulse delivered. The quality of the resulting ablated surface is poor (roughly etched site with deep large-scale structures) as the thermal loading on the polymer film is high and the beam penetrates relatively deeply into its surface. The exposure of these polymers at fluences down to at least one order of magnitude less than
the threshold value can result in ablation after a sufficient number of incubating pulses have been delivered to the surface. The production of diene and triene groups as well as carbonyl groups was observed during the incubation process. The increase of absorption at 193 nm was probably due to the growth of olefinic bonds. The quality of the ablated surface after incubation was superior (smooth shallow pit) as thermal loading was lower and radiation penetration was confined to a much shallower level.

Similar observations were made by another group, where PMMA thin film was incubated with a KrF excimer laser or continuous (cw) UV light sources. Production of unsaturated species was detected which increased the absorption of the film. This way, the incubated PMMA film could be efficiently ablated with a XeCl excimer laser.

2.3. Laser induced-plasma

Emission spectra in the visible and ultraviolet range of polyimide exposed to 193, 248 and 351 nm laser radiation were used to investigate the laser etching process. It was obvious that the emission derived from two distinct components: a fast one that appeared simultaneously with the laser excitation and a slower one whose propagation speed was about $4 \times 10^5$ cm.s$^{-1}$. Such behaviour is typical of laser-produced plasma and was described as the “shell” (fast) and the “core” (slow) emission components. Thus, plasma is created in the laser etching process.

Mermet et al. studied the role of buffer gas and the laser wavelength in ignition of the plasma. Photographs were taken after about 1,000 laser shots on the same area of a copper target. This choice was based on earlier findings that the optical emission signal evolves during the first laser shots and is stable thereafter. The experimental conditions used to obtain the images of the plasmas corresponded well with the operating conditions used in commercial LA-ICP-MS apparatus. The results were the following.

- plasma produced by IR radiation in argon buffer gas was complex and had a poor reproducibility,
• plasma produced by IR radiation in air buffer gas was complex (two hot spots), but its reproducibility was better,
• plasma produced by UV radiation in argon buffer gas was simple (one single plasma) and its reproducibility was considerably better.

In the experiments with IR radiation, the lack of reproducibility of the plasma ignition probably explained the poor reproducibility observed in LA-ICP-MS measurements.

The images suggested the following physical interpretation. When a high-power laser is focused on a metal target, the intense radiation leads to rapid heating and evaporation of the solid. At the same time, free electrons are created, either by thermoelectric emission, by multiphoton emission or by multiphoton ionisation of the metallic vapour or the ambient gas. These electrons absorb the incoming photons by inverse Bremsstrahlung. This is necessarily a three-body process for reasons of conservation of both energy and momentum. The third body can be either an atom or an ion, but the cross-sections are several orders of magnitudes greater for ions than for atoms. Therefore, the heating of the electrons begins slowly, before they acquire enough energy to ionise the gas collisionally. This starts the cascade that leads to breakdown. In addition, since the inverse Bremsstrahlung cross-section of the ions relates to the wavelength as \([1-\exp(-hc/\lambda kT)]\lambda^3\), the plasma will be much more absorbing in the IR than in the UV.

With IR radiation, the absorption by the plasma was so strong that the energy was deposited at the leading edge of the plasma where it could lead to secondary or multiple breakdowns. This was not the case with UV laser produced plasmas where no breakdown of the buffer gas was observed.

As a consequence of its higher absorption cross-section, the IR plasma is hotter than the UV plasma and less energy in the laser beam interacts directly with the sample surface. The plasma produced by the IR laser acts as a shield that only transfers a small part of the incoming laser energy to the solid surface.

With UV radiation, the direct laser interaction regime lasts the duration of the laser pulse (6 ns) whereas the importance of the plasma erosion is negligible. The risk of selective vaporisation is therefore minimised. With IR radiation, the direct laser interaction regime lasts only a fraction of the laser pulse (the time to reach breakdown, probably less than 1 ns) and, with the fact that the plasma is considerably hotter, the
plasma erosion with an IR laser was found to be very important for the crater formation and possibly also for the removal of the material. The lateral spatial resolution of laser sampling for metallic targets is given by:

- the laser focal spot size in the case of UV laser,
- by the plasma size for the IR laser.

Ruso et al.\(^9\) developed a model for the formation of laser-induced plasma using thermal evaporation and inverse Bremsstrahlung processes. The model showed that plasma shielding starts at approximately 0.3 GW.cm\(^{-2}\) for a brass sample. This result was in agreement with experimental data where the mass ablation rate of a brass sample showed a roll-off at this same fluence value (excimer laser \(\lambda=248\) nm, pulse width 20 ns).

The same group demonstrated, using ICP-AES monitoring of the ablated material, that the onset of plasma shielding could be detected for ns and ps laser interaction with solids\(^10\). For laser pulses of the order of 10 ns, as the laser intensity was increased past the point that a plasma formed above the surface of the target, the rate of increase in AES intensity markedly slowed. This roll-off is the evidence that the mass removal rate as a function of laser intensity changes after the formation of a dense plasma. At high intensities, it was proposed that the plasma above the surface could absorb almost all the laser light, thus shielding the target. For laser pulses of the order of 10 ps, atoms and ions do not travel sufficiently far to establish a substantial collisional zone for inverse Bremsstrahlung plasma shielding to occur during the laser pulse. Therefore, for ps laser pulses, differences in the gas atmosphere should not affect material removal. However, it was shown that at low intensities, the gas atmosphere influences the composition of the material removed even for ps laser ablation.

The influence of noble gases on the laser-material interaction and on the formation of the laser-induced plasma has been observed by Russo et al.\(^11\). The amount of ablated material from a brass sample was influenced by change of the gas environment; the amount of ablated material was highest in He and decreased as the ionisation potential of
the gas decreased. Data indicated that the ionisation potential of the gas might have an effect on plasma screening by shifting the point at which roll off occurred.

Fusso et al.\textsuperscript{12} studied plasma temperature and density as a function of time after the arrival of the laser pulse. The laser used was a XeCl excimer laser ($\lambda=308$ nm, pulse width 16 ns). Rather large electron density values ($n_e$) were found, especially in the first stages of the plume expansion ($n_e \sim 6 \cdot 10^{18}$ cm$^{-3}$ at 5 ns after the arrival of the pulse on the target). The decrease of $n_e$ as a function of time was approximately linear. Alternatively, the temperature had a non-monotonic behaviour and attained its maximum value for $t=15$ ns, i.e. just before the end of the laser shot. This phenomenon can be understood considering that the plasma is heated mainly by absorption of the laser radiation through inverse Bremsstrahlung processes, thus the plasma temperature increases as long as the laser pulse irradiates the plume.

2.4 Pulse width

It has been observed that the quality of the laser spot border can be improved with the use of ps laser pulses, compared to nanosecond ablation where pronounced melt dross formation at the border of the spot is exhibited\textsuperscript{13}

Femtosecond-pulse visible laser processing of transparent material was investigated by Kruger et al.\textsuperscript{14}. The interaction between visible light and practically transparent materials like glasses and fused silica is expected to be negligible, however, femtosecond-pulse laser processing at 620 nm allowed precise microstructuring of transparent dielectrics without disruption of the remnant material. Two different photon absorption mechanisms have been observed. The first occurs during the initial laser pulses in the incubation range. There, multiphoton absorption results in moderate energy volume densities. These are sufficient to generate morphological changes and optical defect sites (colour centres) which provide a much higher absorptivity relevant for the second mechanism. It results in gasification without prior melt.
Another group studied the ablation of oxide ceramics with different pulse durations\textsuperscript{15} (30 ns and 500 fs). The ablation threshold fluence was found to be generally lower with sub-ps pulses than with ns pulses. Using ns pulses, "plasma mediated ablation" dominated, whereas in the case of fs pulses, the process was controlled by multi-photon absorption.

Many experiments have shown that ultra short laser pulse widths improve the quality of the ablation crater as well as providing higher ablation yield. This points out the importance of the energy deposition per unit time in ablating material from the target.

2.5. Ablation products.

At fluence levels below the threshold for etching of PMMA or polyimide, the ejection of diatomic species such as C\textsubscript{2} and CN has been observed by laser-induced fluorescence\textsuperscript{2}. Peak velocities were as large as $6 \times 10^5$ to $7 \times 10^5$ cm.s\textsuperscript{-1}. Atoms (C) and ions (C\textsuperscript{+}) were also seen. CH has been observed in emission from PMMA ablated at 193 nm.

The products of UV laser ablation have been analysed for a few polymers, in every instance, there appears to be a diversity of products ranging from atoms and diatomics to small polyatomic molecules and small fragments of the polymer.

The product composition is also wavelength-dependent.

From PMMA, of initial number-average molecular weight $M_n=10^6$, the products are:

- at 193 nm: oxides of carbon, MMA (the monomer) and low molecular weight ($M_n < 1500$) fragments of the polymer,
- at 248 nm: the principal product is a low molecular weight fraction ($M_n = 2500$) of the polymer.

There is a difference in the translational temperatures between a polyatomic product and a transient diatomic product from the same polymer, which suggests that they may be formed by different reaction paths\textsuperscript{2}.

Garrison et al.\textsuperscript{16} studied the velocity distributions of molecules ejected in laser ablation. They proposed an analytical expression based on the Maxwell-Boltzmann distribution.
imposed on a stream velocity modified to account for a range of stream velocities in the ejected plume. The simulation clearly showed that the dynamics of material ablation provide different ejection conditions for molecules, depending upon after their original depth in the substrate. Moreover, there are collisions in the plume that tend to accelerate the motion of the molecules that ablate early, and consequently, slow down the molecules near the end. For the entire depth of material, there is nearly a linear dependence of the mean axial velocity on the initial position under the surface. The radial velocities of ejected material have no significant correlation with the initial position under the surface. It is associated with the thermal motion of the ejected plume. The final temperature of the ejected plume results from the fast cooling of the ejected material due to an explosive matrix disintegration in the ablation process and a slower gradual cooling during the plume expansion.

2.6. Effect of debris formation.

Singleton et al.\textsuperscript{17} studied the importance of the debris on cone formation as a function of laser fluence, optical pulse duration and cut diameter, for polyimide and polyethylene, at $\lambda = 308$ and 222 nm. The formation of conical shaped structures was observed in the crater after ablation; this phenomenon has been related to the presence of impurities in the polymer; they could not be ablated at low fluences and acted as a screen to prevent cutting of the polymer below the impurity site. These cones were in great abundance for cuts made near the ablation threshold, but could be essentially eliminated at higher fluences. However, Singleton et al. also showed that the debris width that corresponded to no cone formation increases with the size of cut. Since the debris width was increased by raising the fluence, this implies that higher fluences were required to totally remove the cone formations from large cuts. This observation, combined with the fact that the debris originating from within the cut always fell within a well-defined debris width and that the debris width shrunk to zero near the ablation threshold, was consistent with the cones being the result of the screening effect produced by the agglomeration of debris.
products within the cut diameter which could not be ablated any further and which could not be ejected from the cut region.
Thus, cone formation is due to ablated debris and not to impurities in the polymer. It should be then more difficult to remove cones from deep cuts (cut depth > cut diameter) since debris will be increasingly likely to hit the side walls and not be removed from the cut site.

2.7 Sample surface after ablation.

Short pulses of far-UV radiation (e.g., 193 nm) have been observed to ablate organic material cleanly\(^\text{18}\), the sample exhibiting a precisely defined pit. For longer wavelength radiations, visible or infrared light, damaged samples were generally observed.
A study of the ablatives photodecomposition dependence on the laser wavelength, the laser fluence and sample properties\(^\text{3}\), demonstrated that the 193 nm laser wavelength was not unique in its ability to produce good etching (smooth, with no flow of boundaries and with reasonable etch rates) of polyimide; indeed, the 248 and 351 nm laser wavelengths could do so as well, provided a sufficiently high laser fluence was used.

2.8. Doping.

Ablation is initiated by the absorption of laser light, and therefore the etch depth per pulse (etch rate) depends upon the absorbance of the polymer substrates. It was found that ablation could be achieved by doping a certain amount of light absorbing species into polymer films, even if the films did not absorb the laser photons.
In one investigation\(^\text{2}\), it was found that the introduction of acridine, a small molecule (\(M_w=179\)), in a concentration of 1 to 8% by weight into PMMA progressively reduced the threshold for ablation at 248 nm and also sensitised it to laser etching at 308 nm.
Studies on dopant-induced laser ablation were carried out for PMMA, poly(dimethyl glutarimide) and chlorinated poly(methylstyrene) doped with pyrene, benzophenone, 4-amino-benzoylhydrazide and 2-(2'-hydroxy-3',5'-diisopentyl-phenyl) benzotriazole.

The use of dopant led to the following observations:

• the ablation threshold decreases with an increasing dopant concentration,
• optimal conditions exist for generating clean and smooth etching:
  - at low dopant concentration, the etched surface is rough,
  - at high dopant concentration, clean and smooth etch patterns are obtained at a relatively low fluence.

Pyrene (Py) is a typical dopant used in such experiments\textsuperscript{19}. Py and its derivatives form an excimer in concentrated solution and molecular assemblies. It was found that the aggregated state of Py or 1-ethylpyrene (Epy), in the vicinity of a polymer/substrate interface, was different from that in the bulk of polymer film; and that the intensity ratio of the excimer fluorescence to the monomer one decreased with the number of laser shots and with increasing laser fluence. These results indicated that the change of the aggregated state of Epy proceeded with increasing the number of laser shots and that a high fluence led to a larger change compared with low fluence. Also, aggregated states of Epy were affected by the laser ablation process in a region about 20 \textmu m around the ablated area. Since the excitation energy could not migrate as far as 20 \textmu m, another effect must have caused this change of Epy aggregation. When materials were ablated by the laser, the fast thermal and volume expansion were considered to occur simultaneously with explosive desorption of the ablated mass. These expansions were transmitted through the PMMA matrix to unirradiated and unablated areas and possibly led to a different distribution of the dopant and to changes in the physicochemical properties of PMMA.

