APPLICATION OF SPECTROMETRY ISOTOPE DILUTION MASS (IDMS) TO TRACE ANAYISIS. STUDY DETERMINATION OF MOLYBDENUM IN A CERTIFIED REFERENCE MATERIAL

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INDEX

OBJECTIVE

The objective of this study is to determine Molybdenum in a Standard Reference Material (CRM) by applying the isotope dilution technique by Mass Spectrometry (IDMS). This involves learning ICP-MS technique and quantification by isotope dilution.

INTRODUCTION

1. Molybdenum

Chemical element symbol Mo, atomic number 42 and atomic weight 95.94 is one of the transition elements. Silver-gray metal. It is an important tool in seawater in the form of molybdates (MoO_4^{2-}) amount, and living things can easily absorb this.

The human body contains about 0.07 mg of molybdenum per kilogram. It occurs in high concentrations in the liver, kidneys and vertebrae. Molybdenum is also present in the enamel of human teeth and may help prevent deterioration. Pork, lamb and beef liver each have about 1.5 ppm of molybdenum. Other significant dietary sources include green beans, eggs, sunflower seeds, wheat flour, lentils and cereal grains.

The average daily intake of molybdenum varies between 0.12 and 0.24 mg, but depends on the molybdenum content of food. The acute toxicity has not been seen in humans, and depends largely on the chemical state. Although human toxicity data are not available, studies in animals have shown that chronic intake of more than 10 mg / day molybdenum can cause diarrhea, stunted growth, infertility, and low birth weight. It can also affect the lungs, kidneys and liver. Sodium tungstate is a competitive inhibitor of molybdenum, and diet reduces the concentration of molybdenum in tissues.

Dietary deficiency of molybdenum from its concentration on the Earth's surface has been associated with higher rates of esophageal cancer in parts of China and Iran. Compared with the United States, which has a greater supply of molybdenum in the soil, people living in these areas have an approximately 16-fold increased risk for esophageal squamous cell carcinoma.

2. Trace analysis

   2.1.   Concept Definition

   The term "trace analysis" corresponds to the analytical methodology implicated in identifying or quantifying the amount of a given component when it is in very low concentrations.

The term "very low concentration" has evolved over time because initially was available techniques were not able to quantify below 0.01% and today it is possible to "ultra trace analysis" on the concentrations are determined below 0.0001%. It should be noted that when dealing with extremely low concentrations is not appropriate to talk about percentages and therefore the units will be used in the form mass/mass or mass/volume.

2.2.   Problematic

One of the problems involved in the determination of trace components is the possible existence for losses or contamination during the analytical process (from sampling to measure) behave as they made a grave error for measurements at such low concentrations.

Another aspect to consider is the high ratio of matrix / analyte mass must not exceed 106 order because they can cause interference mass. In the case of matrix interference effect it is eliminated by performing calibration standard additions.

The choice of measurement technique is very important in trace analysis because it must be sensitive enough to quantify the analytes in the desired level of concentration; for this, sometimes a preconcentration step is necessary.

The lack of Certified Reference Materials (CRM) is a problem regarding the validation of the results obtained.

2.3.   Importance

The analysis of trace components is very important in sectors such as industry, environment (limit pesticides), legislative, health (diagnose or prevent diseases), etc.

3.   IDMS in trace analysis

3.1.   Introduction

3.1.1.   Nature of the elements Isotope

The thought of the possible existence of isotopes of the elements occurred in the late XIX century when it was observed that the light elements had atomic weights near integers, but instead the atomic weight of chlorine was 35,5.

In 1913, Thomson calibrated the first mass spectrometer and later his student Aston determined the isotopic abundances of different elements thus explaining the anomaly of chlorine. A few years later, Nier introduced the magnetic sector analyzer.

Most elements have at least two stable isotopes of the elements being of interest carbon (of 100 atoms, 1 is ^{13}C and 99 are ^{12}C).

When making use of the source of elemental ionization (as ICP) mass spectra obtained indicate the isotopic abundances of atoms and these will be considered invariant in nature, therefore it can predict when isotopic ratios are altered with respect its abundance in nature. The same applies to the physical and chemical properties of isotopes as they are considered identical for the same item.

3.1.2.   The concept of isotope dilution

To determine the number of chickpeas there in a packet of 1Kg you could have one to one but this way is costly and can lead to error (we can fall any on the table, the account is lost by fatigue and boredom ...) . If you have sachets containing 1000 black chickpeas (the existence of some white chickpea despises) and one of them is mixed with a packet of 1Kg white chick peas (black chickpeas that may have despise) you can determine the number of chickpeas in the package of 1Kg by the formula:

$$\frac{X}{1000} = \frac{B}{N} \quad (1)$$

where:

- ▪ X = number of white chickpeas
- ▪ B = white chickpeas that are in the handful *i*
- ▪ N = black chickpeas that are in the handful *i*

The uncertainty that applies is the standard deviation of all measurements. Any aliquot of the mixture has the same ratio B/N therefore any loss (after mixture) sample does not affect the result. Aliquots larger provide better accuracy and therefore more reliable values.

3.2.   Fundamentals of isotope dilution analysis

Isotope dilution is based on alteration of the isotopic abundances of the element to be determined in the sample by adding to it a known amount of enriched isotope of the same one element (tracer). The element to be determined must have 2 stable

isotopes, or a stable and a long half-life radioactive, which can be measured without spectral interference by a mass spectrometer.

The principle of isotope dilution consists in mixing a sample with a tracer. In the sample one of the two isotopes (eg: a) of an element is more abundant; however, in the tracer isotope b of the same element is present in greater proportion than to as shown in *Figure 1*. In the mixture abundances of the two isotopes are intermediate between the sample and tracer.
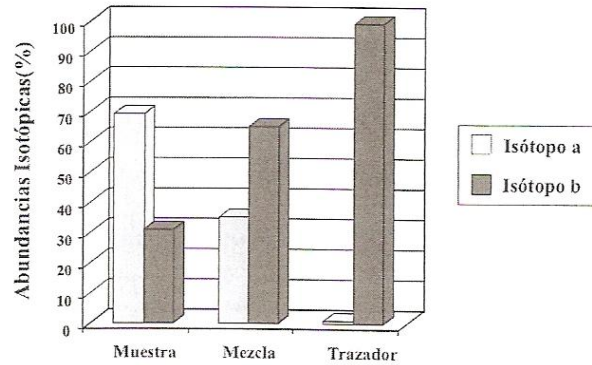

Figure 1. Basis of isotope dilution for an item that contains two isotopes (a and b).

Through isotope dilution equation the initial concentration of the element in the sample is calculated by measuring the isotopic ratio in the mixture. If N_s is the number of moles of a poly-isotopic element present in the sample, N_t is the number of moles of the same element in the tracer:

$$N_m = N_s + N_t \quad (2)$$

where N_m is the number of moles of the element in the mix.

If we take into account the existence of two isotopes *a and b* mass balances are:

$$N_m^a = N_s^a + N_t^a \quad (3)$$

$$N_m^b = N_s^b + N_t^b \quad (4)$$

The isotopic ratio *a/b* in the mixture (R_m) is obtained by dividing (3) between (4) and taking into account the isotopic abundances in the sample and the tracer:

$$R_m = \frac{N_m^a}{N_m^b} = \frac{N_s^a + N_t^a}{N_s^b + N_t^b} = \frac{N_s A_s^a + N_t A_t^a}{N_s A_s^b + N_t A_t^b} \quad (5)$$

Solving N_s in equation (5):

$$N_s A_s^b R_m + N_t A_t^b R_m = N_s A_s^a + N_t A_t^a \quad (6)$$

$$N_s A_s^a - N_s A_s^b R_m = N_t A_t^b R_m - N_t A_t^a \quad (7)$$

$$N_s(A_s^a - A_s^b R_m) = N_t A_t^b R_m - N_t A_t^a \quad (8)$$

$$N_s = N_t \cdot \frac{A_t^b R_m - A_t^a}{A_s^a - A_s^b R_m} \quad (9)$$

Therefore it is observed that knowing the isotopic composition of tracer (A_t^a and A_t^b), the sample (A_s^a and A_s^b), the number of moles added tracer (N_t) and measure the isotopic ratio (R_m) in the mixture; the number of moles of the element present in the sample is calculated.

