Fe determination in environmental water using ICP-MS-IDA

QU0943 - Degree Final Project

UNIVERSITAT JAUME·I

Degree in Chemistry

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Contents

INTRODUCTION

The determination of the composition of a sample, which is the objective and purpose of Analytical Chemistry, whatever it is done qualitatively or quantitatively, has been evolving towards the improvement of its precision, accuracy, detection and quantification limits and the optimization of analysis times and costs. This constant improvement has been made possible with the development of better instrumental techniques and better analytical instruments.

This way, lower and lower concentrations of analytes were enabled to analyse and quantify, opening the door to a whole new analytical field: trace analysis. Most of the quantitative analytical determinations (either elemental or molecular, for major components or trace elements) are methods based on the use of calibration curves. Although calibration curves provide an easy way to obtain the relationship between analyte concentration and instrumental signal by measuring solutions containing increasing known analyte concentrations, it is a quite time-consuming methodology.

In this context of trying to optimise the analysis time while maintaining the quality of the analytical determination, the Isotope Dilution Analysis is a fast and reliable elemental method, traceable directly to primary standards, that has become an alternative to the more traditional calibration curve-based determinations in Mass Spectrometry with Inductively Coupled Plasma as ion source for elemental determinations.

TRACE ANALYSIS

The term ‘trace analysis’ is widely used to describe the application of analytical chemistry under circumstances where the amount of analyte is very small. Although its wide use, the term ‘trace analysis’ has no unambiguous definition. Some analyst apply the term to determinations made at or below the part per million level (i.e. 1 ppm ≡ 1 µg/g ≡ 0.0001% ≡ 1 mg/L) while others define the term more generally as applying to an analysis where the concentration of the analyte is low enough to cause difficulty in obtaining reliable results. But generally, all applications that require special precautions to be taken are considered to fall into trace analysis, precautions such as low concentration in the matrix, difficulties derived from analyte losses, contamination or interferences and applications where the samples are only available in small portions (forensic or clinical analyses).

As such, its scope is as broad as that of analytical chemistry itself: the range of inorganic analytes is relatively small comprising the elements and organometallic compounds, but in the field of organic chemistry several million compounds are known to exist and many are of interest at trace levels.

The ability of resolve and separate very low concentrations of analyte from complex mixtures provided by the instrumental development has been of interest in diverse applications such as environmental and consumer protection, forensic science and clinical analysis.

TRACEABILITY

The traceability of an analytical result is that basic characteristic of it that implies its unequivocal relationship with standards or appropriated reference materials through an uninterrupted series of comparisons and which uncertainty can be expressed en basic terms of the international system of units. In a physicochemical measurement, methods or procedures used must be traceable to the basic units of the international system of units (kilogram, mole, ampere, second, etc.) either directly or through a series of comparisons. The methods traceable directly to the international system of units do not require methodological calibration, they are known as “Primary Methods” and they are generally used for reference material preparations and for the validation of other analytical methods.

Under certain conditions of measure, the Isotope Dilution Analysis can be considered a Primary Method of analysis, which is the only one that can be applied generally in trace analysis and it is often used for certification of reference materials and method validation. In contrast, methods based on the construction of calibration curves require the bi-univocal concentration-signal relationship, so they cannot be considered as primary methods.

In recent years, Isotope Dilution Analysis has been used also for routine analysis due to the commercialization of enriched isotopes at relatively low cost and the easiness, rapidity and robustness of the ID-based methodologies.

ISOTOPIC NATURE OF ELEMENTS

In the late 1800s, the existence of isotopes of chemical elements was suspected, based on the measure of atomic weights of the elements. While most of the lighter elements would tend to be integer numbers (hydrogen 1, carbon 12, nitrogen 14, oxygen 16, sodium 23, etc.), the remarkable exception of chlorine with its 35.5 atomic weigh kept scientists shocked. Meanwhile, studies on radioactivity demonstrated that mineral lead and lead obtained from the uranium and thorium radioactive decay had different atomic weigh.