The photoetching characteristics of PMMA film at 308 nm, doped with different molecules, have been investigated\textsuperscript{29}. The study was carried out systematically varying the dopant concentration and the laser fluence. Pyrene was added to the polymer at different concentrations to make the ablation of the film possible. When the pyrene concentration was raised, the threshold fluence value decreased. That is, as the absorption coefficient of the medium increased, more photon energy was absorbed near
the surface region and consequently the threshold for ablation was reduced. It was observed that for a given laser fluence, the increase of dopant resulted in an increase of etch depth until it reached a maximum and then declined at higher dopant concentrations.

2.9 Non representative subsampling.

A serious problem associated with LA-ICP-MS is non-representative subsampling or fractionation. This phenomenon enhances or reduces relative analyte signal intensities and sensitivities.

- Fractionation during a phase change is most common
  Volatile elements and compounds are particularly prone to fractionation and it was shown that the use of low fluence, near the ablation threshold, can produce significant segregation and fractional ablation. These effects are enhanced by repetitive ablation of a single area of the sample. In practice, it was found that the extent of fractionation was reduced at higher laser fluence (10 - 100 J cm\(^{-2}\)). A reduced number of laser pulses per unit area also reduces fractionation, but this may require a large sample surface area for extended analysis
- Fractionation also occurs during transport.
  This problem is discussed in paragraph 2.10 that follows.

Cromwell suggested that for metal alloys, the extent of fractionation could be qualitatively predicted from the binary-phase diagram of the corresponding analyte matrix\(^21\). The energy deposition into the sample is governed by the reflectivity and absorbance of the material at the laser wavelength, but can also be influenced by plasma absorption above the surface. The heat conduction away from the surface is dominated by the thermal conductivity of the material, especially in the case of metals; for materials such as polymers or glasses, the thermal conductivity is lower.

When the laser beam is applied on the material, the surface reaches the melting point of the solid; a melt front starts to move in the sample. For high enough laser fluence, the
surface temperature exceeds the boiling point and a second phase front will start to propagate. Violent eruption of material occurs because of the high transient pressures generated by material expansion during phase changes. After the laser pulse, the material will start to cool and the phase fronts will move back to the new surface as the material re-solidifies\textsuperscript{21}. Examination of solid-liquid binary phase diagrams for homogeneous materials showed that some systems of elements are immiscible above certain temperature. In some cases, an element will segregate from a solid mixture into a pure liquid when the temperature rises above the melting point of the element. During low fluence ablation, when a small amount of sample material is melted, a relative large volume of the bulk can be above the melting point of the segregated elements or species. The segregated element can form a pool of molten material below the melt front and may erupt like a volcano because of the pressures associated with the phase change. This phenomenon leads to an enrichment of that element in the ablated material and consequently increases its signal\textsuperscript{21}.

Results were obtained that were higher than the theory predicted; a possible explanation for this was that non-equilibrium effects at the solid/liquid interface cause increased enrichment within the near surface of the material during solidification by a process analogous to "zone refinement". In zone refinement, a melt front is repeatedly propagated through a bar of metal with the result that impurities are segregated to the end of the bar. As the melt propagates, elements which thermodynamically prefer the liquid phase tend to stay in this phase\textsuperscript{21}.

Segregation occurs when the melt front is faster than the time required to reach the equilibrium between solid and liquid. In laser ablation, segregation would occur during solidification, leading to an enrichment of the near-surface layer in certain elements\textsuperscript{21}.

In the case of metal alloys, a complication to this model arises, due to the speed of the melt front; this additional behaviour which is quite significant is called "solute trapping". For materials such as polymers, glasses, etc., whose thermal diffusivities are lower, and hence have slower melt fronts than metals, solute trapping will be less important, and segregation and fractional ablation may be more prevalent\textsuperscript{21}.

As the laser fluence increases, the total amount of material ablated increases and the ablation depth approaches the melt depth. There are likely to be regions where element segregation and enrichment occur, but their relative contributions to the total amount of
material ablated decrease as the fluence increases. Enhanced segregation due to repetitive melt front propagation also is minimised because most molten material is ejected and does not solidify in the ablation zone. Thus at higher laser fluence (10 - 100 J cm$^{-2}$), the ablated material is likely to be more representative of the bulk composition of the sample\textsuperscript{21}.

On the other hand, if the laser fluence is too high, vaporisation of some species becomes important and they will be discriminated against during transport\textsuperscript{21}.

At present, except perhaps for high purity metals or simple metal alloys, the interpretation of fractionation by binary-phase diagrams is not practical. A possible aim of future work would be to develop a quantitative model of fractionation and obtain correction factors to improve the accuracy of semi quantitative analysis\textsuperscript{21}.

Longerich et al.\textsuperscript{22} studied the behaviour of fifty-three elements during laser ablation and ICP-MS detection of NIST glass reference materials. It was found that the elements fell into five distinct clusters and that the elements within these clusters correlate well with each other.

The clusters were the following:

- **Au cluster.** The Au signal did not correlate well with any of the fifty-three elements studied. The high ionisation potential of Au, which leads to a low fractional ionisation in the plasma may contribute to the anomalous behaviour of this element. Unfortunately, the other precious metals were absent from the material studied.

- **Chalcophile cluster.** Ten chalcophile elements (Ag, Te, Bi, Tl, Ga, Sb, In, Ge, As and Pb) formed a distinct cluster.

- **Lithophile cluster.** The largest cluster contained thirty-eight elements, most of which could be described as lithophile in character. The alkaline earth elements (Ca, Sr and Ba), the rare earths (Sc, Y, La to Lu), the high field strength elements (Zr, Hf, Nb, Ta) and the actinide (U), were correlated very closely. Also included in this group were Mn, Cs, V and Si. Less strongly correlated were the light elements Mg and Be, which might have
been affected by their low mass. Ti, Cr, Rb, Co, W, Mo, Sn and Re were more loosely correlated with the core elements of this group.

- B cluster. B had a significantly dissimilar ablation behaviour to the other lithophile elements.
- Zn, Cu and Cd cluster. These three elements, while appearing in the same cluster, were only very weakly correlated. However, their closeness in periodic properties support their grouping.

While the elemental or crystal parameters which vary in a periodic relationship for the elements must be controlling their behaviour, no single parameter, such as ionisation potential, electronegativity, etc, provided a complete explanation of the groupings. Rather, the elements appeared to be correlated accordingly to Goldschmidt's geochemical classification of the elements - lithophile, siderophile and chalcophile groupings\textsuperscript{2}. These result from a combination of elemental properties that distribute elements within a three phase system consisting of silicate, metallic Fe, and sulphide liquid.

Similar results to these were observed from several natural rock-forming minerals, confirming that fractionation phenomena were substantially independent of the sample matrix.

Under carefully controlled conditions, it is possible to minimise the fractionation. However, it was suggested that internal standard should be chosen from the cluster enclosing the elements of interest.

Jeffries et al.\textsuperscript{23} studied the behaviour of elements during the ablation of the silicate glass reference material NIST SRM 610 with IR and UV lasers. It was found for both IR and UV conditions that the effects of laser ablation extended far beyond the diameter of the laser beam and the resulting crater; the effect being greater with the IR laser. Indeed, on an ablation traverse with a crater diameter of 40 \textmu m, the fractionation observed on Pb disappeared if the interval between the analysis points exceeded 150 \textmu m for the UV laser, but fractionation was still observable for an interval of 250 \textmu m with the IR laser. Whilst local temperatures of the sample could cause elemental fractionation, it was not
clear to what extent re-sampling deposited material around the crater affected precision and contributed to fractionation.

During UV and IR ablation, two groups of elements were distinguished in relation to their correlation with Si. The alkali, alkaline earth metals, some low z transition metals and large ion lithophile elements showed an increasing fractionation trend with respect to Si, whereas the REEs and the high field strength elements showed a decreasing fractionation trend.

During IR ablation, it was also found that there was a linear relationship between the ionic radius of REEs and their degree of fractionation relative to Si, the fractionation increasing with the ionic radius.

For UV ablation, active focusing of the laser beam onto the target was found to improve analytical precision. However, no fractionation trends were observed for either the active focus or the normal focus ablation.

The influence of three wavelengths (1064, 532 and 266 nm) was studied on the fractionation effect on elements contained in glass as a function of the focus point of the laser onto the target (z) (or irradiance). The eleven elements studied were Na, Al, Fe, Ni, Zr, Ru, Ba, La, Ce and Nd. The elemental response as a function of z could be classed into two groups of behaviour when 532 and 1064 nm ablation was used. The first group included Ba, Ce, Nd, La, Zr and Al, the signals obtained for these elements was independent of the laser focus. The second group included Si, Ru, Ni, Na and Fe which were dependent of the laser focus. The observed elemental bias was related to the elements' oxide melting points. It was concluded that 1064 and 532 nm ablation produced local surface heating of the sample, which volatilised the more volatile species and/or produced large particles that, instead of being fully digested in the ICP, were partially dissociated and thermally extracted for the more volatile species.

Laser ablation at 266 nm did not exhibit elemental fractionation as a function of irradiance. However, when too high an energy was used, too much sample was introduced in the ICP-MS. The excess sample loading gave rise to increased space charge effect within the interface of the spectrometer, leading to mass biased signal suppression. Under these conditions, the signals of the lighter mass isotopes are suppressed more than heavier isotopes because they have less momentum and their paths
through the mass spectrometer are affected more by these space charge effects. Other consequences of overloading the plasma were clogged cones, and signal saturation.

A study on elemental fractionation conducted with an ArF laser on NIST 612 showed a change in analyte behaviour as the crater became deeper. A progressive volatile element enrichment was observed at shallow hole depth followed by an enrichment in refractory elements as the ablation pit deepened further. The element fractionation behaviour was explained as a reflection of a change in the ablation process from photothermal dominated to plasma dominated ablation.

2.10. Entrainment and transport.

Ideally, the ablation cell and transfer tube should entrain and transport particles over a size distribution broader than that produced in the primary source. However, it appears that the cell and tube need only to transport particles up to some size limit, corresponding to the fall-off in the response of the secondary source. Indeed, it is preferable to modify the primary source distribution to favour smaller particles by, for example, using a short-duration laser pulse, rather than overloading the plasma or depositing out large particles with consequent reduction in transport efficiency and possible poor transient response and memory effects.

Arrowsmith and Hugues developed a cell for fast transfer of ablated material with short signal decay time to allow rapid sampling at different locations in samples of arbitrary size and shape.

This ablation system consisted of two parts:

- an outer box which was gas tight and filled with plasma support gas at ~ 4 torr above atmospheric pressure to provide a pressure gradient along the transfer tube for transport of ablated material into the ICP. The purposes of the excess inlet flow and the vent were to flow clean gas in and around the cell and to provide an alternative outlet for any ablated material that escapes the cell.
A small ablation cell that enclosed the plume of material but did not form a seal to the sample surface. The inlet gas flowed in through an annulus to form a symmetric gas sheath around the base of the cell. The width of the annulus at the base of the cell was $\sim 1$ mm and the inner diameter of the inner tube was 10 mm to avoid deposition on the walls.

A useful feature of this design is that only an initial purge of the cell and transfer tube is required before the ICP is started; and samples can be changed rapidly without extinguishing the ICP as the sheath of inlet gas around the base of the cell excludes air. A dependence of the signal upon the transfer gas flow rate was observed. At low flow, the signal increased with flow, indicating improved transport efficiency. At high flow, the signal decreased, possibly due to cooling of the secondary source, resulting in reduced vaporisation and ionisation efficiency.

The entrainment efficiency was determined to be 92%, with good agreement between different ablation periods. Hence, only 8% of the ablated particles escaped to the outer box and were not detected. Moreover, 50% of ablated material was more likely to be lost by gravitational deposition within the transfer tube, due to the primary source distribution having a significant mass fraction within particles having a diameter greater than 5 $\mu$m.

These problems were reduced when the ablation cell and transfer tube had a sufficiently broad transfer function to overlap the largest particle sizes produced by the primary source. For a fixed transfer gas flow rate, this condition was approached with a small diameter cell and transfer tube to give high gas flow velocities that minimised gravitational deposition.


3.1. First considerations.

The 193 nm laser wavelength is not unique in its ability to produce good etching and that the 248 and 351 nm laser wavelengths can do so as well. This suggests, then, that
the absorbed photon energy per unit volume $\alpha F$ - where $\alpha$ is the linear absorption coefficient and $F$ the laser fluence - is an important parameter that controls the laser etching process, rather than the laser fluence itself.\(^8\)

Thermal coupling and etch rate measurements\(^3\) on polyethylene terephthalate and polyimide films irradiated at excimer wavelengths of 193, 248 and 308 nm suggested the existence of a threshold fluence ($F_T$). Below $\alpha F_T$, thermal energy balance was observed and the ablation of a material absorbing an energy density $> \alpha F_T$, was rapid, carrying away excess energy $A(F-F_T)$. Then for sufficiently thick targets, the energy remaining in nonablated film was $\sim A F_T$ and was constant.

3.2. Microscopic models by Srinivasan and Garrison

In 1984, Garrison and Srinivasan attempted to explain ablation processes by microscopic models for photochemical and thermal processes\(^{18}\).

**Photochemical model: 193 nm**\(^{18}\) (Fig.3). The absorption of UV radiation by organic molecules was known to involve an electronic transition to a higher state. The following processes could then occur:

- if the transition leads to a level above the dissociation limit, then the molecule can dissociate almost immediately,
- there may also be a curve crossing to a repulsive state which again leads to dissociation,
- an intersystem crossing can occur, by which the molecule ends up in the ground state.

In the first two cases, the excitation at 193 nm produced a change in volume occupied by monomers. There is a repulsive interaction among the reacted monomers or new photochemical products, and between these new species and the remaining sample; consequently, all of the photochemically reacted species will eventually ablate.
The predictions of the photochemical model are as follows:

- the reacted material ablates without melting the remainder of the sample,
- the average perpendicular velocity of the ablated material is 1000-2000 m.s\(^{-1}\),
- the angular spread is within 25-30 degrees of normal and peaked in the direction normal to the surface,
- the material ablates layer by layer.

Fig 3  Photochemical Model  Reproduced from B.J Garrison, R Srinivasan, J.Appl Phys, 1985, 57, 8, 2909.