If you want express mole concentrations instead of isotopic ratios are defined in the sample and the tracer as follows:

$$R_s = \frac{A_s^b}{A_s^a} \quad (10)$$

$$R_t = \frac{A_t^a}{A_t^b} \quad (11)$$

And the equation (9) is the following manner:

$$N_s = N_t \cdot \frac{\frac{A_t^b}{A_t^b}}{\frac{A_s^a}{A_s^a}} \cdot \frac{A_t^b R_m - A_t^a}{A_s^a - A_s^b R_m} \quad (12)$$

$$N_s = N_t \cdot \frac{A_t^b R_m - A_t^b \cdot \frac{A_t^a}{A_t^b}}{A_s^a - A_s^a \cdot R_m \cdot \frac{A_s^b}{A_s^a}} = N_t \cdot \frac{A_t^b}{A_s^a} \cdot \left(\frac{R_m - R_t}{1 - R_m \cdot R_s}\right) \quad (13)$$

Using the expressions:

$$N_s = \frac{C_s \cdot m_s}{M_s} \quad (14)$$

$$N_t = \frac{C_t \cdot m_t}{M_t} \quad (15)$$

where:

- C_s and C_t are the concentrations of the element in the sample and the tracer respectively.
- m_s and m_t are taken sample mass and added mass tracer, respectively.
- M_s and M_t are the atomic weights of the element in the sample and the tracer, respectively.

Finally, the equation of isotopic dilution in which all parameters are known except R_m corresponding to the extent provided by the Mass Spectrometer and therefore calculation of the concentration of the element in the sample C_s is immediately obtained:

$$C_s = \frac{N_s \cdot M_s}{m_s} = N_t \cdot \frac{A_t^b}{A_s^a} \cdot \left(\frac{R_m - R_t}{1 - R_m \cdot R_s}\right) \cdot \frac{M_s}{m_s} = C_t \cdot \frac{m_t}{m_s} \cdot \frac{M_s}{M_t} \cdot \frac{A_t^b}{A_s^a} \cdot \left(\frac{R_m - R_t}{1 - R_m \cdot R_s}\right) \quad (16)$$

The first advantage provided by the isotope dilution analysis is observed directly from equation (16) because no parameter depends on the instrumental sensitivity. This fact suggests that any variation due to instrumental instabilities (signal drift, matrix effects, ...) does not have influence on the final value of C_s.

Another advantage of is that the uncertainty in the measurement of the concentration (C_s) depends solely on R_s, R_t and R_m sometimes being known R_s and R_t can be determined or can be also known whether a certificate tracer used. Therefore, high precision and accuracy in the measurement is obtained R_m since only depends on the mass spectrometer.

The third advantage is that once the isotopic equilibrium achieved any loss of substance in the mixture does not affect the final result since all have the same R_m aliquots (no need to have knowledge of the dilution carried out, preconcentration, ...).

In this case it is not necessary to know the total amount of analyte that is isolated or analytical performance of each step as in other techniques.

For all these advantages the isotope dilution analysis method is considered a "reference" or "absolute". Measurement directly gives the concentration R_m therefore faster analysis because performing calibration is not necessary is achieved.

For all the above is truthful should consider:

➢ Any loss of substance before the equilibrium is a source of considerable error.
➢ The isotope enriched added should behave identically to the natural element.
➢ Measurement of the intensities of the isotopes must be free of interference.
➢ Factors affecting a precise must be controlled.
➢ Should be monitored white values for possible contamination.

3.3.   Practical aspects of application

3.3.1. Measure isotope ratios by ICP-MS for elemental analysis and speciation

a) Factors affecting the accuracy of measurement of isotope ratios

➢ *Blank*

A major source of error in IDMS lies in the possible contamination of reagents or materials used for the analysis. This does not usually occur due to high concentrations and the low sample treatment necessary for this technique.

In cases where the target has a similar isotopic composition of the sample it is necessary to perform a separation element of interest in the target.

The experiments IDMS targets are needed to determine the detection limit of the method. In elementary IDMS, the detection limit is calculated by multiplying the standard deviation by three, and so it is possible to directly subtract the concentration found in blank instead of subtracting the signal from the target samples. Blank uncertainty should be taken into account for the calculation of the uncertainty of the sample.

➢ *Spectral interferences*

Elemental isotope dilution analysis can only be carried out if at least two isotopes of the element are free from spectral interferences and this is achieved by using a mass spectrometer double focusing high resolution as this power is increased resolution decreasing the slit width of the slit source and collector.

An alternative to equipment dual approach are analyzers type mass quadrupole collision cell and reaction in which a cell (between the plasma source and analyzer) pressurized with collision gas or reaction in order to install eliminate or reduce interfering ions. Depending on the gas used will collision cell (if the gas used is inert, helium or xenon) or reaction (if the reactive gas is used, hydrogen or ammonia). The following figure shows interference from argon dimers on selenium are observed. In this case it is possible elimination reaction cell using hydrogen and the result obtained is a free interference spectrum (*Figure 3*).
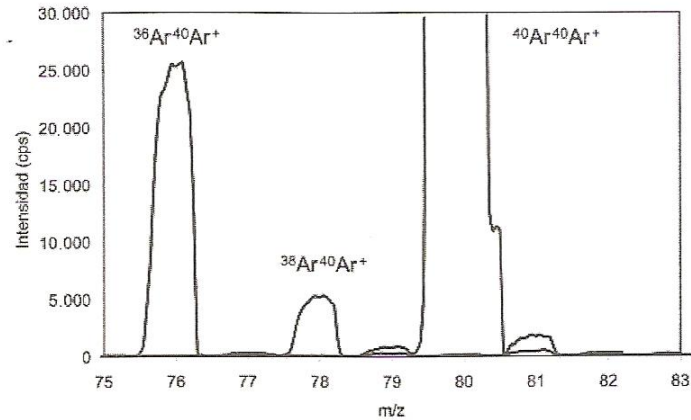
Figure 2. ICP-MS spectrum of a reagent blank without using collision gas in the spectral region of selenium. When using the collision gas argon dimers disappear.
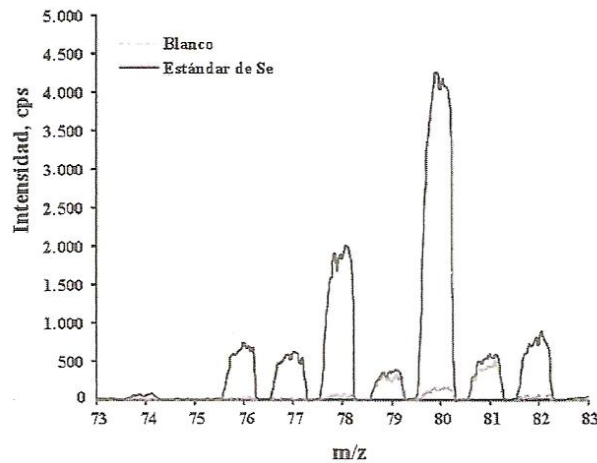

Figure 3. ICP-MS spectrum of a reagent blank and a standard Se using H_2 as the reaction gas in a collision cell.

In majority of occasions, it is possible to eliminate interference during the chromatographic separation though there are cases where this does not happen and detection of additional isotopes and subsequently using equations correction is necessary.

➢ *Detector dead time*

In ICP-MS detectors are the most used electron multipliers and pulse counting systems. In the pulse counting systems, if the speeds are very high (> 10^6 counts/sec) the number of registered accounts is less than real. This problem becomes even more important if the abundances of the isotopes are very different between them. In these cases the instrumental sensitivity to obtain good results for the less abundant isotope although it the most abundant appear more affected by the downtime is increased. Therefore this effect must be corrected by the following formula:

$$I_{corrected} = \frac{I_{measure}(cps)}{1 - I_{measure}(cps) \cdot \tau(s)} \qquad (17)$$

where τ is the dead time of the detector (s).