After calibration of the first mass spectrometer with different gases, J. J. Thomson obtained the first evidence of the isotopic nature of elements in 1913, discovering two isotopes of neon with masses of 20 and 22. In the successive experiments carried out by one of his students, the chlorine anomaly was explained as being a mixture of two stable isotopes at masses 35 and 37 with relative abundances of 0.758 and 0.242, respectively. In the next 20 years, more and more isotopic abundances of different elements were determined, explaining also the case of lead, which showed that the existence of different isotopes of elements were more a rule than an exception.

As can be seen in the following chart, most of the elements have two or more stable isotopes, with a few exceptions such as fluorine (^{19}F) and phosphorus (^{31}P).

Table 1. Exact masses and relative abundances of several isotopes of different elements.

Isotope / nominal mass	Exact mass	Abundance
^{1}H	1.007825	0.99985
^{2}H	2.014102	0.00015
^{10}B	10.012938	0.1980
^{11}B	11.009305	0.8020
^{12}C	12.000000	0.9890
^{13}C	13.003355	0.0110
^{14}N	14.003074	0.9963
^{15}N	15.000109	0.0037
^{16}O	15.994915	0.99762
^{17}O	16.999131	0.00038
^{18}O	17.999159	0.00200

Isotope / nominal mass	Exact mass	Abundance
^{19}F	18.998403	1.0000
^{28}Si	27.976928	0.9223
^{29}Si	28.976496	0.0467
^{30}Si	29.973772	0.0310
^{31}P	30.973763	1.0000
^{32}S	31.972072	0.9502
^{33}S	32.971459	0.0075
^{34}S	33.967868	0.0421
^{36}S	35.967079	0.0002
^{35}Cl	34.968853	0.7577
^{37}Cl	36.965903	0.2423

Mass Spectrometry measures show the isotopic abundances of atoms and molecules. So, when an elemental ionization source (such as ICP) is used, the mass spectres obtained will show the isotopic abundances of atoms (like in the chart above). However, if a molecular ionization source is used, molecular isotopic distribution information will be obtained. An example can be seen in the spectrum below (Fig. 1), which shows the calculated isotopic distribution of a peptide with molecular formula $C_{68}H_{107}N_{17}O_{25}$ where all of the elements involved have different stable isotopes.

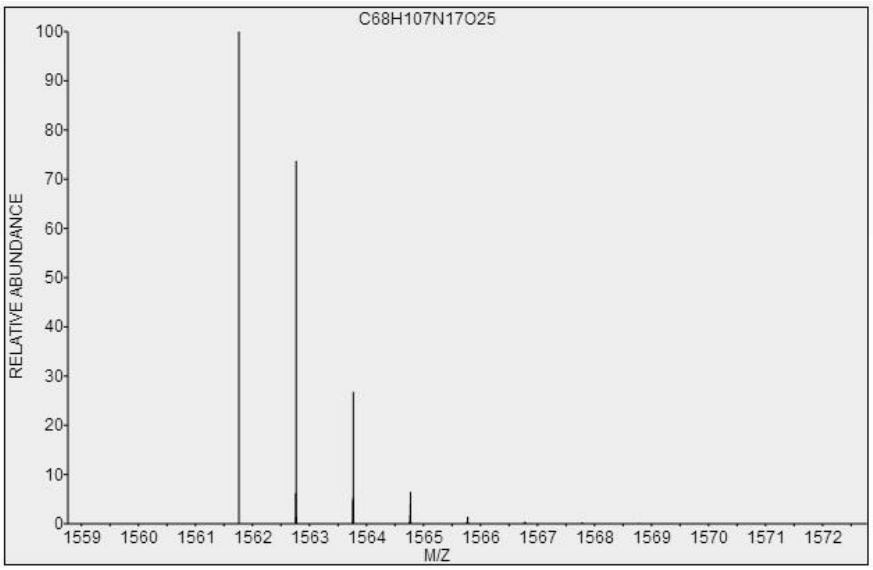

Fig. 1. Isotopic distribution of a peptide (calculation made at www.chemcalc.org).