*Thermal model: 532 nm (Fig.4).*

The energy available is less than chemical bond strength. One photon cannot force the molecule to undergo an electronic transition such that a bond is broken. It seems plausible that the photon energy excites vibrations within the molecules. The ablation of the material corresponds to an evaporation rather than volume explosion. For evaporation, several quanta of laser energy are required in one bond so that it might break. During the time that the energy is accumulating in this bond, other regions of the sample are becoming vibrationally excited and possibly melted. Moreover, the velocity vector of each irradiated unit is randomly oriented. During this time of collisions between the irradiated or energised units and surrounding solid occur, energy is transferred to the solid. Some of the monomers may lose sufficient energy such that they are trapped in the solid and do not ablate.
The predictions of the thermal model are as follows:

- the remaining sample is distorted and melted,
- the angular spread is twice as large as that from the photochemical model,
- the material does not necessarily ablate layer by layer.

![Thermal Model](image)

Fig. 4: Thermal Model. Reproduced from B J Garrison, R. Srinivasan, J Appl Phys, 1985, 57, 8, 2909

3.3. The dynamic model of Keyes, Clarke and Isner. Theory of photoablative cutting\(^2\).

The theory of photoablation was further developed in 1985, by Keyes, Clarke and Isner\(^2\). The important variable of their theory is the density of unbroken bonds. When a bond breaks, any excess energy will be transferred to the resulting fragments of the original chain. If these fragments remain attached to the surface of the material for \(t > t_{\text{characteristic}}\), the energy may flow into the interior as heat, if \(t < t_{\text{characteristic}}\) the fragments will carry the energy with them and no heating occurs. Small fragments leave
more quickly than large fragments; then, the condition for no heating seems to be that a 
chain is broken down to sufficiently small n-mers before \( t_{\text{characteristic}} \).

Two conclusions derive from this model:

First, a low-intensity excimer laser should heat the material being cut. For low intensity, 
the time between bond breakage will be long, and the excess energy from the initial cuts 
of a particular chain will have time to become heat. A threshold intensity for 
photoablation should exist.

Second, the only possible source of heat in the model is the “excess” photon energy with 
respect to the bond energy. Thus a laser with photons matched perfectly to the bond 
energy should cut non-thermally.

3.4. The dynamic model of Sutcliffe and Srinivasan[28].

In 1986, Sutcliffe and Srinivasan proposed a novel dynamic model, which aimed at 
relating the time evolution of the ablation process to experimental parameters[28]. 
Fragmentation products such as atoms, diatomics, small molecules and small fragments 
of the polymer chain were all observed. The ablation process was believed to be a 
volume explosion that would produce a significant fraction of small molecules. 
The model generally accepts that the absorption of UV photons results in electronic 
excitation. Then, several processes can occur: photofragmentation, leading to stable 
photoproducts or relaxation back to the reactant ground state which would degrade the 
energy without engendering any photodecomposition.

The basic new idea of the dynamic model was the notion of an absorbed photon flux 
threshold below which photofragmentation was negligible. Above this threshold level, 
relaxation back to the ground state reached a steady-state and photofragmentation might 
then successfully compete.

Two new constants are introduced:
• \( \pi \), the flux, defined as the number of photons absorbed per time and per unit volume, it is proportional to the time-dependent laser intensity, at a given depth \( x \):

\[
\pi(t,x) = I(t,x) (\alpha \lambda /hc)
\]

all absorbed quanta above \( \pi_T \) are available for efficient fragmentation, where \( \pi_T \) is the flux threshold. \( \pi_T \) defines the concentration of photons absorbed per unit time required to overcome the various relaxation paths.

• \( \rho \), the time-dependent effective concentration of absorbed photons above threshold at depth \( x \):

\[
\rho(t,x) = \int_0^T \theta \left[ \pi(t',x) - \pi_T \right] dt
\]

\[
\theta(z) = \begin{cases} 
0, & \text{if } z < 0 \\
1, & \text{if } z \geq 0
\end{cases}
\]

In order to ablate spontaneously, the irradiated sample must reach a critical density of broken bonds corresponding to a threshold level \( \rho_T \) for the effective concentration of absorbed photons. Once the ablation condition is reached, \( \rho(t,x) \geq \rho_T \), then the internal stress due to the change in volume occupied by the fragments is sufficient to drive them out of the bulk.

The flux threshold \( \pi_T \) and the ablation condition \( \rho_T \) are constants, characterising a particular polymer, and do not depend upon irradiation conditions.

In contrast to previously accepted ideas on UV laser ablation, the key role played by the pulse time profile was considered, the fluence of the incoming laser beam not being the only important parameter.

Below the flux threshold, the dynamic model assumed a conversion of the total amount of absorbed energy into heat. With increasing fluence, the thermal component reaches an asymptotic value. This thermal contribution is given by integrating the intensity below the threshold level over the whole laser pulse duration.
This model envisages a possible shielding of the incoming beam by the ejected fragments. The photoproducts accumulate below the “moving interface” within each laser pulse and also from pulse to pulse. The ablation condition is therefore reached progressively and possibly only after several laser shots. The bulk encountered by the etch beam is thus constantly changing its properties according to its photochemical history. Only a fraction of the very first laser pulse sees a virgin bulk sample and is, in this sense, unique. The following simplification was made: as long as the ablation condition was not reached, the change in absorption of a layer below the interface caused by the breakdown of long chain molecules was neglected.

A major new feature introduced with the dynamic model was certainly the crucial importance of the pulse width. Irradiating a polymer with a continuous light source merely heats the surface because the intensity threshold is never reached. The concept of a gradual chemical change below the interface explains the dependence of the etch rate on the number of laser pulses.

This dynamic model was applied to the photodecomposition of PMMA and polyimide. These two polymers are dissimilar in their chemical compositions and spectroscopic properties, and were well suited to evaluate the performance of the model.

The non-linearity of the etch curve was well accounted for, in contrast to the usual treatment predicting a linear relationship between the etch depth and the logarithm of the fluence. Near the fluence threshold, the behaviour of the curve was very sensitive to \( \pi_T \), whereas \( \rho_T \) prevailed at higher fluences.

In the case of the photodecomposition of PMMA, the experimental results followed the model, whereas, in the study on polyimide, the model did not work, except at fluences just above threshold.
4. Conclusion.

Laser-material interactions involve numerous variables related to the laser, the sample and the atmosphere above the sample. Among these are the wavelength, the energy, the pulse width and the spatial form of the laser beam, and, the chemical and physical properties of the sample such as the heat capacity, the thermal conductivity and the absorption characteristics. The nature of the surrounding gas adds to the complexity of the ablation mechanism as photons from the laser beam can be absorbed by inverse Bremsstrahlung process. More or less complex plasmas can form above the sample, acting partially as shields as well as being partly responsible for removal of sample material.

The ablation process is so complex that many models have been developed to describe it, but each only pertains to a separate component of the interaction and is applicable only under limited conditions. Practically, useful information can be, however, obtained from specific case studies where the influence of key parameters is defined by empirical investigation.


Chapter 6:

Investigation on
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1. Introduction.

A new method of calibration has been investigated for the quantitative analysis of solid samples using LA-ICP-MS. It involved the use of aqueous standard solutions whose absorption characteristics were modified by the addition of a chromophore, in order to obtain the desired degree of coupling with the laser energy. Initial work on this project employed poly(sodium 4-styrene sulfonate) as an additive in standard solutions to be used with an excimer laser, emitting at 248 nm. Work was done on NIST glass and the method of calibration was applied to bone samples from patients suffering from osteoporosis.

However, further work was needed to find new chromophores for other wavelengths, e.g., 266 nm, to improve the modified standard solutions, to develop a systematic method of use for the standards, to validate the results obtained and to investigate the use of appropriate internal standards (i.e., the minor isotope of a major element of the sample matrix).

2. Selection of chromophores.

A conventional standard solution, mainly composed of water and one or two per cent of nitric acid, does not absorb most of the laser wavelengths which are commonly used for laser ablation. An exception is the excimer line of the ArF laser, emitting at 193 nm, which is significantly absorbed by nitric acid. Therefore, the addition of a chromophore to the standard solution is indispensable to make a selected laser beam couple with the liquid standard and ablate it.

Initial trials to produce reliable modified standard solutions, using various chromophores, defined appropriate criteria for the selection of the chromophore. It would seem logical that an ideal chromophore should be resistant to photo-
degradation, but as the results presented in the next section show, this is not the critical factor.

More importantly the ideal chromophore should have the following characteristics.

- absorbs strongly at the lasing wavelength used for ablation,
- be soluble in one to two per cent of nitric acid,
- does not precipitate when in contact with the analytes,
- be non-toxic.

A suitable chromophore combining these four characteristics was selected for each lasing wavelength. Our efforts were focused on producing standard solutions for UV laser ablation as this results in a more efficient ablation of solid materials than IR ablation and is less prone to fractionation\textsuperscript{27}. The chromophores are listed below with their corresponding specific absorptivity and maximum solubility in acid solution.

For 193 nm excimer laser, two chromophores were found

- nitric acid
  \[ \varepsilon_{193} = 31 \text{ g}^{-1} \text{ cm}^{-1} \]
  used at 1~2\% in solution.

- poly(sodium 4-styrene sulfonate) (Fig. 1a)
  \[ \varepsilon_{193} = 851 \text{ g}^{-1} \text{ cm}^{-1} \]
  maximum solubility in acid solution 4 g l\(^{-1}\)

![Fig 1a: poly(sodium 4-styrene sulfonate)](image-url)
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For 248 nm excimer laser:

- m-hydroxybenzoic acid (HBA) (Fig 1b)
  \( \varepsilon_{248} = 30 \, \text{l g}^{-1} \, \text{cm}^{-1} \)
  maximum solubility in acid solution: 3 g l\(^{-1}\)

![Figure 1b: m-hydroxybenzoic acid](image)

For 266 nm frequency quadrupled Nd:YAG laser:

- 2-thiobarbituric acid (TBA) (Fig 1c)
  \( \varepsilon_{266} = 80 \, \text{l g}^{-1} \, \text{cm}^{-1} \)
  maximum solubility in acid solution: 4 g l\(^{-1}\)

![Figure 1c: 2-thiobarbituric acid](image)

3. Stability of the signal from the ablation of a modified standard solution.

The chromophores selected for 248 and 266 nm were found to be unstable under UV radiation from a mercury pen lamp (257 nm). The absorbance of the standard solutions varied due to the formation of photo-products. This resulted in a slight
increase of absorbance at 248 nm for a HBA solution and a decrease of absorbance at 266 nm for a TBA solution. Figs.2a-2b and Figs.3a-3b show the evolution of absorption of modified solutions (respectively 0.04 g l⁻¹ of m-hydroxybenzoic acid and 0.006 g l⁻¹ of 2-thiobarbituric acid in 2% nitric acid) exposed to a mercury lamp.

Fig.2a: Influence of the exposure of an aqueous solution containing 0.04 g.l⁻¹ of HBA to a Hg pen lamp during 0, 1, 1.5 and 2 minutes.

Fig.2b: Increase in the absorption at 248 nm of an aqueous solution containing 0.04 g.l⁻¹ of HBA exposed to a Hg pen lamp.
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Fig. 3a: Influence of the exposure of an aqueous solution containing 0.006 g.l⁻¹ of TBA to a Hg pen lamp during 0, 1, 1.5 and 2 minutes.

Fig. 3b: Decrease in the absorption at 266 nm of an aqueous solution containing 0.006 g.l⁻¹ of TBA exposed to a Hg pen lamp.
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Fig. 3a: Influence of the exposure of an aqueous solution containing 0.006 g.l\(^{-1}\) of TBA to a Hg pen lamp during 0, 1, 1.5 and 2 minutes.

Fig. 3b: Decrease in the absorption at 248 nm of an aqueous solution containing 0.006 g.l\(^{-1}\) of TBA exposed to a Hg pen lamp.
Fig. 4a and Fig. 4b show the signal obtained by laser ablation of modified standard solutions:

- for 248 nm: 0.4 g l$^{-1}$ of HBA and Mg, Al, Cr, Co, Zn, Sb and Pb at 5 μg g$^{-1}$ in 2% nitric acid, ablated at 75 mJ and 10 Hz,
- for 266 nm: 3 g l$^{-1}$ of TBA and Fe, Mo and W at 10 μg g$^{-1}$ in 2% nitric acid, ablated at 580 volts and 10 Hz.

Fig. 4a: Signal stability of a modified standard solution containing 0.4 g l$^{-1}$ of HBA and Mg, Al, Cr, Co, Zn, Sb and Pb at 5 μg g$^{-1}$ in 2% nitric acid, ablated at 248 nm, 75 mJ and 10 Hz.
Fig. 4b: Signal stability of a modified standard solution containing 3.5 g l⁻¹ of TBA and Fe, Mo and W at 10 µg g⁻¹ in 2% nitric acid, ablated at 266 nm, 580 volts and 10 Hz.

These figures show that the photo-stability of the chromophore is not critical to obtaining a stable ablation signal. There are two principal reasons for this; first, most of the volume of aqueous standard strongly irradiated by the laser beam is efficiently ablated and therefore removed, unless the energy threshold value has not been reached; second, the liquid state of the standard offers a renewable surface of fresh solution during the ablation event. Further to these points, making the reservoir volume (typically 1 ml) very much larger than the ablation volume ensures that a large excess of fresh chromophore is always present. Thus the chromophore used to modify the absorbance of the solution does not have to be photo-stable to yield stable ablation over a long period of time.
Initial work on the project involved the use of poly(sodium 4-styrene sulfonate) in modified standard solutions for ablation at 248 nm because of the stability of its absorbance at this wavelength. Indeed, when a solution of this additive was exposed to UV radiation, the evolution of its absorbance showed a stable cross-over point around 248 nm. It was therefore thought to be an ideal chromophore to use at this wavelength. Disadvantage however were that its absorbance at 248 nm was poor and its solubility in acid solution low, and these limited its use. Given the previous observations made for m-hydroxybenzoic acid (HBA) and 2-thiobarbituric acid (TBA), poly(sodium 4-styrene sulfonate) can also be expected to be an efficient chromophore at 193 nm where it has a high specific absorptivity (85 l g⁻¹ cm⁻¹).


Once a chromophore has been selected to be used to modify standard solutions for a particular laser, its concentration in solution has to be determined. For this purpose, the effect of the laser energy on the ablation yield was investigated for modified standards with different concentrations of additive at 248 nm and 266 nm.

