Day 4 (morning)

Isotope ratio by ICP-MS

A- Sample preparation (crushing, milling, dissolution)

B- Problems:

- **Instrument:**
  - Quadrupole or Magnetic sector
  - Single collector or multicollector
- **Mass Bias**
  - Matrix induced
  - Instrumental
  - Mass Bias correction
- **Sample introduction system itself:**
  - Solution:
  - Laser ablation:
- **Detector**:
  - Ion counting device: Dead Time Correction:
  - Faraday cups: Calculation of the gain of the amplifier
- **Sensitivity (Counting statistics)**
- **Interference**
- **Standardisation (calibration)**
- **Background (Sample Contamination-Interference)**:

C- Acquisition

- **Tuning**
- **Faraday Cup position**
- **Peak Centre - Mass Calibration**
- **Method**

Day 4

Isotope ratio by ICP-MS

A- Sample preparation (crushing, milling, dissolution)

B- Problems:

- Instrument:

Isotope ratio precision will depends on the type and the design of the instrument used.

- Quadrupole or Magnetic sector

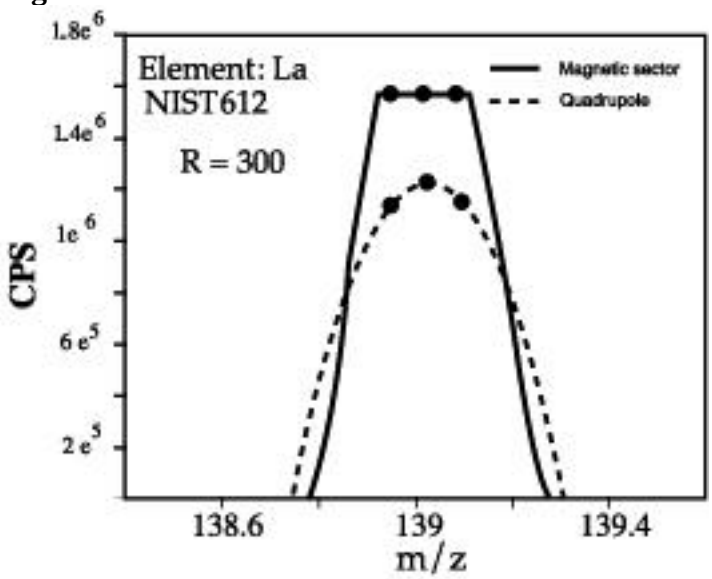


Figure 4.2: Magnetic sector provides a flat top peak shape, in comparison to quadrupole instrument. This figure shows the intensity of La, while ablating a NIST612 at resolution 300. The precision on the measurement of the La intensity will therefor be higher using magnetic sector.

- Single collector or multicollector

Simultaneous measurement of multiple isotopes will provide a better precision in isotope ratio measurement, in comparison to single isotope collection. The noise introduces by the sample introduction system and the flickering of the plasma will be reduced.

- Mass Bias

The mass bias derives from the differential transmission of ions of different mass from the point at which they enter the sampling device until they are finally detected by the electron multiplier or Faraday Cups. The mass bias effects occur in the interface region in magnetic sector ICP. Several processes are considered to contribute to the mass bias effect, including the space charge effect in the plasma or vacuum interface regions. The space-charge effect results in the preferential transmission of the heavier ions because the lighter ions tend to migrate to the exterior of the plasma and are focussed less efficiently into the mass analyser (see day 1).

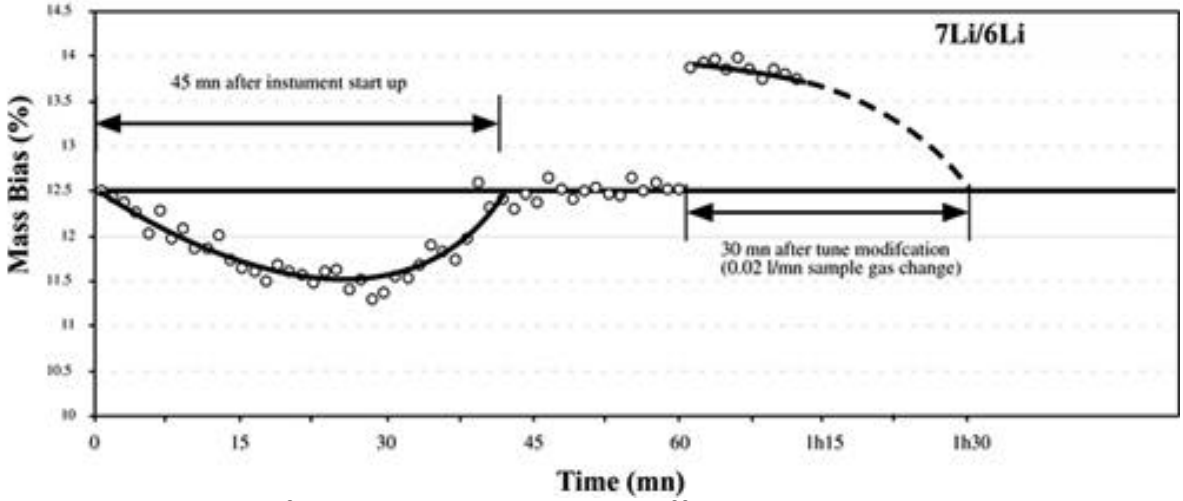


Figure 4.3: Evolution of the mass bias (percentage difference between the measured and true value of Li^7/Li^6) during the warm-up of the instrument. After 1 hour, a slight modification of the sample gas flow has a huge effect on the accuracy of the ratio.

There are two types of mass bias:

Matrix induced mass bias, related to the quality of your chromatographic separation and the use of external standardisation. If the solution is pure lead then you can use Tl internal standardisation to correct for the mass bias. If the solution isn't pure lead you will have to consider the use of a well-characterised external standard which will produce similar bias to your instrument.

Instrumental mass bias, mainly instrumental dependant and sensitive to lenses and gas flow settings (figure 4.3).