From an analytical standpoint, we will consider here that isotopic abundances of elements are constant in the nature so natural isotopic abundances can be predicted for every element and molecule in a mass spectrometer, and therefore detect whether measured isotopic abundances have been altered respect the natural abundances.

OBJECTIVE

The main objective of this Degree Final Project has been the approach to a powerful analytical instrumental technique that is the ICP-MS for measuring and to learn and apply the concentration calculation method of Isotope Dilution Analysis, both well-understood techniques and used in many analytical applications and applied in this case for the elemental determination of Fe in water with the purpose of broaden the knowledge acquired during the previous grade courses.

In the realization of this assignment, different objectives have been accomplished:

- **Use of ICP-MS**. I have been able to familiarize myself with one of the most useful present-day analytical instruments, handling it and making the required measures, that consisted in:
    - Understanding the parts and elements of the instrument, and the processes that occur inside it, knowing its advantages and disadvantages.
    - Handling the instrument and its software, from start-up to shut-down, making the required optimizations and checks to assure that the measure conditions are correct. This included programming methods and sample analysis sequences.

- **Technique comparison**. The Fe determination has been carried out by two existing methods: external calibration and isotope dilution analysis. This has provided an overview of the accuracy and precision of each technique aside from learning and applying the IDA, which includes:
    - Understanding the fundamentals and concept of IDA.
    - Deduction of the fundamental IDA equation.
    - Take into account the error sources in the measurements and how to apply the necessary corrections.

- **Laboratory work**. In the present project, not much laboratory work has been necessary due to the simplicity of the matrix, which has made unnecessary a large sample preparation step. However, some usual laboratory tasks have been performed:
    - Dilution preparation by weighing of stock solutions, calibration curve points and preparation of samples with added tracer.
    - Typical and specific cleaning procedures in trace analysis laboratories.

Besides these academic learning, I have also been able to experience the research and professional environment from the inside, which has given a complementary view of a possible future after graduation, together with the work placement period.

ICP-MS

Inductively Coupled Plasma Mass Spectrometry is an analytical technique developed in the late 1970's and commercially available since the early 1980's, product of the junction of two already existing instrumental techniques, namely ICP and MS. In the 1990's computer-controlled ICP-MS were introduced as the technique was gaining popularity. It was further developed with the inclusion of Collision/Reaction Cell systems in the late 1990's, which allowed a rapid expansion in almost every analytical field for the determination of trace, minor and major elements.

Fig. 2. ICP-ORS-MS Agilent 7500c used at Universitat Jaume I.

The most important characteristics and strengths of ICP-MS are:

- Wide elemental coverage: virtually all elements can be measured.
- Performance: its high sensitivity and low background noise give very low detection limits, in the range of ppb or even ppt.
- Fast analysis times: wide mass/charge range scanning can take only a few minutes in simple quadrupole analysers.
- Wide analytical linear range: up to 9 orders in a single acquisition.
- Isotopic information: making also possible the Isotope Dilution Analysis.
- Technique coupling: ICP-MS is suitable as an excellent detector for chromatographic techniques.

COMPONENTS

The ICP-MS analysis involves a series of processes from the introduction of the sample to the final obtained signal, these processes and the parts of the instrument in which they occur will be explained in this section and they are shown in the following figures.