Fig. 5a and Fig. 5b show the effect of the energy of the laser beam respectively on:

- 248 nm: HBA at 0.17, 0.45 and 0.6 g l⁻¹ with 1 µg g⁻¹ of Co in 2% nitric acid ablated at 15, 20, 25, 30, 40 and 50 mJ and 10 Hz.
- 266 nm: TBA at 1, 1.8, 2.6 and 3 g l⁻¹ with 5 µg g⁻¹ of Co in 2% nitric acid ablated at 570, 580, 590, 600, 610, 620, 630, 640 and 650 volts and 10 Hz.

The addition of chromophore to the standard solutions reduces the threshold fluence value; the threshold fluence value being the fluence value at which a significant ablation begins to occur. This phenomenon has also been observed in experiments involving the doping of solid materials in order to improve their ablation at selected wavelengths. Using the response curve (Fig. 5a or 5b), modified standard solutions suitable for the analysis of a given sample type can be prepared.
Fig. 5a: Influence of the laser energy on the ablation yield of modified standard solutions at 248 nm, prepared with 1 μg/g of Co and different chromophore concentrations.
Fig. 5b: Influence of the laser energy on the ablation yield of modified standard solutions at 266 nm, prepared with 5 μg/g of Co and different chromophore concentrations.
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Ablation of the sample under different conditions (laser energy, pulse frequency and beam size)

Fractionation

Yes

No

Select chromophore concentration to be added to the standard solution for efficient ablation at the selected energy

Analysis

Fig. 6: Scheme for the preparation of modified standard solutions for the analysis of a given sample.
The selective addition of the chromophore offers the user the freedom to prepare standards that give a signal of the desired amplitude, when ablated with a fluence pre-selected to be optimal for the ablation of the sample. Therefore, the analyst has to first determine the laser energy that is optimal to ablate the sample. Knowing this energy value, it is possible to determine the concentration of chromophore to be added to the standard solution using figures 5a or 5b.

For example, for the analysis of a sample requiring a relatively low laser fluence to produce an efficient ablation, a relatively high chromophore concentration will be selected in order to decrease the threshold fluence value and to obtain an efficient ablation (and hence an appropriate analyte count rate) of the standard solution. For a sample requiring a relatively high laser fluence to be ablated, a relatively low chromophore concentration will be selected to produce a significant ablation of the modified standard at the pre-selected laser energy. In this latter case, the use of a too high chromophore concentration was found to produce a violent explosive ablation event yielding large aerosol droplets that were visibly deposited onto the ablation chamber walls.

From these observations, a systematic approach for the use of the modified standard solutions can be derived as shown in Fig.6.

5. Fractionation.

Initial investigations were made on the modified standard solution to see if the response of the analytes relative to the internal standard was varying with the concentration of additive in the standard and with the laser energy used for ablation. For modified standard solutions containing different concentrations of additive, ablated at different laser voltages, the ratios “analyte CPS / internal standard CPS” were observed.
Fig. 7a: Al CPS / Co CPS ratios for modified standard solutions with different concentrations of additive, ablated at different laser energies, at 248 nm.
Fig 7b: Cr CPS / Co CPS ratios for modified standard solutions with different concentrations of additive, ablated at different laser energies, at 248 nm.
Fig. 7c: Zn CPS / Co CPS ratios for modified standard solutions with different concentrations of additive, ablated at different laser energies, at 248 nm.
Fig. 7d: Sb CPS / Co CPS ratios for modified standard solutions with different concentrations of additive, ablated at different laser energies, at 248 nm.
Fig. 7e: Pb CPS / Co CPS ratios for modified standard solutions with different concentrations of additive, ablated at different laser energies, at 248 nm.
Fig. 8: Co CPS / C CPS ratios for modified standard solutions with different concentrations of additive, ablated at different voltages, at 266 nm.
For the LA-ICP-MS system ablating at 248 nm, the behaviours of elements selected across the mass range were compared with Co, which was the element selected as internal standard. Modified standard solutions containing 0.17, 0.45 and 0.6 g l^{-1} of m-hydroxybenzoic acid, with 5 μg g^{-1} of Mg, Al, Cr, Co, Zn, Sb and Pb, were ablated at 20, 25, 30, 40 and 50 mJ. The CPSs obtained for Mg, Al, Cr, Zn, Sb and Pb were ratioed to the ones obtained for Co. Results were plotted in Fig. 7a-7f. The CPS ratios obtained were directly comparable as all the modified standard solutions contained the same concentrations of elements. Error bars representing the noise of the two signals that were ratioed were included. For each concentration of additive selected, the amplitude of the error bars decreased as the laser energy increased. This was probably due to two reasons; firstly, the amplitude of the signal would increase as more material was ablated; secondly, the increase of energy may produce an ablation yielding a finer spray that would therefore be more efficiently transported. For each set of data, it was obvious that the ablation of the standard at the lowest laser energy resulted in a signal too noisy to be usable. Still, the value of the counts ratios obtained for the different modified standard solutions did not show any significant variation for the different laser energies and concentrations of additive used. Unfortunately, due to difficulties encountered with the excimer laser, no additional data were acquired for this experiment at 248 nm in order to confirm the latter observation with more precise data.

For the LA-ICP-MS system ablating at 266 nm, the behaviour of the analyte Co was compared with ^{13}C, which could be used as an internal standard when analysing polymers. Modified standard solutions containing 1, 1.8, 2.6 and 3 g l^{-1} of 2-thiobarbituric acid, with 5 μg g^{-1} of Co, were ablated at 600, 610, 620, 630, 640 and 650 volts. In order to compare results obtained from the different standard solutions, i.e., containing different concentrations of ^{13}C, the results were normalised to a ^{13}C concentration equal to one. The CPS obtained for Co and ^{13}C were ratioed. Results were plotted in Fig. 8. Modified standard solutions with a low concentration of additive and ablated at low laser voltages resulted in ^{13}C signals too small to be integrated. Error bars on the signal ratios were much less significant than previously. This probably indicates that the range of laser energy used was suitable for producing
an efficient ablation of the modified standard solutions prepared with the selected concentrations of additive. The data presented in Fig 8 show CPS ratios laying between 11 and 14 ± 2 for the different conditions used. Therefore the influence of the laser voltage and the additive concentration did not seem to produce any fractionation

6. Investigation of the ablation mechanism of the standard solutions.

6.1. Experiments.

To study the ablation mechanism of the modified standard solutions, solutions were prepared having different properties. The following experiments were carried out using the quadrupled frequency Nd YAG laser (266 nm)

The first experiment involved two standard solutions where the additive, 2-thiobarbituric acid, was in solution with two different solvents: H₂O and D₂O. The two solutions were made up at 3 g l⁻¹, giving the same absorption at 266 nm. They were ablated for one minute; the mass losses after ablation were compared. The mass losses due to the argon flow above the solution were monitored to allow the ablated mass to be calculated from the total (evaporation + ablation) mass loss.

A second experiment involved two different chromophores, absorbing at 266nm: 2-thiobarbituric acid (TBA) and 1,10-phenanthroline (PNT). The two solutions were made up in water to have the same absorption at 266nm (i.e.: 2.13 g l⁻¹ of TBA and 1.43 g l⁻¹ of PNT). As previously, the mass losses, after 45 seconds of ablation, were recorded and compared.

For all these experiments, each mass loss measurement was repeated ten times in order to apply to them statistical tests to check the validity of the results.
6.2 Results and discussion

The results of the H$_2$O - D$_2$O experiment are presented in Table 1. As the masses measured were of the order of a milligram, a two-tailed t-test was applied to the results to check their validity. It was found that there was a significant difference between the two means at the 99.9% confidence level. The mass loss due to ablation from the aqueous solution was 2.6 fold greater than from the deuterated solution.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>2-thiobarbituric acid</th>
<th>2-thiobarbituric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>H$_2$O</td>
<td>D$_2$O</td>
</tr>
<tr>
<td></td>
<td>Ar flow effect</td>
<td>Total mass loss</td>
</tr>
<tr>
<td>Average of mass loss (mg)</td>
<td>1.5</td>
<td>2.8</td>
</tr>
<tr>
<td>RSD (%) n=10</td>
<td>12.8</td>
<td>9.2</td>
</tr>
<tr>
<td>Mass loss due to ablation (mg)</td>
<td>1.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 1: Comparison of ablation yield of standard solutions with different solvents (H$_2$O and D$_2$O)

The process by which the energy absorbed by the chromophore is coupled into the water matrix is complex and could proceed by a variety of routes. However, the direct conversion of several electron volts of energy into translational motion of a single molecule is unlikely when that molecule is firmly embedded in the elastic water matrix$^{14}$. Whether the transfer route is via direct quenching, internal conversion or dissociation, the final step in the energy cascade is most likely to occur through a vibrational process. The experiment with D$_2$O seeks to verify this hypothesis. The physical properties of H$_2$O and D$_2$O are not very different. The boiling point$^{15}$ of D$_2$O is 101.4°C compared with 100°C for H$_2$O and similarly, the enthalpy of vaporisation is 169.9 kJ mol$^{-1}$ for H$_2$O and 174 kJ mol$^{-1}$ for D$_2$O. These data derive from the fact that
the O-H covalent bond is stronger in water than in D₂O, which in turn leads to a weaker H bond in H₂O compared with the equivalent bond in D₂O. However, these properties are insufficient to account for the differences found in the experiments. Such differences could only be accounted for if the initial energy transfer from the chromophore to the H₂O or D₂O matrix is resonantly coupled through a principal or overtone vibrational transition of the solvent. H₂O and D₂O have significantly different absorption band patterns in the IR. An example of this highly specific type of energy cascade has been described for the sensitizer [tetrakis(4-sulfonatophenyl)porphine] (TPPS) excited at 532 nm. In this case the triplet excited state of TPPS is quenched by O₂ which in turn is excited to its singlet state. The measurement of the lifetime of the O₂ singlet excited state showed the extent of its coupling with the solvent. This lifetime was found to be shorter when the solution was prepared in H₂O than in D₂O because H₂O has an overtone that directly overlaps with an absorption band in O₂. Attempts to maintain a degassed solution in our experimental arrangement proved unsuccessful and therefore we were unable to establish whether O₂ was playing a significant role in the energy transfer process.

The results obtained for the experiment involving two chromophores: TBA and PNT are shown in Table 2. As previously, a two-tailed t-test shows that there is a significant difference between these two means at the 99.9% confidence level. The solution containing PNT produced an explosive ablation compared to the one with TBA. Four times more solution was removed during the explosive ablation.

Two reasons can be advanced to explain the difference found. TBA and PNT were respectively at 14.7x10⁻³ mol l⁻¹ and 8x10⁻³ mol l⁻¹ to give the same absorbance at 266 nm. Therefore the laser energy was absorbed by approximately twice the number of TBA molecules compared with PNT. This contributes to a more dispersed partitioning of the laser energy into the TBA solution.
Chapter 6  
Investigation on the modified standard solutions

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>2-thiobarbituric acid</th>
<th>1,10-phenanthroline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>H₂O</td>
<td>H₂O</td>
</tr>
<tr>
<td>Ar flow effect</td>
<td>0.97</td>
<td>1</td>
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<tr>
<td>Total mass loss</td>
<td>1.14</td>
<td>1.64</td>
</tr>
<tr>
<td>Average of mass loss (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSD (%) n=10</td>
<td>9.32</td>
<td>4.8</td>
</tr>
<tr>
<td>Mass loss due to ablation (mg)</td>
<td>0.17</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Table 2: Comparison of ablation yield of standard solutions with different chromophores (2-thiobarbituric acid and 1,10-phenanthroline).

Additionally, as shown in Figs 9a and 9b, TBA molecules present more sites of interaction with the solvent than PNT, therefore, the energy of its excited state is released in a more dispersed way to the solvent. This results in the creation of a fine aerosol that is readily transportable to the plasma. PNT produces a more localised coupling to the solvent, resulting in the removal of large droplets that are not efficiently transportable beyond the ablation cell. Contamination of the cell with large water droplets was readily observable under these conditions.

Fig. 9a: Interaction of 2-thiobarbituric acid with water.

Fig. 9b: Interaction of 1,10-phenanthroline with water.
The end result of coupling the laser energy to the liquid appears to be a rapid and local increase in temperature and pressure leading to nebulisation of the bulk solution. This is important, as such a mechanism should be free of fractionation effects. These experiments underlined the fact that the quality of aerosol produced (i.e., the transportable mass) is equally important to the initial ablation yield.

6.3 Further investigation.

The influence of the additive concentration on the ablation yield was observed for a given laser energy. Modified standard solutions with 0.17, 0.3, 0.45, 0.6 g l\(^{-1}\) of m-hydroxybenzoic acid and 1 µg g\(^{-1}\) of Co were ablated at 30 mJ, with the excimer laser (Fig 10a). Another set of modified standard solutions prepared with 1, 1.8, 2.6, 3 g l\(^{-1}\) of 2-thiobarbituric acid and 5 µg g\(^{-1}\) of Co was ablated at 610 V with the Nd:YAG laser (Fig 10b). Examination of the plots in Fig. 10a and 10b, obtained respectively for 248 nm and 266 nm, indicate an approximately exponential relationship between ablation yield and chromophore concentration and were suggestive of a process that might be modelled by simple application of Beer's law. This however would be difficult to confirm. A simple form of Beer's law used for LA modelling\(^{20}\) is.

\[
P_c = P_o e^{-k_o L_o}
\]

Where

- \(P_c\) is the incident power,
- \(P_o\) is the threshold power required for ablation to begin,
- \(k_o\) is the absorption coefficient of the sample,
- \(L_o\) is the depth of material ablated by the pulse.
Fig. 10a: Influence of the chromophore concentration on the ablation yield of modified standard solutions, with 1 μg/g of Co, ablated at 248 nm, 30 mJ and 10 Hz.
Fig. 10b: Influence of the chromophore concentration on the ablation yield of modified standard solutions, with 5 μg/g of Co, ablated at 266 nm, 610V, and 10 Hz.
Investigation on the modified standard solutions

The use of Beer's law as a model of the ablation of the modified standard solutions would be difficult to demonstrate practically as when the absorption coefficient is increased, the threshold fluence value is decreased as well as the depth of penetration of the laser beam as it will be more rapidly absorbed, closer to the liquid surface. These three parameters being dependent, they would have to be monitored to check the validity of Beer's law in this case. The two first parameters are easy to monitor, but the depth of material removed would be difficult to measure precisely.