Mass Bias correction: There are three ways to correct for mass bias, although the internal standardisation technique is considered to be more accurate than the external one but also more dedicate to multicolletor ICP-MS:

* External corrections, using a standard of well know isotopic composition, such as NIST SRM 981 for lead. The external standard is periodically measured within the sequence, using the same method, between samples. And the difference between the measured ratio and the true ratio unable the use of a mass bias correction on the sample. This is the easiest technique (also called sample bracketing) but it also relies on the assumption that there isn't any change of mass bias between the sample and the standard (matrix effect or changes in the plasma condition). This method is maybe also better for single collection so that no time is wasted while scanning over the internal standard, which improve the precision of the ratio.

* Internal corrections
  - Natural stable ratio: Sr, Nd, Hf
  - Addition of Tl to the Pb solution (NB: some authors refer to this method as an external correction as well).

  - 3 mathematical expressions have been used to correct for mass bias: a linear (1), power (2) and exponential law (3).

$$(1) \rightarrow R_{true} = R_{obs}(1+C)$$

or

$$\rightarrow \%C = \left(\frac{R_{true}}{R_{obs}} - 1\right) * 100$$

$$(2) \rightarrow R_{true} = R_{obs}(1+\Delta mC)$$

$$(3) \rightarrow R_{true} = R_{obs}(1+C)^{\Delta m}$$

The exponential law give the most consistent results. T_{rue}/R_{Meas} is the certified to measured ratio. Δm is the mass difference between the isotope of interest. C is the mass bias factor.

Example: Pb isotope measurements using the $^{205}Tl/^{203}Tl$ ratio

$$\left(\frac{^{208}Pb}{^{206}Pb}\right)_t = \left(\frac{^{208}Pb}{^{206}Pb}\right)_m \left(\frac{Mass_{208Pb}}{Mass_{206Pb}}\right)^f$$

with

$$f = \frac{\ln \dfrac{(^{208}Pb/^{206}Pb)_m}{(^{208}Pb/^{206}Pb)_t}}{\ln \dfrac{Mass_{208Pb}}{Mass_{206Pb}}}$$

where the subscript m and t denote the measured and true ratio respectively.

- Sample introduction system itself:

Solution:

This is the main source of noise in single collection ICP-MS. Three main improvement should be consider although plasma flickering remain as a main source of noise.

- use of free aspiration and/or microliter nebulizer
  - Free aspiration: improve precision and reduce the noise related to perilstatic pump pulsing
  - Microliter nebulizer: Low uptake nebulizer: reduce the sample dilution, increase concentration, improve signal and counting statistics
- use of a Cyclonic-Scott type spray chamber to improve stability,

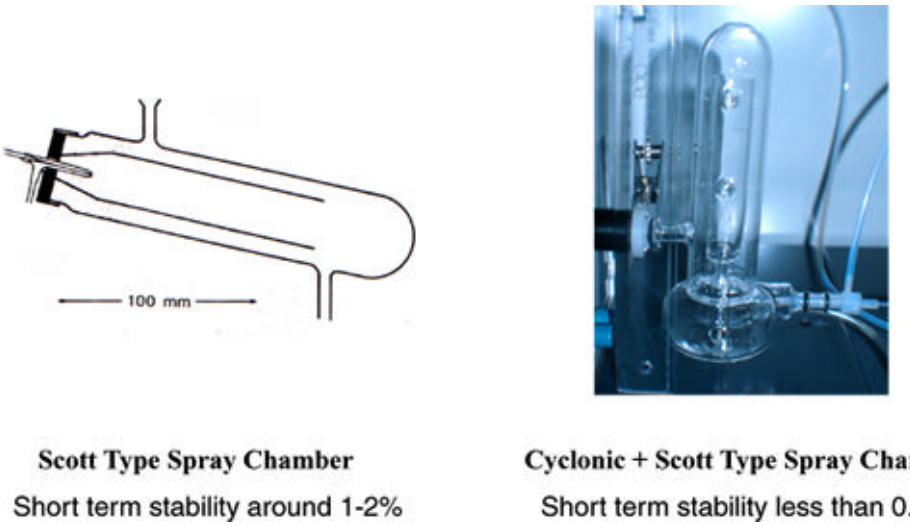


Figure 4.4: Comparison between a classic Scott type spray chamber (left) and a new cyclonic + Scott spray chamber (right).

- Laser ablation:

Laser ablation is responsible for inter-elemental fractionation. So the precision of the isotopic ratio will depend on whether we analyse isotopes from single element (e.g Hf isotopic composition of a zircon) or isotopes from two elements having different behaviour during the ablation process (e.g U/Pb ratio in a zircon).

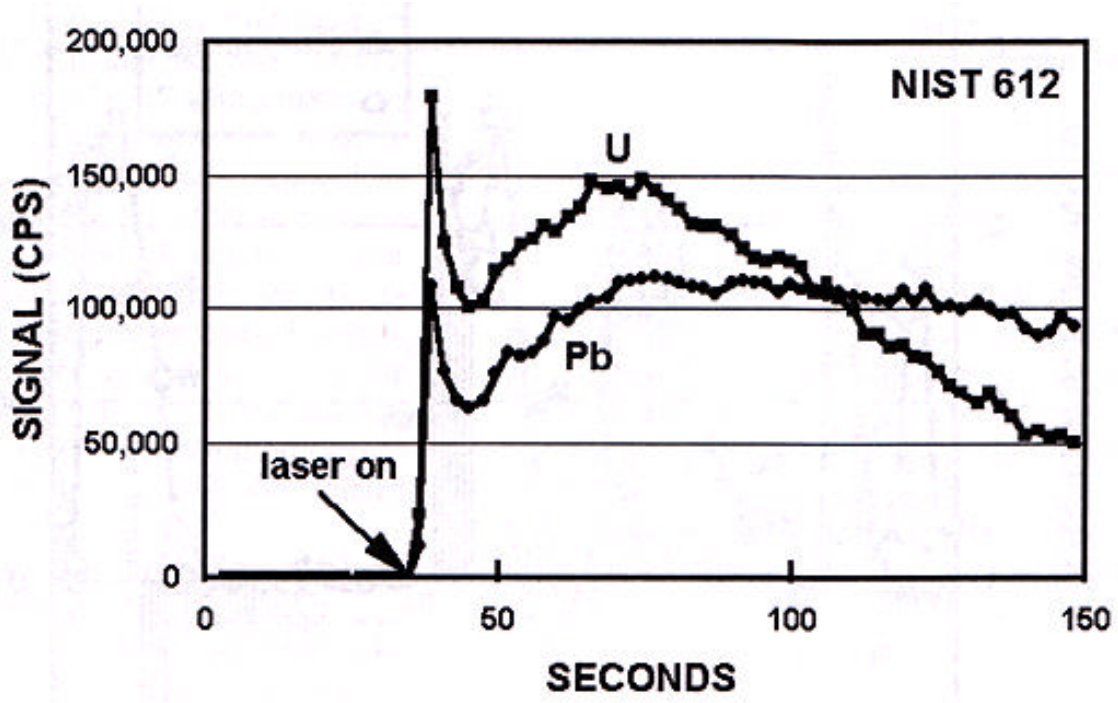


Figure 4.5: Evolution of the U and Pb signal through time. Fractionation of the U/Pb ratio during the analysis (Jackson 2001).

