Chapter 3

The measurement technique of isotope dilution inductively coupled plasma mass spectrometry (ICP-MS)

3.1 Introduction

Total metal analysis, including trace and ultra trace elemental analysis of geological materials, have traditionally been performed using analysis methods such as atomic absorption spectroscopy (AAS), X-ray fluorescence (XRF), instrumental neutron activation analysis (INAA)[22]. Other methods include flame emission spectrometry, spectrophotometric analysis, ion selective electrode potentiometry, UV/VIS spectroscopy, candoluminescence, etc[10, 11]. Over the past 30 years more versatile measurement techniques have been developed in the form of inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

The first requirement for this study was to re-certify SARM 1 to 6 using a definitive technique with the potential to be a primary reference measurement procedure (primary method) as defined in Chapter 1[2]. Firstly, the method must be performed at the highest level of accuracy (trueness and precision)[2, 23]. Secondly, a complete measurement model must be defined in terms of SI units to facilitate the complete evaluation of all contributions to the measurement uncertainty in accordance with the Guide to the Expression of Uncertainty of Measurement (ISO GUM)[4].

Isotope dilution mass spectrometry is a direct ratio method which has been identified by the Consultative Committee for Amount of Substance (CCQM) of the International Committee for Weights and Measures (CIPM) to have the potential to be a primary method [1]. Isotope dilution measurements can be made with inductively coupled plasma mass spectrometry (ICP-MS), which is specifically suited to trace and ultra trace elemental analysis of geological materials.

3.2 Isotope dilution mass spectrometry (IDMS)

The principle of isotope dilution can be explained with the following illustration: In a large box you have a mixture of white soccer balls and rugby balls, where the one cannot be distinguished from the other. We want to know the number of soccer

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balls, but there are too many to count. So, what kind of method can we use to determine the number of soccer balls?

Put 100 red soccer balls into the box with the white soccer balls and rugby balls, and mix them completely. By doing this, the original white soccer balls are diluted with the red ones. Now, take 50 soccer balls out of the box and count the number of red ones. If the number is 5, then we know the ratio of the red soccer balls to all the soccer balls is 0.1 ($=\frac{5}{50}$). This ratio does not change before or after taking the soccer balls out of the box. Before taking the soccer balls out of the box, the number of red soccer balls in the box was 100, so the total number of soccer balls in the box had to be a 1000, suggesting that the original number of white soccer balls was 900. Thus we are able to establish the total number (though it is an approximate value) by measuring the ratio of the marked (red) soccer balls to the unmarked (white) soccer balls in a sample from the box, after mixing them.

This is the principle of isotope dilution analysis, where the white soccer balls correspond to the analyte in the sample and the red soccer balls correspond to the spiked analyte, which is added to the sample in a known quantity. The rugby balls correspond to the matrix.

Isotopes of an element are the atoms which have the same atomic number as the element, but have different mass numbers (numbers of neutrons in their nuclei). They are classified as stable isotopes and radioisotopes. In isotope dilution analysis, an enriched radioisotope or stable isotope is used as the 'marked' analyte. It behaves in the same way as the analyte and is called a 'spike' (also a 'marker' or a 'label'). The analyte in the sample is mixed with a defined amount of spiked analyte (then called the diluent). By measuring the specific activities or isotope ratio of the diluent and the diluted sample, it is possible to know the degree of dilution and calculate the quantity of the analyte in the sample. There is essentially no difference between the principles of radio and stable isotope dilution analysis. But, in the case of stable isotope dilution analysis, there is no corresponding radioactivity to measure, so the degree of dilution must be measured mainly by using mass spectrometry. Therefore, the development of stable isotope dilution analysis coincided with improvements in mass spectrometers.

Isotope dilution mass spectrometry (IDMS)[24] is based on addition of a known amount of enriched isotope (called the 'spike') to a sample. After equilibration of the spike isotope with the natural isotope of the element in the sample, mass spectrometry (MS) is used to measure the altered isotopic ratio(s). The measured isotope ratio (R_m) of isotope A to isotope B can be calculated as follows:

Basic equation:

$$R_m = \frac{A_x C_x W_x + A_s C_s W_s}{B_x C_x W_x + B_s C_s W_s} \text{ .... } (3.1)$$

where

A_x, B_x = the atom fractions of isotopes A and B in the sample, relative to all isotopes

A_s, B_s = the atom fractions of isotopes A and B in the spike

C_x, C_s = the elemental mass concentrations in the sample and the spike, respectively

W_x, W_s = the weights of the sample and the spike, respectively

The concentration of the element in the sample can then be calculated from this ratio:

$$C_x = \left(\frac{C_s W_s}{W_x}\right) \cdot \left(\frac{A_s - R_m B_s}{R_m B_x - A_x}\right) \text{ .... } (3.2)$$

A major advantage of the technique is that chemical separations, if required for accurate ratio measurement, need not be quantitative (after equilibration). In addition, ratios can be measured very reproducibly and, thus, concentrations can be determined very precisely. The technique is based directly on primary standards and the processes of weighing and mass spectrometric isotope ratio measurement. Thus, the weighing process ties the technique to the fundamental SI unit, the kilogram. The mass spectrometric isotope ratio measurement process ties the technique to the relative atomic masses of the elements, linking mass to amount of substance and thus to the mole, the fundamental unit of chemistry.

Accurate quantification with IDMS requires calibration of the isotopic abundances and concentration of the enriched stable isotope spike. Typically the enrichment of the stable isotope spike is known, but the concentration may not be accurately known. The concentration of the spike is then determined by a reverse isotope dilution procedure: The spike is mixed with known amounts of the natural material of the analyte of interest using solutions prepared from primary standards or high-purity materials of the analyte of interest. The isotopic composition of the natural material samples must also be determined for the few elements for which natural variations are expected (e.g., Pb).

The direct link between the amount content of an element in an unknown sample and a primary chemical standard is illustrated in **Figures 3.1** and **3.2**. The accurately known chemical composition of the primary assay standard (a standard with accurately know isotopic abundances as well as quantitative chemical composition), is used to obtain an accurate value of concentration for the spike solution by isotope ratio measurement of a mixture of these two solutions. This procedure is called "spike calibration", and the process of quantitatively diluting the highly-enriched ^{206}Pb atom fraction in the spike solution with the isotopically natural assay standard, is often referred to as "reverse isotope dilution" or "double isotope dilution". The spike calibration is an important and integral part of the isotope dilution process, making the analysis of the sample a "double ratio" process, through the spike, to the primary assay standard.

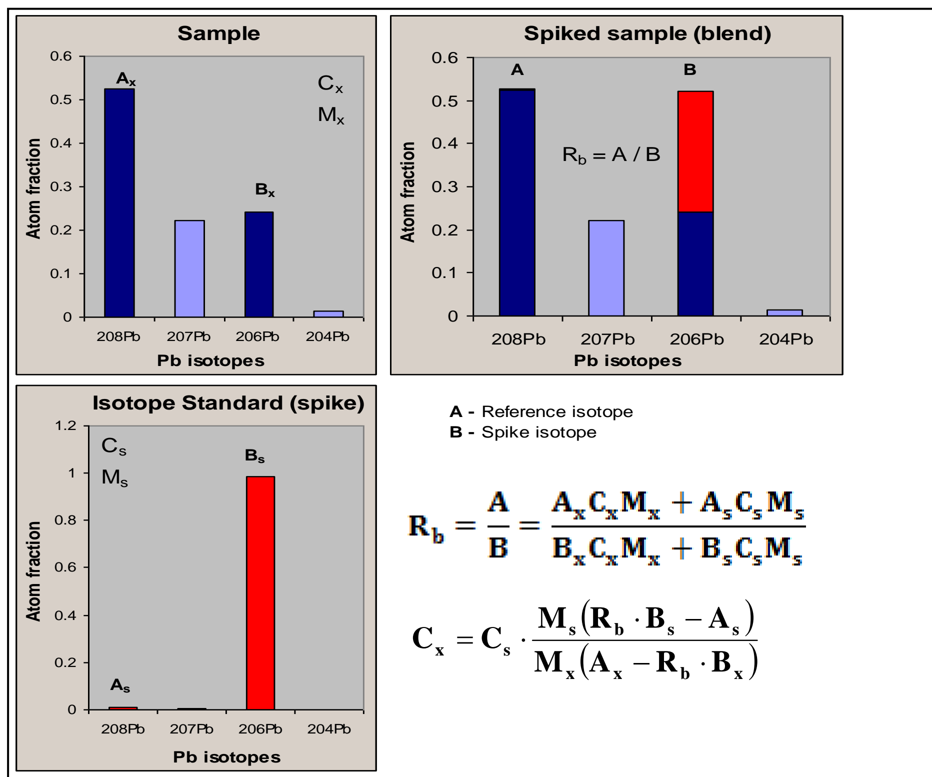

Figure 3.1: Illustration of the natural sample which is spiked with the enriched stable isotope standard to produce a stable isotope sample spike blend

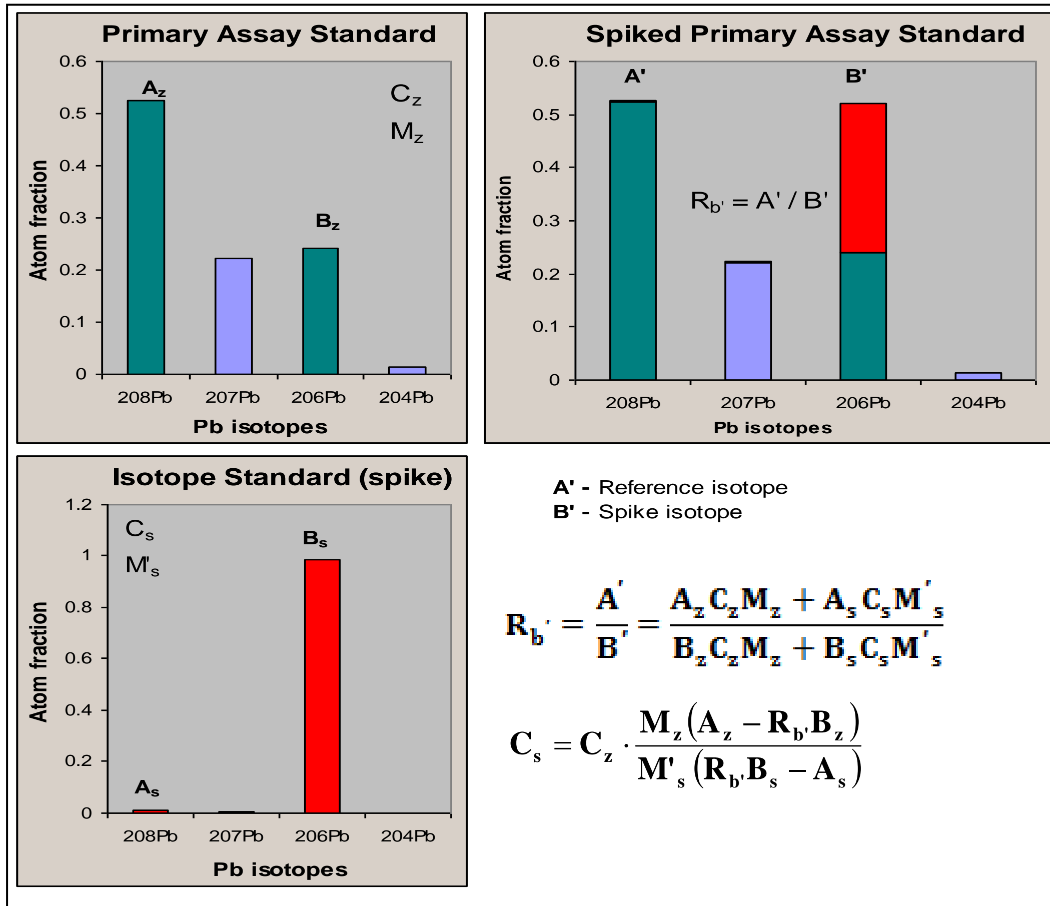

Figure 3.2: Illustration of the primary assay standard which is spiked with the enriched stable isotope standard to produce a stable isotope primary assay standard spike blend

The double isotope dilution technique is based on the use of a primary assay standard. The accurately known concentration of the primary assay standard is utilised to obtain an accurate value of the elemental concentration for the spike isotope standard through the measurement of the isotope ratio (R_b) of a mixture of these solutions. Therefore, double isotope dilution analysis requires accurate measurement of the isotope ratios of two mixtures (blend solutions), i.e. spike:unknown (R_b) and spike:assay standard ($R_b^{'}$).

