

Day 2

Trace elements by ICP-MS

A- Sample Introduction System: liquid

- A1- Sample preparation
- A2- Problems:
 - Solution saturation
 - Drift (calibration and sample induced)
 - Matrix effects
 - Interference
 - Standardisation (calibration)
- A3- Acquisition:
 - Plasma ignition
 - Mass Calibration
 - Method
 - Sequence
- A4- Data reduction
- A5- Applications

B- Sample Introduction System: solid

- B1- Sample preparation
- B2- Problems:
 - Matrix effects
 - Element fractionation
 - Standardisation (calibration)
- B3- Acquisition
 - Tuning
 - Mass Calibration
 - Method
 - Sequence
- B4- Data reduction
- B5- Standardisation

A- Sample Introduction System: LIQUID

A1- Sample preparation

A2- Problems:

- *Solution saturation*

Element stability are different in different solvent and different matrix.

- *Drift*

It can have a dramatic effect on all analyses performed using ICP-MS. Drift arises when an instrument response changes with time. Drift appears to be directly dependent on the matrix of the solution introduced to the ICP-MS. Typically, samples with moderate to high total dissolved solids contents will deposit salts on the cone orifices. This plating action results in a drop in sensitivity over time. The drift could be: **a) linear as a function of time; b) a non-linear function of time but is independent of mass; c) Instrument response is a non-linear function of time and mass (see discussion on calibration below).**

- *Matrix effects*

The role that matrix plays is complex and varied, and can lead to dramatically reduce the accuracy. Complex geological matrices generally result in a suppression of the analyte, although enhancements have been observed.

- *Interference:*

Apart from isobaric overlap, recombination of ions leads to the formation of interferences. There are different types of interferences:

- The argon plasma: Ar⁺, Ar²⁺

- Polyatomic species: Contribution from the solvent and combination with the analyte species: (H₂O⁺, H₃O⁺, OH⁺, ArH⁺ etc....). Incomplete dissociation of the sample matrix will lead to recombination in the plasma tail, usually in the form of oxide MO⁺ (or MO₂⁺, MO₃⁺). The oxide formation will depend on the oxide bond strength of the element (quite high for REE for example).

- Air entrainment and gas impurity (N⁺, O₂⁺, NO₂⁺, etc...)

- Material eroded from the cones (isotopes of Ni, Cu, Mo etc...)

- *Standardisation (calibration):*

Three methods for quantitative analysis available for the ICP-MS:

- **Standard additions:** In the case of standard additions, the technique involves taking the sample, dividing it into equal aliquots, and adding to each increasing amounts of a reagent containing the element(s) under consideration. The increments usually consist of equal volumes, and a minimum of four mixtures is required per sample. Therefore, a set of standard addition "spikes" must be prepared and calibrated in addition to the preparation of the sample. Thus, for each sample analysed by standard additions at least four solutions must ultimately be measured. Standard additions can routinely yield data that is better than 2%

- **Isotope dilution:** Isotope dilution, while being a potentially extremely accurate technique, is also labour intensive and more costly than standard additions. Isotope dilution mass spectrometry is based on the addition of a known amount of enriched isotope (called the "spike") to a sample. After equilibration of the spike isotope with the natural element in the sample, the ICP-MS is used to measure the altered isotope ratio. The difference between the isotopic ratio in the mixture and the natural isotope ratio can be used to accurately calculate the concentration of the element in the sample. While the addition of spike is not particularly time consuming, the initial time spent in preparing the spike solutions is. Additionally, the initial cost of purchasing the spike solution can be high. A further disadvantage of isotope dilution is that the concentration in the unknown is generally a non-linear function of the isotope ratio of the standard-spike mixture. This non-linearity leads to error magnification, which becomes a serious problem when the isotope ratio in the sample-spike mixture approaches that of either the natural value or the spike value. Avoiding error magnification requires some knowledge of the concentration before spiking. IDMS produces data better than 1%.

- **External standardisation:** External standardisation minimises effort but often sacrifices precision. In the external standard calibration method, the blank-subtracted signal intensities for the element of interest in a group of standards are plotted against the known concentration of the element in those standards. A calibration curve is fitted to the data points. This technique is not as labour intensive as standard addition or isotope dilution, however it is not as accurate. Using a straightforward classical approach, under optimal conditions of instrument tuning and maintenance, the ICP-MS produces results with a maximum precision for analysis of geological materials (i.e., complex matrices) in the range of 5 to 10 %.

The main problems associated with external calibrations are:

- *Dynamic range*: Typically in the commercially available ICP-MS instruments, the linear dynamic range, the range over which the response of the instrument is linear with respect to analyte concentration, is greater than six orders of magnitude. As such, the curve fitted to the standard data should be linear. The slope of the line defined by the standards is proportional to the concentration in the standards. The unknown sample is run and its signal intensity is plotted against the curve to determine the concentration.

- *Matrix effects*: The role that matrix plays is complex and varied, and can lead to dramatically diminished accuracy. Complex geological matrices generally result in a suppression of the analyte, although enhancements have been observed. One common suggestion is to match the matrices of the standards and unknowns. Using a suite of United States Geological Survey (USGS) standards encompassing the entire range of igneous rock compositions from basalt to granite (e.g., BIR-1, DNC-1, W-2, BHVO-1, AGV-1, GSP-1, and G-2) results in non-linear calibration curves for the rare earth elements (REE). The maximum range in concentrations in rare earths in this suite is less than 4 orders of magnitude, and thus is well within the linear dynamic range of the instrument. The non-linear portion of the calibration curves involves AGV-1, GSP-1 and G-2, the 3 non-basaltic members of this suite. However basaltic rocks should be analysed against basaltic standards and granites against granitic standards.

- *Drift*: It can have a dramatic effect on all analyses performed using ICP-MS. Drift arises when an instrument response changes with time. The drift could be:

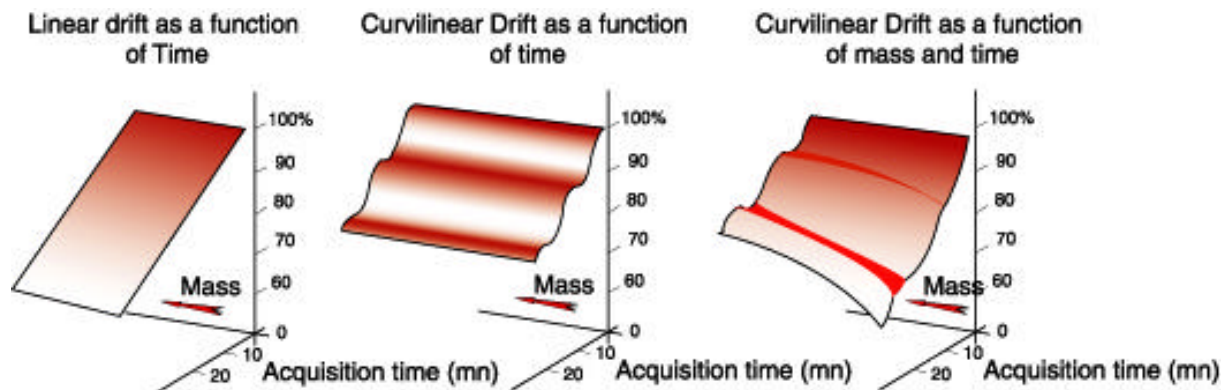


Figure 3.1: linear as a function of time; a non-linear function of time but is independent of mass; a non-linear function of time and mass (from Cheatham et al 1993).

Instrument response is a non-linear function of time and mass.

In reality, the analysis of geological samples with complex matrices is indeed a complex function of time and mass, and that neither simple recalibration nor internal standardisation adequately corrects for it. So long as matrices of samples and standards are well matched, the drift is the single most important factor limiting analytical precision in ICP-MS analysis. Ideally, the matrix would have to be removed to avoid matrix effect, but the chemical processing required for matrix removal is generally labour intensive. Matrix removal also introduces two other potential sources of analytical error: blank and yield. The development of a method of drift correction is preferable to remove the matrix effect.