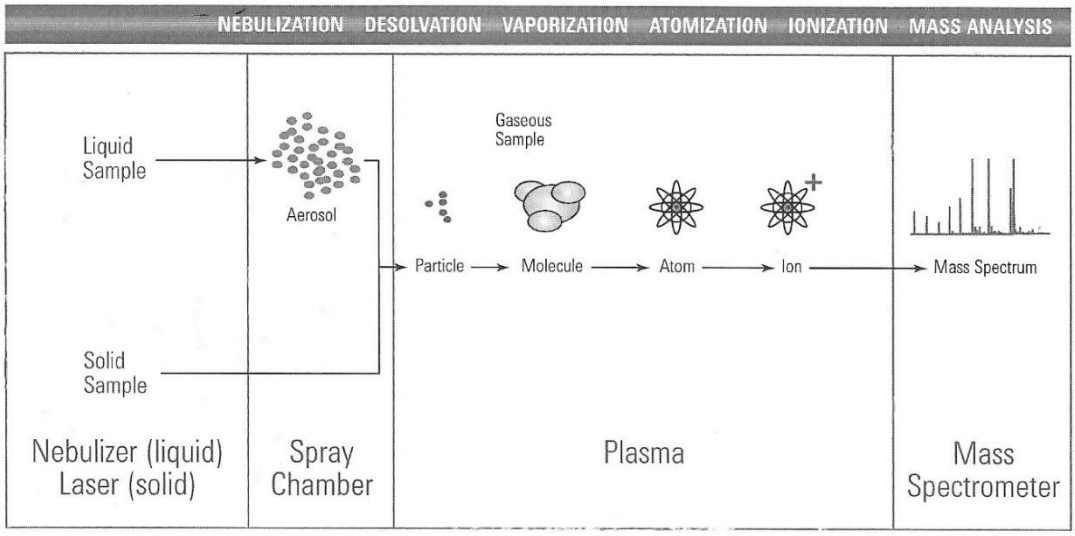

Fig. 3. Processes occurring to analytes in an ICP-MS measure (from "ICP-MS: Inductively Coupled Plasma Mass Spectrometry". A. Primer. Agilent Technologies (2005)).

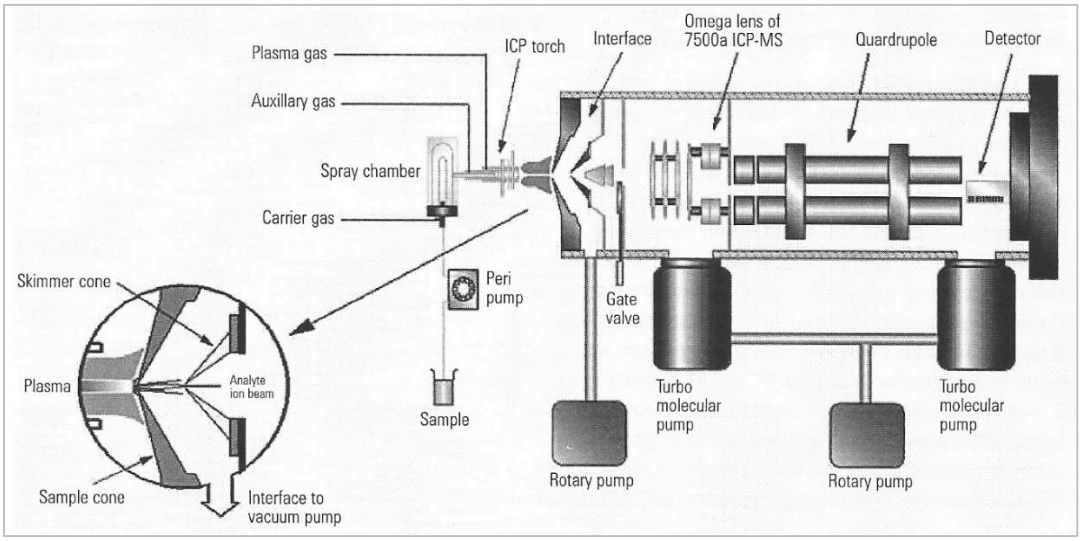

Fig. 4. Parts of an ICP-MS instrument, without Collision/Reaction Cell system (from "ICP-MS: Inductively Coupled Plasma Mass Spectrometry". A. Primer. Agilent Technologies (2005)).

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 Fig. 5.

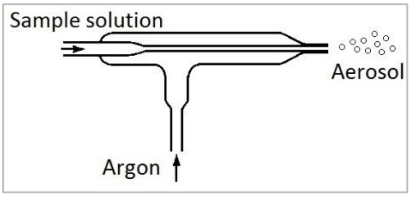

Fig. 5. Concentric nebulizer (from "Principios de Análisis Instrumental". D. A. Skoog, F. J. Holler, T. A. Nieman. McGraw Hill. 5a Edición (2001)).