$$R_b = \frac{A}{B} = \frac{A_x C_x M_x + A_s C_s M_s}{B_x C_x M_x + B_s C_s M_s} \text{.....................(3.3)}$$

If you make C_x the subject of the equation, then

$$C_x = C_s \cdot \frac{M_s (R_b \cdot B_s - A_s)}{M_x (A_x - R_b \cdot B_x)} \text{............................(3.4)}$$

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$$R_{b'} = \frac{A'}{B'} = \frac{A_z C_z M_z + A_s C_s M_s'}{B_z C_z M_z + B_s C_s M_s'} \text{..........................(3.5)}$$

If you make C_s the subject of the equation, then

$$C_s = C_z . \frac{M_z (A_z - R_{b'} B_z)}{M_s' (R_{b'} B_s - A_s)} \text{..................................(3.6)}$$

Then you substitute C_s in **equation 3.4**

$$C_x = C_z . \frac{M_z (A_z - R_{b'} .B_z)}{M_s' (R_{b'} .B_s - A_s)} \frac{M_s (R_b .B_s - A_s)}{M_x (A_x - R_b .B_x)} \text{...................... (3.7)}$$

If the conditions of ratio measurement are consistent between the spike calibration and the sample measurement, and assuming accurate weighing, potential systematic errors in the measurement process are cancelled or minimised in the final result. The calculation of the mass fraction of the analyte in the unknown sample is carried out according to the final equation (**equation 3.8**):

$$C_x = C_z . \frac{M_z .M_s (A_z - R_{b'} B_z)(R_b .B_s - A_s)}{M_s' .M_x (R_{b'} B_s - A_s)(A_x - R_b .B_x)} \text{.................(3.8)}$$

where,

x - index for the sample

s - index for the spike

z - index for the primary assay standard

b - index for the blend of fractions of sample and spike

b' - index for the blend of fractions of the primary assay standard and spike

C_z - Amount content or mass fraction of the primary assay standard

M_s - Mass of the spike in blend b

M_z - Mass of the primary assay standard in blend b'

M_x - Mass of the sample in blend b

M_s' - Mass of the spike in blend b'

R_b - Determined isotope ratio of blend b

$R_{b'}$ - Determined isotope ratio in blend b'

A_x, B_x = the atom fractions of isotopes A and B in the sample, relative to all isotopes

A_s, B_s = the atom fractions of isotopes A and B in the spike

A_z, B_z = the atom fractions of isotopes A and B in the assay standard

Equation 3.8 can be simplified further by substituting atom fractions with ratios.

$$C_x = C_z \cdot \frac{M_z.M_s.(R_z - R_{b'}).(R_b - R_s)}{M_{s'}.M_x.(R_{b'} - R_s).(R_x - R_b)} \text{............ (3.9)}$$

where

R_b = Determined isotope ratio in the sample blend, b

$R_{b'}$ = Determined isotope ratio in the standard blend, b'

R_x = Determined isotope ratio in the sample

R_z = Determined isotope ratio in the assay standard

A typical experiment for double isotope dilution analysis of a single sample requires the preparation and analysis of six solutions. The set of six sample solutions (see **Figure 3.3**) are prepared under identical conditions and includes: rock sample, rock sample with added isotope spikes, primary standard, and primary standard with added isotope spikes, reagent blank and reagent blank with added isotope spikes.

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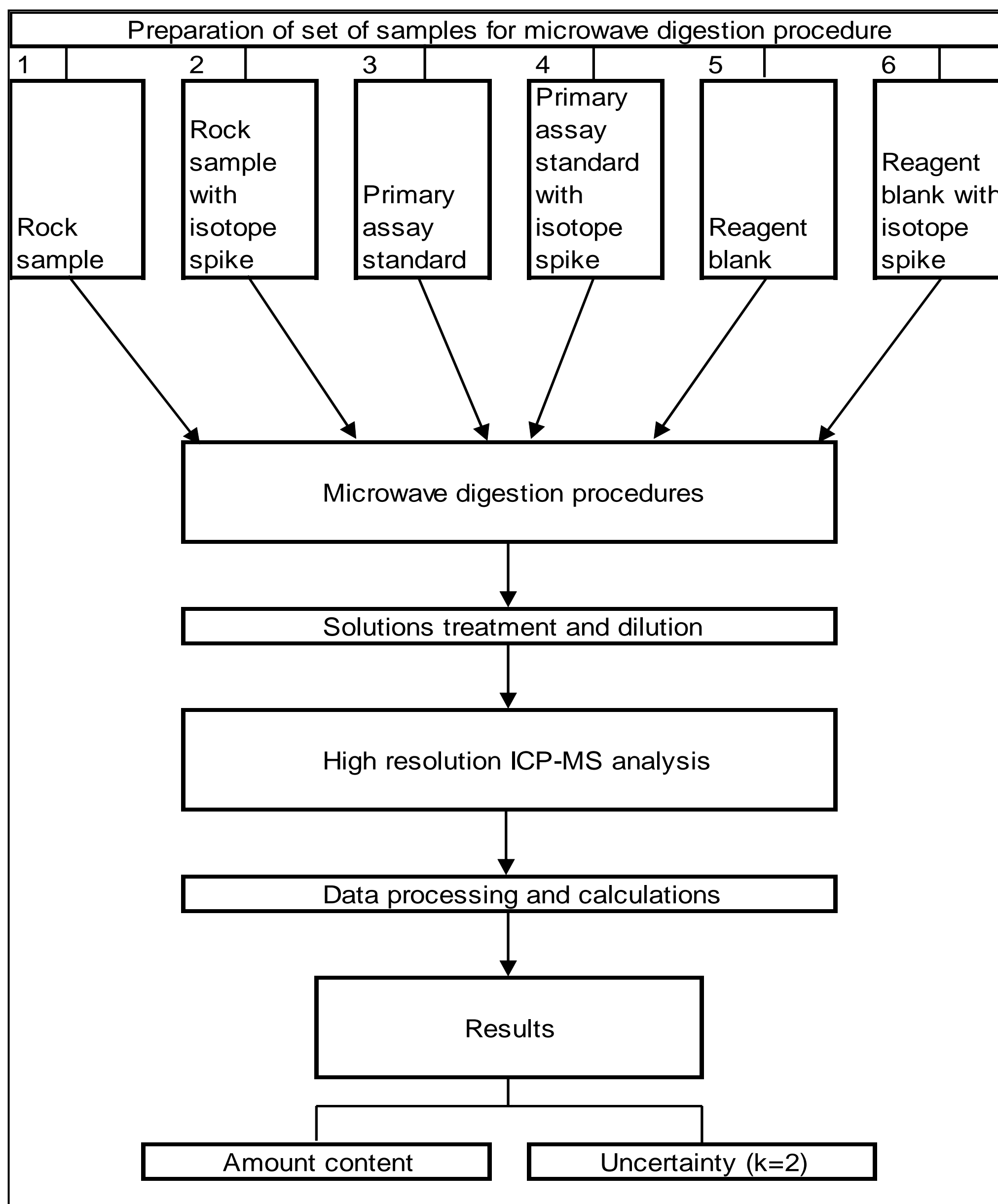

Figure 3.3: General scheme for the double isotope dilution HR-ICPMS analysis

There are three possible sources of systematic error in IDMS[24], i.e. sample preparation, mass spectrometric analysis, and the concentration of the spike standard solution, which must be accurately known and therefore traceable. Because double ID ICP-MS requires equilibration of the spike isotope and the natural isotope(s), the spiked sample must be completely dissolved into solution. During this stage of the procedure the analyst must be aware of pitfalls. If the sample does not completely dissolve, if the spike or sample isotopes are selectively lost before equilibration, or if contamination occurs in the dissolution process, the measured isotopic ratio will not reflect the accurate ratio of added spike atoms to sample atoms for that element. One advantage of IDMS is that the chemical separation of an element need not be quantitative. Once equilibration is achieved,

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the isotopic ratio defines the elemental concentration and this ratio will not change with non-isotope selective element loss.

There are two dominant aspects of accurate isotopic ratio measurements[24], i. e., isobaric interferences and instrumental discrimination/fractionation effects. Isobaric interferences can result from elemental interferences, molecular ion interferences that can arise from the sample, residual gases in the mass spectrometer, or multiply-charged ions. It is difficult to generalise about the potential effects of isobaric interferences because they are dependent on the specificity of the mass spectrometric method, and the sample. Isobaric interferences, which result from the sample matrix itself, present greater difficulties. Measurement of natural isotopic abundances for the unspiked samples should be a prerequisite for accurate isotope dilution analysis.

The best IDMS measurements require an optimum mixture of the spike and sample. The error magnification factor (the propagation of the uncertainty in concentration from the uncertainty in ratio measurement) can be calculated[25] and becomes large if the spiked sample ratio approaches the spike ratio ('overspiking') or the natural ratio ('underspiking'). The effect of the error magnification factor is dependent on the mass spectrometric precision, and the relative enrichment of the spike isotope and natural isotope. From an error propagation standpoint alone, the 'best' mole ratio occurs when the determined ratio, R_m, equals the square root of the product of the ratios of the spike and the natural isotope. In practice, other factors are considered. For example, the best mass spectrometric precision is achieved for ratios near one. When the element to be determined is near the detection limit, the ratio of spike isotope to natural isotope should be greater than one (≈ 10), so that noise contributes only to the uncertainty of the natural isotope and not to the spike isotope[25].

Several sources of noise exist in any analytical measurement performed by ICP-MS. The two major sources of noise that can have an impact on the ultimate precision obtained for an isotope ratio measurement are flicker noise and shot noise. Flicker noise ia a non-fundamental source of noise relating primarily to the sample introduction system and the ICP. Sources of flicker noise include peristaltic pump pulsation and changing droplet size distributions for solution nebulisation. Sources of flicker noise for solid sampling include shot to shot laser fluctionations and changing particle size distribution from one moment to the next. These and other effects cause a fluctuation in the number of analyte ions that generate the signal used for analytical purposes. Flicker noise increases directly with increasing signal level. For example, if a given signal has a strength of 1000 and a standard deviation of 100 (RSD=(100/1000) x 100 =10%), a corresponding signal of 10 000 would have a standard deviation of 1000 or an RSD of 10% as well.

Shot noise, otherwise known as Poisson Statistics or Counting Statistics, is a much different and fundamental source of noise that is directly proportional to the square

root of the signal. Shot noise is due to the random arrival rate of particles (photons, electrons, ions) at a detector. Using the previous example of signal strength of 1000, the shot noise component woud be $1000^{\frac{1}{2}}$ or 31.6 yielding an RSD of 3.16% and a signal of 10 000 could give an RSD of 1%. It is evident from this simple example that increasing the amount of signal accumulated will improve the shot noise component of the overall statistical variance of a measurement.

Ultimately, the noise of any measurement depends on which source of noise becomes the dominant limiting factor towards the precision of the measurement result. Shot noise usually becomes the precision limiting source of noise with very low signals. Conversely, the contribution of shot noise to the overall noise level in high signals becomes small, and flicker noise dominates the precision of the measurement result.

Thus,

Flicker noise: $\sigma \propto s$ ....(3.10)

Shot noise: $\sigma \cdot s^{1/2}$ ....(3.11)

RSD = σ/s ....(3.12)

where

σ = standard deviation (noise)

s = signal required

At the shot noise limit, substituting (3.11) into (3.12) yields

$$RSD = s^{1/2} \quad \text{.......................................(3.13)}$$

Measurement of high precision isotope ratios presents unique challenges for ICP-MS. When an isotope ratio is taken, not only are the isotopes of interest measured, but also the flicker noise component is minimised. Ideally, the only noise component is from shot noise; flicker noise is completely eliminated. Using a sequential ICP-MS device, this ideal condition is sought by peak hopping very rapidly between the two isotopes of interst. The rapid peak hopping process is necessary in order to minimise the time between the measurement of the isotopes of interest. This is done to minimise flicker noise, but it introduces higher levels of shot noise since the amount of signal collected during each measurement sequence is reduced as the integration time for each isotope is kept small. Using a sequential ICP-MS system the result is a conundrum. One must introduce elevated levels of shot noise in order to remove flicker noise.