- **Detector**:

Ion counting device: **Dead Time Correction**:

A minimum time difference between the impact of two ions on the detector (electron multiplier) is necessary to identify those as two different events. Therefor the dead time value has to be enter in the software of the spectrometer so that all the ions are counted, otherwise the number of ions counted by the detector will be smaller than the real number of ions detected. For isotope ratio, it means that the measured ratio changes with the intensity of the ion beam. There are two different ways to calculate the dead time value although the use of solution with different isotopic ratio seems to be the best.

- *Using solution at different concentrations*: You need to take two isotopes with very contrasting natural abundances such as ^{175}Lu (97,4%) and ^{176}Lu (2,6%) (^{204}Pb and ^{208}Pb could also be used). Prepare three sets of solution which results in a count rate of about (1) 2.10^6 cps; (2) $0.8:10^6$ cps and (3) 200000 cps for the most abundance isotope (^{175}Lu) for example. Create 3 methods for the different solution in a way that the same amount of ions per each isotopes will be collected at the multiplier (by changing the sample time). Measure the ^{175}Lu /^{176}Lu ratio and correct the dead time so that the three calculated ratios are equal for the three solutions.

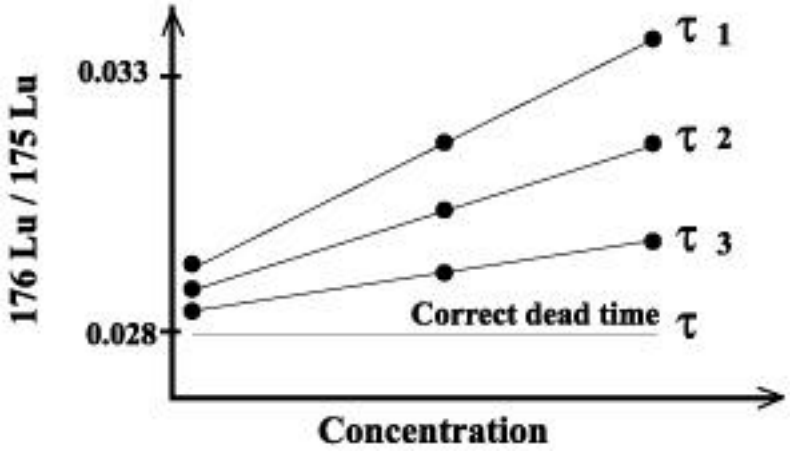


Figure 4.6: Variation of the concentration and the Lu^{176}/Lu^{175} ratio as a function of the dead time (τ)

- *Using solution with different isotope ratio*: (the easiest and most accurate method): Use three set of solution at different concentration. Measure the same ratio with the same method in all three solutions. Calculate the ratio for each of the sample using different dead time value and plot a curve (Dead time chosen versus measured ration/certified ratio). The curves should intersect at the right dead time value.

Example with different uranium samples of various known isotopic composition and concentrations:

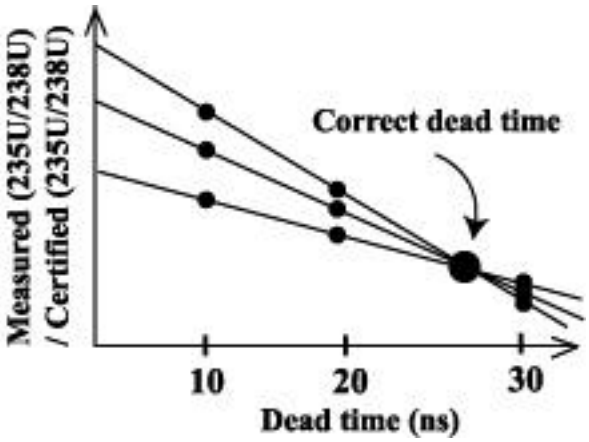


Figure 4.7: Variation of the dead time value (ns) in function of the ratio between the measured 235U/238U ratio and the certified value.

- To correct the measured intensities, use the following equation:

$$C_{true} = \frac{C_{obs}}{(1 - C_{obs}\tau)}$$

with C_{true} as the true intensity, C_{obs} as the observed intensity and τ as the dead time in second. An alternative is to plot the true ratio/measured ration versus the intensity of the most abundant isotope. This last technique yield a straight line, the slope being

$$m' = \frac{(C_{true} - 1)}{\tau}$$

Taking into account the mass bias, the dead time could be finally.

NB: The further the measured isotope ratio lies from unity, the more susceptible the ratio is to dead time correction.

NB: The dead time value is in the range of the nanosecond and usually is around 25ns. It varies with the age of the detector but doesn't change with the mass of the element analyse.
NB: The measured ratio has to be corrected for mass bias using to element with similar sensitivity. Once the mass bias correction factor has been calculated (I_{true}/I_{meas}), we can measured the mass bias per mass unit and use it to correct the ratio of interest.