The produced aerosol should be homogenised, so the larger droplets have to be removed. This is accomplished employing a spray or nebulization chamber (as shown in Fig. 6) 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.

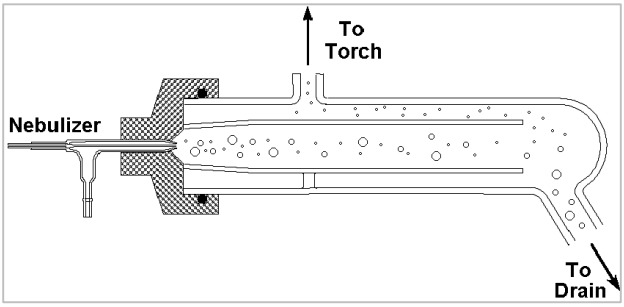

Fig. 6. Nebulization chamber (from http://analyticalprofessional.blogspot.com.es/2013/06/inductive-coupled-plasma-optical.html).

Ion source. Plasma

The ion source for the mass spectrometry analysis is provided by the plasma torch, whose purpose is to form positively charged ions from the sample aerosol. Plasma is generated in a torch composed by three cylindrical, concentric quartz tubes: the inner for the carrier gas containing the sample, the central for the auxiliary or coolant gas flow and the outer for the plasma gas. The plasma gas, Argon, is firstly ionised by a spark and then retained by a radio frequency load coil that induces a rapid oscillation and friction of Ar^+ ions and free electrons; thus forming a stable, hot plasma (up to 10,000 K). The auxiliary gas, Ar as well, is used to centre and keep the plasma away from the quartz tube to prevent melting it. Finally, the resulting "plasma ball" is pierced by the central gas flow, giving the characteristic donut-like shape in which central path the sample is ionised.

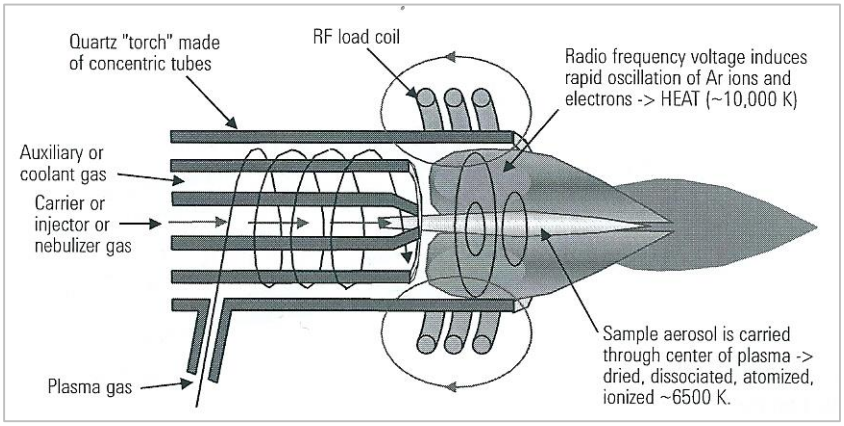

Fig. 7. Inductively Coupled Plasma torch system (from "ICP-MS: Inductively Coupled Plasma Mass Spectrometry". A. Primer. Agilent Technologies (2005)).

Sample droplets carried into the hot plasma through the central channel are rapidly desorpted from the aqueous matrix, the remaining dissolved compounds are vaporised to gaseous state and then atomised and ionised (as explained before in **Fig. 3**).

To ensure good results, plasma loading should be optimised to maintain high ionization temperatures while retaining good sensitivity. The higher the plasma loading, the higher will be the sensitivity, but the ionisation will be poorer, and vice versa. If the plasma is too much loaded, the aerosol will not be completely ionised, as can be seen in Fig. 8.