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Similar to the single signal case, the shot noise or theoretical lowest limit of a ratio ($RSD_{A/B}$), can be calculated from the following equations.

$$RSD^2_{A/B} = RSD^2_A + RSD^2_B \quad \text{................................ (3.14)}$$

Substituting in equation (3.13) yields

$$RSD^2_{A/B} = \left[\left(s_A^{-1/2} \right)^2 + \left(s_B^{-1/2} \right)^2 \right] \quad \text{.................... (3.15)}$$

or

$$RSD_{A/B} = \left(s_A^{-1} + s_B^{-1} \right)^{1/2} \quad \text{............................... (3.16)}$$

From equation (3.16), it can be seen that the $RSD_{A/B}$ will become smaller as s_A and s_B increase. There are several ways for the signal required for each of the isotopes to increase. First, the concentration of the isotopes can be increased. Second, since s_A and s_B represent the total signal measured and not the signal rate, the integration time of the measurement can be increased.

Increasing the concentration of the isotopes can be done to a certain extent and is a valuable tool for improving the ratio measurement. The original sample, sampling conditions, and detector saturation considerations will undoubtedly dictate the concentration regime that can be used in any measurement.

Increasing the integration time is a very effective tool for improving the measured precision of an isotope ratio for a simultaneous measurement system. However, the fact remains that a sequential system must peak hop or scan very rapily in order to minimise flicker noise. The impact of this peak hopping or scanning can be very dramatic on the quality of the data. Plasma conditions cannot be completely matched at each moment in time. This implies that atomisation and ionisation conditions, polyatomic formation and dissociation, ion extraction and ion transmission parameters fluctuate on a very rapid time-scale. Thus, even when rapid peak hopping is incorporated, deviation from the ideal precision of the measurement is observed.

Example 1: 1:1 isotope ratio (Similar to ^{107}Ag:^{109}Ag where ^{107}Ag is 51.8% naturally abundant and ^{109}Ag is 48.2% naturally abundant).

Count rate for A = 10 000 counts per second (cps)

Count rate for B = 10 000 cps

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Integration time = 1 second

s_A = 10 000 counts

s_B = 10 000 counts

$RSD_{A/B} = (10\ 000^{-1} + 10\ 000^{-1})^{1/2}$

$RSD_{A/B}$ = 0.014 = 1.4%

The above calculation indicates that the theoretical lower limit of the precision for this isotope ratio is 1.4% using a 1 second integration time. When the integration time is increased:

Example 2: 1:1 isotope ratio

Count rate for A = 10 000 counts per second (cps)

Count rate for B = 10 000 cps

Integration time = 10 seconds

s_A = 100 000 counts

s_B = 100 000 counts

$RSD_{A/B} = (100\ 000^{-1} + 100\ 000^{-1})^{1/2}$

$RSD_{A/B}$ = 0.0044 = 0.44%

The improvement in precision demonstrated is from 1.4% to 0.44% (improved by $10^{1/2}$) by increasing the integration time from 1 second to 10 seconds with the same count rate. Increasing the concentration (count rate) by the same factor of 10 and leaving the integration time at 1 second would have had an identical effect.

Another point that should be brought out from equation (3.16) is the effect of the ratio itself. In **Examples 1** and **2**, a total of 10 000 cps + 10 000 cps = 20 000 cps were taken. However, if the ratio changes, the theoretical limit of the RSD also changes.

Example 3: Ratio = 3:1

s_A = 15 000 cps

s_B = 5 000 cps

Integration time = 1 second

$RSD_{A/B} = (15\ 000^{-1} + 5\ 000^{-1})^{1/2}$

$RSD_{A/B} = 0.0163 = 1.63\%$

3.3 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS has matured into one of the most successful methods in atomic spectrometry, because of its sensitivity and ability to make multi-element measurements[26]. Since it was introduced for elemental analysis, the ICP has developed into one of the most successful sources. Initially, it had been used as an electronic excitation source, primarily in combination with emission spectroscopy. During the past 20 years, it has been widely used as an ion source for mass spectrometry (MS). Certain technological problems related to the sampling of ions had to be resolved for a successful combination of ICP and MS into ICP-MS.

In the ICP, ions are generated at atmospheric pressure; whereas for operating a mass spectrometer, a pressure of less than 10^{-5} mbar is a prerequisite. The bottleneck in between is the interface, which is used for ion extraction and pressure reduction. In the early days of ICP-MS, this was realised simply by a single, water-cooled, nozzle-like orifice with a diameter of only 50 to 70 µm. The problem with this arrangement was that, in the cool boundary layer in front of the cone, many different molecular ions were generated. This problem was overcome by increasing the diameter of the entrance orifice to about 1 mm, so that the boundary layer is punctured and ions are directly sampled from the “undisturbed” plasma. This technique became known as continuum sampling, and therefore the cone became known as the “sampler”.

Because the gas flow through this sampler is much larger than before, the pressure must be reduced by differential pumping in two or more steps. This is why a second nozzle is placed downstream of the sampler and the space in between is evacuated by a fore pump with a high pumping rate. Because of the high difference in pressure between the ICP and the first pumping stage, the ions are sucked into the interface and accelerated to supersonic velocities.

To avoid turbulence at the second cone, it was machined with sharp edges to skim the ions from the supersonic beam, and therefore the name “skimmer” became widely used. The arrangement, consisting of a sampler and a skimmer cone with diameters of about 1 mm, became known as the “interface”. This was the breakthrough in ICP-MS that made ion extraction more effective, and thus improved intensity, and decreased spectral interferences by orders of magnitude.

Although ICP-MS is much less prone to spectral interference compared to ICP-OES, these nevertheless occur and must be eliminated as far as possible for the successful implementation of ID-ICP-MS. Spectrometric interferences are caused by atomic or molecular ions having the same nominal mass as the analyte isotope of

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interest. The resulting signal may disturb, or even obscure, the true analytical signal; so the accuracy of the determination as well as the detection limits may be considerably deteriorated. The sources from which the interfering species may arise are many; so far, no generally accepted model exists to explain all of the contributing factors, but it is now well accepted that the interface still plays an important role in the appearance of molecular species.

Spectrometric interferences may be subdivided into isobaric atomic ions, multiply-charged ions, intense adjacent signals, and polyatomic ions of various origins. Isobaric overlap exists when isotopes of different elements coincide at the same nominal mass. For each element, with the exception of indium (In), at least one isotope can be found that is free from isobaric overlap, but in many cases this will not be the most abundant isotope. Multiply-charged ions will be found in the mass spectrum at a position *m/z*. Mainly, doubly charged ions of the major matrix components, and multiply-charged ions of the discharge gas argon, contribute to the mass spectrum. The signals of neighbouring ions with a very high intensity, such as those coming from a matrix element, may contribute to the signal of an adjacent isotope by tailing, if the abundance sensitivity i.e. the ratio of a signal intensity at m/z $(m+1)$ to that at m, is not sufficient. Polyatomic ions may consist of atoms of the discharge gas and its contaminants, plus components of the solvent and matrix.

Of all these different groups of spectrometric interferences, polyatomic ions cause the most severe problems. Polyatomic ion interferences may be introduced by the analytical sample itself. For example, oxides can survive passage through the hot zone of the plasma, because of their higher bond strength. The majority of polyatomic interferences arising from the sample do so because of the water introduced with the sample. Laser ablation and solvent desolvation introduction systems substantially reduce oxide interferences. Polyatomic ions may also be produced as contaminants from either the chemical pre-treatment stage, or from the discharge gas, or possibly from air trapped in the plasma. Spectroscopic interferences of this kind can, in principle, be separated from the affected analyte isotope by high mass resolution.

A mass spectral interference will be resolved from the analyte signal depending on their mass difference and the instrument resolution. Mass resolution (R) is generally defined as $\frac{m}{\Delta m}$, in which Δm is the mass difference necessary to achieve a valley of 10% between two neighbouring peaks of identical intensity at a mass m and mass $m+\Delta m$. Because the intensities of neighbouring peaks are rarely identical, an alternative definition will be much more useful. In this definition, Δm is derived from the peak width at the points in the profile that correspond to 5% of the height. This approach will lead to the same value as in the 10% definition mentioned before, if the neighbouring peaks are equally high. It should be pointed out that, in general, the theoretical value is only a lower estimation for the resolution required, because most

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often the signal intensity of the interfering species exceeds the analyte intensity by orders of magnitude.

One of the most often discussed examples of a spectral interference is $^{56}Fe^{+}$ and $^{40}Ar^{16}O^{+}$. The latter is a product created from the discharge gas argon and from oxygen contained in the solvent used. In this example, the isotopes $^{54}Fe^{+}$, $^{57}Fe^{+}$ and $^{58}Fe^{+}$ can be used alternatively for analysis, but the $^{58}Fe^{+}$ is isobarically interfered with by the isotope $^{58}Ni^{+}$. Whereas, the others are interfered with, to a certain extent, by $^{40}Ar^{14}N^{+}$ or $^{40}Ar^{16}O^{1}H^{+}$, the best choice overall is to use $^{57}Fe^{+}$. However, as its natural abundance is only 2.2 %, the detection limit for this element is extremely poor if low resolution instruments are used. Nevertheless, a resolution of less than 2500 is sufficient to separate the spectral interference from the $^{40}Ar^{16}O^{+}$ ion from the interfered analyte isotope at a *m/z* of 56.

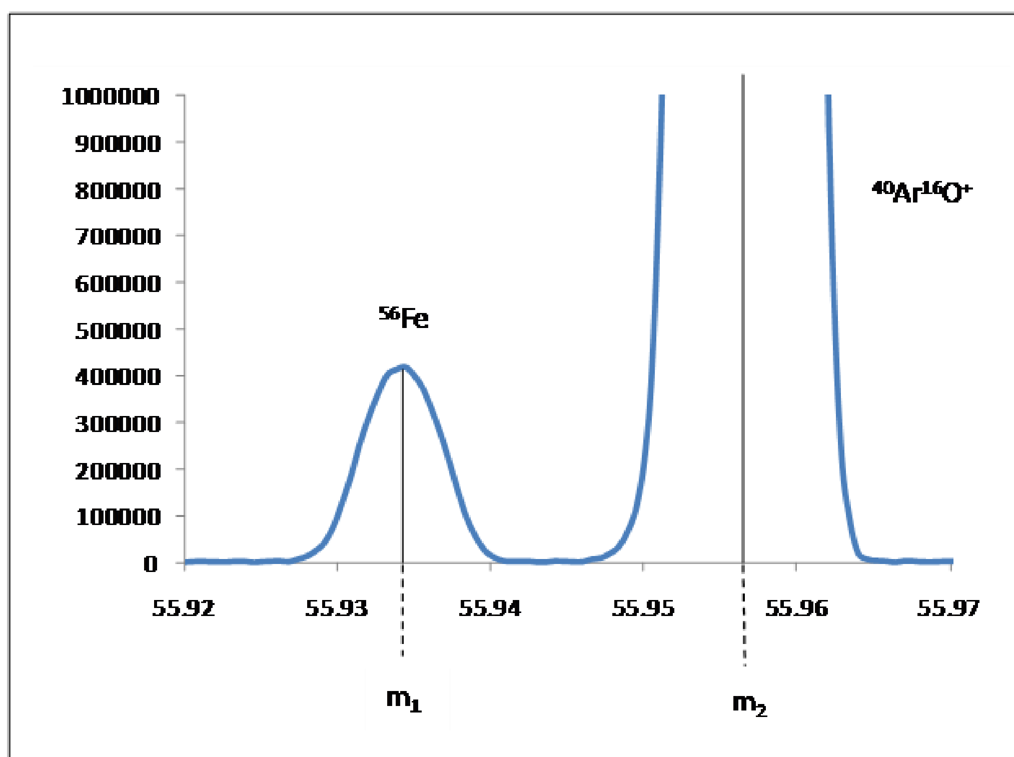

Figure 3.4: A schematic illustration of the effective resolution of the Finnigan Mat ELEMENT2 applied to the example of ^{56}Fe and $^{40}Ar^{16}O^{+}$

In **Figure 3.4** the nuclidic mass of $^{40}Ar^{16}O+$ is m_2 = 55.9565 and the nuclidic mass of ^{56}Fe is m_1 = 55.9345, then $\Delta m = m_2 - m_1$ = 55.9565 – 55.9345 = 0.022. Thus, the needed resolution for the instrument is calculated as $R = \frac{m}{\Delta m}$ = 2543.