Additionally to this practical limitation:

- This simple analysis assumes that power is absorbed more or less instantaneously before the ablation process begins, which may be true with ps lasers, but not with lasers such as those used here with 15 ns pulse widths.
- There will be attenuation of the beam by coupling to the plasma formed above the liquid surface.

7. Observation and comment on the particular behaviour of m-hydroxy-benzoic acid as a chromophore in standard solution.

It was observed that standard solution freshly made with m-hydroxybenzoic acid would turn progressively yellow after a few days. Additionally, the slow kinetics of this reaction was found to be influenced by the presence of the analytes in solution; the effect occurring more rapidly with a greater analyte concentration. When ablated with the same energy, the yellow standard solution produced a higher ablation yield than a freshly made solution prepared with the same initial m-hydroxybenzoic acid concentration. Determination of the changes that occurred in the modified solution would be indicative of the chemical or physical parameters that are important in the ablation mechanism of the modified standard solutions. The compounds present in the yellow solution were extracted from the acid medium, analysed by MS, $^1$H NMR and GC-MS and compared with results obtained from analysis of the starting material: m-hydroxybenzoic acid (HBA).
Initial MS analysis of the aged yellow standard solution showed a peak at $M + 46$, which indicates the presence of a nitrated form of the initial chromophore. Comparative analyses were then performed by $^1$H NMR (Fig. 11a-11c) and GC-MS (Fig. 12) between m-hydroxybenzoic acid, a nitrated isomer of m-hydroxybenzoic acid, 3-hydroxy 4-nitro benzoic acid, and the mixture of unknown compounds extracted from the aged modified standard solution.

The $^1$H NMR analysis of the unknown mixture showed the presence of several compounds (Fig. 11a). Identification of these compounds was achieved by comparison of the latter spectrum with spectra obtained for the following compounds: the starting material m-hydroxybenzoic acid (Fig. 11b) and one of its nitrated form 3-hydroxy 4-nitro benzoic acid (Fig. 11c). This confirmed the presence of those two compounds in the aged solution.

For the analysis by GC-MS of the mixture of compounds extracted from the aged modified standard solution, m-hydroxybenzoic acid and 3-hydroxy 4-nitrobenzoic acid, the samples were methylated using BF$_3$/methanol to make the chromatography easier. The analysis confirmed that the yellow solution was mainly a mixture of the initial chromophore, m-hydroxybenzoic acid, with 3-hydroxy 4-nitro benzoic acid; various ketones and diesters were formed at very low concentrations.

Four peaks remained unidentified in the $^1$H NMR spectrum of the unknown mixture. The compounds related to those NMR peaks probably originate from the nitration of m-hydroxybenzoic acid; unfortunately, no other nitrated form of m-hydroxybenzoic acid was available to perform further comparative analyses. Additionally, although the $^1$H NMR spectrum (Fig. 11a) showed that this unidentified compound(s) is present in solution in the same proportion as the two other identified ones, the GC-MS analysis does not show more than two main peaks. It could be that the unknown compound(s) was an isomer of the nitrated form of m-hydroxybenzoic acid and was not separated during the GC-MS analysis.
Fig. 11a. $^1$H NMR spectrum of the mixture of compounds extracted from the aged modified standard solution.
Fig 11b. $^1$H NMR spectrum of 3-hydroxybenzoic acid.
Fig 11c. $^1$H NMR spectrum of 3-hydroxy-4-nitrobenzoic acid.
Fig. 12. GC-MS spectra obtained after methylation of:

a) 3-hydroxybenzoic acid

b) 3-hydroxy 4-nitrobenzoic acid

c) mixture of compounds extracted from the aged modified standard solution
3-hydroxy 4-nitro benzoic acid was found to be much less soluble than m-hydroxybenzoic acid in 2% HNO$_3$. Therefore, the ablation of a solution containing this molecule would be of a similar type to the one observed for 1,10-phenanthroline where the release of laser energy, absorbed by the chromophore, is less dispersed in the solvent in comparison with a more soluble molecule, producing a more localised heating and a higher ablation yield. As the m-hydroxybenzoic acid in modified standard solution gets progressively nitrated, the concentration of 3-hydroxy-4-nitrobenzoic acid increases, leading to a greater ablation yield.

8. Conclusion.

The preparation of modified standard solutions is simple, rapid and provides standards whose elemental composition is readily variable. The great advantage of this type of standard over matrix-matched solid standards is the possibility of varying their absorption characteristic in order to achieve ablation under conditions that are optimal for the ablation of a given type of sample. This very important feature makes them potentially suitable for the analysis of a wide variety of sample types. Initial investigations on the ablation mechanism of the modified standard solutions provide insights into the nature of the ablation event. The ablation mechanism seems to be a three-step process. The chromophore is initially excited by absorption of a photon; the energy is then transferred to the surrounding solvent through vibrational coupling, this creates localised spots of heat and pressure which leads to the nebulisation of the bulk liquid. Obviously a great deal more work would be required to provide a quantitative estimate of the ablation yield for such a complex process.
Chapter 6

References

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20. B.L.Sharp, Loughborough University.

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Chapter 7:

Application of the new calibration strategy to polymers and steel
Chapter 7 Application of the new calibration strategy to polymers and steel

1. Introduction.

The modified standard solutions were used to produce calibration curves for elements across the mass range (amu 27-208 Al, Mg, Cr, Co, Zn, Sb and Pb). The new technique of calibration was then applied to the quantitative analysis of different types of sample: low density polyethylene (LDPE), polyketone (PK) and stainless steel. The results obtained by LA-ICP-MS analysis were compared to nominal values or to results obtained by a reference analysis.

2. Calibration curves.

Calibration curves were obtained by LA-ICP-MS with the KrF excimer laser (248 nm) and the Nd:YAG laser (266 nm).

Reagents

Standard solutions were prepared from 1000 ppm stock reagents (Grade Specpure, Johnson Matthey, and Spectrosol, BDH). Dilution was made with 2% nitric acid solution and 18 MΩ de-ionised water. The additives used for the modification of the standard solution were m-hydroxybenzoic acid (Aldrich, Gillingham, Dorset, UK) and 2-thiobarbituric acid (Merck, Magma Park, Lutterworth, Leicestershire, UK).

2.1. Preparation of calibration curves at 248 nm.

Modified standard solutions were prepared containing 0, 5, 10, 25, 50, 100 μg g⁻¹ of the following elements: Mg, Cr, Zn, Sb and Pb. As the concentration range studied here is relatively high, the amount of chromophore added to the standard solutions had to be small enough in order to obtain analyte signals that would not saturate the detector. The laser energy used was 50 mJ. A concentration of 0.15 g l⁻¹ of m-hydroxybenzoic acid was selected to be added to the modified standard solutions.
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Fig. 5a (Chapter 6). It was not possible to use the $^{13}$C isotope as an internal standard with the PQI instrument because its signal was unstable. For this reason, all standards contained 50 $\mu$g g$^{-1}$ of Co, which was used as an internal standard.

2.2. Preparation of calibration curves at 266 nm.

Calibration curves were obtained for the same elements with the Nd:YAG laser system. Modified standard solutions were prepared with 0, 0.25, 0.5, 1, 5 and 12.5 $\mu$g g$^{-1}$ of the analytes. The laser energy for the ablation was 600 volts, the concentration of chromophore added to the standard solutions was determined to be 2.8 g l$^{-1}$ (using the curve in Fig. 5b, in Chapter 6). Use of the PQII+ ICP-MS instrument resulted in a stable signal for the isotope $^{13}$C; this minor isotope of carbon was therefore used as an internal standard with this system.

2.3. Results of calibration at 248 and 266 nm.

Each standard solution was continually ablated for five minutes. The acquisition of the ablation signal was preceded and followed by a minute of non-ablation. This non-ablation blank was subtracted from the ablation signal before any calculations; in this way, any signal interfering with the elements of interest was monitored. The origins of such interferences are from the argon gas and the surrounding environment of the plasma (i.e. CO$_2$ and N$_2$). The blank solution was treated as a point on the calibration curves. The five-minute ablation acquisition was divided into five contiguous portions of one minute each. The analyte responses were normalised to the internal standard (i.e.: $^{59}$Co for the 248 nm laser and $^{13}$C for the 266 nm laser). A standard deviation was calculated for each point. Calibration curves obtained at 248 nm are given in Figs. 1a-1e; those obtained at 266 nm are given in Figs. 2a-2g. A weighted regression line was calculated for each element. Error bars represent three standard deviation. Errors in the slope and intercept of the regression lines are given respectively for 248 nm and 266 nm in Table 1a and 1b.
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Fig. 1a: Calibration curve for $^{25}$Mg, obtained at 248 nm.

Fig. 1b: Calibration curve for $^{53}$Cr, obtained at 248 nm.
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Fig 1c: Calibration curve for $^{64}$Zn, obtained at 248 nm.

Fig. 1d: Calibration curve for $^{121}$Sb, obtained at 248 nm.
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Fig. 1e: Calibration curve for $^{208}$Pb, obtained at 248 nm.

Fig. 2a: Calibration curve for $^{25}$Mg, obtained at 266 nm.
Fig. 2b: Calibration curve for $^{27}$Al, obtained at 266 nm.

Fig. 2c: Calibration curve for $^{53}$Cr, obtained at 266 nm.
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Fig. 2d: Calibration curve for $^{59}\text{Co}$, obtained at 266 nm

Fig. 2e: Calibration curve for $^{64}\text{Zn}$, obtained at 266 nm
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Fig. 2f: Calibration curve for $^{121}$Sb, obtained at 266 nm.

Fig. 2g: Calibration curve for $^{208}$Pb, obtained at 266 nm.
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Isotope | Regression equations | Corr. coeff. $r^2$ | error on slope | error on intercept |
---------|-----------------------|-------------------|----------------|-------------------|
$^{25}\text{Mg}$ | $y = 158x + 50$ | 0.9937 | +/- 12 | +/- 603 |
$^{53}\text{Cr}$ | $y = 113x - 70$ | 0.9988 | +/- 4 | +/- 184 |
$^{64}\text{Zn}$ | $y = 87x + 148$ | 0.9993 | +/- 2 | +/- 110 |
$^{121}\text{Sb}$ | $y = 112x + 88$ | 0.9991 | +/- 3 | +/- 152 |
$^{208}\text{Pb}$ | $y = 383x + 900$ | 0.9987 | +/- 20 | +/- 941 |

Table 1a: Regression line equations, correlation coefficients and errors in slope and intercept for the calibration curves obtained at 248 nm.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Regression equations</th>
<th>Corr. coeff. $r^2$</th>
<th>error on slope</th>
<th>error on intercept</th>
</tr>
</thead>
</table>
$^{25}\text{Mg}$ | $y = 8388.9x + 131.7$ | 0.9998 | +/- 724 | +/- 3994 |
$^{27}\text{Al}$ | $y = 58643x + 9478.4$ | 0.9992 | +/- 2340 | +/- 12903 |
$^{53}\text{Cr}$ | $y = 3992.6x - 296$ | 0.9981 | +/- 251 | +/- 1385 |
$^{59}\text{Co}$ | $y = 31790x + 2463$ | 0.9998 | +/- 599 | +/- 3306 |
$^{64}\text{Zn}$ | $y = 15972x + 1048$ | 0.9999 | +/- 315 | +/- 1742 |
$^{121}\text{Sb}$ | $y = 12028x + 1117$ | 0.9996 | +/- 333 | +/- 1838 |
$^{208}\text{Pb}$ | $y = 42840x + 1320.5$ | 0.9998 | +/- 580 | +/- 3202 |

Table 1b: Regression line equations, correlation coefficients and errors in slope and intercept for the calibration curves obtained at 266 nm.

The use of $^{59}\text{Co}$ as an internal standard provided correlation coefficient values greater than 0.9937. Satisfactory results were expected as the internal standard was in this case of the same nature as the elements of interest. However, the use of $^{13}\text{C}$ as an internal standard also proved to be successful even though it was of a different nature to the analytes being part of the chromophore, an organic molecule. In the latter case, most analytes had a correlation coefficient greater than 0.999. The same behaviour was observed for $^{13}\text{C}$ and the analytes during the repeated ablations indicating that the ablation of the modified standard solution occurred without fractionation for these selected elements across the mass range. The small magnitude of the standard deviations of the signals obtained for the calibration curves showed that the analytes contained in the standard solutions were homogeneously distributed. Therefore,
unlike solid standards, the modified standard solutions do not require to be ablated at several sites in order to give a representative response.

3. Calculation of elemental concentrations from LA-ICP-MS acquisition data.

As previously described for the calibration curves, each acquisition of the ablation signal, for the standards and the samples, was preceded and followed by one minute of non ablation. An example of the signals produced during these periods of non ablation, caused by non-specific instrumental background and molecular ions, are shown in Fig.3, for the $^{26}$Mg, $^{27}$Al and $^{52}$Cr isotopes. The interferences at those particular masses are produced by the following molecular ions: $^{12}$C$^{13}$C$^1$H$^1$H, $^{12}$C$^{13}$C$^1$H$^1$H and $^{13}$C$^{13}$C$^1$ at mass 26; $^{12}$C$^{14}$N$^1$H$^1$H and $^{12}$C$^{15}$N at mass 27 and $^{40}$Ar$^{12}$C at mass 52. The "non ablation blank" was subtracted from the corresponding ablation signal, prior to any calculation.

The calculation of the results comprises two steps:

- the calculation of a Correction Factor (CF) which involves the concentration and the counts per second of the internal standard in the sample and in the standard\(^1\). The CF allows correction for differences in transport of ablated material and sensitivity occurring between the sample and the standard.

$$\text{CF} = \frac{[(\text{CPS IS sample}) \times (\text{concn. IS std})]}{[(\text{CPS IS std}) \times (\text{concn. IS sample})]}$$

- the calculation of the concentration of each analyte in the sample.

$$\text{concn. elt} = \frac{[(\text{CPS elt sample}) \times (\text{concn. elt std})]}{[\text{CF} \times (\text{CPS elt std})]}$$

where elt = element

std = standard

concn. = concentration

CPS = counts per second
Fig. 3: Signals obtained before and after ablation of a modified standard solution, from spectroscopic interferences, on mass 26, 27 and 52.
Heterogeneity in the sample is a consequence of the sample manufacturing process and therefore needs to be included in the estimate of the limits of detection for the method. The limits of detection were calculated as being equal to three times the standard deviation obtained from repeated ablations on different sites of a sample.