The temperature of the plasma and the alignment and distance respect the sampling cone are optimisable parameters that affect the amount of oxides and double charged ions formed in the plasma that finally reach the analyser and so interfering with the measure. These parameters are optimised employing a tuning solution containing Cerium and adjusting the instrument to lower as much as possible the intensity ratios between m/z equal to 156 and 140 for oxides ($^{156}CeO^{+}/^{140}Ce^{+}$), and m/z equal to 70 and 140 ($^{140}Ce^{2+}/^{140}Ce^{+}$).

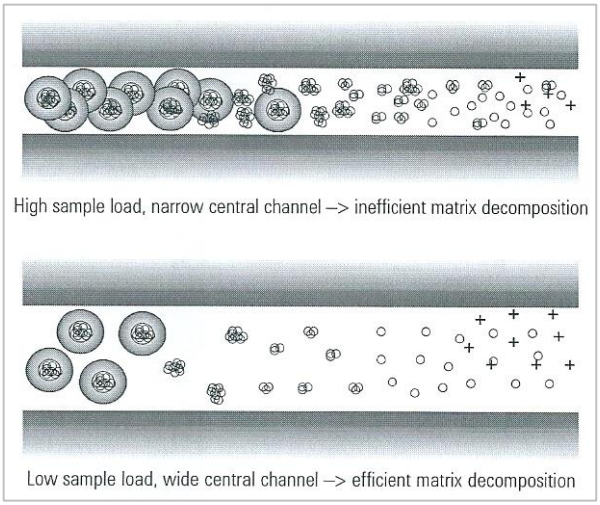

Fig. 8. Effect of plasma loading on matrix decomposition (from "ICP-MS: Inductively Coupled Plasma Mass Spectrometry". A. Primer. Agilent Technologies (2005)).

Interface, vacuum system and ion focusing

The ICP-MS comes from the union of two instrumental techniques, as we have seen, using the ICP as ion source for the MS analyser. At this point, one can notice a fundamental problem, while the ICP works at a certain pressure, giving a constant flow of Argon gas carrying the ionised species, the MS analysis requires a high vacuum to work properly. This difference make necessary an interface to adequate the conditions and make the coupling possible.

The role of the ICP-MS interface is to extract a representative sample of the plasma ion population and transfer it efficiently to the higher vacuum regions in which the ion focusing, mass spectrometer and detector systems are located.

This reduction of pressure cannot be achieved efficiently in a single step, so it is performed in 3 steps instead. The first step involves a drop from atmospheric pressure (1 bar approximately) to about 1 mbar. This first low pressure zone is that between the sampling cone, in direct contact with the plasma, and the skimmer cone (see **Fig. 10**). This sudden pressure decrease leads to a supersonic expansion of the extracted ion beam, and the position of the skimmer cone respect of the sampling cone is very important to keep the representativeness of the extracted ions. Moreover, the orifice size and shape of the cones affect the sensitivity, mass response, oxide and double-charged species formation.

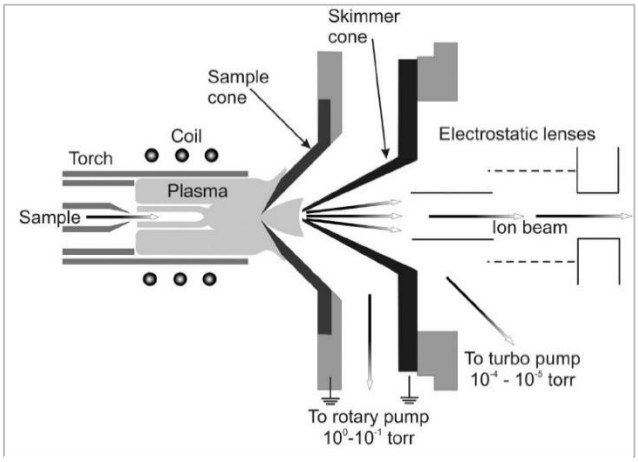

Fig. 10. 3-step ICP-MS interface system (from "Present Trends and the Future of Zircon in Geochronology: Laser Ablation ICPMS". J. Košler, P. Sylvester. Reviews in Mineralogy and Geochemistry, January 2003, v. 53, p. 243-275).