A more problematic example is $^{75}As^{+}$, if chloride ($^{40}Ar^{35}Cl^{-}$) is present in the analyte sample. In the case of a mono-isotopic element, no alternative isotope can be chosen and the required resolution must be increased to about 7800. However, a resolution of 3000 will be sufficient to eliminate more that 90% of the interferences

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caused by polyatomic ions. Commercial high-resolution magnetic sector field ICP-MS instruments have a maximum resolution somewhere between 7 500 and 12 000.

3.4 High resolution inductively coupled plasma magnetic sector field-mass spectrometry (HR-ICP-MS)

High mass resolution is usually achieved with a double-focusing instrument on the basis of combining magnetic and electric sector fields[26]. These instruments have an even longer tradition in mass spectrometry than do quadrupoles, but they are technically more sophisticated and therefore more expensive. The heart of a double-focusing instrument is a magnetic sector field. If ions of uniform kinetic energy and different mass are injected perpendicular to a magnetic sector field, they pass the field on a circular trajectory because of the Lorentz force. The radius of the trajectory depends on the mass of the ion, leading to a mass dispersion.

If the ion beam diverges from an entrance slit with a certain angle, then the beam focuses (directional focusing) behind the magnetic sector. Mass separation can now be realised if a slit is positioned behind the sector field just at this focus point, resulting in a well-defined radius and selection of a specific mass. Decreasing the slit width can be used to increase the mass resolution, but only if the ions are mono-energetic, because any spread in energy will deteriorate the beam width at the focus point itself. From this point of view, the ICP is not an ideal ion source. The energy distribution of ions is far too broad to be accepted by a magnetic sector device operated in high mass-resolution mode.

Therefore, the energy dispersion of an electric sector field is used to exactly compensate for the energy dispersion of the magnet so that, in the whole device, only mass dispersion is left. Both magnetic and electric sector instruments have angular focusing properties, and the combined system focuses by angle and energy. This is why these instruments are called double focusing.

Different geometries for combining a magnetic and an electric sector are possible, but double-focusing conditions can be realised with a well-defined combination of electric and magnetic sector angles only. The position sequence of the two analyser components is optional. Traditionally, the electric sector is placed before the magnetic sector field. A 90° electrostatic sector combined with a 60° magnetic sector became widely known as Nier-Johnson geometry. Nowadays, the so-called “reverse geometry” with the electric sector behind the magnetic sector is usually considered advantageous, because the high ion currents from the source are first reduced by mass analysis, and only ions of the selected mass are subjected to the subsequent energy analysis. This configuration helps improve abundance sensitivity as well as reduce noise.

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In normal sector field arrangements, double-focusing conditions are obtainable at only one point, where the exit slit is located. Some very special arrangements have been developed, which guarantee double focusing in a whole plane. Such arrangements have been used for simultaneous detection by photoplates or by multicollector Farraday cup equipment. The latter is advantageous, especially for high-precision (small relative standard deviation) isotope ratio measurements, because all isotopes of an element can be measured simultaneously. Therefore, precision is not limited by time-dependent fluctuations of the source. Although often not designed for high mass-resolution, precise isotope ratio measurements with double-focusing instruments are an important application, for example in dating geological samples or taking measurements at nuclear power plants.

A schematic of an ICP double-focusing MS instrument is shown in **Figure 3.5**. An ion source, a sampling interface, and a subsequent lens system are necessary, similarly to standard, low-resolution quadrupole-based instruments. A major difference is the need for an accelerating voltage of up to 8000 V. A special lens system is normally used, shaping beams and focusing ions into the mass analyser.

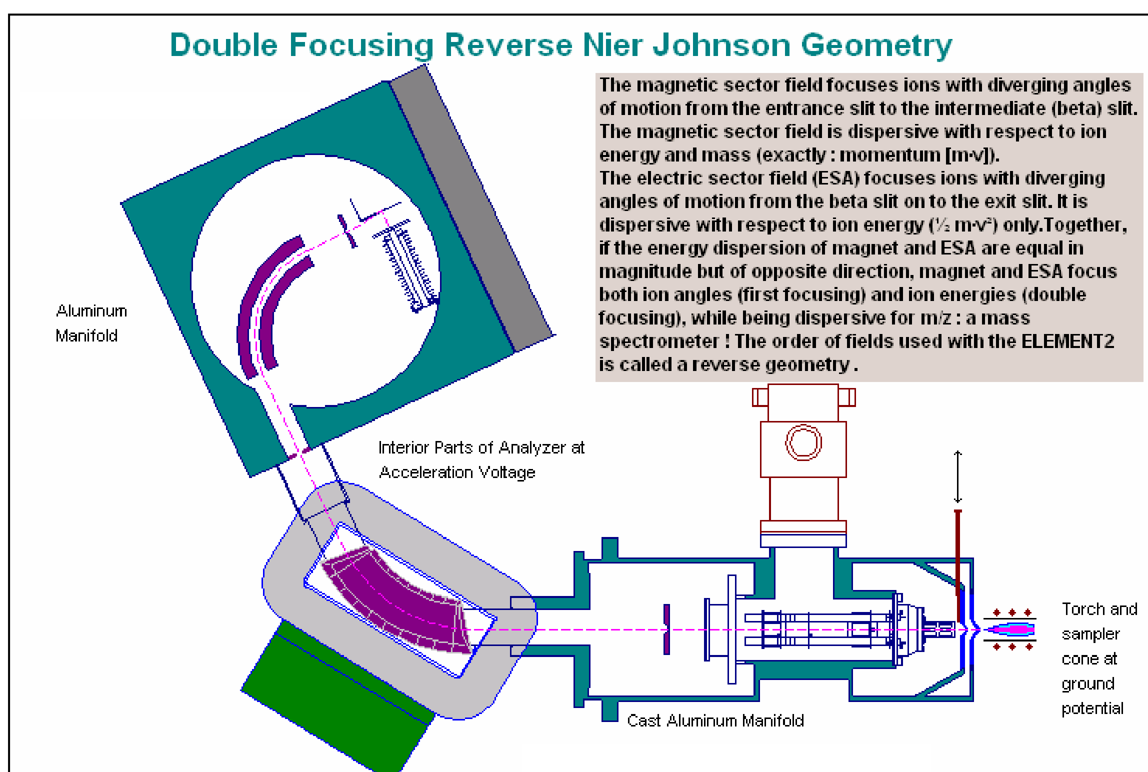

Figure 3.5: A schematic diagram of the ion optics of the Thermo FINNIGAN MAT Element 2 HR-ICP-MS

The resulting bent geometry of double-focusing instruments provides certain advantages when compared with the linear geometry of quadrupoles, because it keeps the noise level low and guarantees a high transmission. No ion losses occur

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at otherwise offset lens systems or photon stop arrangements, as is the case with quadrupole instrumentation. For these reasons, sensitivities of up to 10^9 cps (counts per second) per µg.mℓ$^{-1}$ for the low-resolution mode and noise levels of less than 0.1 cps have been reported. Reducing noise and improving sensitivity can improve detection limits by orders of magnitude, even when the instruments are operated in low-resolution mode.

The first HR-ICP-MS instrument with Nier-Johnson geometry on the market was the Plasmatrace I, introduced in 1988 by VG Elemental. Design of the ion source and the interface was based on quadrupole ICP-MS systems by the same manufacturer. Nowadays, double-focusing instruments with high-resolution capabilities are available from different manufacturers.

Some peculiarities of double-focusing instruments should be mentioned. At first, the peak shape looks different compared to those from quadrupoles. Quadrupoles are operated with constant peak width and therefore linearly increasing resolution with mass. However, double-focusing instruments are operated (for a fixed slit width) with constant resolution, and therefore the absolute peak width increases with mass. For normal-resolution settings, the peaks have a trapezoidal peak shape, which looks needle-like at low masses, and are broader at high masses. The scan speed with which a mass spectrum can be acquired is lower than that obtainable with quadrupoles, even with modern laminated magnets, because double-focusing instruments require a longer settling time for achieving stable magnetic-field conditions. This limits the number of isotopes that can be investigated when data acquisition is by special sample introduction systems such as laser ablation.

Of course the most important capability of double-focusing instruments is high mass resolution. Increasing resolution results in decreased peak width. The interfering molecule can be separated from the analytical isotope, but not without a reduction in sensitivity. It should be noted that increasing the resolution from 400 to 4 000 decreases sensitivity by about 1 order of magnitude. Even in this case, the detection limits are better than that of quadrupole instruments by an order of magnitude.

Chapter 4

Experimental: Sample preparation and isotope ratio measurements

4.1 Development of the methodology for sample preparation

The analysis technique used during this study was double isotope dilution inductively coupled plasma magnetic sector field mass spectrometry (ID-ICP-MS). For the isotope dilution analysis it was a requirement to convert the rock samples to solutions. The two most common approaches to the decomposition of geological samples are acid digestion and fusion[22]. Other decomposition methods include slurry nebulisation (where the sample is introduced to the ICP in a semi-solid state), solvent extraction, pyrolysis, combustion, etc.

A slurry may be defined as a uniform suspension of small particles[22]. The slurry must be of low viscosity to be of practical use as a method of introducing samples into an ICP. The transport properties of a slurry should be similar to those of an aqueous solution, since the behaviour of the slurry in the spray chamber, torch and plasma will then be similar to that of a solution. If these criteria are fulfilled, it should then be possible to calibrate the system using aqueous calibration solutions. However, depending on the samples, matrix effects could be pronounced and internal standardisation will typically be required. In an ideal slurry, all particles would be of uniform small size (< 5 µm) so that they will remain suspended in a fluid medium during an analytical run.

In ICP-AES applications, slurries are typically analysed at concentrations between 1 and 30 % m/v. However, for analysis by ICP-MS it is necessary to limit the levels of total solids (or total dissolved solids) to less than 2000 $\mu g.m\ell^{-1}$ in order to prevent blocking of the sampling cone orifice. For good accuracy and precision, samples need to be very homogeneous, which could be problematic to achieve for geological samples, which are generally polymineralic.

Slurry nebulastion is a useful alternative method of sample introduction for the direct analysis of solids. Provided that the sample can be reduced to a sufficiently small and uniform particle size, measured data should be of comparable quality to that obtained by solution nebulisation. The technique is best applied to materials for which alternative methods of sample preparation are unsuitable and for the determination of elements which are lost as volatile species during other methods of

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sample preparation. Problems of contamination and particle size reduction currently limit the widespread application of slurry nebulistion.

Fusion is usually employed when the matrix does not allow for complete decomposition of the sample by acid digestion. Fusion can be performed using a wide range of fluxes specifically suited to the matrix of the sample. Fluxes include sodium peroxide (Na_2O_2), lithium borate ($LiBO_2$) lithium metaborate ($Li_2B_4O_7$) and sodium metaborate ($Na_2B_4O_7$) for acidic rocks, which are igneous rocks containing more than two thirds silicon dioxide (SiO_2), and sodium hydroxide (NaOH), potassium hydroxide (KOH) for basic rocks, which are silicate minerals or rocks that are rich in magnesium and iron, etc. The major disadvantage of fusion for trace and ultra trace analysis at high levels of accuracy is the limited levels of purity of the fluxes.

The hotplate was traditionally used for acid digestion with different combinations of acids specifically suited to decompose the matrix of the sample. For example, a combination of hydrofluoric acid (HF), nitric (HNO_3) and hydrochloric acid (HCl) can be used for silicate rocks similar to the samples analysed during this study. Acid digestion was also performed in an open or closed configuration on the hotplate. In open acid digestion the samples with the acids were left open on the hotplate and the acids were allowed to evaporate to dryness. When a closed configuration of acid digestion on the hotplate (atmospheric pressure refluxing) was performed, the beakers with the samples and acids were covered with watch glasses to allow for dissolution of the samples under reflux of the acids.

With the advent of microwave technology, industrial microwave ovens were developed for specific application in acid digestion of samples for chemical analysis. A variety of microwave procedures were developed either in closed or open configuration for the decomposition of geological samples[27].

During this study a method was developed for the decomposition of the rock samples with acid digestion in a microwave oven with a high temperature and pressure programme. An attempt was made to develop a one step method for the complete dissolution of the samples. The idea was to have a simple digestion method to prevent loss of sample and to facilitate the use of the methodology for more routine applications. Some measure of pre-concentration of the samples was also required for the accurate determination of the low concentrations of especially nickel, cadmium and molybdenum in the samples.