Dead time is calculated by measuring isotope ratios of an element at different concentrations using different values of dead time (*equation 17*) so that when the correct value is entered isotope ratio does not vary according to the concentration (*Figure 4*).
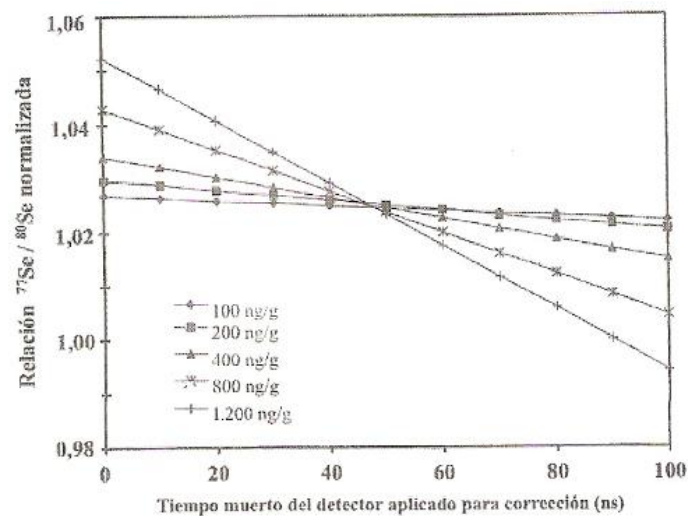
Figure 4. Isotope ratio $^{77}Se/^{80}Se$ to different concentrations of Se for calculating the dead time of the detector.

> ➤ *Discrimination mass (κ)*

It refers to a preferred transmission fact happen both through the extraction interface as the mass spectrometer heavier ions against the lighter that will lead to erroneous value R_m. In ICP-MS originates both extraction interface (hole effect) as in the system of ion lenses (space-charge effect).

The space-charge effect is repulsion suffering ions between them when leaving the separator cone and causes the number of transmitted ions is less because the lighter suffer a degree of greater than heavier deflection (these remain in the center of the ion beam). This effect also depends on the ionic current produced by the sample (the higher potential less space-charge effect).

Mass discrimination ICP-MS is corrected using a standard known isotopic composition or certified (isotopic MR) and the appropriate equation for calculating this purpose it is as follows:

$$R_{corrected} = R_{measure} \exp{(F\Delta m)} \qquad (18)$$

where $R_{measure}$ is the isotope ratio, F factor discrimination more per unit mass and Δ_m the mass difference between isotopes. The *Picture 1* shows the results obtained for a pattern of natural isotopic abundance of molybdenum measured by ICP-MS multicollector.

Picture 1. Measurement of isotopic ratios for molybdenum in an ICP-MS Multicollector equipment.

Relación isotópica	R_{med}	R_{teor}	$Ln(R_{med}/R_{teor})$	Diferencia de masa
92/98	0,54356	0,61500	−0,12348	6
94/98	0,35318	0,38334	−0,08195	4
95/98	0,62089	0,65976	−0,06072	3
96/98	0,66357	0,69126	−0,04087	2
97/98	0,38790	0,39577	−0,02010	1
100/98	0,41469	0,39909	0,03835	−2

b) Factors affecting the measurement accuracy of isotopic ratios

➤ Ion counting statistics

If an electron multiplier detector is used as the accuracy is limited by the ion counting statistics, since the use of highly sensitive instruments accuracy is improved experimental measurements.

Sequential measures transient signals that change rapidly over time are associated errors in measurement of isotopic ratios as the effect of spectral shift, especially important in these cases occurs. The number of readings is distributed among the number of isotopes in a limited signal time, therefore the sensitivity and accuracy decreases as the number of measured isotope cause distortion peaks and errors in quantification.

➤ Stability of the ion current

The peak shape can influence the stability of the ion current even when there is temporal fluctuations. The peaks with narrow peaks require an exact measurement sequence as the minimum fluctuation in the m/z axis carries a significant deterioration in accuracy. In the case of ICP-MS dual approach resolving power under the peaks generated by the equipment have trapezoidal shape so there will be slight variations in measurements.

> ➤ Optimization of the amount of tracer added simple

One of the parameters that have a significant influence on the end result is the amount of added tracer. This amount can be optimized by calculating the optimum range of *sample/tracer* in which statistical errors are minimized. From *equation (16)* the variance of the concentration in the sample is obtained:

$$
s(C_s)^2 = \left[\frac{\partial C_s}{\partial m_t}\right]^2 s(m_t)^2 + \left[\frac{\partial C_s}{\partial m_s}\right]^2 s(m_s)^2 + \left[\frac{\partial C_s}{\partial M_t}\right]^2 s(M_t)^2 + \left[\frac{\partial C_s}{\partial M_s}\right]^2 s(M_s)^2
$$
$$
+ \left[\frac{\partial C_s}{\partial A_t^b}\right]^2 s(A_t^b)^2 + \left[\frac{\partial C_s}{\partial A_s^a}\right]^2 s(A_s^a)^2 + \left[\frac{\partial C_s}{\partial R_s}\right]^2 s(R_s)^2 + \left[\frac{\partial C_s}{\partial R_t}\right]^2 s(R_t)^2
$$
$$
+ \left[\frac{\partial C_s}{\partial R_m}\right]^2 s(R_m)^2 \quad (19)
$$

Applying partial derivatives is obtained:

$$
\left[\frac{s(C_s)^2}{C_s}\right] = \left[\frac{s(m_t)}{m_t}\right]^2 + \left[\frac{s(m_s)}{m_s}\right]^2 + \left[\frac{s(M_t)}{M_t}\right]^2 + \left[\frac{s(M_s)}{M_s}\right]^2 + \left[\frac{s(A_t^b)}{A_t^b}\right]^2 + \left[\frac{s(A_s^a)}{A_s^a}\right]^2
$$
$$
+ \left[\frac{R_m R_s}{1 - R_m R_s}\right]^2 \left[\frac{s(R_s)}{R_s}\right]^2 + \left[\frac{-R_t}{R_m - R_t}\right]^2 \left[\frac{s(R_t)}{R_t}\right]^2
$$
$$
+ \left[\frac{R_m(1 - R_t R_s)}{(R_m - R_t) - (1 - R_m R_s)}\right]\left[\frac{s(R_m)}{R_m}\right]^2 \quad (20)
$$

Considering that the measurement of the isotope ratio in the sample and the tracer does not influence the result, the magnification factor of error is defined:

$$
f(R) = \left[\frac{R_m(1 - R_t R_s)}{(R_m - R_t)(1 - R_m R_s)}\right] \quad (21)
$$

Therefore the magnification factor only depends on the variable R_m and R_s and R_t are constants. If $f(R)$ represents R_m against range in which the magnification error is minimal and of this form optimizing the amount of tracer added is achieved is obtained.
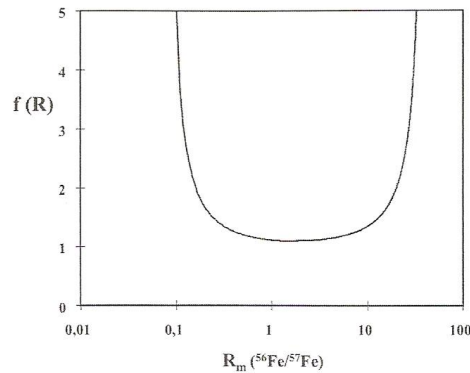
Figure 5. Curve magnification error for a tracer isotope ^{57}Fe-enriched to 92,45%.

As shown in *Figure 5*, the optimal range where the relative error in concentration is equal to the relative error in measurement is 0.2 to 10.

3.4.   New tendencies

3.4.1.   Deconvolution isotopic profiles

The definition of isotopic profile is the set of isotopic abundances relative all stable isotopes of an element and the sum of all the relative abundances of all isotopic is always 1, it also being possible to apply this concept in the case of chemical compounds.

The natural isotopic abundances of the elements are tabulated and their uncertainties, as they are considered constant throughout the Earth and therefore calculating them is easy. An element or compound is said isotopically enriched isotopic profile is altered as the relative abundance of one or more stable isotopes is greater than what is found in nature while the remaining elements of low abundance.

Isotopic deconvolution profiles is the mathematical process that allows calculation of the contribution of natural isotopic profile and altered in the mixture in a single compound or measured by mass spectrometry element. The result is expressed as a mole fraction of each isotope in the sample profile.

The deconvolution process is not limited to use of a single altered isotopic profile and a demonstration of this is the next in isotopic considers three profiles; one natural and two altered of the same element.

The case in which the sample containing an unknown amount of both the element of natural isotopic abundance as one of altered isotopic profiles and the other altered

isotopic profile, the sample is added is analyzed, containing a known amount of the object element study. The mass balance is given by:

$$N_m = N_{nat} + N_{p1} + N_{p2} \quad (22)$$

where N_m is the number of total moles of the element in the sample, the number of unknown N_{nat} moles of natural isotopic abundance element, N_{p1} and N_{p2} moles of corresponding to the two profiles altered isotopic element in the sample.