The technique is based on the analysis of a 'drift correction' standard after every 4 or 5 samples. The sample and standards are mixed with an internal standard (e.g. 10ppb of Indium). A first correction is applied for physical drift, while recalculating each sample's drift based on the signal given by the first standard (Figure 3.4). After the first drift correction for Indium, a polynomial curve is fit to each isotope analysed, and a correction is applied, based on this curve to the measured intensity of the respective isotope in both sample and standard solutions. Using this technique, the ICP-MS produces results with a maximum precision for analysis of geological materials (i.e., complex matrices) in the range of 5 to 2 percent or below for elements such as the Rare Earth Elements.

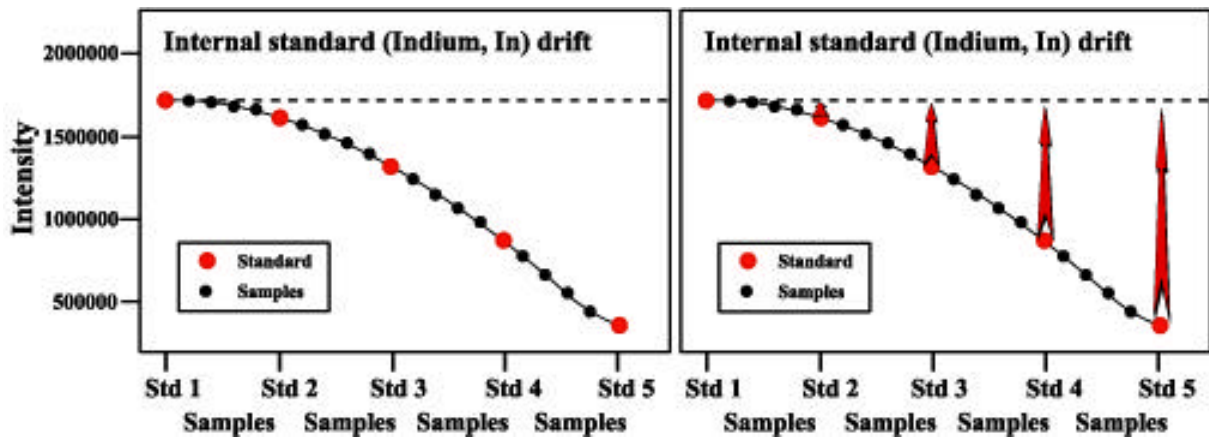
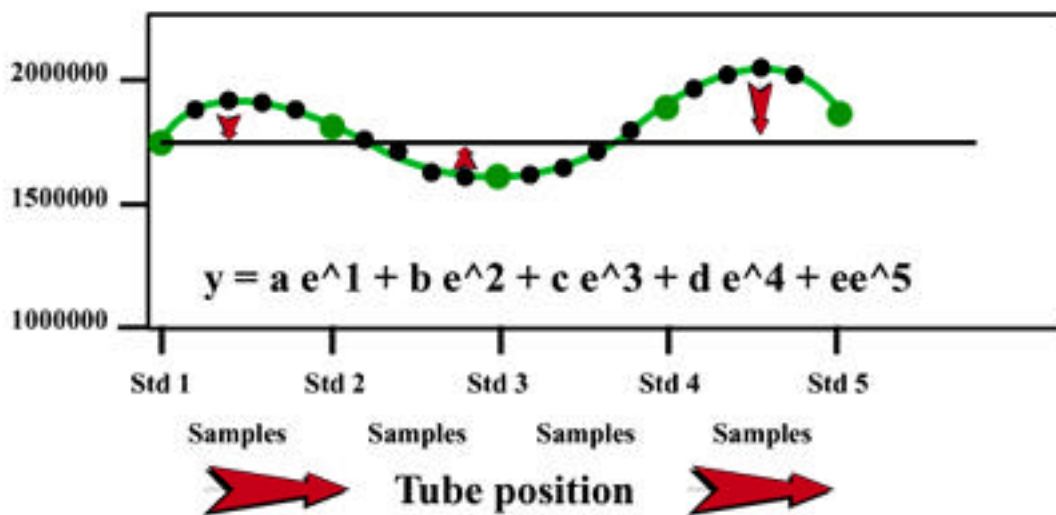
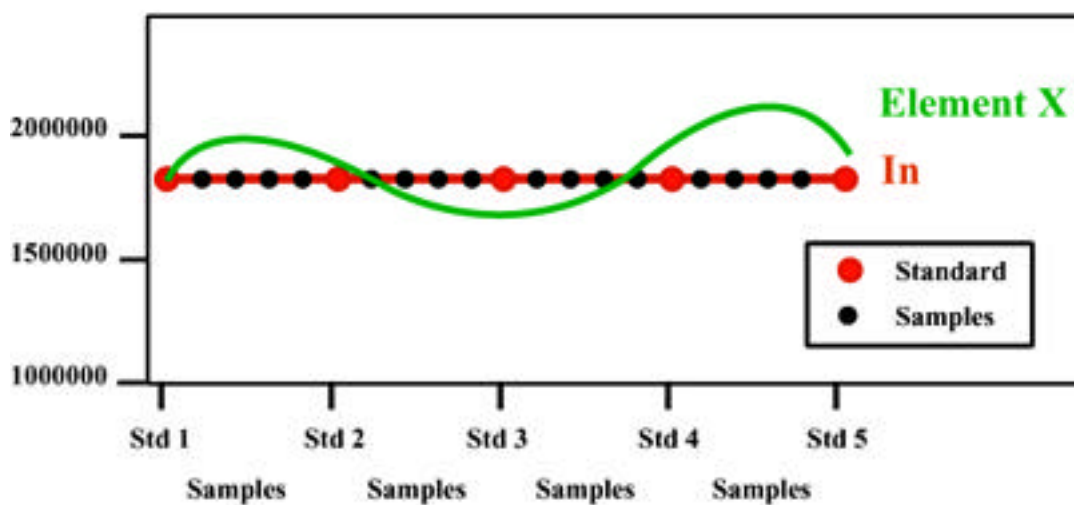


Figure 3.4: Physical drift correction based on Indium for example.

Matrix Effect : Chemical effect



**Calcul of a, b...e from the polynomial
 for each element as a function of the tube position**

Figure 3.5: Chemical Drift correction for each elements, based on the response for each standard, after calculating the polynomial curve.

A3- Acquisition

Plasma Ignition

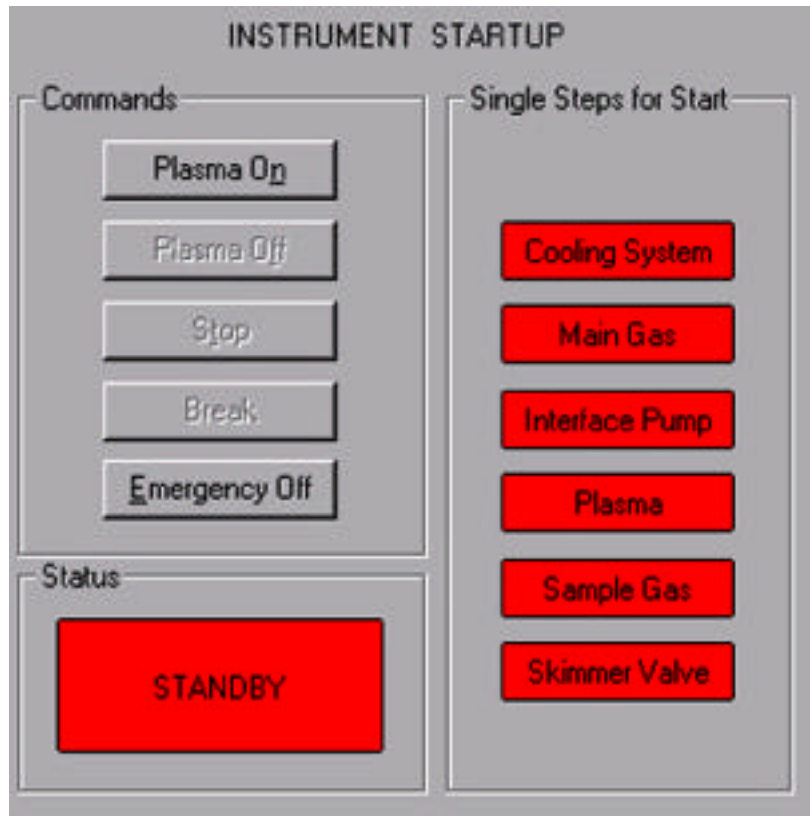


Figure 3.6: The 'Start-up' window of the Element. When 'Plasma ON' is pressed, the ICP perform a series of operation from switching the cooling system ON, turning the mai gas (cool, auxiliary and sample) ON, switching the interface (to decrease the vaccum i the interface area, between the two cones), switching the plasma ON and finally open the skimmer valve which separate the ICP from the analyser.