The samples were first digested with the one step method proposed by Barbaro *et al.*[28]. Aliquots of 0.5 g sample of SARM 3 and SARM 4 were dissolved in a microwave oven using 2 mℓ HCl, 5 mℓ HNO_3 and 6 mℓ HF under pressure. Afterwards the samples were dried on hotplate before the samples were diluted with 10% HNO_3. SARM 4 did not dissolve completely during the one step microwave digestion, most probably due to the high concentration of silica, as well as calcium-,

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magnesium- and iron oxide, compared to SARM 3 and SARM 2. After evaporation on the hotplate, the samples also did not completely redissolve in 10% HNO_3. Experiments were done with different amounts of HF to see if the samples would dissolve in a one step digestion procedure. Care was taken to keep the amount of acid added to the samples to a minimum to prevent the samples from venting during the microwave procedure. Different amounts of HF did not improve the dissolution of the samples. HF is a very dangerous and corrosive reagent. The amount of HF in the acid mixture was kept to a minimum for safety reasons and also to protect the glassware and sample introduction system of the ICP.

A two step microwave digestion procedure was then developed[29], where the sample aliquot was reduced to 0.2 g. During the first step the samples were digested with 4 mℓ HNO_3, 3 mℓ HCl and 1 mℓ HF. During the second step another 1 mℓ HF was added with 15 mℓ 5% H_3BO_3 to dissolve the precipitate of fluorosilicates that precipitated during the digestion of SARM 4. The boric acid reacted with the fluorosilicates that precipitated during the digestion of SARM 4 to form borofluorosilicates in solution to produce a clear solution after the two-step digestion procedure. A possible drawback with the addition of a high volume of boric acid is the possibility of contamination, this necessitates the use of super-boiled or ultra-pure boric acid in these experiments.

4.2 Experimental work

4.2.1 Instrumentation

- High resolution inductively coupled plasma mass spectrometer, Element 2, Thermo Finnigan GmbH, Bremen, Germany.
- Self-aspirating nebuliser of 100 or 50 µℓ.min^{-1}, suitable for nebulisation of solutions containing HF, an HF-resistant spray chamber and appropriate nebuliser tube for solutions containing HF.
- Desolvating sample introduction system, Aridus, Cetac Technologies Inc., Omaha, USA.
- Autosampler, ASX-100, Cetac Technologies Inc, Omaha, USA.
- Semi-micro analytical balance, Model: Genius ME215P, Sartorius AG, Goettingen, Germany.
- Eppendorf Variable Reference micropipettes (10 to 100 µℓ and 100 to 1000 µℓ) and Eppendorf Variable Research Pro (100 to 5000 µℓ), Eppendorf-Netheler-Hinz GmbH, Hamburg, Germany.

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- Microwave Digestion System, Ethos 1600, Milestone S.r.l., Sorisole, Italy, with automatic temperature control.
- Drying oven, Ecoterm, Labotec.
- Water purification systems, Option 7/15 Plus and Elgastat Maxima Analytical, USF Elga, Bucks,UK.

Figure 4.1: Sartorius GENIUS ME215P semi-micro analytical balance

4.2.2 Test samples and certified reference material (CRM)

Experimental work was carried out using the following rock-type materials:

SY-4, Diorite Gneiss, Canadian Certified Reference Material, CANMET

SARM 2, Syenite, South African Reference Material (NIM-S)

SARM 3, Lujavrite, South African Reference Material (NIM-L)

SARM 4, Norite, South African Reference Material (NIM-N)

4.2.3 Reagents, standards and laboratory ware

4.2.3.1 Reagents

- Nitric acid 65%, Ultrapur, Merck KGaA, Darmstadt, Germany.

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- Hydrochloric acid 30%, Ultrapur, Merck KGaA, Darmstadt, Germany.
- Hydrofluoric acid 40%, Environmental grade, Merck KGaA, Darmstadt, Germany.
- Boric acid 99,9999%, Suprapur, Merck KGaA, Darmstadt, Germany , and 5% solution.
- Deionised water, 18 Mohm.cm.

4.2.3.2 Standards

- Certified single element ICP-MS calibration standard, NIST SRM 3136; Lot no. 000612; 9.738 ± 0.022 mg.g^{-1} Ni; k =2,31.
- Certified single element ICP-MS calibration standard, NIST SRM 3114; Lot no. 011017; 9.993 ± 0.016 mg.g^{-1} Cu; k =1,99.
- Certified single element ICP-MS calibration standard, NIST SRM 3128; Lot no. 991504; 9.98 ± 0.03 mg.g^{-1} Pb; k =2.
- Certified single element ICP-MS calibration standard, NIST SRM 3134; Lot no. 891307; 9.99 ± 0.03 mg.g^{-1} Mo; k =2.
- Certified single element ICP-MS calibration standard, NIST SRM 3108; Lot no. 890312; 9.116 ± 0.025 mg.g^{-1} Cd; k =2,36.
- Certified single element ICP-MS calibration standard, NIST SRM 3168a; Lot no. 001402; 9.99 ± 0.02 mg.g^{-1} Zn; k =2,05.
- Certified single element ICP-MS calibration standard, NIST SRM 3104a; Lot no. 992907; 9.93 ± 0.03 mg.g^{-1} Ba; k =2.
- Certified ICP-MS calibration standard, Lot no. 219323, 1000 ± 3 µg.ℓ$^{-1}$ Sr, High Purity Standards, USA. The standard concentration has been certified by spectrometric analysis against an independent source, which is directly traceable to NIST SRM 3153a, Lot no. 990906 Density 1.01010 g.mℓ$^{-1}$ at 20 °C.
- Certified ICP-MS Calibration Standard M, Lot no. 510217, High Purity Standards, USA. The standard concentration has been certified by spectrometric anlaysis against and independent source, which is directly traceable to NIST SRM no. 3100 series.

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- ^{206}Pb stable isotope standard solution of 10 mg.ℓ$^{-1}$, Claritas PPT, Spex CertiPrep, USA.
- ^{135}Ba stable isotope standard solution of 10 mg.ℓ$^{-1}$, Spectrascan, Teknolab A/S, Norway.
- ^{67}Zn stable isotope standard solution of 10 mg.ℓ$^{-1}$, Spectrascan, Teknolab A/S, Norway.
- ^{65}Cu stable isotope standard solution of 10 mg.ℓ$^{-1}$, Spectrascan, Teknolab A/S, Norway.
- ^{61}Ni stable isotope standard solution of 10 mg.ℓ$^{-1}$, Spectrascan, Teknolab A/S, Norway.
- ^{86}Sr stable isotope standard solution of 10 mg.ℓ$^{-1}$, Spectrascan, Teknolab A/S, Norway.
- ^{97}Mo stable isotope standard solution of approximately 3233 mg.ℓ$^{-1}$ prepared by nitric acid digestion of the pure metal, Cambridge Isotope Laboratories, USA.
- ^{111}Cd stable isotope standard solution of 10.7965 mg.ℓ$^{-1}$, IRMM, Belgium.

The isotopic compositions of the stable isotope standards are given in **Appendix E**.

The general procedure for IDMS to be used in this study was the exact matching method where the samples would be spiked with an enriched isotope standard of the elements of interest to obtain a calculated isotope ratio close to 1. This could be achieved with relative ease during this study, because from the original certification study for SARM 1 to 6 the concentrations of the elements of interest in this study was fairly accurately known. However, the idea was to prepare a multi-element isotope standard spike solution containing all the elements of interest instead of spiking each sample with each spike isotope standard solution separately, to simplify the procedure.

Wherever necessary, intermediate isotope standard solutions were prepared from the stock isotope standards, using appropriate dilutions with high-purity deionised water and nitric acid. A multi-element isotope standard spike solution containing ^{61}Ni, ^{65}Cu, ^{67}Zn, ^{97}Mo, ^{111}Cd and ^{206}Pb in optimal concentrations, was prepared from the corresponding source spike solutions for the four samples.

Due to the high concentrations of barium and strontium in SARM 2 and SY-4, strontium and zinc in SARM 3 and the strontium in SARM 4 it was not practically possible or economical to add the isotope spike to the sample aliquots before

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digestion. Individual ^{135}Ba and ^{86}Sr spikes were performed after digestion to accurately weighed aliquots of the digested sub-samples of SARM 2 and SY-4 due to the high concentrations of these elements present in the respective samples. For SARM 3 the ^{86}Sr and ^{67}Zn spikes were added after digestion and for SARM 4 only the ^{86}Sr spike was added after digestion.

It was still expected that complete equilibration between the naturally occurring isotopes and the enriched spike isotopes would occur even if the spike is added after digestion, because the chemical form of the elements in the digested solution was nitrates due to the dominance of nitric acid in the digestion reagents and the isotope spikes were also added to the digested samples in the chemical form of nitrates.

4.2.3.3 Laboratory ware

- PTFE (Teflon®) and polypropylene vials, 3 cm^3 volume capacity.
- Stainless steel weighing boat.
- Microwave digestion PTFE vessels with caps.
- Polypropylene graduated test tubes with caps.
- Polypropylene micropipette tips for Eppendorf Reference and Research Pro micropipettes.
- Weighing glass bottles with caps.
- Set of calibrated mass pieces, traceable to the SI unit, the kilogram.

4.3 Sample preparation procedures

4.3.1 Moisture content

The procedure used for the determination of the moisture content in the test samples was as follows:

- Approximately 1 to 3 g of the solid test samples were weighed on an analytical balance with 5 significant digits in suitable glass weighing bottles. The samples were capped immediately after the transfer took place.
- The weighing bottles (with caps removed) were placed in a drying oven at 105 ^{o}C for a minimum of 24 hours.

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- After drying, the weighing bottles with samples were closed and the bottles were transferred directly into a desiccator. The vessels were left to cool down to room temperature (22 ± 1 ^{o}C) and were then weighed several times.
- The moisture content (as % moisture and dry mass correction factor) was calculated from the difference in the sample weights found. The uncertainty includes contributions from the weighing process and the uncertainty of the mean of the weighings. The standard uncertainty associated with the weighing of materials in various mass ranges, was derived from experimental data, taking into account the repeatability and absolute bias in the weight measurements (see **Section 5.3.3**).

4.3.2 Preparation of isotope dilution samples prior to microwave digestion

The test samples for this study were obtained from one bottle of each of the reference materials. The bottles were homogenised prior to taking the samples by shaking the sample bottles. During the development of the microwave digestion method, the experiments started with a sample aliquot of 0.5 g. However, a clear completely dissolved sample solution could not be obtained with any of the tested methodologies and the sample aliquot was then reduced to 0.2 g.

During the original certification study the homogeneity of the SARM 1 to 6 materials were tested with three different methods: the chemical analysis of a synthetic mix, X-ray fluorescence analysis and gamma-scintillation counting[13]. A new check on the between bottle homogeneity of the materials was not performed during this study, but is a proposal for further work towards the complete re-certification of the remaining units of SARM 1 to 6.

The set of samples for each isotope dilution experiment were prepared gravimetrically, using an analytical balance with 5 significant digits, prior to microwave digestion. All samples, primary assay standards, reagents and blends were subjected to the same treatment conditions throughout the analysis to minimise the uncertainty.

All microwave vessels utilised in the preparation of the test samples were cleaned with a mixture of acids and a specific microwave program prior to use. When not in use, the vessels were stored filled with high purity water. The vessels were thoroughly rinsed with high purity water prior to use. The procedure for preparation of samples prior to microwave digestion was as follows:

The accuracy of the analytical balance was confirmed with a set of calibrated mass pieces with stated traceability.

- Microwave digestion vessel no.1: Rock sample.

Approximately 0.2 g of sample was accurately weighed to 5 significant digits (±0.01 mg) into a tared sample boat. The reading was recorded. The sample was then transferred to the first microwave vessel and the empty boat was re-weighed. The reading was recorded again and the actual sample weight transferred was calculated.

- Microwave digestion vessel no.2: Rock sample with multi-element isotope spike.

The procedure for microwave digestion vessel no. 1 was repeated for microwave vessel no.2 with the same solid sample. The weighing of the multi-element isotope spike standard was performed using clean Teflon® vials. The actual mass of the aliquots were calculated after re-weighing the empty vials.

- Microwave digestion vessel no.3: Primary assay standard.

An aliquot of the primary assay standard was accurately weighed in a Teflon® vial according to the experimental design. The content of the vial was transferred into microwave vessel no.3 and the empty vial was re-weighed.

- Microwave digestion vessel no.4: Primary assay standard with multi-element isotope spike.