The modified standard solutions were used for the analysis of a polymeric sample: low-density linear polyethylene (LDPE). The polymeric material, presented as beads, was provided by the CSL Food Science Laboratory, Norwich, UK. These beads had been prepared to be used as matrix-matched standards to determine the presence of catalyst residues in polymeric material used in food packaging.

The analysis was carried out with the excimer laser system (248 nm). The results obtained by LA-ICP-MS were compared with those obtained by conventional analytical methods (sample digestion + ICP-MS and AA analyses). The elements of interest were Mg, Cr, Co, Zn, Sb and Pb.

Reagents

Reagents used for the LDPE sample digestion were a borate flux, (120A: 80% lithium tetraborate, 20% lithium fluoride, Johnson Matthey, Royston, Hertfordshire, UK), Aristar nitric acid (Merck), tartaric acid (A.R. Grade, Fisher Scientific, Loughborough, UK). Standard solutions were prepared from 1000 ppm stock reagents (Specpure Grade, Johnson Matthey, and Spectrosol, Merck). Dilution was made with 2% nitric acid solution and 18 MΩ de-ionised water. The additive used for the modification of the standard solution was m-hydroxybenzoic acid (Aldrich, Gillingham, Dorset, UK).
4.1 Analysis of the LDPE sample by conventional methods

As the polymeric sample was not a certified reference material, it was digested and analysed by ICP-MS and furnace AA. The digestion procedure\(^3\) used a lithium borate mixture to fuse inorganic materials that were not directly soluble in acidic solution. The sample (150 mg) was previously ashed in a platinum crucible with lid, above a gas burner flame. The ashes were fused in the molten flux at 950°C in a muffle furnace. The fused solid, when cool, was dissolved in an acidic solution (4% nitric acid / 0.5% tartaric acid) and made up to 50 ml to give an overall dilution of 333.1. Two replicates were made this way.

Standard solutions at 0, 30, 50, 100 and 200 ng g\(^{-1}\) of the analytes were made up in the same lithium borate matrix for calibration of the ICP-MS instrument. \(^{9}\)Be, \(^{89}\)Y and \(^{209}\)Bi were used as internal standards, respectively for light, medium and heavy mass isotopes to compensate for mass discrimination which could occur due to the high content of dissolved flux in the solutions.

4.2 Analysis of the LDPE sample by LA-ICP-MS.

A blank solution and a standard solution (7.5 \(\mu\)g g\(^{-1}\) of analytes), both containing 0.3 g l\(^{-1}\) of m-hydroxybenzoic acid, were prepared. They were both ablated at 60 mJ, as well as the LDPE sample and a LDPE blank, known to be free of the analytes of interest. The ablation of this LDPE blank allowed correction for isobaric interferences due to carbon compounds from the LDPE matrix. Table 2 summarises the composition of the modified standard solutions and the laser parameters.
Table 2: Summary of the composition of the modified standard solutions and the laser parameters for the analysis of the LDPE sample.

4.3. Results.

The concentrations of the elements found by the three different analytical techniques are shown in Table 3. Data found for the same sample during a previous study by other workers\(^2\) are shown in Table 4.

<table>
<thead>
<tr>
<th>Element</th>
<th>Digestion+ICP-MS (µg g(^{-1}))</th>
<th>RSD (%)</th>
<th>Digestion + AA (µg g(^{-1}))</th>
<th>RSD (%)</th>
<th>LA-ICP-MS (µg g(^{-1}))</th>
<th>RSD (%)</th>
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<tbody>
<tr>
<td>(^{25})Mg</td>
<td>57.6</td>
<td>5.6</td>
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</tr>
<tr>
<td>(^{53})Cr</td>
<td>30.3</td>
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<td>1.6</td>
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<tr>
<td>(^{59})Co</td>
<td>28.5</td>
<td>8.2</td>
<td>32.1</td>
<td>2.1</td>
<td>Internal Std</td>
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<td>(^{64})Zn</td>
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<td>48.3</td>
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<td>17.6</td>
</tr>
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<td>(^{121})Sb</td>
<td>62.3</td>
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<td>64.8</td>
<td>1.9</td>
<td>62.6</td>
<td>61.2</td>
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<td>1.1</td>
<td>57.7</td>
<td>4.5</td>
<td>52.5</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Table 3: Results for analysis of LDPE.
Chapter 7  Application of the new calibration strategy to polymers and steel

<table>
<thead>
<tr>
<th></th>
<th>nominal concentrations mg g⁻¹</th>
<th>MD* ICP-MS mg g⁻¹</th>
<th>NAA mg g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>51.6</td>
<td>61.6</td>
<td>51.7</td>
</tr>
<tr>
<td>Cr</td>
<td>51.9</td>
<td>40.8</td>
<td>26.4</td>
</tr>
<tr>
<td>Co</td>
<td>49.2</td>
<td>34.6</td>
<td>29.0</td>
</tr>
<tr>
<td>Zn</td>
<td>49.3</td>
<td>48.8</td>
<td>39.2</td>
</tr>
<tr>
<td>Sb</td>
<td>69.8</td>
<td>74.8</td>
<td>52.0</td>
</tr>
<tr>
<td>Pb</td>
<td>62.6</td>
<td>68.3</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*MD: microwave digestion

Table 4: Results for analysis of LDPE from other source².

For the LA-ICP-MS analysis, n=6 represents the number of separate sites (200 µm diameter) ablated on the same sample to obtain representative concentrations for the bulk of the material. The high RSD for antimony indicated its heterogeneity in the LDPE matrix. The results obtained by LA-ICP-MS were in very good agreement with those found by digestion-ICP-MS and graphite furnace AA. The experimental values were significantly different to the nominal values given in Table 4. This illustrates the difficulty of preparing homogeneous matrix-matched polymer standards of known composition.

5. Application of the new method of calibration to a polyketone sample (PK).

5.1. Sample

Boron and palladium were the two elements of interest in the polyketone matrix. Polyketone pellets doped with different concentrations of the two analytes had been prepared initially in the BP laboratories, in order to be used as matrix-matched solid standards for the analysis of polyketone samples by LA-ICP-MS.
Initial attempts to ablate these pellets were conducted in BP laboratory\textsuperscript{4}, using the first harmonic of a Nd:YAG laser (1064 nm). As shown on Fig.4a, a large rim around the crater was observable.

Fig.4a:
IR ablation of polyketone.

The rim could originate from the redeposition of molten material ejected from the deep crater and/or thermal effects. The border of the crater presented a vitreous aspect which indicated the occurrence of chemical and physical changes of the polyketone during the IR ablation. During the first two minutes of the IR ablation, the intensities of the counts continuously increased for all the elements, but not at the same rate for C and Pd. The ratio Pd/C was increasing steadily during this period and then reached a steady state (both in terms of signal intensity and ratios). A three-minute pre-ablation was required before obtaining a usable signal. These observations confirmed that IR ablation could give non-representative signals which could easily lead to erroneous results.

The same polyketone pellet was ablated with the fourth harmonic of the Nd:YAG laser (266 nm) as shown in Fig.4b. Though a thin rim of molten material surrounded the crater, no dramatic physical changes, such as the ones observed after the IR ablation, were noticed.
The ablation of the polyketone sample by the UV laser gave a satisfactory signal, which did not show any fractionation. UV ablation was performed on a raster in order to obtain a relatively long signal without ablating the target too deeply.

Fig. 4b: UV ablation
of the polyketone pellet.

The new method of calibration was applied to the analysis of three of the home-made polyketone solid standards to test its validity with this particular matrix. This study was performed on the BP LA-ICP-MS system (i.e., Nd:YAG laser + PQII+ ICP-MS). Estimated concentration values for B and Pd were given with the polyketone pellets. Additionally, a sample of each of the pellets was analysed by a conventional analytical technique (digestion + atomic absorption analysis) to verify their Pd content. It was found that the concentration values for Pd, which were estimated from their preparation, were unreliable. Therefore, the results obtained for Pd by LA-ICP-MS were compared to the experimental results. Unfortunately, no reference method was available to determine the concentration of boron in the polymer; therefore, the real B concentrations could not be checked.
5.2. Analysis of the polyketone pellets by LA-ICP-MS.

5.2.1. Determination of the optimal laser energy.

The optimal laser energy for the ablation of the sample was determined observing the influence of the laser voltage on the ablation yield (Fig. 5a-5b).

![Graph showing ablation yield of $^{11}$B and $^{108}$Pd in polyketone as a function of the laser voltage.](image)

Fig. 5a: Ablation yield of $^{11}$B and $^{108}$Pd in polyketone as a function of the laser voltage.
As shown in Figs. 5a and 5b, the ablation yield was increasing steadily until 605 volts. From this observation, the maximum laser voltage tested, 605 volts, appeared to give the best energy possible to ablate the polyketone sample.

However, the plot of the ratio “CPS of the analyte/CPS of the internal standard” against the laser voltage showed a progressive decrease of the ratio $^{11}\text{B}/^{13}\text{C}$, whereas the ratio $^{108}\text{Pd}/^{13}\text{C}$ was not affected (Fig. 6).

This phenomenon could be due to mass discrimination. This effect is widely observed in solution ICP-MS when a solution with a high content of dissolved material is introduced into the ICP. The light mass elements are deflected outwards from the ion beam and lost when the ions are extracted and focused. This results in a non-representative detection of the light mass isotopes. It appeared that the same phenomenon happened with the introduction of solid material by laser ablation if a too great amount of ablated material was transported to the ICP. A relatively low laser voltage should therefore be selected to minimise the effect of mass discrimination.
Fig. 6: Influence of the laser voltages on the ratios B/C and Pd/C
Another explanation could be that the decrease of the $^{11}\text{B}/^{13}\text{C}$ ratio with laser voltage increase was due to thermal effects during the ablation. Indeed, thermal effects occurring during the ablation of polyketone, at low laser voltages, would show an enrichment in B which forms volatile compounds. As the laser voltage was increased, the thermal effect would be minimised and the B to C ratio would decrease and tend towards a stable value. This is observed over the laser voltage range from 590 to 605. Therefore, a laser voltage at the upper end of the range of the ones tested should be selected for the analysis of the polyketone samples.

Unfortunately, only one laser voltage was used for the analysis of the samples, corresponding to the lowest value tested. According to the data in Fig 6, this choice of the laser voltage only affected the results for B, as Pd did not seem to be influenced by this parameter.

5.2.2. Preparation of the modified standard solutions.

Reagents.

Reagents used were 1000 ppm stock reagents (Specpure Grade, Johnson Matthey, and Spectrosol, Merck), dilution was made with 2% nitric acid solution and 18 MΩ deionised water. The additive used for the modification of the standard solution was 2-thiobarbituric acid (Merck).

As a relatively low laser voltage was selected for this particular sample, a high concentration of chromophore had to be added to the standard solution to produce an efficient coupling of the solution with the low energy of the laser beam (Fig 5b Chapter 6). Unfortunately, it was impossible to prepare a modified standard solution to be efficiently ablated at 565 volts, as Pd precipitated with the high concentration of the chromophore 2-thiobarbituric acid. A concentration of TBA equal to 4 g l$^{-1}$ would have been necessary, but a smaller concentration of chromophore had to be used in order to avoid formation of the precipitate. The maximal chromophore concentration that could be used in the standard solution containing 10 µg g$^{-1}$ Pd was 3 g l$^{-1}$. With
this chromophore concentration, the laser voltage used to ablate the modified standard solution had to be increased, a laser voltage of 600 volts was therefore selected for the ablation of the standard. In this experiment, the laser energy selected to ablate the sample was different to the one required to ablate the modified standard solutions. At first, it appears that this circumstance would prevent a satisfactory analysis, but the use of the internal standard and the invariance of the elemental ratios with power solve this problem. Ablating each material at its optimum power has the considerable benefit of producing a fine aerosol and minimum fractionation.

Table 5 summarises the composition of the modified standard solutions and the laser parameters.

<table>
<thead>
<tr>
<th>TBA concentration (g l⁻¹)</th>
<th>analyte concentration (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>3</td>
</tr>
<tr>
<td>Standard (B)</td>
<td>3</td>
</tr>
<tr>
<td>Standard (Pd)</td>
<td>3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Frequency (Hz)</th>
<th>Mode of ablation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>565</td>
<td>10</td>
</tr>
<tr>
<td>Standards</td>
<td>600</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 5: Composition of the modified standard solution and laser parameters.

5.3 Results and discussion.

The results found for the three solid polyketone standards are given in Table 6a for B and in Table 7a for Pd.
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Application of the new calibration strategy to polymers and steel

The limits of detection corresponding to the heterogeneity of the different pellets are given in Table 6b for boron and Table 7b palladium, for the particular conditions of ablation used during these analyses (i.e., 60 μm diameter crater, 565 V. and 10 Hz).

<table>
<thead>
<tr>
<th>B</th>
<th>LA-ICP-MS</th>
<th>RSD (%)</th>
<th>Nominal Values (μg·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyketone standard 1</td>
<td>37</td>
<td>31.5</td>
<td>16</td>
</tr>
<tr>
<td>Polyketone standard 2</td>
<td>30</td>
<td>8.2</td>
<td>20</td>
</tr>
<tr>
<td>Polyketone standard 3</td>
<td>43</td>
<td>12.5</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 6a: Boron concentrations in three polyketone in-house solid standards determined by LA-ICP-MS and nominal values.

<table>
<thead>
<tr>
<th>B</th>
<th>Standard 1</th>
<th>Standard 2</th>
<th>Standard 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD (μg·g⁻¹)</td>
<td>32</td>
<td>7.4</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 6b: Limits of detection for boron.

The results obtained for B appeared very unsatisfactory in comparison with the given nominal values (at +/- 125%). Three reasons contribute to this observation. Firstly, the B concentration found for the first polyketone standard was too close to the LOD to be quantified. Additionally, the B concentrations found by LA-ICP-MS were all greater than the nominal values. This could imply the presence of enrichment in B during the ablation of the polyketone samples. That would confirm the presence of a thermal effect occurring at low laser voltages. In fact, $^{13}$C, which is a light mass isotope, was not affected by the laser voltage. Thus the variation in B signal was more likely due to a B enrichment than a fractionation effect. Therefore, the use of a higher laser voltage value could have improved the results. Finally, it was found for Pd that...
the estimated concentration values given for the polyketone pellets were not reliable. Boron is more difficult to incorporate successfully into solid standard than Palladium and therefore the estimated values are suspect. No alternative data were available for the B concentration and therefore, it was not possible to estimate the accuracy of the results found for B by LA-ICP-MS.