Mass Calibration

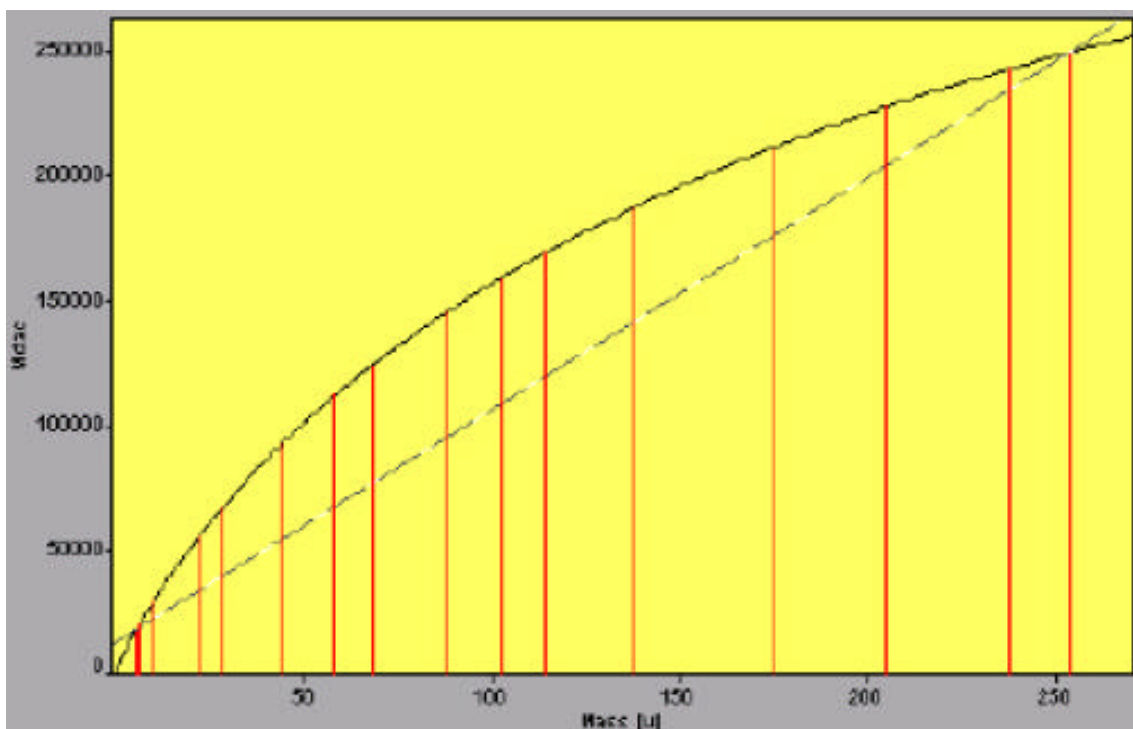


Figure 3.8: Part of the 'mass calibration' window of the Element, which check the position of each of the isotopes.

Method

Isotope	Mass amu	Mass Window %	Mass Range amu	Magnet Mass amu	Settling Time s	Sample Time s	Sample per Peak	Segment Duration s	Search Window %	Integration Window %	Detection Mode
Li7	6.0145	100	6.005-6.025	6.005	0.1	0.005	20	0.1	100	100	Counting
Si29	28.987	100	28.971-28.992	28.971	0.04	0.005	20	0.1	100	100	Analog

Figure 3.9: Example of the 'method' window of the Element when analysing solutions

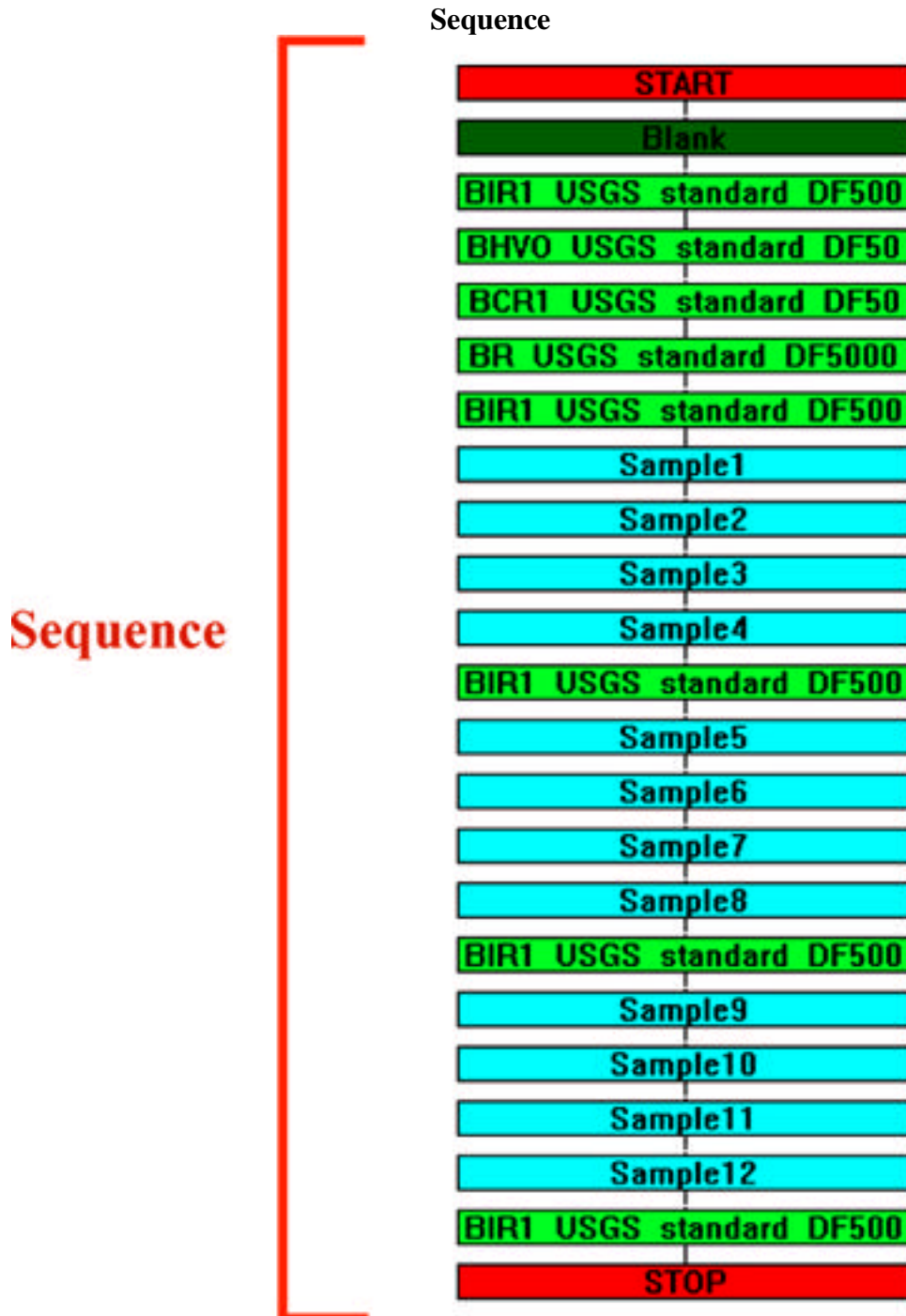


Figure 3.10: The 'sequence' window of the Element

A4- Data reduction

External calibration curve after drift and matrix effect correction (see above)