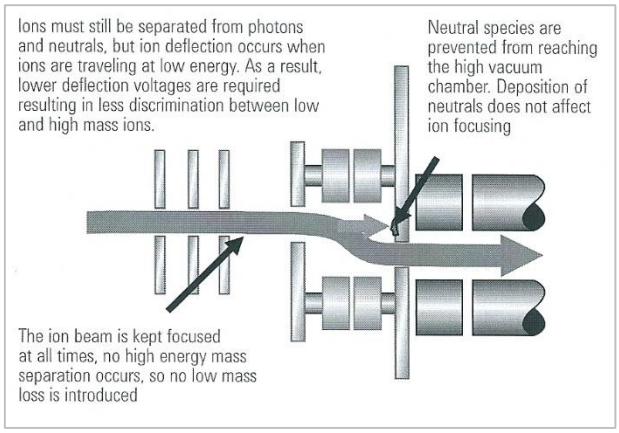

Fig. 9. Schematic off-axis ion lens system (from "ICP-MS: Inductively Coupled Plasma Mass Spectrometry". A. Primer. Agilent Technologies (2005)).

The ions extracted by the skimmer cone enter then in the high vacuum space (10^{-4}-10^{-5} torr) in which electrostatic plates, known as ion lenses, focus the expanding ion cone-shaped beam. At this point, photons and neutral species are separated by guiding ions through an S-like turn to the analyser. Only the ions are affected by the lenses, so photons and neutral atoms go in a straight line and do not reach the analyser (see Fig. 9).

Mass analyser. CRC

Ions pass from the ion lens system (with or without CRC) into the final or analyser vacuum stage, where they are separated according to their mass to charge ratio by the quadrupole, by far the most widely used mass analyser in ICP-MS due to its ease of use, robustness, mass range, high scanning speed and relatively low cost.

The quadrupole is a sequential mass filter, which separates ions based on their mass to charge ratio (m/z). It comprises of two pairs of parallel cylindrical or hyperbolic rods, arranged in a square, on the axis of the ion beam (see Fig. 11). The variation of AC and DC currents between each pair of confronted rods produces a narrow bandpass filter that allows only a narrow range of masses to be transmitted, other m/z than the selected will take an unstable trajectory ending either out of the quadrupole or on it (producing neutral atoms and eliminating them through the pumping system).

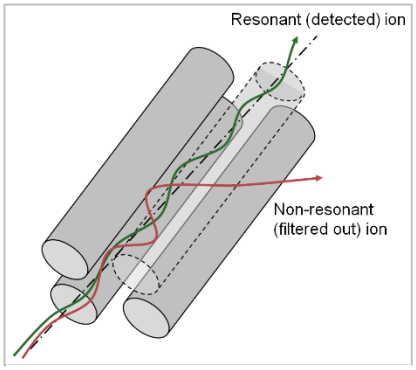

Fig. 11. Quadrupole mass analyser. Selected mass ions resonate and reach the detector, while non-resonant ions have unstable trajectories (from http://chemwiki.ucdavis.edu/Analytical_Chemistry/Instrumental_Analysis/Mass_Spectrometry/Mass_Spectrometers_(Instrumentation)/Mass_Analyzers_(Mass_Spectrometry)).

A very common source of spectral interferences, which will be reviewed later on, is the formation of polyatomic species in the plasma that have the same mass to charge ratio than that of the analyte. To solve this problem, Collision/Reaction Cells are mounted between the ion lenses and the quadrupole analyser (see Fig. 12). CRC systems consist in an octopole (sometimes an hexapole) enclosed in a small internal volume cell that can be pressurized with a gas and is mounted on-axis to the quadrupole, the interaction between polyatomic ions and the cell gas leads to the removal of interference. This CRC systems can operate in 3 different modes:

- No-gas mode: without gas in the cell, non-interfered m/z measures can be determined with a higher sensitivity than with gas.