In case you want to consider the mass balance for each of the isotopes present:

$$N_m^i = N_{nat}^i + N_{p1}^i + N_{p2}^i \quad (23)$$

where the term *i* refers to either an isotope.

Equation (23) can be expressed as a lineal combination of the total quantity of the element in each of the isotopic profiles of known isotopic abundances in each profile:

$$N_m \cdot A_m^i = N_{nat} \times A_{nat}^i + N_{p1} \times A_{p1}^i + N_{p2} \times A_{p2}^i \quad (24)$$

where A_m^i, A_{nat}^i, A_{p1}^i and A_{p2}^i are the isotopic abundances of the isotope i in each of the isotopic profiles. If equation (24) by equation (22) is divided the following mathematical expression is obtained:

$$A_m^i = x_{nat} \times A_{nat}^i + x_{p1} \times A_{p1}^i + x_{p2} \times A_{p2}^i \quad (25)$$

where:

$$x_{nat} = \frac{N_{nat}}{N_{nat} + N_{p1} + N_{p2}} , x_{p1} = \frac{N_{p1}}{N_{nat} + N_{p1} + N_{p2}} , x_{p2} = \frac{N_{p2}}{N_{nat} + N_{p1} + N_{p2}} \quad (26)$$

are the mole fractions of each of the x_{nat}, x_{p1} and x_{p2} isotopic profiles that contribute isotopic profile observed in the sample.

In the event that the element used stable isotopes possess n (n ≥ 3) can define an equation of isotopic abundances and mole fractions (*equation 25*) for each isotope expressed in matrix notation is:

$$\begin{bmatrix} A_m^1 \\ A_m^2 \\ A_m^3 \\ ... \\ A_m^{n-1} \\ A_m^n \end{bmatrix} = \begin{bmatrix} A_{nat}^1 & A_{p1}^1 & A_{p2}^1 \\ A_{nat}^2 & A_{p1}^2 & A_{p2}^2 \\ A_{nat}^3 & A_{p1}^3 & A_{p2}^3 \\ & ... & \\ A_{nat}^{n-1} & A_{p1}^{n-1} & A_{p2}^{n-1} \\ A_{nat}^n & A_{p1}^n & A_{p2}^n \end{bmatrix} \begin{bmatrix} x_{nat} \\ x_{p1} \\ x_{p2} \end{bmatrix} + \begin{bmatrix} e^1 \\ e^2 \\ e^3 \\ ... \\ e^{n-1} \\ e^n \end{bmatrix} \quad (27)$$

In the event that n> 3 are more equations than unknowns (mole fractions) and it has to include an error vector in *equation (27)*. The values of x_{nat}, x_{p1} and x_{p2} and

uncertainties, unknowns are obtained by least-squares fitting error vector using the technique of multiple least squares. This process (calculation of the mole fractions using equation (27)) is called "deconvolution isotopic profiles."

Now relations x_{nat}/x_{p2} and x_{p1}/x_{p2} matching mole ratios N_{nat}/N_{p2} and N_{p1}/N_{p2} respectively are calculated. As the added amount of tracer 2 (N_{p2}) it is known is possible to determine the amount of natural and tracer element 1 in the sample.

This form of calculation IDA (Isotope Dilution Analysis) presents a number of advantages over other possible equations. One advantage is that it serves for any system in which elements or isotopically labeled compounds (two isotopic profiles: natural and altered) are used. Another advantage is the possibility of working with multiple isotopic profiles, which is necessary in most cases. Finally, to correct systematic errors (discrimination mass spectral interferences,...) without using certified standards, since it works with more isotopes strictly necessary for IDA.

4. ICP-MS

ICP-MS or Inductively coupled plasma mass spectrometry is an analytical technique used for elemental determinations. The technique was introduced in the market in 1983 and has gained general acceptance in many types of laboratories. Geochemical analysis laboratories were the first to adopt the ICP-MS technology because of its superior detection capabilities, especially for rare earth elements (REEs).

Figure 6. ICP-ORS-MS Agilent 7500c used at Universitat Jaume I.

The ICP-MS analysis involves a series of processes from the introduction of the sample to the final obtained signal and they are shown in the following figures:
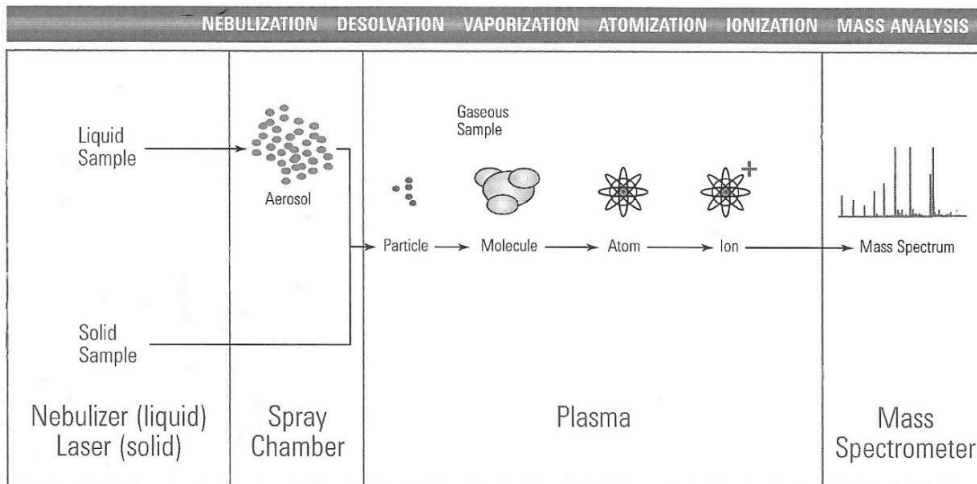
Figure 7. Processes occurring to analytes in an ICP-MS measure

ICP-MS has many advantages over other techniques elemental analysis such as atomic absorption and optical emission spectrometry, including ICP atomic emission spectroscopy (ICP-AES), because:

- The detection limits for most elements are equal to or better than those obtained by atomic absorption spectroscopy graphite furnace (GFAAS).
- Performance higher than GFAAS.
- Ability to handle both simple and complex matrices with a minimum of interference from the matrix due to the high temperature of the ICP source.
- Capacity than ICP-AES detection in the samples analyzed.
- Ability to obtain isotopic information.

An ICP-MS combines high temperature ICP (inductively coupled plasma) source with a mass spectrometer. The ICP source converts the atoms of the elements of the sample ions. These ions then separated and detected by the mass spectrometer.

Figure 8. Parts of an ICP-MS instrument, without Collision/Reaction Cell system

4.1. Sample introduction

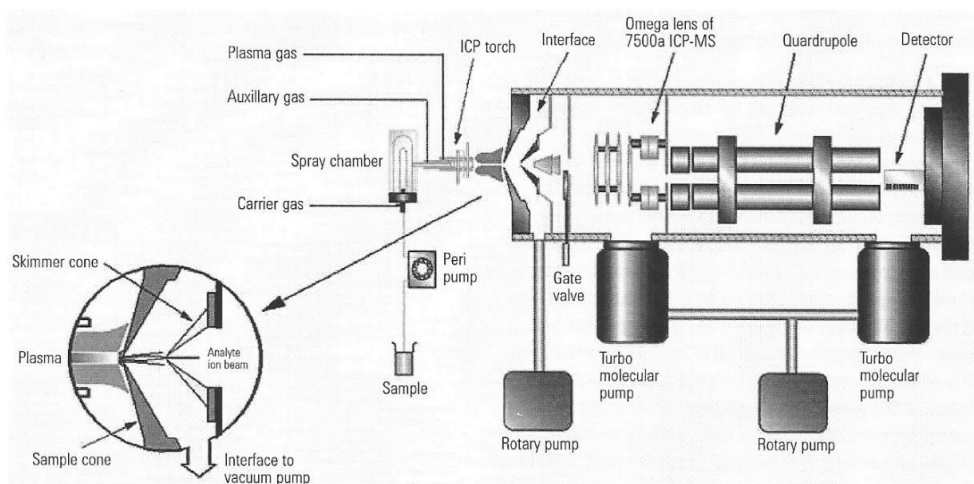The sample introduction system is one of the most important components of the entire ICP-MS system. It must transport the sample, in the form of a homogeneous aerosol of little droplets, into the centre of the plasma. Large droplets and wide size range must be avoided in order to maintain the plasma temperature and repeatability/reproducibility of measures.