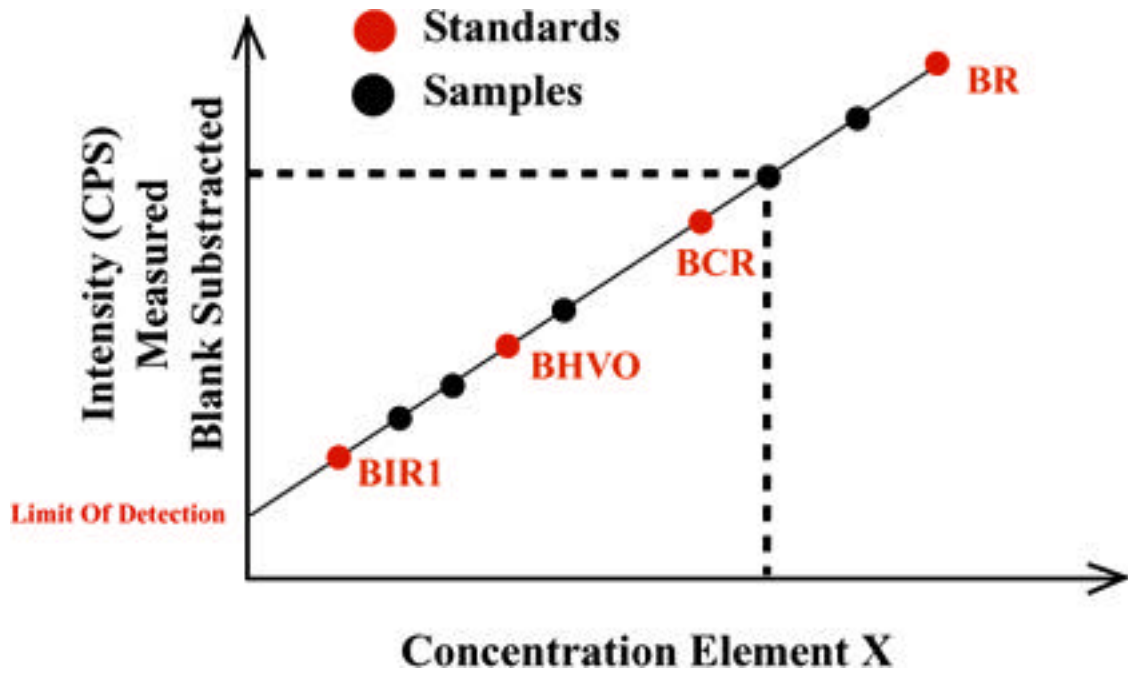


Figure 3.11: Final external standardisation step using USGS standards. The concentration of the element X is calculated using calibration lines passing through matrix-matched standards against corrected intensity for the drift and the blank (see above)

Concentration are calculated using a regression line. Both slope (b) and intercept (a) are subject to errors. The following equations are from Odegard et al (1998) and initially from Miler JC & Miller JN (1994): statistics for analytical chemistry. Ellis Horwood Limited, publishers, Chichester. Halsted ress: adivision of John Wiley & sons, New York, chichester, rsbane, toronto, 2nd edition.

$$S_{x_0w} = \frac{S_{(y/x)_w}}{b} \sqrt{\frac{1}{w_0} + \frac{1}{n} + \frac{(y_0 - \bar{y}_w)^2}{b^2(w_i x_i^2 - n\bar{x}_w^2)}}$$

Y_0 = experimental value of y for which the concentration of x_0 is to be determined.

S_{x_0w} = estimated standard deviation of the predicted x_0

N = number of calibration standard

W_i = weighted factor

$$S_{(y/x)_w} = \sqrt{\frac{w_i(y_i - \hat{y}_i)^2}{n - k}} \quad \bar{y}_w = \frac{w_i y_i}{n} \quad \bar{x}_w = \frac{w_i x_i}{n}$$

The most accurate technique used a mixture of external drift correction and enriched isotope internal standardisation (Eggs et al, 1997). In this case the optimal concentration level to "spike" the sample can be determined from the following equation;

$R^{i/j}$ is the ratio of isotope i to j in the spike, sample and mixture

$$R_{mixture}^{i/j} = \sqrt{R_{spike}^{i/j} * R_{sample}^{i/j}}$$

A5- Applications

ICP-MS is the method of choice for trace element measurements, because of its ease of use, large sample output and low limit of detection, in comparison to other analytical technique such as TIMS and INAA. A listing of the applications of trace element measurements by ICP-MS is beyond the scope of this lecture. The calculated Limit Of Detection using the Element, are shown on Figure 3.12 and are typically between the PPQ to the PPT range, dependant on the m/z ratio.

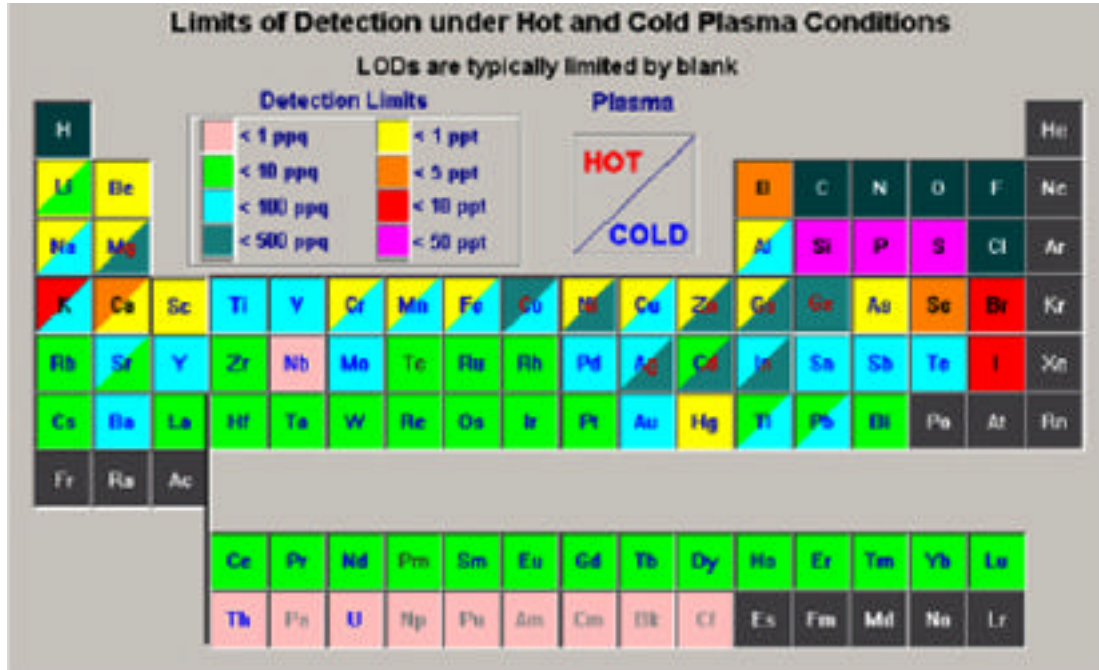


Figure 3.12: Calculated limit of detection under hot and cold plasma conditions using the Element.

B- Sample Introduction System: SOLID

B1- Sample preparation:

In general sample preparation is straightforward. Polishing is usually necessary if the electron microprobe is to be used for internal standardisation before loading the sample into the sample cell. Because the laser sample cell is not under vacuum, outgazing of the support material is not a problem.

Powdered samples should be treated in a similar way to XRF analysis and stabilised either by

- (a) compacting the sample into a pellet with or without a binding agent,
- or
- (b) fusing the sample to a borate glass or using a strip heater.

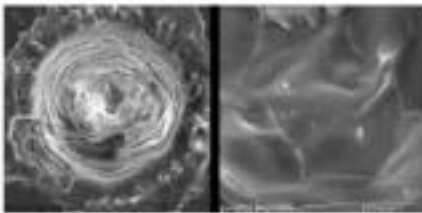
B2- Problems:

Several problems are associated with the quantitative analysis of trace elements by laser ablation ICP-MS:

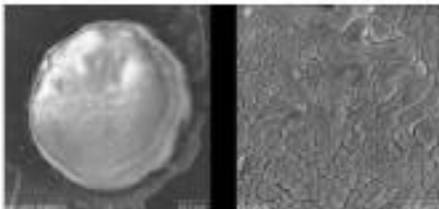
Matrix effects

Dependant on the colour of the mineral and its absorption characteristic of the specific wavelength of the laser ablation system used. Different volume of sample will be ablated. Therefore, two minerals having the same concentration will generate different signal dependant on their physical characteristics (colour, cleavage etc...).