Faraday cups: Calculation of the gain of the amplifier

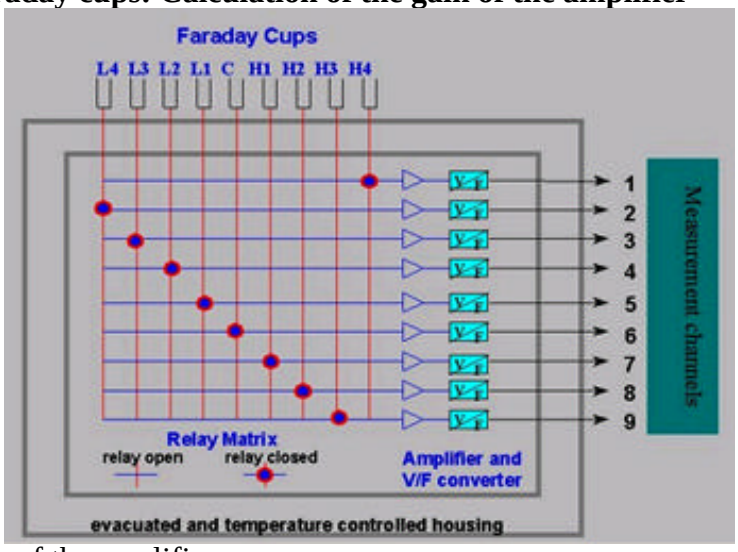


Figure 4.8: Schematic of the amplifier

- **Sensitivity (Counting statistics)**

$$Ratio\frac{A}{B}_{Optimal} = \sqrt{\frac{1}{Intensity\_A * Time(s)} + \frac{1}{Intensity\_B * Time(s)}}$$

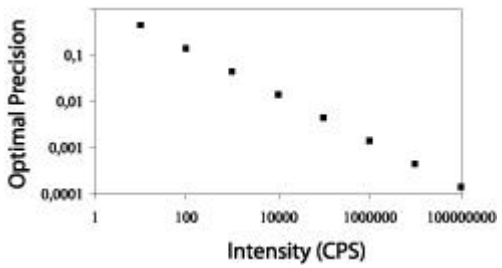


Figure 4.9: Using the equation above, the intensity versus optimal precision shows a linear correlation on this log-log figure.

- Interference

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

- 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…)

Use of different resolution:

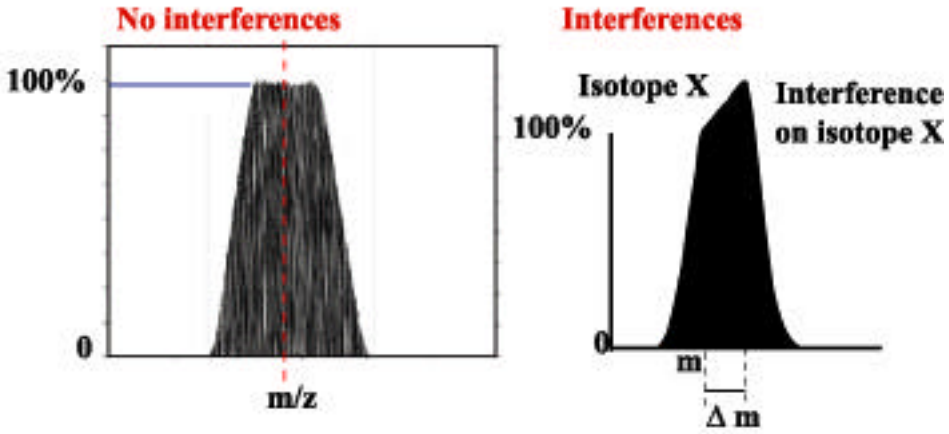


Figure 4.10: Schematic representation of the influence of an interference on the peak shape at low resolution.