The liquid sample is pumped with a peristaltic pump with a controlled and optimised flow rate and it is nebulised into a spray chamber. There are some different nebulizer types, but the concentric nebuliser is the most widely employed. The liquid is turned into an aerosol with a gas carrier (Argon) as shown in *Figure 9*.
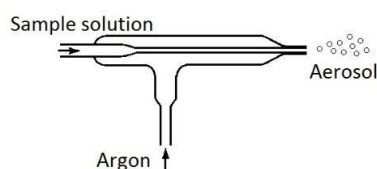
Figure 9. Concentric nebulizer

The produced aerosol should be homogenised, so the larger droplets have to be removed. This is accomplished employing a spray or nebulization chamber (*Figure 9*) allowing only a small portion of the droplets to reach the plasma torch, the rest is drained as waste. Also, the chamber is usually kept at low temperature to condense the water vapour and make the plasma more stable.
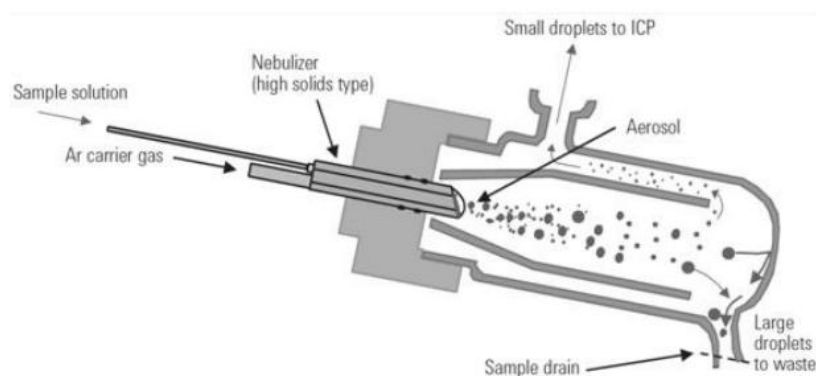

Figure 10. Scheme conventional spray chamber.

4.2. Ion source. Plasma

Plasma is a highly ionized gas and electrically conductive. An ICP plasma formed when an inert gas, usually argon, is introduced into a quartz torch consisting of a coil to which is applied a potential, and it surrounds three concentric tubes: central tube (drag the spray shows a nebulizer generated by flowing Ar), intermediate tube (focuses the plasma by flowing Ar) and external (cooled torch).

The ion source for mass spectrometry analysis is provided by the plasma torch, whose purpose is to form positively charged ions of the sample spray. *Figure 10* shows a schematic representation of a source of ICP in a ICP-MS. The argon gas flows into the concentric channels ICP torch. RF load coil is connected to a radiofrequency generator (RF). As energy load coil generator is supplied, oscillating electric and magnetic fields are set at the end of the torch. When a spark is applied, argon flows through the ICP torch, electrons are stripped of argon atoms, forming argon ions. These ions are trapped in the oscillating fields and collide with other argon atoms, forming a plasma discharge or argon.
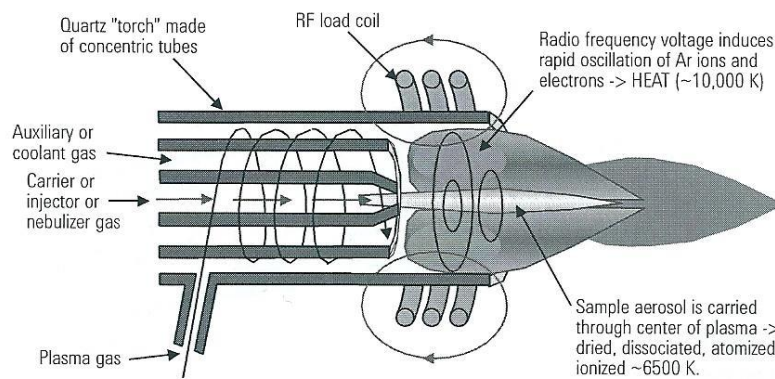
Figure 11. ICP torch showing the destination of the sample.

The sample is typically introduced into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into a nebulizer or using a laser to directly convert solid samples into an aerosol. Once the sample aerosol is introduced into the ICP torch, it is completely desolvated and the elements in the aerosol are converted first into gaseous atoms and then ionized towards the end of the plasma.

The most important things to remember about the argon ICP plasma are:

- The argon discharge, with a temperature of around 6000-10000°K, is an excellent ion source.
- The ions formed by the ICP discharge are typically positive ions, M^+ or M^{+2}, therefore, elements that prefer to form negative ions, such as Cl, I, F, etc., are very difficult to determine via ICP-MS.

- The detection capabilities of the technique can vary with the sample introduction technique used, as different techniques will allow differing amounts of sample to reach the ICP plasma.
- Detection capabilities will vary with the sample matrix, which may affect the degree of ionization that will occur in the plasma or allow the formation of species that may interfere with the analyte determination.

4.3.   Interface

Once the elements in the sample are converted into ions, they are then brought into the mass spectrometer via the interface cones. The interface region in the ICP-MS transmits the ions traveling in the argon sample stream at atmospheric pressure (1-2 torr) into the low pressure region of the mass spectrometer ($<1 \times 10^{-5}$ torr). This is done through the intermediate vacuum region created by the two interface cones, the sampler and the skimmer (*Figure 12*).
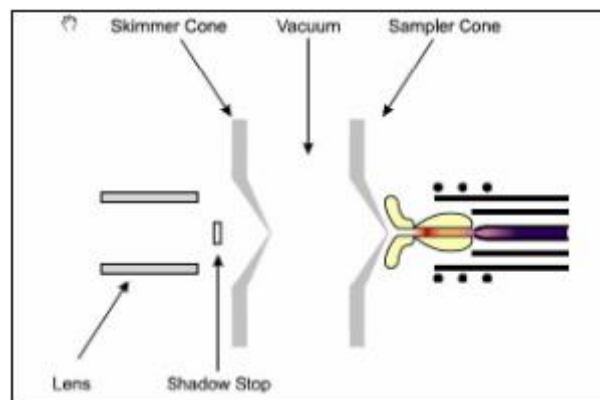
Figure 12. The interface region of an ICP-MS.

The sampler and skimmer cones are metal disks with a small hole (~1mm) in the center. The purpose of these cones is to sample the center portion of the ion beam coming from the ICP torch. A shadow stop (*Figure 12*) or similar device blocks the photons coming from the ICP torch, which is also an intense light source. Due to the small diameters of the orifices in the sampler and skimmer cones, ICP-MS has some limitations as to the amount of total dissolved solids in the samples. Generally, it is recommended that samples have no more than 0,2% total dissolved solids (TDS) for best instrument performance and stability. If samples with very high TDS levels are run, the orifices in the cones will eventually become blocked, causing decreased sensitivity and detection capability and requiring the system to be shut down for maintenance. This is why many sample types, including digested soil and rock samples must be diluted before running on the ICP-MS.

The ions from the ICP source are then focused by the electrostatic lenses in the system. Remember, the ions coming from the system are positively charged, so the electrostatic lens, which also has a positive charge, serves to collimate the ion beam and focus it into the entrance aperture or slit of the mass spectrometer. Different types of ICP-MS systems have different types of lens systems. The simplest employs a single lens, while more complex systems may contain as many as 12 ion lenses. Each ion optic system is specifically designed to work with the interface and mass spectrometer design of the instrument.

4.4.   Mass analyzer. CRC

Once the ions enter the mass spectrometer, they are separated by their mass-to-charge ratio. The most commonly used type of mass spectrometer is thequadrupole mass filter. In this type, 4 rods (approximately 1 cm in diameter and 15-20 cm long) are arranged as in *Figure 13*.
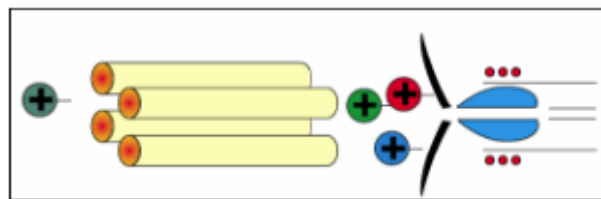
Figure 13. Schematic of quadrupole mass filter.