Transparent Garnet



Dark Garnet



Ablation volume (elemental abundance) is matrix dependant

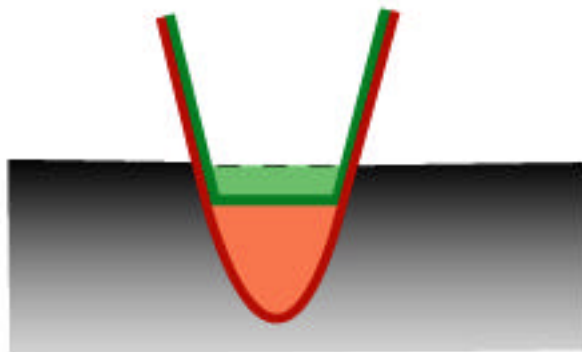


Figure 3.14: Comparison between the ablation of a dark and a light mineral.

Element fractionation

Selective removal of some elements and material can be caused by the laser interaction with the sample, a process termed "elemental fractionation".

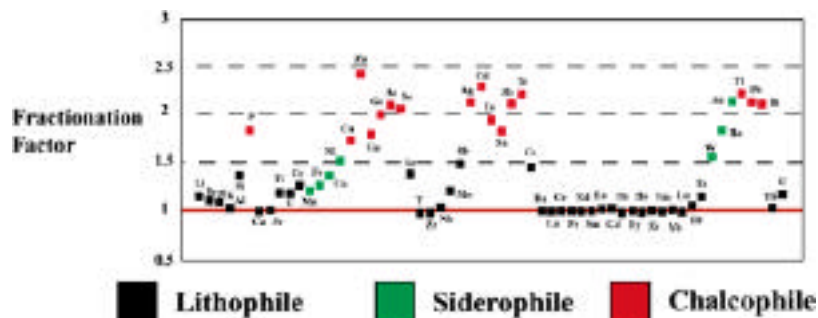


Figure 3.15: Fryer et al (1995) have ratioed the signal from the first two minutes over the last two minutes and calculated a fractionation factor while ablating a synthetic glass standard (NIST610). The fractionation intensity seems to follow the Goldschmidt classification of elements (lithophile, chalcophile and siderophile).

Several process contribute to the fractionation process between element during the ablation:

Crater size/depth ratio (Eggins et al, 1998; Mank and Mason, 1999):

At constant laser fluence, the principle parameter, which appears to control fractionation behaviour, is the aspect ratio of the ablation pit.

For the deeper craters the three structural regions of an ablation crater can be defined as follows:

-Regions A, at the base, The ablation front: The glass appears to have been removed cleanly from the surrounding sample and there is little evidence for the condensation or re-deposition of ablated material. However some very small melt globules (<10 µm) are sometimes seen in this region and the smooth nature of the walls may be due to re-melting by the plasma following ablation.

-Regions B: The intermediate region: Characterised by thermal cooling cracks on the walls of the crater. This part of the ablation crater is where particles escape from the ablation front, some of which are deposited on the walls where they may be re-ablated by reflected light and heated by the secondary plasma that penetrates into the ablation crater. Heating in this region may also lead to volatilisation of elements with the particles that are ablated from deeper in the crater.

-Region C: Crater opening: Where large amount of particles redeposition and melting have been taken place. Fracturing of the sample is most apparent in this region and may be related to stress during cooling or recrystallisation of thin molten layers. Deposition around the crater on the surface of the glass sample can be extensive and is dependant upon the amount of material removed during the ablation event, the viscosity or density of the gas in the sample cell and the dynamics of flow of the gas in the sample chamber.

The model can be applied under all power density, repetition rate and static focus parameters that have been applied in this study. The formation and relative influence of each structural unit is controlled by the depth/diameter ratio of the ablation crater.(Mank and Mason, 1999). For minimal fractionation it is essential to maintain power density well above the ablation threshold giving a crater of similar diameter from the top to the base. A crater/depth ratio lower than 6 is recommended to reduce the level of fractionation.

Laser wavelength:

Ablation mechanisms are influenced by the photon energy of the laser. Shorter wavelengths offer higher photon energies for bond breaking and ionisation processes. The ablated volume in different matrix will be similar for shorter wavelength in the standard and the unknown, which limit fractionation effect between the two and make quantification easier (figure 2.24).

Gas medium

Sensitivity improvement are expected using mixed gas such as nitrogen. Durrant (1994) have shown that the addition of about 1% N₂ in the coolant gas increase the sensitivity by a factor of 3 for some elements. Addition of about 12% N₂ to the cell flow have a similar effect. An improvement by a factor of 5 is also claimed by (Hirata and Nesbitt, 1995) for heavy masses. Moreover, mixed argon-helium atmosphere retards condensation and reprecipitation of ablated material around the excavated crater (Louks, et al., 1995; Eggins et al 1998; Mao et al 1998; Leung et al 1998; Chan et al 1998; Günther and Heinrich 1999) and improve sensitivity by a factor of 5 for some elements

The manner of deposition of material around the top of the crater is very different when ablating in He with a larger diameter blanket of deposited material. However, the material is deposited in a thinner layer of coalesce particles than in the case of the blanket observed when ablating in Ar.

Particle size and entrainment

Particles of different sizes are entrained into the plasma by the carrier gas for different laser wavelength. Recent studies have showed that the particle size distribution in the ICP is the major factor responsible for inter-element fractionation. Therefor other parameter such as **power density** or **focusing conditions** have also an influence.

Interferences

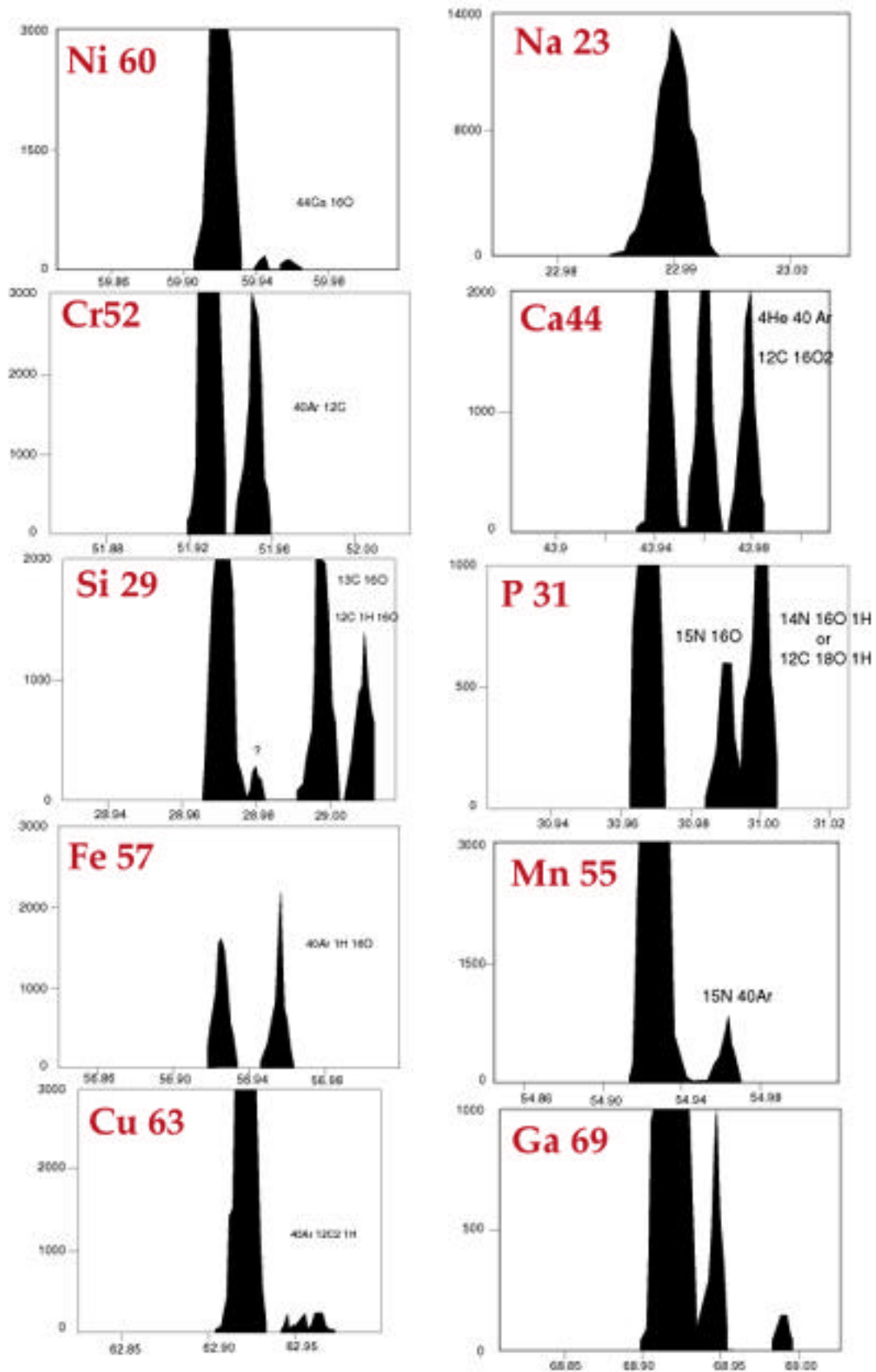


Figure 3.16: Some classic interference mainly due to air entrainment (Si29, P31, Ca44, Fe57, Mn55). The interference are minimal for Ni, Cu and Cr are result mainly from source contamination. Those interference may be reduce by using the medium resolution setting of a high resolution magnetic sector ICP.