The procedure for microwave vessel no. 2 was repeated for microwave vessel no.4. The aliquot of the multi-element isotope spike standard, as reflected in the experimental design, was added. The weighing of the isotope standard spike was performed using a clean Teflon® vial. The actual mass of the aliquot was calculated after re-weighing the empty vial.

- Microwave digestion vessel no.5: Reagent blank with multi-element isotope spike as for microwave vessel no. 4.

- Microwave digestion vessel no.6: Reagent blank.

Reserved for reagent blank only.

The reagents (4 mℓ nitric acid (HNO_3), 3 mℓ hydrochloric acid (HCl) and 1 mℓ hydrofluoric acid (HF)) were added to all the microwave digestion vessels using a micropipette and changing tips for every reagent. The volume of the solutions in each vessel was calculated and appropriate volumes of deionised water were added to each vessel to ensure that all vessels contained the same volume of liquid.

4.3.3 Microwave digestion procedure

The samples prepared in the microwave vessels as described above were covered with the microwave Teflon® caps and placed in safety housing shields. The vessels were then introduced to the rotor segment and tightened using a torque wrench. The rotor segment was inserted into the microwave cavity, and the temperature sensor, positioned into vessel no.1 (rock sample), was connected to the temperature control unit.

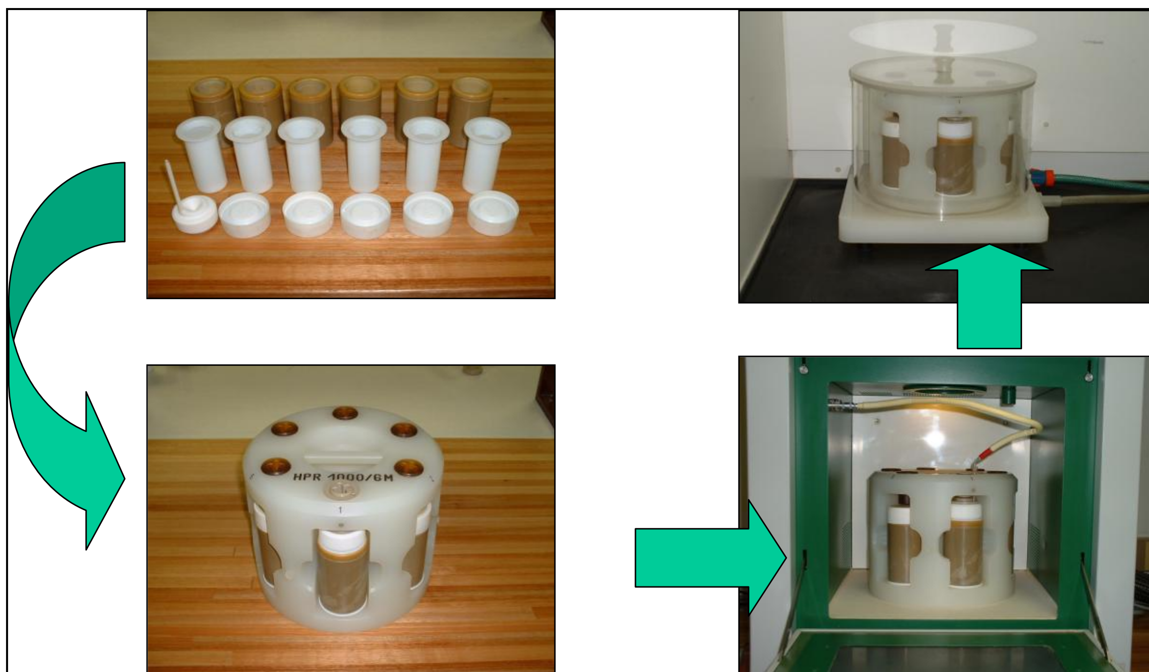

Figure 4.2: Milestone ETHOS 1600 microwave digestion system

The complete digestion of the samples was achieved using a two-stage microwave program. After the first microwave digestion cycle (see **Table 4.1**), the vessels were removed from the microwave system, cooled down in a water bath for approximately 45 minutes and carefully opened under a fume cupboard. Then 1 mℓ hydrofluoric acid (HF) and 15 mℓ 5% boric acid (H_3BO_3) were added to all samples. The sample vessels were closed again and put back into the microwave system for the second microwave program (see **Table 4.2**).

For the microwave digestion, high pressure vessels with a maximum working pressure of 100 bar, were used. The temperature during the digestion process was monitored and automatically controlled to follow the temperature profile of the microwave programs (see **Figure 4.3**) by means of the temperature probe inserted into vessel no.1.

After the first stage of the microwave digestion procedure, a residue due to the precipitation of metal fluorides and fluorosilicates was formed. In order to obtain a complete digestion the second stage of microwave treatment was performed with the additions of H_3BO_3 and HF. The additions of HF and H_3BO_3 resulted in the formation

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of HBF_4, which acted as a releasing agent, the boric acid reacted with the precipitate of metal fluorides and fluorosilicates to form borofluorosilicates, which dissolved in the sample digest to produce a clear sample solution after digestionAfter completion, the vessels were cooled down, opened and the solutions quantitatively transferred into clean 50 mℓ polypropylene graduated tubes. The solutions were left for several hours to reach room temperature (22 ± 1 ^{o}C) and brought to the mark as per the experimental design for the final dilution of the digested sample with deionised water. Appropriate dilutions were prepared according to the experimental designs created for each of the four reference materials. The concentrations of the different analytes in the final measurement solutions ranged from 0.3 to 3.0 ng.mℓ$^{-1}$ depending on the concentrations of the analytes in the different solid samples. On all occasions, nitric acid was added to the diluted samples to correspond to 2% of the total solution volume.

Table 4.1: Microwave program 1

Step	**Time (minutes)**	**Temperature (ºC)**	**Microwave power (W)**
1	10	140	Up to 1000
2	15	185	Up to 1000
3	10	185	Up to 1000
4	10	Venting	0

Table 4.2: Microwave program 2

Step	**Time (minutes)**	**Temperature (ºC)**	**Microwave power (W)**
1	10	175	Up to 1000
2	8	175	Up to 1000
3	10	Venting	0

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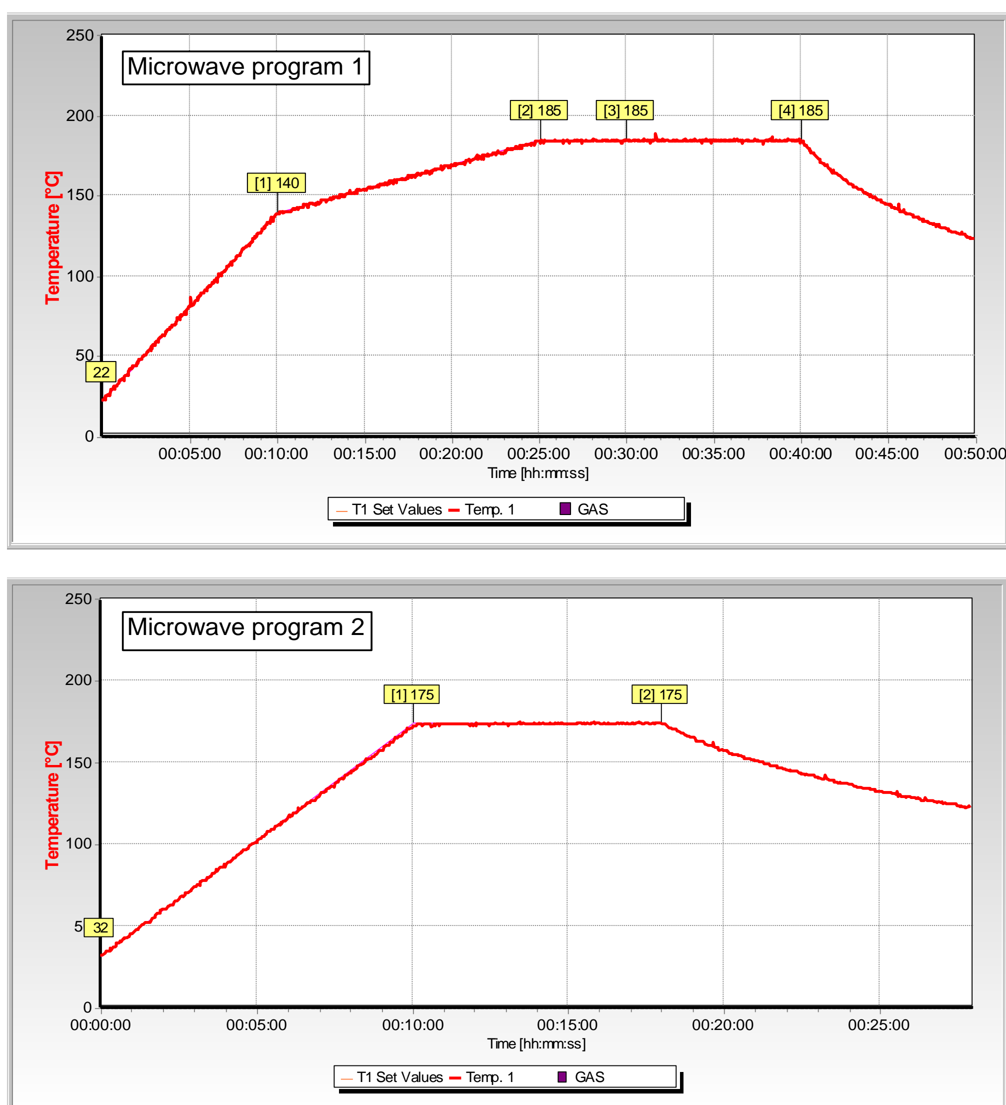

Figure 4.3: Experimental microwave digestion temperature profiles

4.4 ID-ICP-MS analysis and isotope ratio measurements

After appropriate dilutions relevant to every element, the sample digests were subjected to analysis using a magnetic sector (HR) ICP-MS and an autosampler system (AXS-100) with a 24 position sample rack. A self-aspirating nebuliser of 100 or 50 µℓ.min^{-1}, suitable for nebulisation of solutions containing HF, an HF-resistant spray chamber and appropriate nebuliser tube for solutions containing HF was used to prevent corrosion of the sample introduction system due to the HF content in the sample solutions. A desolvating sample introduction system (Aridus) was used to minimise polyatomic interferences due to the introduction of oxides from the water in the samples into the plasma.

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Figure 4.4: ThermoFinnigan MAT Element 2 inductively coupled plasma magnetic sector field-mass spectrometer

4.4.1 HR-ICP-MS parameters

The nature of the IDMS method employed during this study is an approximate matching method similar to the method used by Catterick, *et al.*[30] based on the philosophy of the iterative 'exact matching' method proposed by Henrion[31]. In this study, the 'match' between the isotope ratios for the analytes in the spiked sample blends and the spiked primary assay standard blends was aimed to be within 10% of the ratio of one for optimum counting statistics and mass spectrometric precision.

The mass bias correction factor (K) for each element, was determined by repeated measurements of a natural isotopic abundance standard for all the elements, except for Pb, where the NIST SRM 982-1 certified isotopic standard was used. In the analysis sequence the duplicate analysis of each sample was bracketed by the measurement of the mass bias standard, which in turn was bracketed by the measurement of the wash solution (see **Appendix F**). The measured isotopic ratios of the mass bias standard were individually compared either to the corresponding certified isotopic ratio values of the standard or to the theoretical isotopic ratio values derived from the IUPAC isotopic abundance data (when an isotopic standard with certified isotopic ratios was not available). During this experiment the mass bias

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correction factor that was applied to each isotope ratio measurement was calculated from the average of the ratios measured for the mass bias standard throughout the measurement sequence.

The classical experiment for a double isotope dilution analysis of a single sample requires the preparation and analysis of six solutions. The set of six sample solutions is prepared under identical conditions and includes: the sample to be analysed and the sample with added isotope spikes; the primary assay standard and the primary assay standard with added isotope spikes; the reagent blank and the reagent blank with added isotope spikes.

During this experiment only the sample and sample with stable isotope spike standard blends, as well as one primary assay standard and stable isotope spike standard for each of SARM 2 and SY-4 were digested. All the other solutions required for the double isotope dilution analysis such as the primary assay standard and two additional blends of primary assay standard and stable isotope spike standard for both SARM 2 and SY-4, as well as the blend of the reagent blank and the stable isotope spike standard, were prepared off-line without going through the digestion process. No significant difference was found for the different sample blends between the off-line and digested standard blends.