In a quadrupole mass filter, alternating AC and DC voltages are applied to opposite pairs of the rods. These voltages are then rapidly switched along with an RF-field. The result is that an electrostatic filter is established that only allows ions of a single mass-to-charge ratio (m/e) pass through the rods to the detector at a given instant in time. So, the quadrupole mass filter is really a sequential filter, with the settings being change for each specific m/e at a time. However, the voltages on the rods can be switched at a very rapid rate. The result is that the quadrupole mass filter can separate up to 2400 amu (atomic mass units) per second. This speed is why the quadrupole ICP-MS is often considered to have simultaneous multi-elemental analysis properties.

The ability to filter ions on their mass-to-charge ratio allows ICP-MS to supply isotopic information, since different isotopes of the same element have different masses.

Typical quadrupole mass spectrometers used in ICP-MS have resolutions between 0.7 - 1.0 amu. This is sufficient for most routine applications. However, there are some instances where this resolution is not sufficient to separate overlapping molecular or isobaric interferences from the elemental isotope of interest. *Picture 2* below shows

some commonly occurring interferences that make ultratrace determinations of several important elements difficult, particularly in specific matrices. The resolving power (R) of a mass spectrometer is calculated as $R = m/(|m1-m2|) = m/\Delta m$, where m1 is the mass of one species or isotope and m2 is the mass of the species or isotope it must be separated from; m is the nominal mass.

Picture 2. Example of interference and resolving power needed.

Analyte	Interference	$|\Delta m|$	m	R
$^{75}As = 74.92160$	$^{40}Ar^{35}Cl = 74.93123$	0.00963	75	7788
$^{52}Cr = 52.94065$	$^{37}Cl^{16}O = 52.96081$	0.02016	53	2629
$^{56}Fe = 55.93494$	$^{40}Ar^{16}O = 55.95729$	0.02235	56	2505
$^{40}Ca = 39.96259$	$^{40}Ar = 39.96238$	0.00021	40	190476
$^{87}Sr = 86.90889$	$^{87}Rb = 86.90918$	0.00029	87	300000

4.5.   Detector

Once the ions have been separated by their mass-to-charge ratio, they must then be detected or counted by a suitable detector. The fundamental purpose of the detector is to translate the number of ions striking the detector into an electrical signal that can be measured and related to the number of atoms of that element in the sample via the use of calibration standards. Most detectors use a high negative voltage on the front surface of the detector to attract the positively charged ions to the detector. Once the ion hits the active surface of the detector, a number of electrons is released which then strike the next surface of the detector, amplifying the signal. In the past several years, the channel electron multiplier (CEM), which was used on earlier ICP-MS instruments, has been replaced with discrete dynode type detectors (*Figure 14*). Discrete dynode detectors generally have wider linear dynamic ranges than CEMs, which is important in ICP-MS as the concentrations analyzed may vary from sub-ppt to high ppm. The discrete dynode type detector can also be run in two modes, pulse-counting and analog, which further extends the instrument's linear range and can be used to protect the detector from excessively high signals.
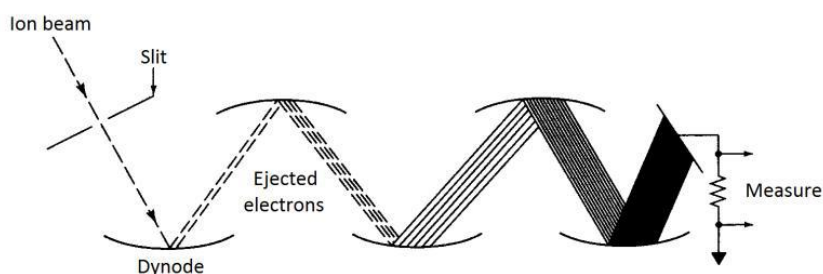
Figure 14. Amplification of a single ion count to a measurable signal in an electron multiplier detector.

EXPERIMENTAL

5. MATERIAL

   5.1. Instrumentation

   - ICP-MS Agilent 7500c
   - Milli-Q Gradient, Millipore, for obtaining de-ionised water, used for dilutions and labware cleaning.
   - Analytical balance (0.0001 g precision)
   - 100 µL, 1000 µL and 5000 µL pipettes
   - 50 mL Falcon plastic tubes for solution preparation
   - Sample vials for ICP-MS auto-sampling system

   5.2. Reagents and Solutions

   - 10,040 ± 37 µg/mL Molybdenum (natural abundances)
   - Standard 987,5 ng/g ^{95}Mo to 2% HCl
   - CRM. TM-25.4, 27.5 µg/L Mo
   - HNO$_3$ 5%

6. ICP-MS TUNING

Before performing any series of measurements in the ICP-MS instrument, some checks must be done and some parameters monitored in order to assure the measure quality.

Once the instrument start-up is done and the plasma is on, a tune configuration without collision gas is loaded. The sampling system is washed and cleaned with nitric acid and de-ionised water and then a tune solution containing Li, Y, Tl and Ce is continuously passed, monitoring signals for ^{7}Li, ^{89}Y, ^{205}Tl, ^{70}Ce/^{140}Ce (double charged), ^{156}CeO/^{140}Ce (no gas oxides).

It is found that the sensitivity of Li, Y and Tl is within the parameters established by the manufacturer. As the same is also done for ^{156}CeO/^{140}Ce and ^{70}Ce/^{140}Ce.

7. RESULTS

First, patterns of natural molybdenum in order to determine the dead time of the detector and the constant mass discrimination are prepared.

Table 1: Values measured intensity by the detector for each of the patterns molybdenum counts per second (cps). Automatically corrected for dead time (τ) of 31.5 nanoseconds (ns).

	^{92}Mo	^{94}Mo	^{95}Mo	^{96}Mo	^{97}Mo	^{98}Mo	^{100}Mo
MO_0.D	1605,151	1079,4395	1736,8317	1841,2435	1085,3755	2717,3123	1143,4448
MO_10.D	76751,961	49717,512	86419,328	92519,336	53923,922	138455,81	56960,926
MO_20.D	143383,7	92839,5	162814,06	173772,58	101301,01	260818,61	107073,82
MO_30.D	210363,98	136434,89	238791,14	254927,8	148734,45	381609,25	157085,58
MO_40.D	296760,78	192253,98	336472,59	359900,91	209977,56	539520,06	221891,38
MO_50.D	370100,63	239316,08	419785,53	447923,75	261191,23	670992,94	276003,25

The detector automatically corrects the data for a time-out set of 31.5 nanoseconds. This requires us to first calculate the values that would have been obtained without the default correction and then consider them as starting values for calculations. Therefore, the calculation is performed in reverse to get the original values without any correction:

Table 2: Intensity values are calculated to simulate the original patterns, without any prior correction.

	^{92}Mo	^{94}Mo	^{95}Mo	^{96}Mo	^{97}Mo	^{98}Mo	^{100}Mo
MO_0.D	1605	1079	1737	1841	1085	2717	1143
MO_10.D	76567	49640	86185	92250	53832	137855	56859
MO_20.D	142739	92569	161983	172827	100979	258693	106714
MO_30.D	208979	135851	237008	252897	148041	377077	156312
MO_40.D	294012	191097	332944	355866	208598	530504	220351
MO_50.D	365836	237526	414307	441692	259060	657104	273624

The formula used for this calculation is:

$$I_{measure} = \frac{I_{corrected}(cps)}{1 + I_{corrected}(cps) \cdot \tau(s)} \qquad (28)$$

7.1. Calculation of dead time detector (τ)

It is calculated according to the dead time ratio ^{98}Mo/^{95}Mo:

Table 3: Ratio of intensities between ^{98}Mo/^{95}Mo for different times.

t(s)	MO_10.D	MO_20.D	MO_30.D	MO_40.D	MO_50.D
0	1,5995	1,5970	1,5910	1,5934	1,5860
1E-08	1,6004	1,5986	1,5932	1,5965	1,5899
2E-08	1,6012	1,6001	1,5955	1,5997	1,5938
3E-08	1,6020	1,6017	1,5977	1,6030	1,5978
4E-08	1,6028	1,6033	1,6000	1,6062	1,6019
5E-08	1,6037	1,6049	1,6023	1,6095	1,6059
6E-08	1,6045	1,6064	1,6047	1,6129	1,6101
7E-08	1,6054	1,6080	1,6070	1,6163	1,6143
8E-08	1,6062	1,6097	1,6094	1,6197	1,6185