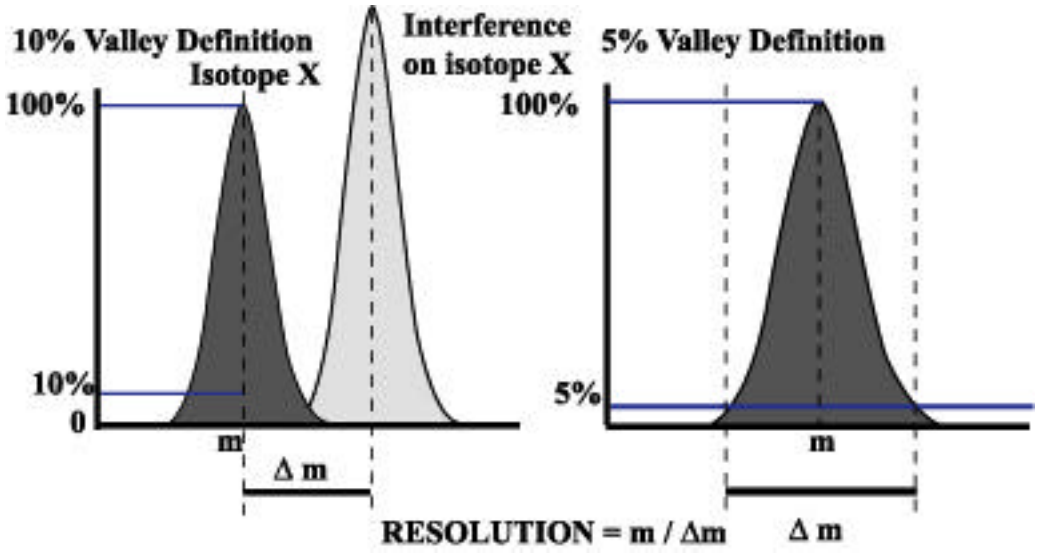


Figure 4.11: Calculation methods for the resolution

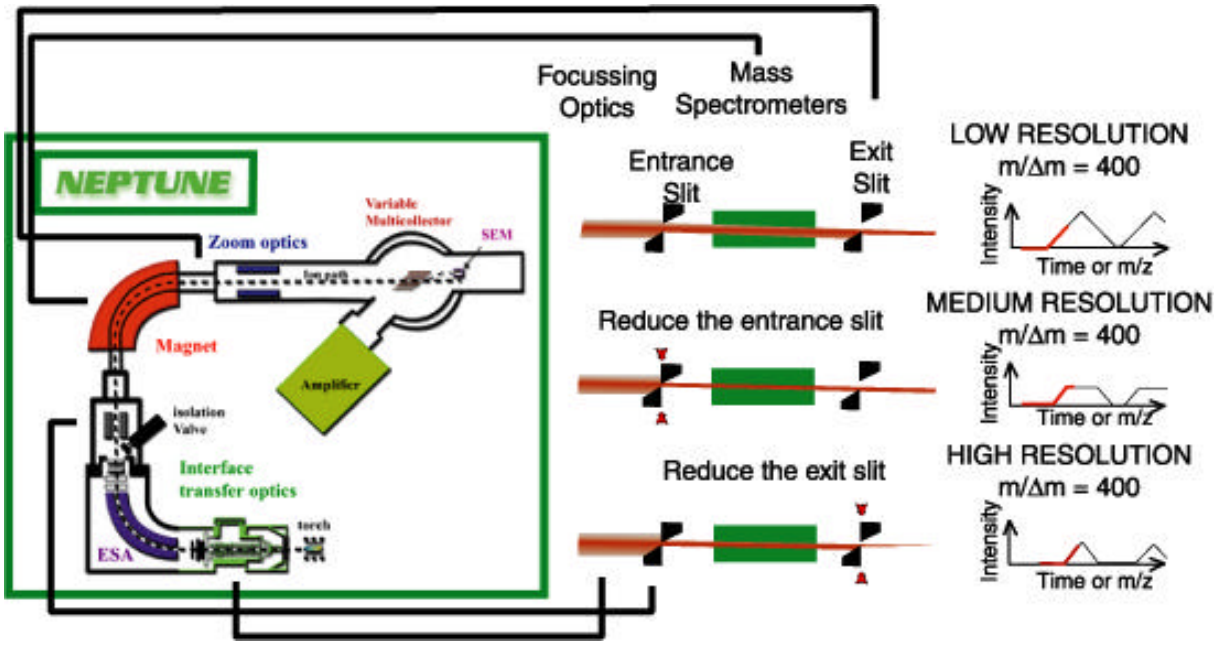


Figure 4.12: Schematic representation of the movement of the entrance and exit slit on the resolution of the Neptune.

Application of High Resolution

Example : in-situ Sr isotopic analysis

In order to perform an accurate measurement of the $^{87}Sr/^{86}Sr$ ratio, the contribution of ^{87}Rb on ^{87}Sr has to be corrected, as well as the ^{86}Kr (deduce from the ^{83}Kr) on the ^{86}Sr intensity.

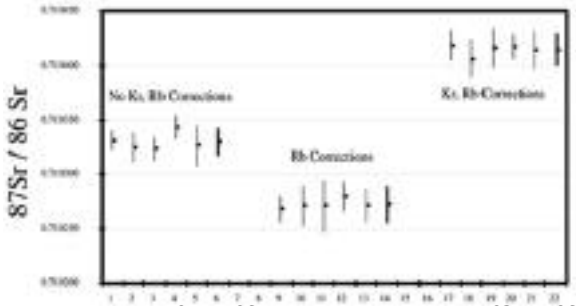


Figure 4_13: Measurement of the $^{87}Sr/^{86}Sr$ ratio without $^{83}Kr/^{86}Kr$ correction and ^{87}Rb correction (left), with ^{87}Rb correction (centre) and with $^{83}Kr/^{86}Kr$ and ^{87}Rb correction (right).

This figure shows that the $^{7}Sr/^{86}Sr$ ratio is overcorrected by ^{86}Kr (calculated from ^{83}Kr). This over-correction might be the result of interference on ^{83}Kr. Kr is a component of the gas and its intensity shouldn't vary during the measurement. The figure below shows the evolution of the signal through time of the ^{83}Kr in the gas blank left and while analysing a standard. The ^{83}Kr signal increases while the ^{86}Sr increase, which indicate that some interference on ^{83}Kr occur. This interference is related to the sample, not to the gas. The figure on the right shows, at high resolution, the intensity of that interference on the ^{83}Kr signal.

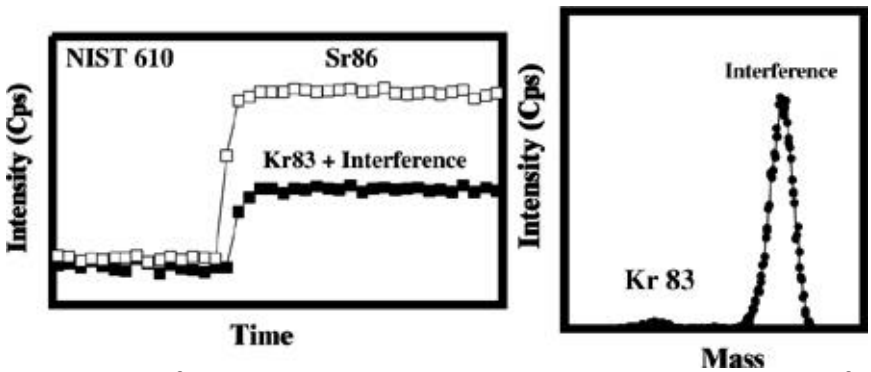
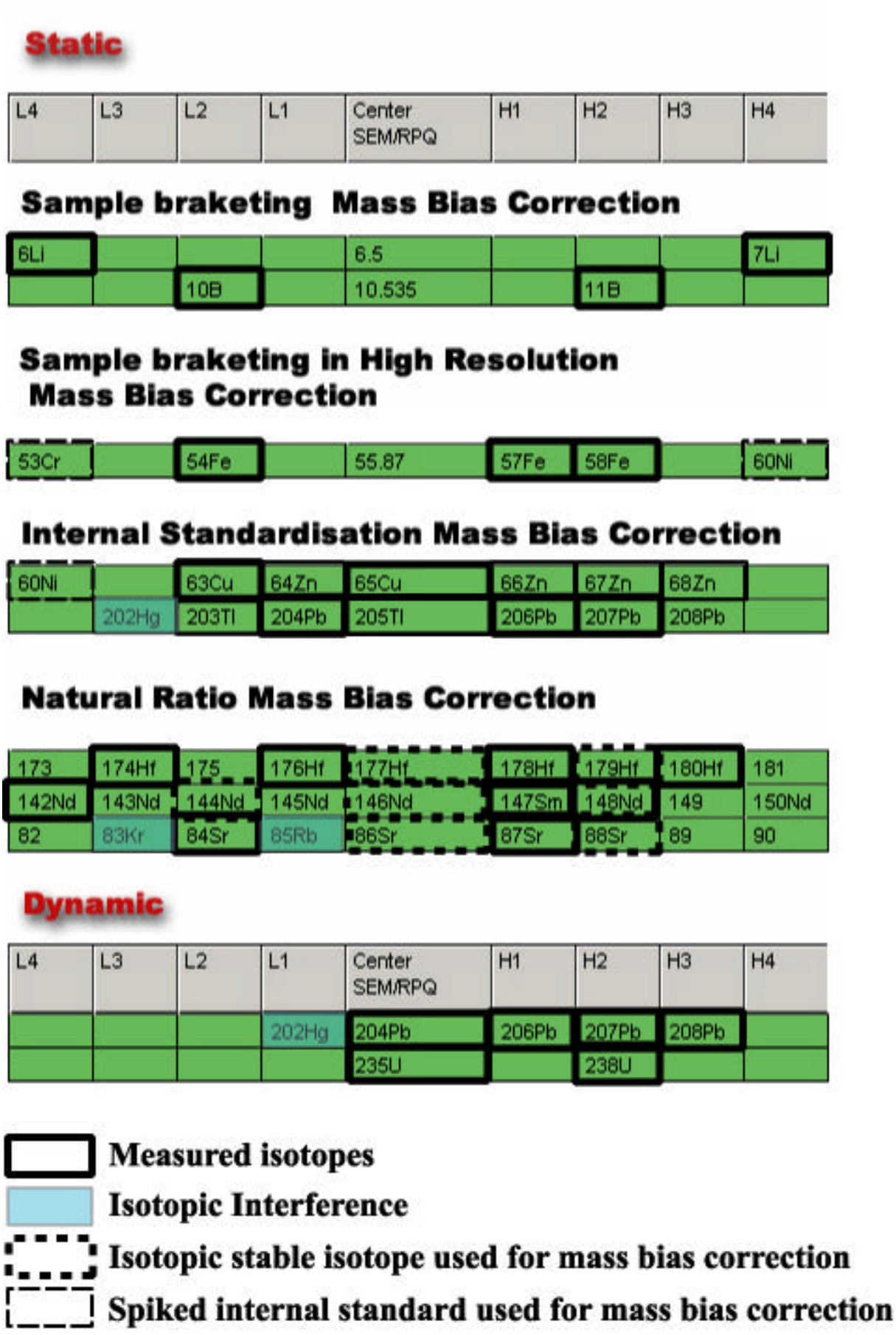