B3- Acquisition

THE FASTER - THE BETTER

NB: Dependant on the type of instrument used different terms are used for the same purpose:

	Quadrupole	Magnetic sector
Total time required for acquisition of intensity information of the complete list of selected mass	Spectrometer sweep time	Total Scan time
Time spent to scan from low to high mass	reading	Scan time
The sum of several reading	Sweep time	
Time spent acquiring data at a particular mass	Dwell time	Sample time
Number of acquisition per mass	Points per peak (From 1 to 3)	Sample window/ number of sample
Time wasted between acquisition	Settling time (0.1-2 ms)	Settling time (0.1 to 100 ms with fast scanning option)

NB: the dwell time is used as the total ablation time with the NewWave laser ablation software.

Tuning and Mass Calibration are the same as for solution analysis

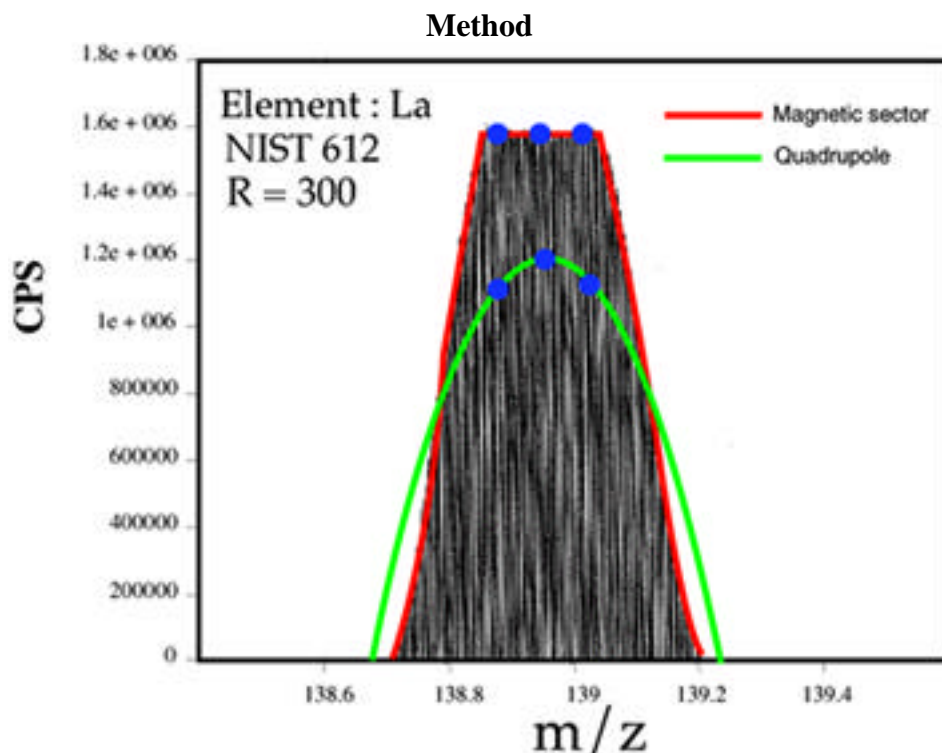


Figure 3.17: Average of 50 scans using a 1 second scan duration which translates to 1000 UV laser shots at the surface of the sample using a magnetic sector ICP. The typical flat topped peak shape produced for La during ablation of NIST 612 (~37 ppm) is characteristic of magnetic sector instruments and should allow the precise measurement of isotope ratios. The precision should be higher to that of a quadrupole instrument, which is characterised by a more gaussian peak shape.

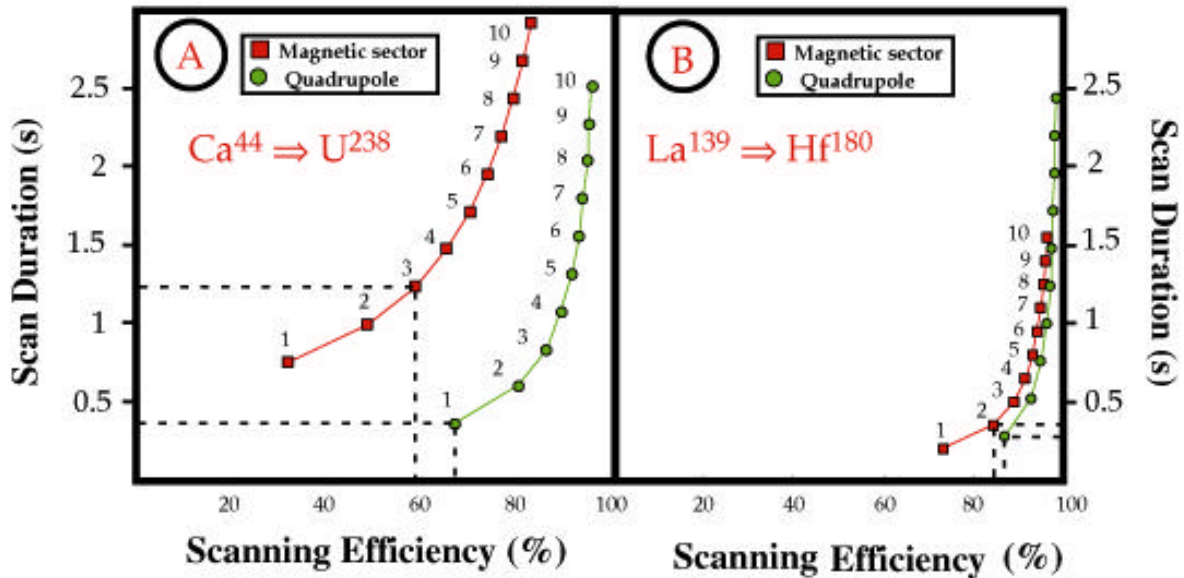


Figure 3.18: The efficiency of the method (time spent analysing / total scan time) will be dependant on the number of isotopes and the scanning range. This figure compare the efficiency of an Element1 and a quadrupole instrument while scanning from Ca44 to U238 (A) and from La to Hf (for REE measurement in a zircon, B). In the first case the magnetic sector instrument reach a maximum of 60% efficiency with a scan duration of 1,2s and with 3 points per peak, while the quadrupole reach a higher efficiency using a lower number of points per peak (1) and a much lower scanning time. In this case the quadrupole instrument is much more efficient. In the second scenario, both instruments reach similar efficiency using 2 points per peak. Since magnetic jumps are slower than electric jumps, magnetic sector will tend to be slower in order to avoid magnet hysteresis. Significant improvement has been made on the second generation of sector field instrument using the fast scanning option (Element2) but quadrupole remain faster and more efficient using classical method involving the measurement of 30-40 elements from Li to U.