The formula used is:

$$R\,98/95 = \frac{I_{measure98_{Mo}} \cdot (1 - I_{measure95_{Mo}} \cdot t(s))}{I_{measure95_{Mo}} \cdot (1 - I_{measure98_{Mo}} \cdot t(s))} \qquad (29)$$

Table 4: Relationship $^{98}Mo/^{95}Mo$ standard.

t(ns)	10	20	30	40	50
0	1,0388	1,0372	1,0333	1,0348	1,0300
10	1,0393	1,0382	1,0347	1,0369	1,0326
20	1,0399	1,0392	1,0362	1,0389	1,0351
30	1,0404	1,0402	1,0377	1,0410	1,0377
40	1,0410	1,0412	1,0391	1,0432	1,0403
50	1,0415	1,0423	1,0406	1,0453	1,0430
60	1,0421	1,0433	1,0421	1,0475	1,0457
70	1,0426	1,0443	1,0437	1,0497	1,0484
80	1,0431	1,0454	1,0452	1,0519	1,0512

Table 5: ^{95}Mo isotopic abundances and natural Mo.

	Abundances	
Isotope	^{95}Mo	Mo natural
92	0,0120	0,1453
94	0,0180	0,0915
95	0,9440	0,1584
96	0,0230	0,1667
97	0,0020	0,0960
98	0,0010	0,2439
100	0,0000	0,0982

$$R_{standard} = \frac{R\,98/95}{\dfrac{Abundance\ Natural\ ^{98}Mo}{Abundance\ Natural\ ^{95}Mo}} \qquad (30)$$

The graphical representation of the relationship $^{98}Mo/^{95}Mo$ normalized versus time in nanoseconds is performed.
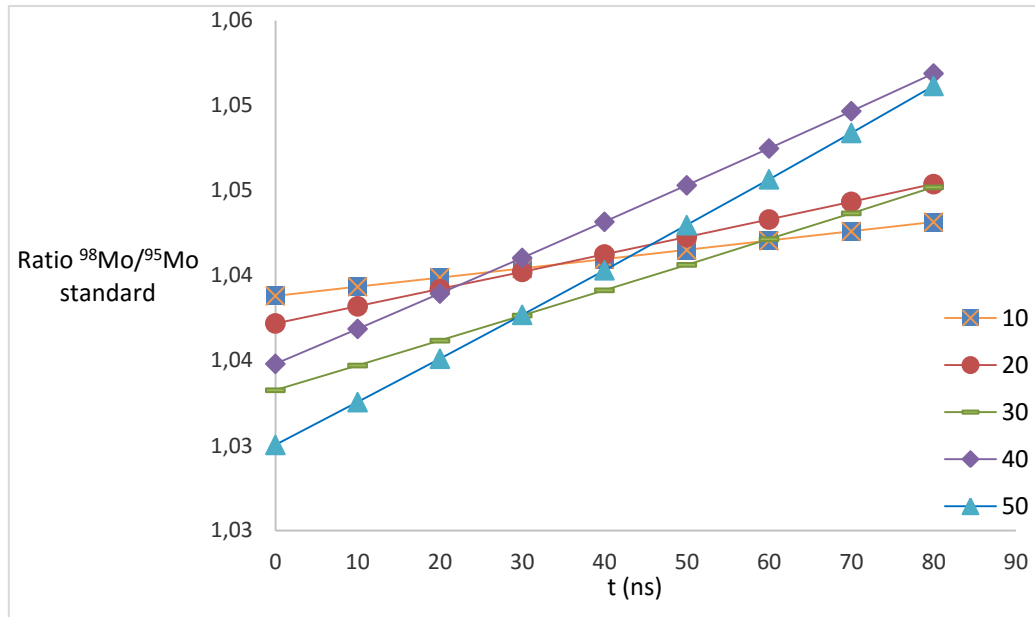
Figure 15. Ratio ^{98}Mo/^{95}Mo standard versus t(ns) at different concentrations of Mo for calculating the dead time of the detector (τ).

The point where all the lines intersect is chosen. In this case, the straight reach not cross all at the same point so the area where the lines are closest is selected, δ = 40ns.

7.2. Calculation of mass discrimination (κ)

The values in *Table 2*, is applied the time correction:

Table 6: δ = 40ns corrected for values.

	MO_0.D	**MO_10.D**	**MO_20.D**	**MO_30.D**	**MO_40.D**	**MO_50.D**
^{92}Mo	1605,173	76802,1	143559	210741	297511,242	371268,587
^{94}Mo	1079,449	49738,5	92912,8	136593	192568,668	239803,886
^{95}Mo	1736,857	86482,9	163040	239277	337437,667	421288,763
^{96}Mo	1841,272	92592,2	174030	255481	361005,282	449635,671
^{97}Mo	1085,386	53948,6	101388	148923	210353	261772,398
^{98}Mo	2717,375	138619	261398	382851	542005,655	674841,86
^{100}Mo	1143,456	56988,5	107171	157296	222310,675	276652,284

Using the following formula:

$$I_{corrected} = \frac{I_{measure}(cps)}{1 - I_{measure}(cps) \cdot \tau(s)} \qquad (31)$$

Table 7: Summary of experimental signals taking ^{98}Mo as a base.

	MO_0.D	MO_10.D	MO_20.D	MO_30.D	MO_40.D	MO_50.D	Average
^{92}Mo	0,5907	0,5541	0,5492	0,5505	0,5489	0,5502	0,5506
^{94}Mo	0,3972	0,3588	0,3554	0,3568	0,3553	0,3553	0,3563
^{95}Mo	0,6392	0,6239	0,6237	0,6250	0,6226	0,6243	0,6239
^{96}Mo	0,6776	0,6680	0,6658	0,6673	0,6661	0,6663	0,6667
^{97}Mo	0,3994	0,3892	0,3879	0,3890	0,3881	0,3879	0,3884
^{98}Mo	1,0000	1,0000	1,0000	1,0000	1,0000	1,0000	1,0000
^{100}Mo	0,4208	0,4111	0,4100	0,4109	0,4102	0,4100	0,4104

The following formula is used:

$$R_{experimental}(98Mo) = \frac{I_{corrected}}{I_{corrected\ for\ 98Mo}} \qquad (32)$$

Table 8: Calculation necessary for representing Ln(Rt/Re) versus the mass difference.

isotope	Abundance	$R_{teo}(^{98}Mo)$	$R_{exp}(^{98}Mo)$	mass dif.	Rt/Re	Ln(Rt/Re)
92	0,1453	0,5957	0,5506	6,0000	1,0821	0,0789
94	0,0915	0,3752	0,3563	4,0000	1,0528	0,0515
95	0,1584	0,6494	0,6239	3,0000	1,0410	0,0401
96	0,1667	0,6835	0,6667	2,0000	1,0252	0,0249
97	0,0960	0,3936	0,3884	1,0000	1,0134	0,0133
98	0,2439	1,0000	1,0000	0,0000	1,0000	0,0000
100	0,0982	0,4026	0,4104	-2,0000	0,9810	-0,0192

Formulas are used:

$$R_{theoretical}(98Mo) = \frac{Abundance_{natural}}{Abundance_{natural\ for\ 98Mo}} \qquad (33)$$

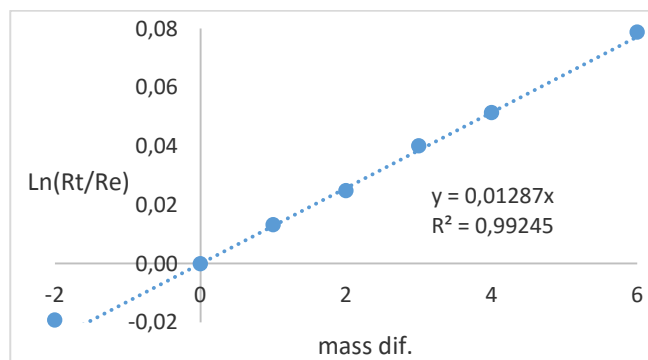$$mass\ dif. = isotopo_i - isotopo_{i-1} \qquad (34)$$

Figure 16. Representation for obtaining constant mass discrimination (slope of the line).