Figure 4_14: Evolution of the signal through time (at low resolution, 350) of mass ^{86}Sr and ^{83}Kr in the gas on the far left and during the analysis of the standard NIST610 (left). The figure on the right shows the interference at resolution 4000.

- Standardisation (calibration)

Usually achieved by analysing Certified Reference Materials (standards) for the isotopic system of interest. The accuracy of the analysis will strongly depend on the certification of the standard for external standardisation technique (e.g. Li7/Li6 isotopes since no internal standards are available and Li has only two isotopes).



- **Background (Sample Contamination-Interference)**:

A measurement of the isotopic composition of the blank may indicate the source of the background (either due to sample contamination or interference).

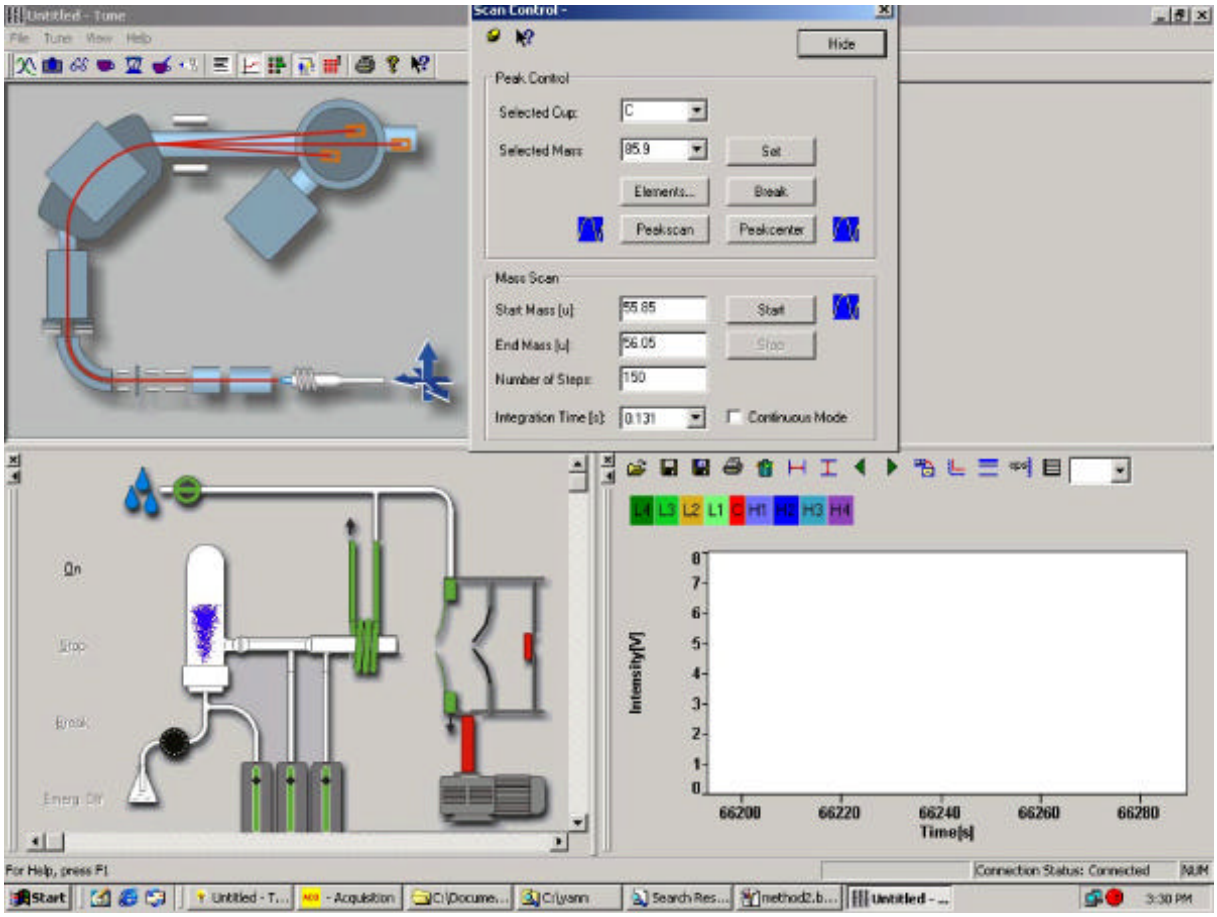
If the isotopic composition of the blank is similar to the sample analysed, then the source of contamination has to be identify and corrected to the sample counts which will lower the precision).