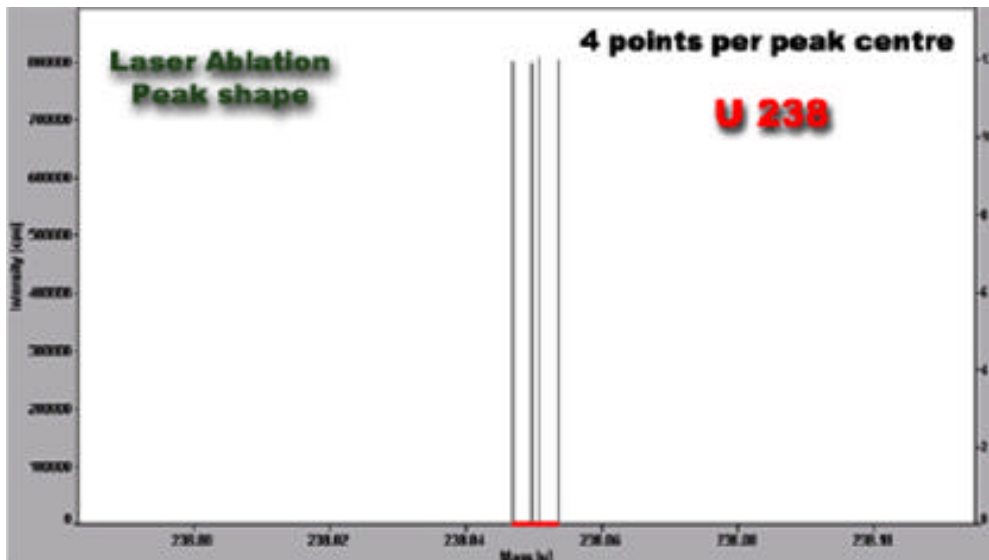


Figure 3.19: Example of a typical laser ablation peak shape (compare with figure 3.15). The centre of the peak top is only analysed (4 points per peak in this case), in order to improve the scanning efficiency.

Isotope	Mass amu	Mass Window %	Mass Range amu	Magnet Mass amu	Settling Time s	Sample Time s	Sample per Peak 100	Segment Duration s	Search Window %	Integration Window %	Detection Mode
Li7	6.0145	4	6.005-6.025	6.005	0.1	0.005	100	0.1	4	4	Counting
Si29	28.987	4	28.971-28.992	28.971	0.04	0.005	100	0.1	4	4	Analog

Figure 3.20: The ,method‘ window of the Element (compare with the method use for solution analysis, figure 3.9). Each elements are analysed using a very small mass window (1%, the very centre of the peak top define during the mass calibration). The magnet mass shows the position of the magnet while it rests between jumps. A sample time (time spent on each channel of points) has been set at 5 ms. Only one point per peak has been chosen. The segment duration will therefor be 5ms for each isotope. All elements has been analysed using the Electric Scan (Escan) and in counting mode (major elements such as Si or Ca, in silicates, will be analysed in Analog mode, in order to protect the SEM).

Sequence

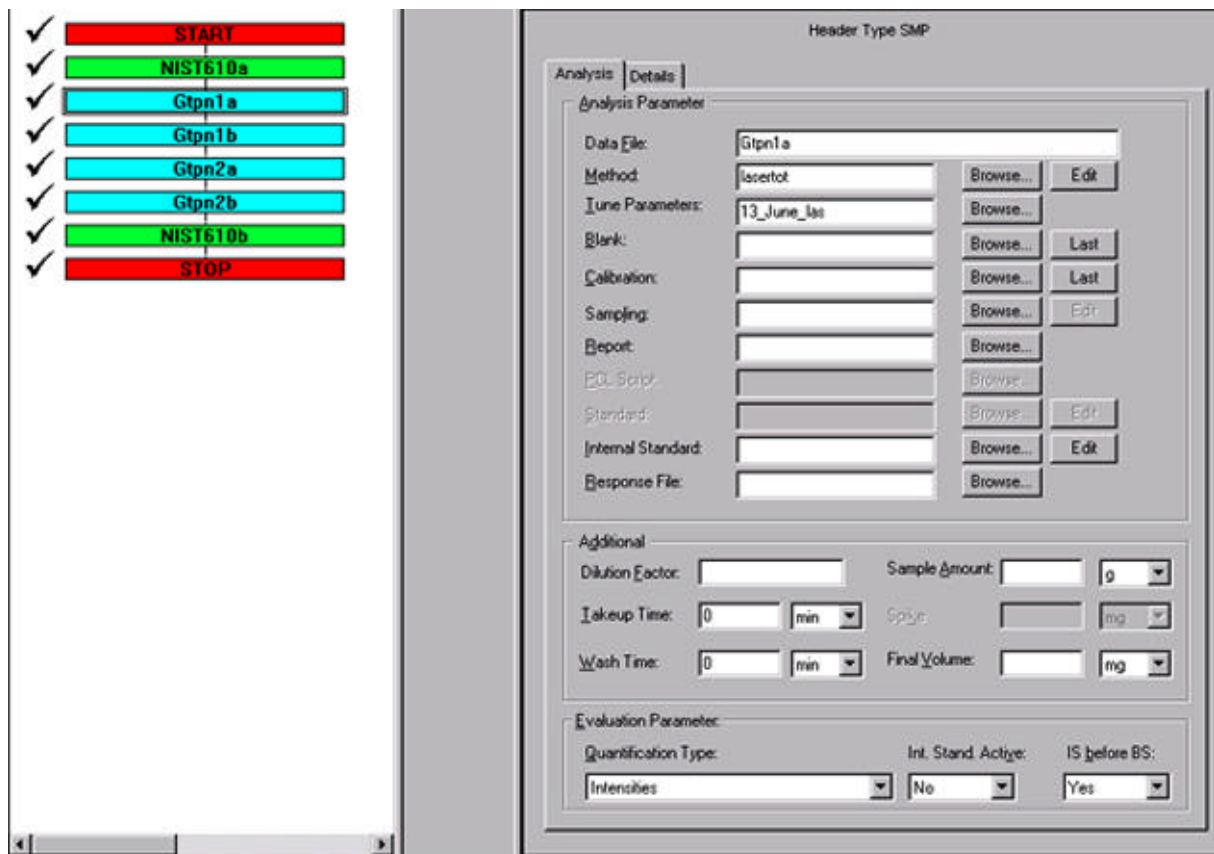


Figure 3.21: The ,sequence‘ window of the Element (compare with the sequence use for solution analysis, figure 3.10). The sequence (left side) will start with the measurement of an external standard such as NIST610, followed by a series of sample before an other external standard etc...A specific method and tuning parameter could be associated to each samples and standards (right side).

NB: the measurement of the blank is a matter of debate: gas blank, gas blank while firing the laser or blank sample (e.g. high purity quartz).

B4- Data reduction

Standardisation (calibration)

Once microparticulate material has been transported by the stream of argon to the plasma, the number of ions which reach the detector depends on (a) the atomic proportions of the element in the source mineral, (b) the amount of material removed during ablation, (c) the ionisation potential of the element in the plasma, and (d) isotopic abundance. Assuming no fractionation during ablation between volatile and other more refractory elements, it is possible to overcome these problems using an internal standard (known concentration of one element in the unknown using another analytical technique). Electron microprobe analysis is usually used to measure the concentration of the element chosen as the internal standard in the unknown. Calibration can then be achieved by comparing the response for the internal standard element in a reference material and the unknown. This element response for the internal standard allows the analyst to apply a correction for other elements included in the selected menu. In order to perform this correction, the geochemist must: (a) assume that the element response in the unknown is similar to that of the reference material (i.e., both matrices are matched); (b) assume that the reference material has a homogeneous trace element composition and distribution; and (c) correctly choose the internal standard in the material analysed (usually a minor isotope of a major element). Once these several operating parameters has been controlled, a typical analytical sequence comprises; (a) analysis of the argon blank; (b) analysis of the reference material; (c) analysis of the unknown; (d) second analysis of the reference material in order to monitor the drift (sensitivity variation of the instrument through time); (e) analysis of other unknowns.