The value of the mass discrimination is obtained directly from the slope of the line, therefore, κ = 0.01287.

7.3. Deconvolution of isotopic profiles (IPD)

Furthermore, six solutions Standard Reference Material fortified ^{95}Mo are prepared:

Table 9. Heavy mass (g) of CRM y ^{95}Mo.

	CRM_2.D	CRM_3.D	CRM_4.D	CRM_5.D	CRM_6.D
m(CRM)	4,7425	5,0948	4,1428	4,5880	4,3477
m(95Mo)	0,0999	0,1000	0,0991	0,1006	0,1001

Table 10. Intensity values measured by the detector for each of the aliquots prepared and fortified in counts per second (cps). Automatically corrected to a dead 31.5 nanoseconds (ns) time.

	^{92}Mo	^{94}Mo	^{95}Mo	^{96}Mo	^{97}Mo	^{98}Mo	^{100}Mo
CRM_1.D	1754,9005	1208,4489	1813,2397	1950,3896	1131,1766	2879,4651	1209,7827
CRM_2.D	206132,81	142304,42	1172709,8	257196,77	137896,45	353837,5	145414,86
CRM_3.D	206695,05	143847,45	1262239,1	258316,11	137855,8	353063,25	145307,28
CRM_4.D	203726,11	140846,33	1184184,1	254259,77	135963,42	349428,84	143814,33
CRM_5.D	197490,94	138414,52	1331004,6	247920,13	130606,43	335338,22	137905,8
CRM_6.D	191132,56	133281,2	1204310,1	238165,45	126615,7	324669,22	133840,3

As can be seen with the naked eye, the value obtained from the first aliquot as different from other aliquots. This fact leads to reject this aliquot results due to errors during preparation.

Table 11. Intensity values are calculated to simulate the original, without any prior correction.

	92	94	95	96	97	98	100
CRM_2.D	204803,0	141669,4	1130932,7	255129,8	137300,1	349937,1	144751,8
CRM_3.D	205358,0	143198,6	1213971,0	256231,2	137259,8	349179,8	144645,2
CRM_4.D	202427,1	140224,2	1141600,4	252239,5	135383,6	345624,5	143165,8
CRM_5.D	196270,0	137813,6	1277445,6	245999,0	130071,3	331833,0	137309,3
CRM_6.D	189988,7	132724,0	1160293,5	236392,0	126112,7	321382,4	133278,4

These values have been calculated in the same way as for the patterns according to *equation (28).*

The values of the intensities calculated for the dead time corrected:

Table 12. Values for δ = 40ns corrected.

Mo	CRM_2.D	CRM_3.D	CRM_4.D	CRM_5.D	CRM_6.D
92	206494,62	207058,83	204079,51	197823,02	191443,58
94	142476,76	144023,55	141015,15	138577,56	133432,36
95	1184517,11	1275928,58	1196224,78	1346235,29	1216765,69
96	257760,28	258884,54	254810,47	248443,68	238648,57
97	138058,27	138017,53	136120,73	130751,58	126752,11
98	354904,92	354126,00	350469,79	336296,79	325567,69
100	145594,82	145486,97	143990,35	138067,64	133992,74

In this case also it proceeds in the same way as for the case of patterns using *equation (31).*

They are also corrected for mass discrimination factor:

Table 13. Values corrected for κ = 0.01287.

mass dif.	CRM_2.D	CRM_3.D	CRM_4.D	CRM_5.D	CRM_6.D
6	223072	223681	220463	213704	206813
4	150004	151632	148465	145898	140481
3	1231146	1326156	1243314	1399230	1264664
2	264481	265635	261454	254922	244871
1	139847	139805	137884	132445	128394
0	354905	354126	350470	336297	325568
-2	141895	141790	140331	134559	130588
SUM	2505349	2602825	2502381	2617055	2441378

The formula used for this calculation is as follows:

$$R_{corrected\ \kappa} = R_{corrected\ \delta} \cdot \exp(\kappa * mass.dif) \qquad (35)$$

Table 14. Corrected abundances.

CRM_2.D	CRM_3.D	CRM_4.D	CRM_5.D	CRM_6.D
0,0890	0,0859	0,0881	0,0817	0,0847
0,0599	0,0583	0,0593	0,0557	0,0575
0,4914	0,5095	0,4969	0,5347	0,5180
0,1056	0,1021	0,1045	0,0974	0,1003
0,0558	0,0537	0,0551	0,0506	0,0526
0,1417	0,1361	0,1401	0,1285	0,1334
0,0566	0,0545	0,0561	0,0514	0,0535

The formula is used:

$$Ab_{corrected} = \frac{R_{corrected\ \kappa}}{\sum R_{corrected\ \kappa\ for\ all\ mass.dif.}} \qquad (36)$$

For determination of molybdenum are taken into account the values of the abundances of the mixture along with those of [95]Mo and natural molybdenum *(Table 5).*

	CRM_2.D	CRM_3.D	CRM_4.D	CRM_5.D	CRM_6.D
χ Mo	0,5769	0,5538	0,5700	0,5220	0,5428
χ 95Mo	0,4237	0,4468	0,4307	0,4788	0,4576
[Mo]	25,8904	26,0432	25,9157	26,0153	25,9439

where *χMo* (molybdenum natural mole fraction) and $\chi\,^{95}Mo$ (molar fraction enriched molybdenum pattern) is obtained by linear estimation and [Mo] is calculated as follows:

$$\frac{\chi_{Mo}}{\chi\,^{95}_{Mo}} = \frac{N_{Mo}/N_{total}}{N\,^{95}_{Mo}/N_{total}} \qquad (37)$$

Simplifying:

$$\frac{\chi_{Mo}}{\chi\,^{95}_{Mo}} = \frac{N_{Mo}}{N\,^{95}_{Mo}} \qquad (38)$$

$$N_{Mo} = \frac{\chi_{Mo}}{\chi\,^{95}_{Mo}} \cdot N\,^{95}_{Mo} \qquad (39)$$

And knowing the data of atomic masses of [95]Mo and natural Mo, 94,976 and 95,94 g/mol respectively, together with the amounts thereof added to the aliquots and standard concentration [95]Mo molybdenum concentration is obtained:

$$[Mo]\,(ppb) = \frac{m(95Mo) \cdot 987,5 \cdot Ar(Mo) \cdot \chi Mo}{m(CRM) \cdot Ar(95Mo) \cdot \chi95Mo} \qquad (40)$$

The value of the mean, standard deviation, coefficient of variation and the relative error is calculated:

$$\overline{[Mo]} = \frac{1}{n}\sum_{i=1}^{n} x_i = 25,96\ ppb$$

$$\sigma = \sqrt{\frac{\sum_{i-1}^{n}(x_i - \bar{x})^2 \cdot f_i}{N}} = 0,07$$

$$cv\ (\%) = \frac{\sigma}{[Mo]} \cdot 100 = 0{,}25\%$$

$$\varepsilon_r(\%) = \left| \frac{[Mo]_{exp} - [Mo]_{real}}{[Mo]_{real}} \right| \cdot 100 = 5{,}6\%$$

CONCLUSIONS

The knowledge obtained in this work have been both theoretical and experimental. Also, they have acquired professional skills highly valued today as handling sophisticated equipment and simulation of real samples.

The completion of this work has allowed us to approach current techniques, especially in the field of research and development, such as elemental mass spectrometry with ionization source plasma (ICP-MS).

It has deepened knowledge of analytical chemistry, through the application of mass spectrometry isotope dilution (IDMS) to trace analysis, hitherto unknown to the student.

Optimizing the amount of tracer added is not performed, since the concentration of ^{95}Mo is known is added the appropriate amount to meet within the optimal range. The fact of working within this range provides greater reliability and less imprecise results.

Nor does it take into account the error due to contamination in blank, as in our case, the chemical element of interest (molybdenum) is not an element present in the water.

It has been chosen technique IPD because it is generic and works with all ions simultaneously.

The certified reference material having a known concentration of molybdenum (27.5 ± 2.29)ppb was obtained and an experimental concentration of 25.96 ppb therefore the result is acceptable since it is within the range and IPD analysis is valid.

The accuracy of the method provides the standard deviation (σ = 0,07) and the coefficient of variation (cv = 0,25%). These values are low enough to assert that the method is accurate.

As for the exact value to consider is the relative error of 5.6% is therefore considered an accurate method.

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