During the ablation of the solid samples and the ablation of the modified standard solution, B did not produce any memory effect which was an advantage compared with its determination by nebulisation ICP-MS. The different values of LOD found for boron showed that the polyketone solid standards had different heterogeneities. Standard 1 gave the highest LOD value and standard 2, the lowest one.

<table>
<thead>
<tr>
<th>Pd</th>
<th>LA-ICP-MS (µg·g⁻¹)</th>
<th>RSD (%)</th>
<th>Digestion+AAS (µg·g⁻¹)ref</th>
<th>Nominal Values (µg·g⁻¹)⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyketone standard 1</td>
<td>47.</td>
<td>8.6</td>
<td>52</td>
<td>74</td>
</tr>
<tr>
<td>Polyketone standard 2</td>
<td>62</td>
<td>13.6</td>
<td>73</td>
<td>94</td>
</tr>
<tr>
<td>Polyketone standard 3</td>
<td>76</td>
<td>4.9</td>
<td>89</td>
<td>114</td>
</tr>
</tbody>
</table>

Table 7a: Pd concentrations in three in-house solid polyketone standards determined by LA-ICP-MS and by digestion AA.

<table>
<thead>
<tr>
<th>Pd</th>
<th>Standard 1</th>
<th>Standard 2</th>
<th>Standard 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD (µg·g⁻¹)</td>
<td>17</td>
<td>29</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 7b: Limits of detection for palladium.

The results obtained for Pd by LA-ICP-MS were compared to the experimental values found by the conventional analytical method. The Pd concentrations found by LA-
ICP-MS were within 15% of the concentrations found by digestion and AA analysis, which for polyketone sample 1 and 2 were within two standard deviations from the mean.


6.1. Interest in applying LA-ICP-MS to metals.

An interest in using LA-ICP-MS for the analysis of steel is the possibility of determining the presence of non-metallic heterogeneities or inclusions, as cleanliness is a critical property affecting the performance of steel. A stainless steel reference material used for XRF analysis was used as a sample for the laser ablation analysis. The reference material contained elements through the mass range, Cr, Co, Fe, Mo and W, and covering a wide concentration range, from a few ppm to tens of percents. A minor isotope of the major analyte ($^{57}$Fe) was used as internal standard. This analysis was performed with the PQII+ ICP-MS instrument.

6.2. Analysis of stainless steel by LA-ICP-MS.

6.2.1. Determination of the optimal laser energy.

The influence of different laser voltage settings on the ablation yield was observed (Fig. 7a-7c). An increase of the signal was observed for Mo and W. The signals of the three other elements, Cr, Fe and Co did not show such a rapid increase as the laser voltage was elevated.

The fusion temperatures of Mo and W are significantly higher than the ones for Cr, Co and Fe. Referring to Mermet's paper, this physical difference should have led to a higher ablation of the elements with a low fusion temperature; the opposite was observed here.
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Fig. 7a: Increase of the ablation yield of Fe and W in stainless steel as a function of the laser voltage.

Fig. 7b: Increase of the ablation yield of Cr and Co in stainless steel as a function of the laser voltage.
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![Graph](image)

The ratios "CPS analyte over CPS internal standard" were plotted against the laser voltage to check if the analytes were all behaving like the internal standard, (Fig. 8a-8d). The minor isotope of Fe, $^{57}$Fe, was selected as internal standard in the stainless steel sample. An apparent enrichment in Mo and W seemed to occur in comparison to Fe, as the laser voltage was increased (i.e., as the amount of material brought to the ICP increased). The isotope of Co showed a less dramatic enrichment and the Cr isotope seemed to behave rather like Fe.

Another way to look at this data was to plot the ratios "CPS analyte/CPS heavier isotope involved (W in this case)" against the laser voltages. Fig. 9a-9d clearly showed that the phenomenon observed here affected mostly the light mass isotopes, i.e. Cr and Fe. Co only showed a slight decrease as the laser voltage was increased. Mo behaved similarly to W. The nominal value of W in the stainless steel was 18.1%. It appeared
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Fig. 8a: Influence of the laser voltage on the ratio Cr CPS / Fe CPS

Fig. 8b: Influence of the laser voltage on the ratio Co CPS / Fe CPS
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Fig. 8c: Influence of the laser voltage on the ratio Mo CPS / Fe CPS

Fig. 8d: Influence of the laser voltage on the ratio W CPS / Fe CPS
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Fig. 9a: Influence of the laser voltage on the ratio Cr CPS / W CPS

Fig. 9b: Influence of the laser voltage on the ratio Fe CPS / W CPS
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Fig. 9c: Influence of the laser voltage on the ratio Co CPS / W CPS

Fig. 9d: Influence of the laser voltage on the ratio Mo CPS / W CPS
that the phenomenon observed was the result of mass discrimination, caused by the space charge effect due to the high content of W in the stainless steel sample. The effect was accentuated as the laser voltage was increased, i.e., as the amount of ablated material brought to the ICP was increased.

The optimal laser voltage selected for the ablation of this particular sample was therefore 580 volts. This voltage gave the highest possible signal without the occurrence of mass discrimination.

6.2.2. Preparation of the modified standard solutions

The laser voltage being relatively low, a high concentration of 2-thiobarbituric acid had to be added to the standard solution in order to obtain an efficient coupling with the laser beam (see Fig 5b Chapter 6). A concentration of 3.5 g l⁻¹ of additive was selected. The elements of interest in this case: Cr, Co, Fe, Mo and W did not show any incompatibility with the chromophore in solution. Table 8 summarises the composition of the modified standard solutions and the laser parameters.

<table>
<thead>
<tr>
<th>TBA concentration (g l⁻¹)</th>
<th>analyte concentration (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>3.5</td>
</tr>
<tr>
<td>Standard</td>
<td>3.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Frequency</th>
<th>Mode of acquisition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>580</td>
<td>10</td>
</tr>
<tr>
<td>Standard</td>
<td>580</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 8: Composition of the modified standard solution and laser parameters.
6.3 Results and discussion.

The results obtained by LA-ICP-MS were compared to the certified value of the analyte concentration in the CRM (Table 9a).

<table>
<thead>
<tr>
<th></th>
<th>LA-ICP-MS (%)</th>
<th>RSD (%)</th>
<th>Certified Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{53}\text{Cr}$</td>
<td>5.1</td>
<td>12</td>
<td>4.80</td>
</tr>
<tr>
<td>$^{57}\text{Fe}$</td>
<td>Internal Standard</td>
<td>-</td>
<td>73</td>
</tr>
<tr>
<td>$^{59}\text{Co}$</td>
<td>0.22</td>
<td>4.5</td>
<td>0.24</td>
</tr>
<tr>
<td>$^{98}\text{Mo}$</td>
<td>0.30</td>
<td>9.3</td>
<td>0.27</td>
</tr>
<tr>
<td>$^{182}\text{W}$</td>
<td>18.4</td>
<td>5.1</td>
<td>18.1</td>
</tr>
</tbody>
</table>

Table 9a: Results obtained for the analysis of a stainless steel CRM by LA-ICP-MS, compared to nominal values.

The results found by LA-ICP-MS fell within 11% of the certified values. The use of a minor isotope of the major element of the matrix, i.e. $^{57}\text{Fe}$, as an internal standard proved to be successful. This is a great advantage as in a real sample, the concentration of such an internal standard is usually known.

Limits of detection are given in Table 9b for the analytes of interest in this particular sample, for the conditions of ablation used in this analysis.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD (%)</td>
<td>1.2</td>
<td>13</td>
<td>0.04</td>
<td>0.06</td>
<td>0.6</td>
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</tbody>
</table>

Table 9b: Limits of detection.
7. Conclusion.

The data presented have demonstrated that aqueous standards having a modified absorption coefficient can be employed in the analysis of solid material by LA-ICP-MS. It was a particular fault of the LA-ICP-MS system at Loughborough that the measurement of $^{13}$C was unstable and subject to unpredictable and inexplicable variation. This phenomenon was not observed using the BP system. It was not possible to resolve this instrumental problem and hence Co was used as an internal standard. The LDPE sample was successfully analysed this way. The following analyses, performed in BP laboratory, were successfully achieved with the use of a minor isotope of the major element of the matrix: $^{13}$C for polyketone and $^{57}$Fe for stainless steel. Results fell within 15% for Pd in polyketone and within 11% for the elements contained in stainless steel. The performance of the new calibration technique could not be evaluated for the analysis of B in polyketone as no alternative analytical method was available to certify the B concentration in the home-made polyketone sample.

The mechanism of ablation of modified standard solutions appeared to be different to that applying to the solid samples. Nevertheless, the use of an internal standard enabled practical analysis to be performed, as long as the analytes in the liquid standard and in the solid sample behaved similarly with respect to the internal standard. One of the great advantages of the modified standard solutions is that simple variation of the additive concentration allows the standards to be ablated at the energy that is optimal for the sample. This characteristic makes their use applicable to a wide variety of sample types. Other practical benefits derived from the use of aqueous standard solutions are that they are easier to prepare than solid standards, their elemental composition is readily variable, the distribution of the elements within the standard is homogenous, they offer a renewable surface during the ablation event and they are inexpensive.
Chapter 7

References

Chapter 8:

Application to real samples
1. Introduction.

A particular interest that BP Chemicals had in the use of LA-ICP-MS was the possibility to determine the concentration of catalyst residues, contained in tiny inclusions called "gels", found in PE thin film. The size of these gels varied from a few tens to a few hundreds of microns. Laser ablation was the ideal sampling method to perform this type of analysis.

The elements of interest were Ti and Zr. The two analytes were present in the PE matrix as residues of organic catalysts. These catalysts were initially inserted in two separate batches of PE beads from which the PE film was made. The beads containing the Ti catalyst and those containing the Zr one were analysed by LA-ICP-MS. The concentrations found for these two analytes were compared with those found by a reference analytical method. A sample of PE thin film containing gels was analysed in the same way. Ablation rasters were performed on the gels and on the normal part of the film in order to compare the concentrations of catalyst residues. Another sample of PE thin film, with no gels this time, was also analysed by LA-ICP-MS. This sample was digested and analysed by ICP-MS. Both sets of results were compared.


2.1 Determination of Ti in polyethylene beads.

2.1.1. Determination of the optimal laser energy

The optimal laser energy for the analysis of the PE beads was determined. The beads were ablated at different laser voltage settings. The signals obtained for $^{13}$C, used as internal standard, and for Ti were observed. As previously, the sample was ablated with the masked laser beam, resulting in 60 $\mu$m diameter craters. The ablation of the beads with the full-size beam (500 $\mu$m) was also tested to see if similar results would be obtained.
Optimal conditions for the ablation of the beads (beam diameter and laser energy) were determined as follows:

- for the 60 μm beam diameter, voltage settings from 610 to 660 volts were tested (Fig.1)
- for the full size beam, voltage settings from 570 to 600 volts were tested (Fig.2). Higher voltage values could not be used as the ablation cell started to become damaged. This was probably due to an excessive amount of ablated material inefficiently transported out of the cell, sticking on the inner side of the top window, making the laser beam couple with this surface.

Fig.1: Signal increase of C (●) and Ti (○) during the ablation of polyethylene beads at 266 nm, with the 60 μm diameter laser beam
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Fig. 2: Signal increase of C (●) and Ti (●) as a function of the laser voltage, during the ablation of polyethylene beads at 266 nm, with the 500 μm diameter laser beam.

For both laser beam diameters, the counts for C and Ti increased regularly with the laser voltage. The wider laser beam generally gave higher counts, up to 2500 counts for Ti, against 400 counts obtained with the small size beam. In both cases, the ratio CPS Ti / CPS C were plotted to check the presence of any change in behaviour between the analyte and the internal standard as the voltage was increased (Fig. 3 for the small size beam and Fig. 4 for the wide beam).

Fig. 3: Titanium CPS / Carbon CPS ratio as a function of the laser voltage. Ablation operated with the small laser beam size.
As shown in Fig. 3 and Fig. 4, the values of the ratios were found to remain constant, not only within a set of laser voltages for each laser beam size, but between the two sets of voltages for the two laser beam sizes also. This showed that the different ablation conditions (beam size and laser energy) did not influence the responses given by the ICP-MS instrument for the analyte Ti relative to the internal standard C.

An optimum laser voltage was selected, for each laser beam size, giving the highest counts possible without risking to damage the ablation cell:

- \( V = 650 \) volts for the 60 \( \mu \text{m} \) laser beam,
- \( V = 595 \) volts for the 500 \( \mu \text{m} \) laser beam.

Both sets of conditions (beam size and laser energy) were tested for the analysis of the beads.
2.1.2. Preparation of the modified standard solutions.

Previous attempts to ablate modified standards at low laser voltages, using the full size beam, were unsuccessful. The area of solution irradiated was so large that the resulting droplets were not efficiently transported out of the ablation cell. The result was significant deposition of droplets on the cell walls. Additionally, the irradiation of a wide area of solution produced a very strong light emission that made any visual observation and control of the ablation impossible via the camera control device. Therefore, the modified standard solutions were ablated with the small beam diameter only. In reference to Fig.5b Chapter 6, a concentration of 3.5 g l⁻¹ of 2-thiobarbituric acid was added to the aqueous standards to be ablated at 595 volts.

<table>
<thead>
<tr>
<th>TBA concentration (g l⁻¹)</th>
<th>analyte concentration (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
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<tr>
<td>Standard</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Beam Ø (µm)</th>
<th>Frequency (Hz)</th>
<th>Mode of acquisition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>595</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>Sample</td>
<td>595</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>Sample</td>
<td>650</td>
<td>60</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 1: Summary of the composition of the modified standard solutions and the laser parameters for the analysis of the beads.