If the isotopic ratio of the blank is different to the sample, then an interference might be blamed and an other isotope, which provides a measure of the level of isobaric interference on the isotope of interest will be include in the data acquisition procedure. Possible isobaric interference has to be taken into account which will depend on the isotope of interest and the sample preparation (example: Hg on ^{204}Pb or $^{183}W^{16}O_7$ on ^{202}Hg if the sample has been crushed using tungsten carbide).

* Acquisition

Tuning

A



B

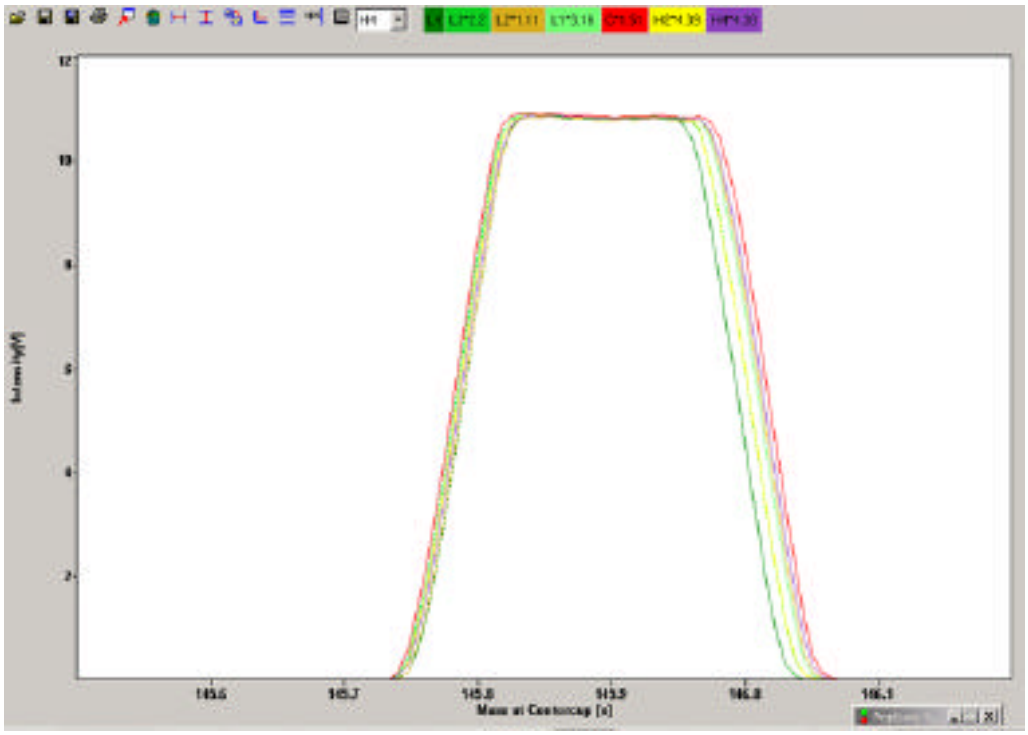


Figure 4-15: The "tuning" window of the Neptune. A. Press On to start the plasma, then monitor and store the gas flow and lens parameters, while watching the intensity on the bottom right figure. B. Check alignment of the cup (example with the Nd isotopes).

Peak Centre - Mass Calibration

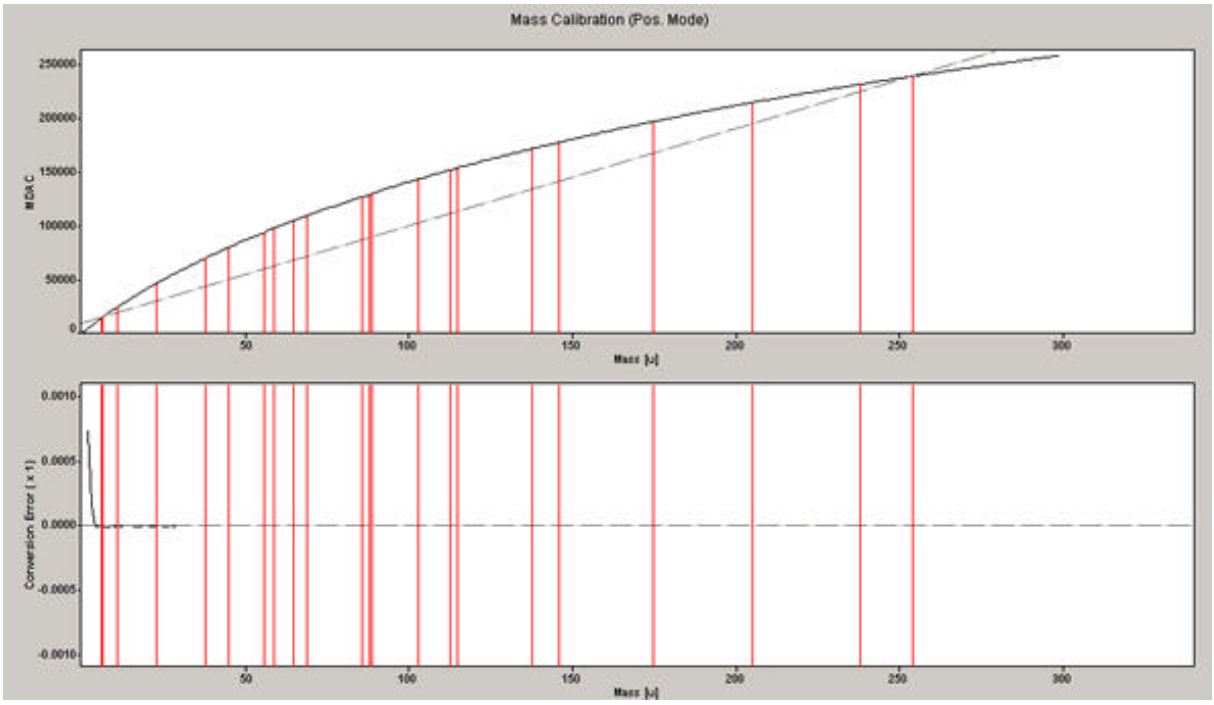
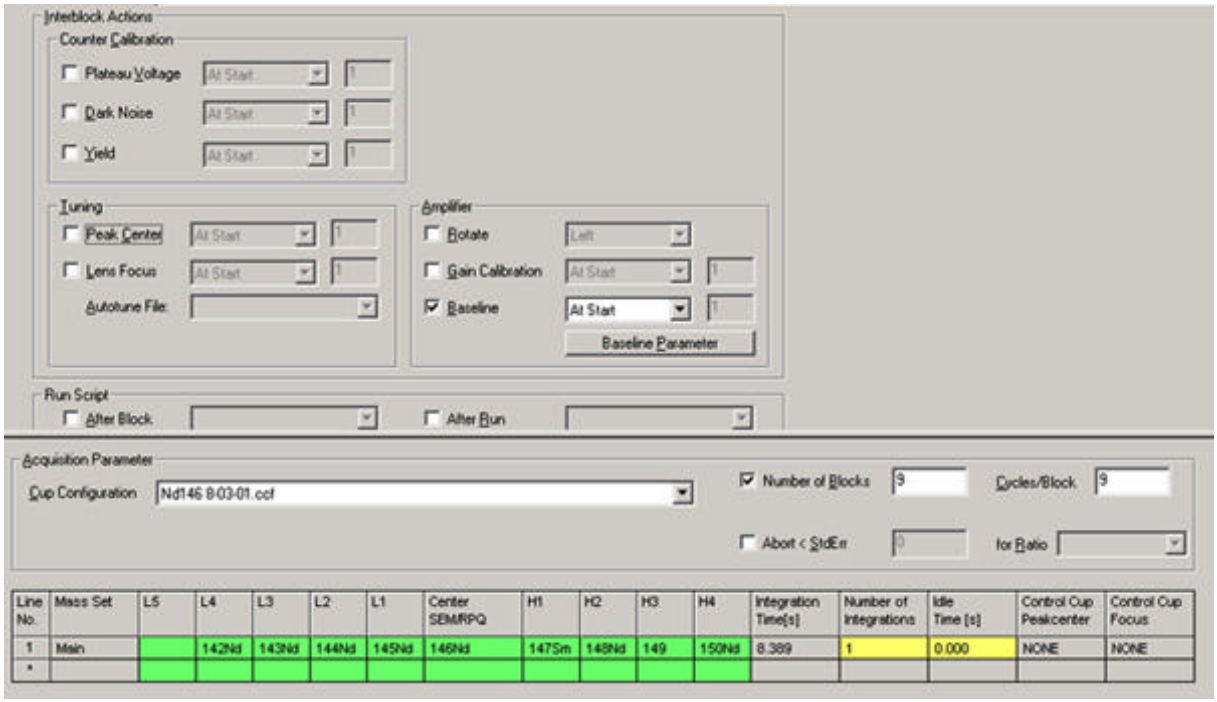