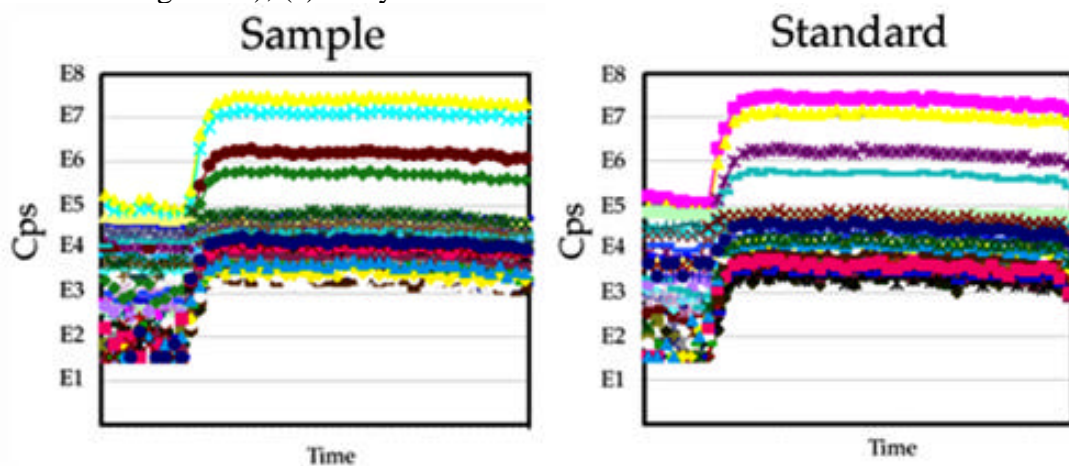


Figure 3.22: These figures show the evolution of the signal (intensity for several isotopes) through time, while measuring a standard and a sample. A gas blank is usually measured for 20-30 seconds, then the laser is firing on the sample and the intensity increase and stabilise (on a log scale). Because of matrix effect, sample having the same concentration will generate different signal, BUT the ratio between elements will stay the same (if there isn't any inter-element fractionation, see above). The average intensity of the gas blank will be subtracted to the average intensity of the sample and standard. These intensities will be ratioed to the internal standard (Ca or Si for silicates for example) and the following equation will be use for quantification.

$$= \frac{\left(\left[\frac{I_{(m,x)}}{I_{(m,I_s)}} \right] * (C_{I_s})_{samp} * (C_{(m,x)})_{std} \right)}{\left(\left[\frac{I_{(m,x)}}{I_{(m,I_s)}} \right]_{std} * (C_{I_s})_{std} \right)}$$

Figure 3.23: Equation use for the calculation of the trace element composition using the internal standardisation technique. $I(m, x)$: Intensity of the element x in the sample or standard; $I(m, I_s)$: Intensity of the internal standard in the sample or standard; C_{I_s} : concentration in ppm of the internal standard in the sample; $C_{(m,x)std}$: concentration of the element x , in ppm, in the standard; $C_{I_s Std}$: concentration of the internal standard in the standard.

Limit Of Detection

The figure below represent a comparison of the limits of detection (LOD) between different analytical techniques such as PIXE, Synchrotron XRF, Ion Probe, IR laserICPQuadMS (with quadrupole mass filter) and UV ICPsectorMS. LOD have been calculated as three standard deviations from the background when ablating a synthetic glass from NIST (NIST612) at 5Hz, 1.5mJ and a crater size of 50 μm . LOD vary from 3 ppb for Sc to 300 ppt for heavier masses such as Pb and U. These LOD can be significantly reduced to the lower ppt range by reducing the size of the element menu or by using a higher laser output energy or repetition rate when analysing elements such as the REE and HFSE which show less fractionation as a result of higher laser pulse energies.

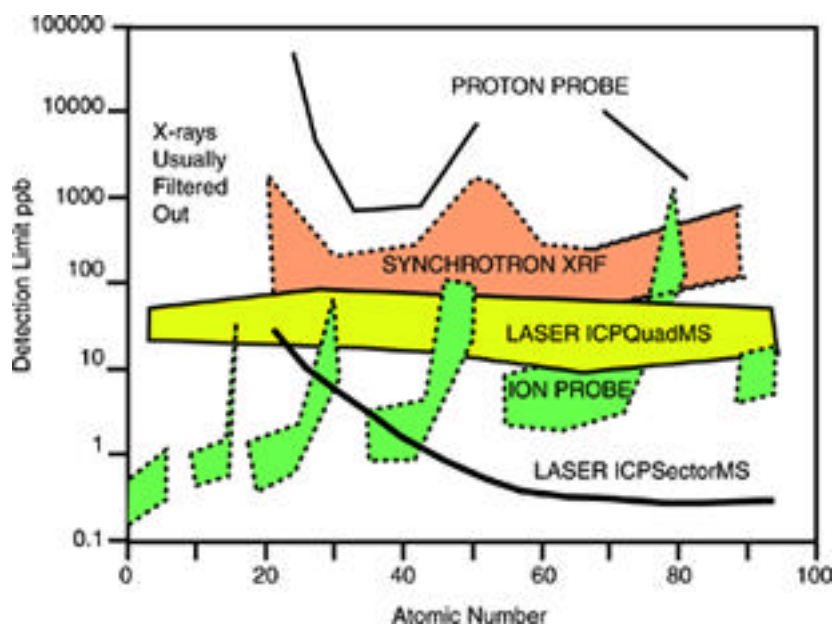


Figure 3.24: Comparison of the limit of detections using different analytical technique such as proton probe, synchrotron XRF, laser ablation quadrupole MS, secondary ion probe and laser ablation Sector MS as a function of the atomic number.

B5- Standardisation:

There are four sets of standard available for quantitative laser ablation analyses of trace elements. Unfortunately they all have a silica-enriched composition. The compositions of these glasses could be found in the appendix.

a- **NIST: Standard Reference Material (SRM) of National Institut of Standards and Technology (NIST):** Information on the original manufacturing of these glasses could be found in Hinton (1999). There are mainly made of a mixture if African sand, Diamond alkali calcium carbonate, Stauffer soda ash, Linde alumina and Olin sodium nitrate. Batches of trace element were made separately and they were latter on mixed together. They are the most widely used for trace element analysis by laser ablation ICP-MS. 4 main types of standards has been made, having different concentration level and wafer thickness: The sixty one elements added to the base glass mix have a final concentration of about 450 ppm (NIST 611-610), about 40 ppm (NIST612-613), 1ppm (NIST 614-615) and less than 100 ppb (NIST 616-617). Those glasses are commercially available see NIST website)

b- **USGS: United State Geological Survey BCR2G, BHVO2G, BIR1G glasses.**

They have been produced by re-melting (1600C) approximately 2kg of the original whole rock powder standard in a 1 litter platinum bowl using a Linderberg heavy duty furnace equipped with high temperature silicon heating elements. To moderate the oxidising environment of the furnace, 100 ml platinum crucible filled with graphite rods were place behind and in front of the platinum bowl containing the standards. The platinum bowl were periodically tipped to facilitate the mixing of the molten material. After 4 hours, the molten material was poured out onto a 40 cm³ platinum sheet and allowed to cool. In the pouring process the molten material spread across the platinum surface, producing a "pancake" of fairly uniform thickness (2cm). Those glasses are available through S. Wilson from the USGS.

c- **DHL:** A new technique for preparing homogeneous glasses has been developed at the **department of geology of Manchester**, using the co-precipitation gel technique (Hamilton & Hopkins, 1995). All component except SiO₂ are contained in single solution as nitrates. About an equal volume of ethanol is stirred into this solution followed by the required mass of tetraethyl orthosilicate (TEOS). The liquid is vigorously stirred until a single solution homogeneous liquid results. Concentrated ammonia solution is now added while vigorous stirring continues in order create a gel with the silica and aluminium hydroxide. The whole content of the beaker should become semi-solid within a few minutes. 3 main standard have been created (DHL6-7 and 8) with concentrations ranging from 1, 70 to 150 ppm. A quartz blank have also been produced using this technique in order to improve blank correction. A PGE standard has also been produced although it has a silica rich matrix. They are commercially available by more expensive than the NIST.

- **MPI-DING:** The last were prepared at the Bayerisches Geoinstitut, Bayreuth following the technique described by (Dingwell et al, 1993). Direct fusion of 50-100g of rock ships at temperature about 1400-1600C were produced except for the peridotitic sample which was a 5:1 mixture of near pure silica. A thin wall platinum crucible was used to contain the melts. These sample could be contaminated with the ZrO₂ insulating boards and the resistive heating elements made of MoSi₂, and previous glasses melt from the same container. The glass were held at that temperature for 1 hour and then place in a second furnace equipped with a viscometer. The melt was stirred at 200 rpm for 12 hours using a Pt80Rh20 spindle. The melt was removed and quench by placing the bottom of the Pt crucible into water. Most of these glasses are homogeneous with the exception of the komatiitic ultramafic glass which shows beautiful olivine spinifex crystallisation feature:

d- **Direct fusion in graphite electrode** (Odegard, 1999): This technique has been used to prepare high purity quartz sample as well as synthetic rutile composition. The fusion time is about 1mn. This technique is fast and cost effective however the presence of gas bubble and some heterogeneity remain.