2.1.3. Results and discussion.

The concentrations of Ti obtained in both cases were compared to results obtained by a reference analytical method where the beads were digested and analysed by ICP-AES (Table 2).
The concentrations of Ti found with both sets of condition of laser ablation were in good agreement with the concentration value found by the other analytical technique. The use of 2-thiobarbituric acid as an additive, containing S atoms, produced an isobaric interference at mass to charge ratio 48, with SO⁺ forming. This was easily corrected by ablating a blank standard solution containing the additive only; the internal standard being part of the additive. The matrix of the PE beads could have also been a source of similar interference. Therefore, a PE blank bead, known not to contain Ti, was ablated. Ten acquisitions were obtained to evaluate this blank. The resulting signal at 48 was varying from a few counts to a more significant signal. This was probably due to the presence of contamination on the top window of the ablation cell, deposited from previous ablations. As the blank beads were ablated in different places, the laser would go through more or less contaminated areas of the cell. The average of the different values obtained at m/z 48 was used and subtracted from the total signal obtained for the sample beads. The overall impact of the interference found in the sample blank was not significant on the Ti concentration results, as the signals produced by the blank were much smaller than those for the beads.

Table 2: Concentration of Ti in PE beads.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Ti concentration (µg.g⁻¹)</th>
<th>± RSD(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650 v - 10 Hz, 60 µm Ø beam</td>
<td>0.7</td>
<td>24</td>
</tr>
<tr>
<td>595 v. - 10 Hz, 500 µm Ø beam</td>
<td>0.6</td>
<td>26</td>
</tr>
<tr>
<td>Digestion + ICP-AES</td>
<td>0.9</td>
<td>11</td>
</tr>
</tbody>
</table>
2.2. Analysis of PE beads containing Zr.

2.2.1. Determination of the optimal laser energy.

As in the previous experiment, the beads were ablated with a set of different laser voltages for the two laser beam sizes:

- from 610 to 660 volts for the masked beam,
- from 570 to 610 volts for the full size beam (Fig. 5).

The major isotope of Zr ($^{90}$Zr) was monitored, as well as $^{12}$C, used as an internal standard. The analyte Zr was not detected when the beads were ablated with the small size beam. The small amount of ablated material produced in these conditions was too small for the analyte to be detected by the ICP-MS instrument. Therefore, only the counts obtained by ablation of the sample with the large laser beam diameter were considered.

![Graph](image)

**Fig. 5:** Signal increase of C (•) and Zr (○) during the ablation of polyethylene beads at 266 nm, with the 500 µm diameter laser beam
Ablation of the beads with the full size beam gave a signal up to four hundred counts. The sensitivities for $^{13}\text{C}$ and $^{90}\text{Zr}$ showed a regular increase with the laser voltages up to 610 volts.

The ratios CPS $\text{Zr}$/CPS $\text{C}$ were plotted to observe if any change in behaviour was occurring between the analyte and the internal standard as the laser voltage was increased (Fig. 6).

![Graph showing Zr/C ratio as a function of laser voltage](image)

Fig. 6: Zr/C ratio as a function of the laser voltage.
Ablation operated with large laser beam size (500 μm).

As shown in Fig. 6, the ratio remained constant therefore no fractionation was occurring for the different laser voltage conditions tested. However, damage of the cell was observed for laser voltages higher than 595 volts. Therefore, 595 volts was the maximum voltage that could be used for the ablation of the beads without risking damage to the cell.
2.2.2. Preparation of the modified standard solutions.

As mentioned previously, due to the difficulty of controlling the ablation of the modified standard solutions with the full size beam, the masked beam was used for this purpose. The selected laser voltage being 595 volts, a concentration of 3.5 g.l\(^{-1}\) was added to the standard solution accordingly to the Fig.5b, Chapter 6. Table 3 summarises the compositions of the modified standard solutions and the laser parameters.

<table>
<thead>
<tr>
<th>TBA concentration (g l(^{-1}))</th>
<th>analyte concentration (µg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>3.5</td>
</tr>
<tr>
<td>Standard</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Frequency (Hz)</th>
<th>Beam Ø (µm)</th>
<th>Mode of acquisition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standards</td>
<td>595</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>Sample</td>
<td>595</td>
<td>10</td>
<td>500</td>
</tr>
</tbody>
</table>

Table 3: Summary of the composition of the modified standard solutions and the laser parameters for the analysis of LDPE sample.

2.2.3. Results and discussion.

The resulting C and Zr signals from the ablation of the beads were smaller than those predicted by the previous experiment (Fig.7). The average CPS obtained was around 350,000 instead of 450,000 for \(^{13}\)C and 100 instead of 250 for Zr. This was possibly due to an attenuation of the laser energy when going through a damaged area of the top window of the ablation cell. However, the signal remained constant amongst the
different spots ablated. The results obtained by LA-ICP-MS were compared to those obtained by a reference analytical method where the beads were digested and analysed by ICP-MS (Table 4).

<table>
<thead>
<tr>
<th>Zr concentration (µg.g⁻¹)</th>
<th>± RSD(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>595 v. - 10 Hz</td>
<td>0.29</td>
</tr>
<tr>
<td>500 µm Ø beam</td>
<td>9.6</td>
</tr>
<tr>
<td>Digestion + ICP-MS</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 4: Concentration of Zr in PE beads.

The concentration of Zr found by LA-ICP-MS was twice the concentration value found by the other method. The very small signal obtained for Zr during the ablation was certainly a source of error in this result. However, the relatively low value of the RSD shows that it was reproducible. An additional problem was the great difference of intensity between the analyte and the internal standard.


3.1. Analysis of gels in polyethylene thin film.

3.1.1. Determination of the optimum laser voltage.

The thin film was ablated at 266 nm with the masked beam at different voltages, from 605 volts to 620 volts. The signals for $^{13}$C, $^{48}$Ti and $^{90}$Zr were monitored (Figs.7a-7b). The film was ablated across its surface following rasters. The laser could only be left on each spot for a short period of time (less than three seconds), as it would quickly
ablate through the thickness of the film. This resulted in an unstable signal and the possibility of picking up contamination due to the eventual ablation of the support material situated below the film.

Fig. 7a: Increase of C signal as a function of the laser voltage.

Fig. 7b: Increase of Ti (•) and Zr (•) signal as a function of the laser voltage.
As shown in Figs. 7a-7b, the signal from the analytes increased regularly with the laser voltage until 620 volts where a slight decrease in signal was observed. This decrease was due to the signal unstability as the beam was quickly going through the thickness of the film at this voltage. The ratios Ti / C and Zr / C were plotted to observe if any change in behaviour was occurring between the analytes (Ti and Zr) and the internal standard C, as the laser voltage was increased (Fig. 8).

![Graph showing Ti/C and Zr/C ratios](image)

**Fig. 8:** Ti / C ratio (●) and Zr / C ratio (●) as a function of the laser voltage.

The ratios "analyte / internal standard" gave a constant value from 605 to 615 volts. It was only at 620 volts that a change for the value of the ratio Ti / C was observed. This was probably due to the imprecision related to the integration of the erratic signal obtained at this particular laser voltage. Therefore, 615 volts was selected as being the optimum laser voltage to give the highest signal possible without going through the film too quickly.
3.1.2. Preparation of modified standard solutions.

Accordingly to Fig. 5b, Chapter 6, a concentration of 2 g.l\textsuperscript{-1} of 2-thiobarbituric acid was added to the standard solutions in order to ablate them efficiently at 615 volts. Table 5 summarises the composition of the modified standard solutions and the laser parameters.

<table>
<thead>
<tr>
<th></th>
<th>TBA concentration (g l\textsuperscript{-1})</th>
<th>Ti and Zr concentration (µg g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Standard</td>
<td>2</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Voltage (V)</th>
<th>Frequency (Hz)</th>
<th>Beam Ø (µm)</th>
<th>Mode of acquisition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standards</td>
<td>615</td>
<td>10</td>
<td>60</td>
<td>acquisitions of one min. each</td>
</tr>
<tr>
<td>Sample</td>
<td>615</td>
<td>10</td>
<td>60</td>
<td>rasters</td>
</tr>
</tbody>
</table>

Table 5: Compositions of the modified standard solutions and laser parameters.

3.1.3. Results and discussion.

Eleven rasters were ablated on the surface of the film, avoiding the gels as shown in Fig. 9. These acquisitions provided concentration values for Ti and Zr in the normal parts of the film.
Eight rasters were performed, passing through the gels as shown in Fig. 10.

The Ti and Zr concentration values found in the gels were then compared to those previously found in the regular part of the film (Fig. 11). A t-test was performed to
Fig. 11: Comparison of Ti and Zr concentrations in normal part of the polyethylene thin film and in gels.
both Ti and Zr. It was found that there was a significant difference between the two sets of data for both elements, at the 95% level of confidence. The Ti and Zr concentrations in the gels were respectively 9 and 4.5 times greater than those found in the normal parts of the film.

Laser ablation was particularly appropriate in this case as it made it possible to determine elemental concentration in the tiny inclusions that are the gels. No analytical technique other than LA-ICP would have made this analysis possible.

3.2. Analysis of a sample of polyethylene thin film without gels.

3.2.1. Preparation of modified standard solutions.

The laser voltage used for the ablation of the film was the same as previously selected 615 volts. However, the concentration of 2-thiobarbituric acid in the standard solutions was altered. Indeed the concentration of chromophore was slightly increased in order to obtain a larger signal for $^{13}$C, the internal standard, during the acquisition of the ablation of the standards. Only the analyte $^{48}$Ti was monitored with $^{13}$C. Table 6 summarises the compositions of the modified standard solutions and the laser parameters.

<table>
<thead>
<tr>
<th>TBA concentration (g l$^{-1}$)</th>
<th>Ti concentration (µg g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>2.7</td>
</tr>
<tr>
<td>Standard</td>
<td>2.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Frequency (Hz)</th>
<th>Beam (µm)</th>
<th>Mode of acquisition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standards</td>
<td>615</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>Sample</td>
<td>615</td>
<td>10</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 6. Compositions of the modified standard solutions and laser parameters.
3.2.2 Results and discussion

Fifteen rasters were acquired across the surface of the film. The signals obtained for $^{48}\text{Ti}$ were in general above 150 counts up to 350 counts. The results obtained by LA-ICP-MS were compared to those obtained by a reference analytical method where the film was digested and analysed by ICP-AES (Table 7).

<table>
<thead>
<tr>
<th>Ti concentration (µg g$^{-1}$)</th>
<th>± RSD(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>615 v. - 10 Hz 60 µm Ø beam</td>
<td>2.1</td>
</tr>
<tr>
<td>Digestion + ICP-AES</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 7: Results for Ti and Zr in PE thin film

The concentration value obtained by LA-ICP-MS was 50% greater than the one determined with the other analytical method. Several reasons could explain this. First, the small amplitude of the signals obtained for Ti. Secondly, a PE bead was used as a sample blank, which obviously has not got the same physical properties as the film and probably contains different additives. Ideally, the sample blank should have been a piece of film containing no Ti.
Chapter 9:

Conclusions and further work
Chapter 9: Conclusions and further work

1. Development and investigation on the modified standard solutions.

Three different chromophores were selected to prepare modified standard solutions for laser ablation analysis at 193, 248 and 266 nm: respectively poly(sodium 4-styrene sulfonate), m-hydroxybenzoic acid, and 2-thiobarbituric acid. The standards obtained present the following advantages:

- they are easy to prepare,
- their elemental composition is readily variable,
- the possibility to change the absorption characteristics of the standard solutions makes them usable for the analysis of samples with different types of matrices,
- they offer a renewable surface of fresh solution below the laser beam during ablation, yielding a stable signal over time,
- they are inexpensive.

A systematic approach was defined for the preparation of modified standard solutions for a given sample. The best ablation conditions have first to be determined for this sample (laser energy, pulse frequency and crater diameter). Then, the right concentration of chromophore to be added into the solutions can be determined by using a graph such as the ones in Fig 5a, 5b in chapter 6. These graphs give the ablation yield obtained at different laser energies for standard solutions with different concentrations of additive.

Initial investigations were made on the mechanism of the ablation of the modified standard solutions. The influence of different parameters on the ablation yield of the standards was observed. It was found that the ablation mechanism could be described as a three-step process, where the chromophore is initially excited by the absorption of the laser beam; this energy is then transferred to the surrounding solvent through vibrational coupling; this creates localised spots of heat and pressure and leads to the nebulisation of the bulk liquid.
2. Applications.

The modified standard solutions were used for the analysis of different sample types. A stainless steel reference material was successfully analysed for a variety of elements across the mass range with a wide range of concentrations. Results fell within $\pm 11\%$ of the certified values. Different polymeric samples were also analysed using the new calibration strategy. Results for those samples fell within $\pm 15\%$ of concentration values determined by other analytical techniques. An internal standard was systematically used during the analyses. It compensates for the different ablation yields from the sample and the standard, it also corrects for the laser shot-to-shot variation. Whenever possible, a minor isotope of a major element of the sample matrix was chosen as an internal standard as its concentration is readily available. The new method of calibration was finally applied to the analysis of inclusions in low density polyethylene thin film. Laser ablation was a particularly appropriate sample introduction method in this case, as the spatial resolution of the laser beam made possible the selective ablation of either the inclusions or the homogeneous part of the polyethylene thin film.

The use of modified standard solutions seems to be an appropriate method of calibration for Laser ablation ICP-MS analyses. The simplicity of the preparation of these standards keeps the overall time of analysis short and the accuracy of the results obtained was satisfactory for the types of samples studied.

3. Further work.

A stainless steel and different polymeric samples were analysed during this project. Though the results obtained for these very different matrices were satisfying, the application of the new method of calibration involving the modified standard solutions should be extended to a much greater range of sample types. This method of calibration could be useful to geochemists for the analysis of glasses and fluid.
inclusions, to forensic scientists for the analysis of biological or inorganic materials (hair, nail, ceramics, glasses, etc), to the steel industry for the analysis of inclusions in steels, to the pharmaceutical industry to determine the repartition of heavy metals from new drugs in different organs, etc. For all those possible matrices, the use of the new method of calibration will have to be tested and a suitable internal standard will have to be found in each case.

Several other aspects should be studied in more details. The behaviour of many more analytes should be observed in the modified standard solutions. Analytes responses from the ablation of standard solutions at different laser wavelengths should be compared to check for the occurrence of elemental fractionation.

Further work would be necessary to understand the mechanism of ablation of the modified standard solutions. However, this would undoubtedly be a major project in its own right, and whist it would be of scientific interest, it is not clear exactly what analytical benefits might be derived from this additional knowledge.