Figure 4_16: The "mass calibration" window of the Neptune. After a peak centre on a precise isotope, the computer check its position according to the other isotopes and calculate a mass calibration curve for all masses.

Method

A



B

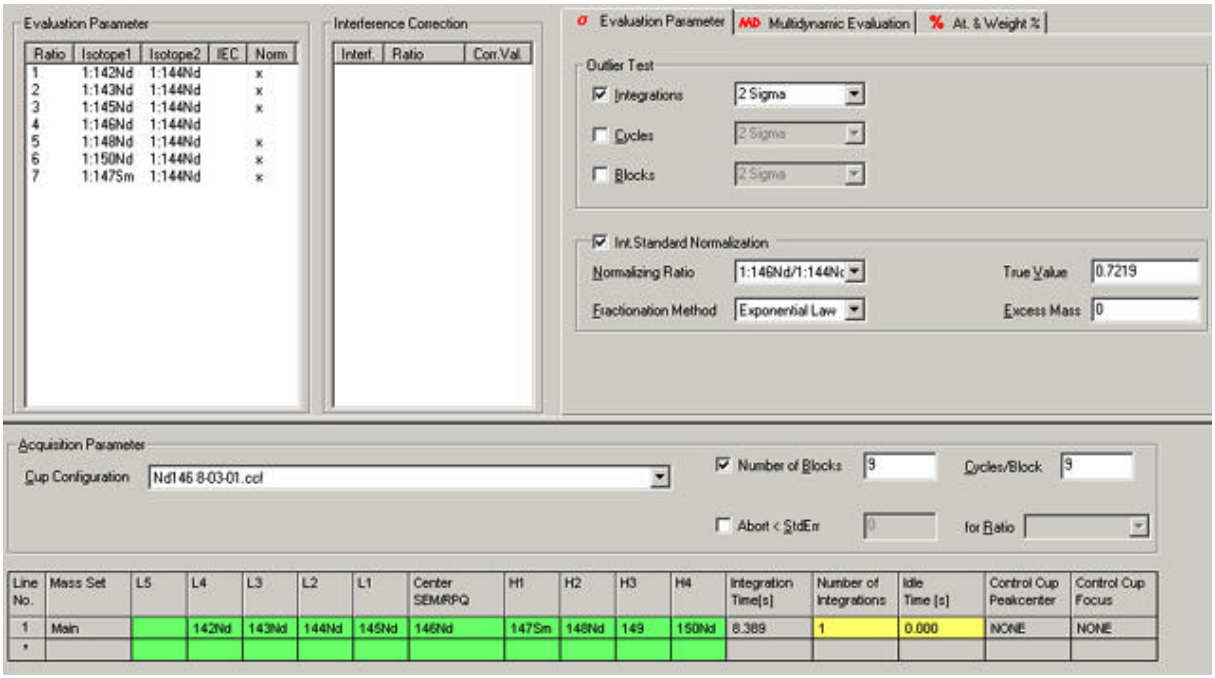


Figure 4_17: The "method " window of the Neptune. For each isotope ratio measurements, a method has to be used. This method will specify:

A. There are few possibilities however a strategy has to be decided for the amplifier only (rotation of the amplifier, gain calibration calculation or baseline calculation). Generally the gain calibration is done separately before the acquisition and a base line is done at the beginning of each measurement. The rotation of the amplifier is an option.

B.

- specify the isotope ratio
- Specify the internal stable ratio for correction (if possible) and its value
- Specify the type of law used for mass bias correction (exponential, power or linear)
- Recall the cup configuration