The aliquots of multi-element stable isotope spike standard, as well as the spikes for Ba and Sr that were added to the samples for the preparation of the sample and stable isotope standard spike blends were varied to within approximately -10% to +10% of the exact matching amount.

Optimisation of the plasma conditions, torch position as well as the peak shapes and mass calibrations, were performed prior to every analysis. The ratios of the following pairs of isotopes for barium, copper, nickel, lead, zinc, cadmium, molybdenum and strontium were measured using separate methods: $^{137}Ba/^{135}Ba$, as well as $^{138}Ba/^{135}Ba$; $^{63}Cu/^{65}Cu$; $^{60}Ni/^{61}Ni$; $^{208}Pb/^{206}Pb$; $^{66}Zn/^{67}Zn$; $^{112}Cd/^{111}Cd$, as well as $^{114}Cd/^{111}Cd$; $^{95}Mo/^{97}Mo$ and $^{88}Sr/^{86}Sr$ (i.e. reference isotope/spike isotope). For some elements the results from two sets of ratios were compared to provide additional information, either to improve the precision of the results, or to overcome the effect of isobaric interference on the reference isotope.

The parameters common to all measurement methods are summarised in **Table 4.3**.

Table 4.3: ICP magnetic sector field MS measurement parameters

	Low resolution	Medium resolution
Coolant gas flow	13.5 ℓ.min^{-1}	13.5 ℓ.min^{-1}
Auxiliary gas flow	0.75 ℓ.min^{-1}	0.75 ℓ.min^{-1}
Carrier gas flow	1.1 ℓ.min^{-1}	1.1 ℓ.min^{-1}
RF forward power	1200 W	1200 W
Runs	1	1
Passes	200	200
Mass window	10 %	120 %
Number of samples per peak	1	24
Sample time	0.01-0.1 s	0.01-0.1 s
Scan type	E-Scan	E-Scan
Detection mode	Counting	Counting
Detector dead time correction	25 ns	25 ns
Measurands	Ba,Sr,Pb,Cd,Mo	Cu,Ni,Zn
Peak integration	80%	80%
Acquisition time, min	3	3

At high count rates, two effects cause counting modes of the detector systems to record fewer counts than actually occur. The most important of these two effects in the Finnigan MAT ELEMENT detection system is dead time. After an ion generates an electron pulse at the conversion dynode, and subsequently an electron pulse in a multiplier, there is a finite time during which the system is incapable of recording another event. The system is effectively "dead" (i.e. unable to process another event) in this interval. There are several reasons for the dead time:

1. Finite width of the output pulse of the multiplier
2. Amplifier discriminator requires an interval to process the data
3. The discriminator emits a pulse of finite width
4. The pulse must be recorded by the data system

A correction should be applied to all ion count rates (counting detection mode) to compensate for this dead time. The detector dead time correction can become significant when accurate isotope ratios are required or for quantitative analysis for samples with high count rates.

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The dead time correction of the Counting Mode uses the following equation:

$$I_{corr} = \frac{I_{meas}}{1 - I_{meas} \cdot \tau_{dead}} \quad \text{.............................. (4.1)}$$

where

I_{corr} = corrected intensity (cps)

I_{meas} = measured intensity (cps)

τ_{dead} = dead time value (s)

For the determination of the dead time correction for the Finnigan MAT ELEMENT 2 ICP-MS spectrometer that was used during this study, four standards were prepared for each element of interest over the expected concentration of the elements in the final solution. The intensities of the reference and spike isotopes of the individual elements were measured with the ICP-MS spectrometer and then a spreadsheet method was used to determine the deadtime correction for each element. In the spreadsheet the calculated ratios of the measured isotope intensities were plotted on a best curve fit. The dead time correction factor was then calculated iteratively on the spreadsheet until the slope of the fitted curve became 0, i.e., the curve became a horizontal line. This horizontal line indicated comparable precision of the determined isotope ratios over the expected concentration ranges of the elements in the final solutions.

The mass window is the scanning range of the instrument around a peak. It is defined with respect to the centre of the peak and its value is entered as a percentage. A mass window of 100% means that, starting from the centre of the peak, half of the peak width on either side of the centre, i.e., one peak width in total is scanned (100% of the peak width). The mass window is also sometimes referred to as the scan window or the mass range. The peak width depends on the mass of the isotope measured and the selected resolution (peak width = m/R), e.g. for ^{63}Cu at mass 62.92 and resolution (R) 3000, the peak width is 0.02097, i.e., this would define a mass window of 100%. Furthermore, the mass range scanned for ^{63}Cu with mass 62.92, peak width 0.02097 and mass window 100%, will be 62.9095 to 62.9304.

The determinations of Sr, Ba, Pb, Cd and Mo were carried out in low-resolution mode. Interference corrections were performed on ^{86}Sr for the isobaric interference of ^{86}Kr in the argon carrier gas. This involved measuring the ^{83}Kr isotope together with ^{86}Kr, ^{86}Sr and ^{88}Sr. The interference correction was calculated with the following equation:

$$Rcorr = \frac{I_{^{88}Sr}}{I_{^{86}Sr}corr} = \frac{I_{^{88}Sr}}{I_{^{86}Sr} - I_{^{83}Kr} \times \dfrac{A_{^{86}Kr}}{A_{^{83}Kr}}} \quad \text{................ (4.2)}$$

where

$I_{^{88}Sr}$ = the measured intensity for the ^{88}Sr isotope

$I_{^{86}Sr}$ = the measured intensity for the ^{86}Sr isotope

$I_{^{83}Kr}$ = the measured intensity for the ^{83}Kr isotope

$A_{^{86}Kr}$ = the IUPAC abundance of the ^{86}Kr isotope

$A_{^{83}Kr}$ = the IUPAC abundance of the ^{83}Kr isotope

The isobaric interference correction on the measured intensity for ^{86}Sr was made for several aliquots of each sample, as well as sample and spike isotope standard blends over the span of the measurement sequence. The corrected ratios for the samples compared well with the primary assay standards and the variations in the measured intensities of the different isotopes were taken into account with the interference correction calculation for each of the aliquots. The contributions to uncertainty from the abundances of the ^{86}Kr and ^{83}Kr isotopes are negligible compared to the precision of the measured intensities for the different isotopes. Therefore, no additional correction factor or uncertainty contribution for the isobaric interference correction was required.

The measurements for $^{63}Cu/^{65}Cu$, $^{60}Ni/^{61}Ni$ and $^{66}Zn/^{67}Zn$ isotope ratios were performed in medium resolution mode in order to eliminate possible spectral interferences as shown in **Table 4.2.**

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Table 4.2: Most probable spectral interferences on the measurements of Ni, Cu and Zn isotopes of interest in the samples

Isotope	Isotope mass	Possible spectral interference	Interference mass
^{60}Ni	59.930788	$^{44}Ca^{16}O$ $^{24}Mg^{36}Ar$	59.95039 59.95259
^{61}Ni	60.931058	$^{23}Na^{38}Ar$ $^{25}Mg^{36}Ar$	60.95250 60.95339
^{62}Ni	61.92835	$^{24}Mg^{38}Ar$ $^{24}Mg^{38}Ar$	61.94778 61.95014
^{63}Cu	62.939598	$^{25}Mg^{38}Ar$ $^{27}Al^{36}Ar$ $^{23}Na^{40}Ar$	62.94857 62.94909 62.95215
^{65}Cu	64.927793	$^{29}Si^{36}Ar$ $^{27}Al^{38}Ar$ $^{25}Mg^{40}Ar$	64.94405 64.94427 64.94822
^{66}Zn	65.926034	$^{28}Si^{38}Ar$ $^{30}Si^{36}Ar$ $^{26}Mg^{40}Ar$	65.93966 65.94132 65.94498
^{67}Zn	66.927129	$^{29}Si^{38}Ar$ $^{27}Al^{40}Ar$ $^{134}Ba^{++}$	66.93923 66.94392 66.95225
^{68}Zn	67.92485	$^{28}Si^{40}Ar$ $^{136}Ba^{++}$	67.93931 67.95228

In **Figure 4.5** the effect of the use of medium resolution for the measurement of Ni is illustrated. For the isotopes of ^{60}Ni, ^{61}Ni and ^{62}Ni in low resolution ($R = 300$) the signals are swamped by interferences from polyatomic ions such as $^{44}Ca^{16}O$ and $^{24}Mg^{36}Ar$, $^{23}Na^{38}Ar$ and $^{25}Mg^{36}Ar$, $^{24}Mg^{38}Ar$ and $^{24}Mg^{38}Ar$, respectively. In medium resolution ($R = 4000$), the nickel peaks are resolved from the peaks of the polyatomic ions. The same effect of medium mass resolution is illustrated for Cu and Ni in **Figures 4.6** and **4.7**. The major interference from Ba^{++} on Zn was eliminated through the use of medium resolution. The other possible interferences on Zn even in medium resolution mode were not likely in these samples because of their low abundance.

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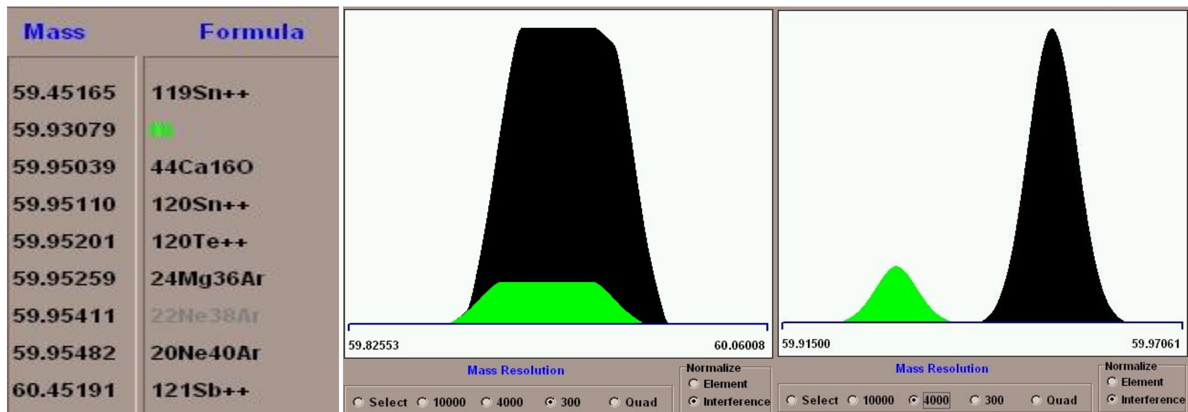
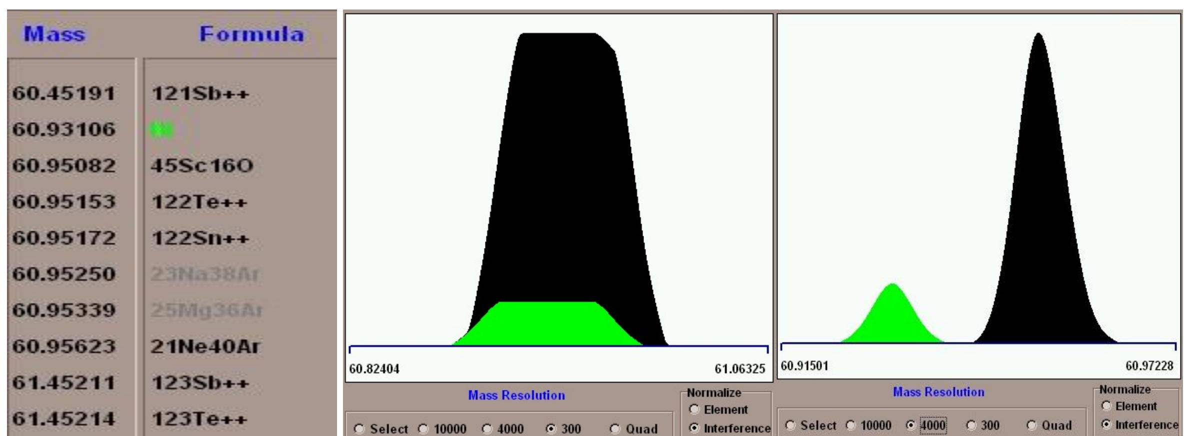
Ni-60



Ni-61



Ni-62

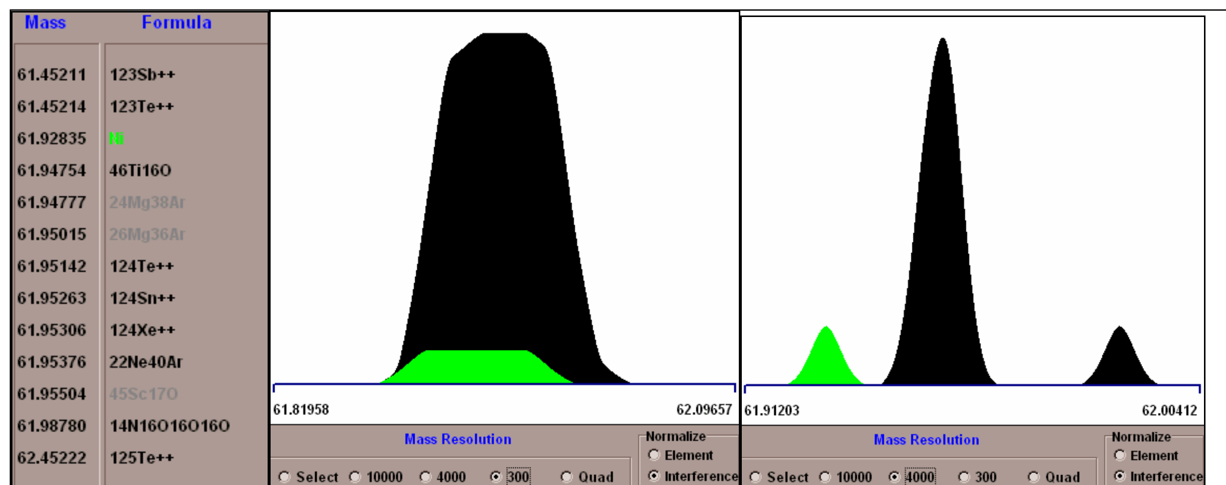


Figure 4.5: Schematic presentation of the effect of medium mass resolution for Ni (Green peak = Ni; Black peaks are the interferences; the peaks represent the same amounts and abundances of the analyte and the individual interferences)

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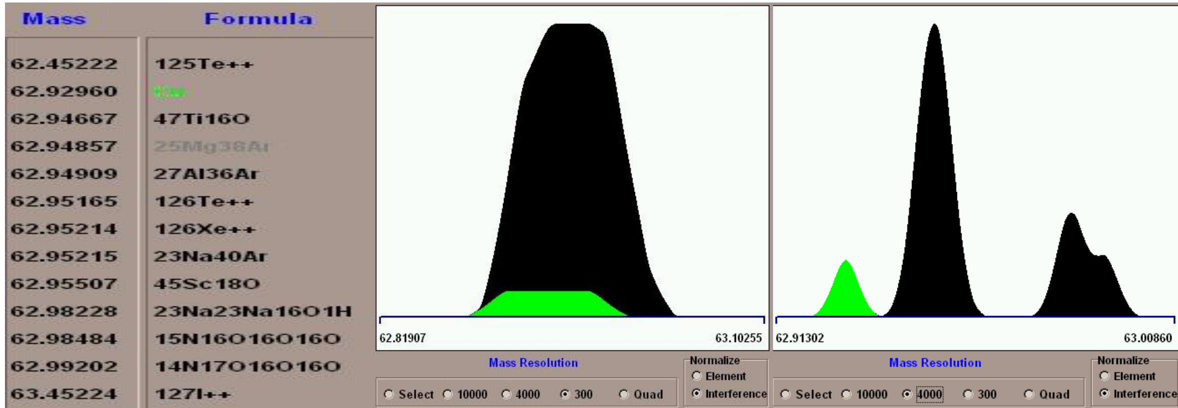
Cu-63



Cu-65

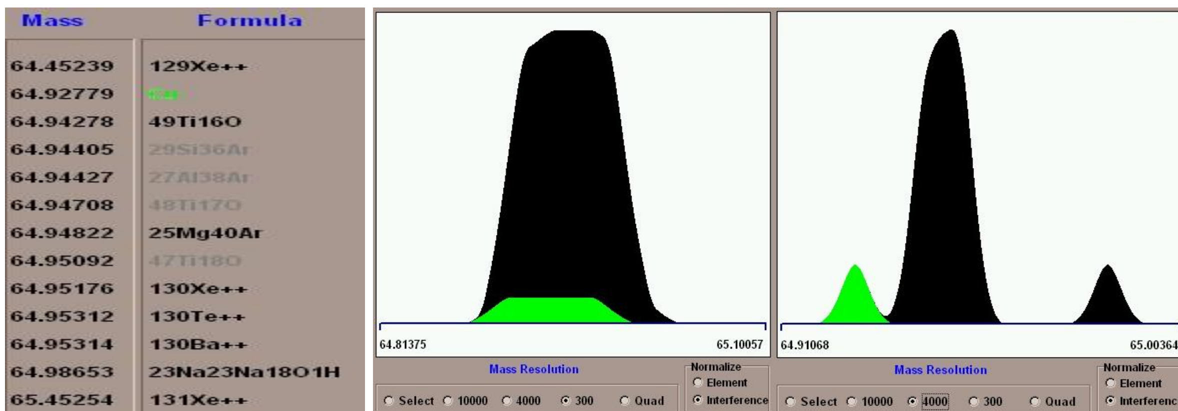
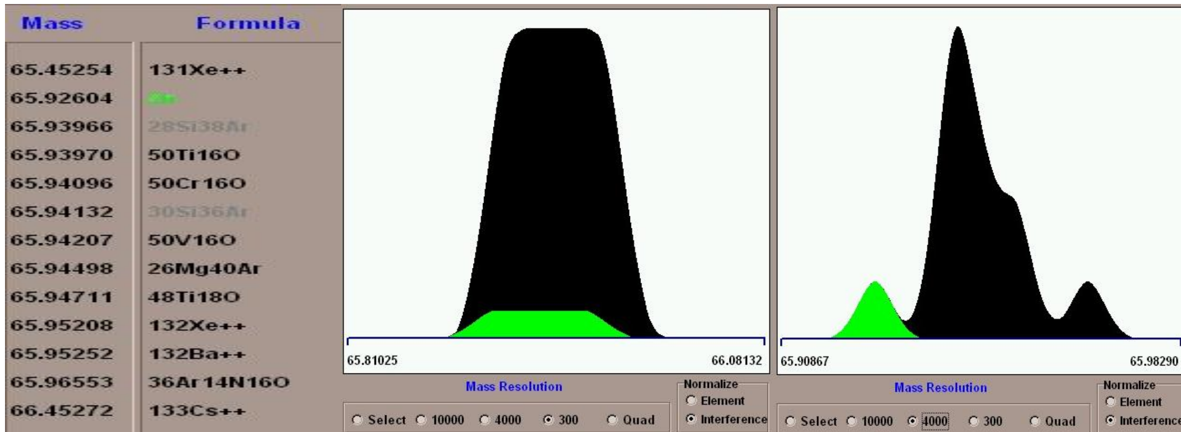
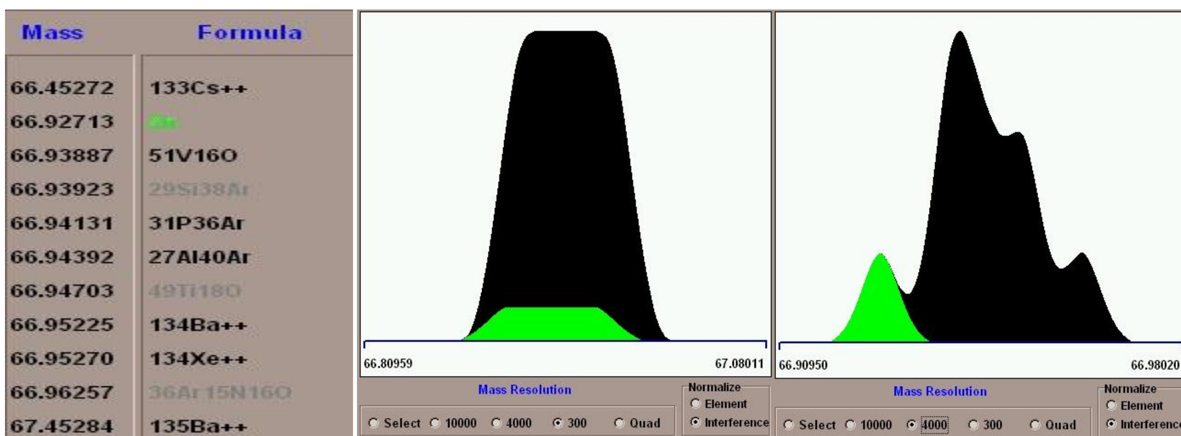


Figure 4.6: Schematic presentation of the effect of medium mass resolution for Cu (Green peak = Cu; Black peaks are the interferences; the peaks represent the same amounts and abundances of the analyte and the individual interferences)

Zn-66



Zn-67



Zn-68

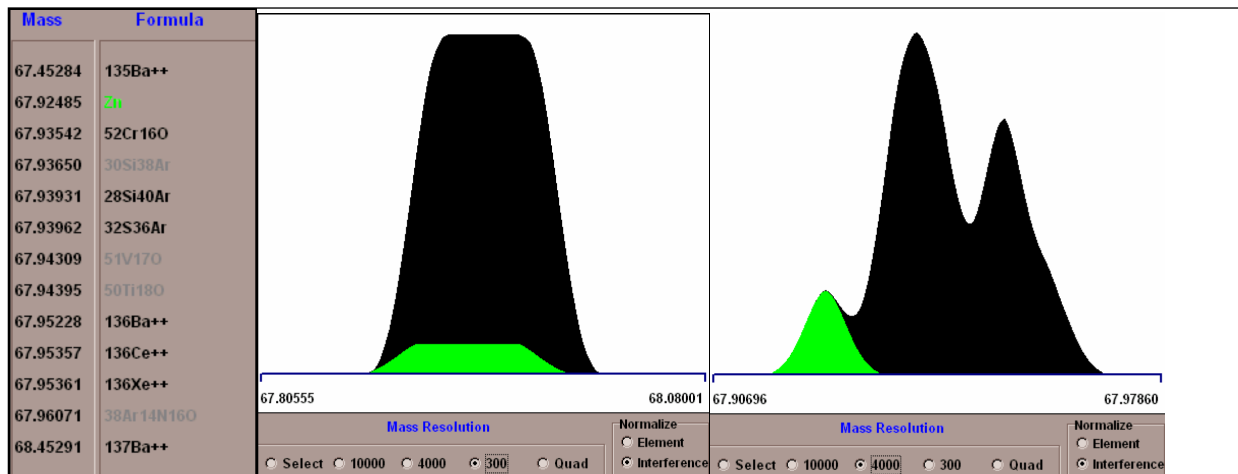


Figure 4.7: Schematic presentation of the effect of medium mass resolution for Zn (Green peak = Zn; Black peaks are the interferences; the peaks represent the same amounts and abundances of the analyte and the individual interferences)

For low resolution each sample solution was split into two independent sample aliquots for analysis and every aliquot was measured in duplicate. In the analysis

sequence every sample was bracketed by a wash solution of 2% nitric acid and a mass bias standard of comparable concentration to the sample (see **Appendix F**). The measurements of this standard throughout the sequence were performed in order to calculate the mass bias correction factor for every analyte. The mass bias correction factor was used to monitor the isotopic ratios of the analyte during the analysis sequence to allow for off-line correction of any possible drift in the mass calibration. The samples with natural isotopic abundances were always analysed before the spiked solutions. Each analyte was determined separately on individual samples.

Every sample is measured with autosampling parameters: Wash time: 140 s (2% nitric acid prior to uptake of sample); Uptake time: 110 s.

4.5 Experimental designs for SARM 2, SARM 3, SARM 4 and SY-4

As part of the developed methodology, experimental designs were created for the determination of Ba, Sr, Zn, Cu, Ni, Mo, Cd and Pb in SARM 2, SARM 3, SARM 4 and SY-4. For optimal precision in the isotope ratio measurements, the necessary spikes of the enriched isotopes were calculated for the ratio of the measured pair of isotopes in the final blend solutions (prior to analysis) to be close to unity. Samples were diluted according to the diagrams presented in **Appendix G** so that the solutions subjected for analysis contained element concentrations suitable to perform measurements in medium (Ni, Cu, Zn) and low (Ba, Sr, Mo, Cd, Pb) resolution.

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