- Helium (collision) mode: the cell is pressurized with He to physically slow down large ions, such as polyatomic species, by collision with He atoms. Because polyatomic ions collide more often than analyte ions, only a small part of the formers and a considerable amount of the latters will reach the quadrupole, thus greatly minimising interferences.

- Hydrogen (reaction) mode: used only for the very few situations where He collision mode is not efficient enough. In reaction mode (with H_2, NH_3, CH_4, etc.), interferences are reacted away by protonation or charge transfer before entering the mass filter region.

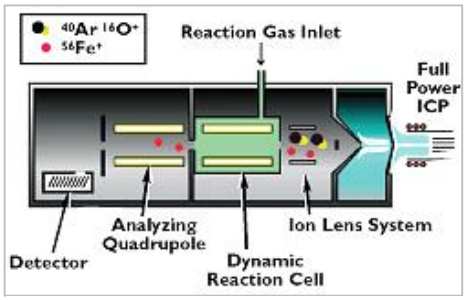

Fig. 12. Polyatomic spectral interference elimination with CRC for the case of ^{56}Fe analysis (from www.wcaslab.com/ tech/drc_vs_rccell.htm).

Detector

The detector in an ICP-MS instrument is largely responsible for the characteristics of a very high sensitivity and low random background, thanks to the electron multiplier detectors used in virtually all modern ICP-MS.

An electron multiplier generates a measurable signal pulse from the impact of a single ion. As a positive ion arrives at the mouth of the detector, it is deflected onto the first dynode, which is held at a high negative voltage. The impact releases several free electrons from the dynode surface, which are repelled from the high negative voltage at the front and strike the next dynode. Each of these electrons produces the same effect in the second

dynode, and so on. By the time the electron cascade reaches the final dynode, the multiplication factor has built up a pulse large enough to be measured as an ion count.

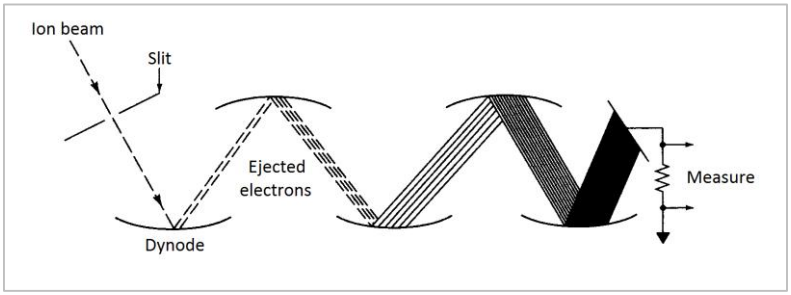

Fig. 13. Amplification of a single ion count to a measurable signal in an electron multiplier detector (from "Principios de Análisis Instrumental". D. A. Skoog, F. J. Holler, T. A. Nieman. McGraw Hill. 5a Edición (2001)).

QUANTIFICATION METHODS

The most typical quantification method used with ICP-MS measurements in liquid samples is external calibration. In this method a calibration plot is constructed, based on the measured signal for the elements of interest against its concentration in a known solution. Since the response of ICP-MS is linear with concentration, in theory a single point plus a blank solution could be used; in practice, 3 to 5 standards plus a blank solution are normally used to define the calibration plot in the concentration range of interest.

Other measurements typically carried out by this technique are those that determine the relative abundances of two or more isotopes of the same element, known as isotope ratio measurements. Isotope ratio analysis is most commonly carried out on elements whose isotopic composition varies in nature, but the measurement of isotope ratios is also used as the calibration method for isotope dilution analysis. Isotope dilution depends on the accurate determination of isotope ratios in a sample after the addition of a enriched spike of one of the isotopes of the analyte element or elements, this method provides excellent precision and accuracy and is independent of recovery or other sample preparation effects, whenever isotopic equilibrium has been reached.

ISOTOPE DILUTION ANALYSIS

CONCEPT

In elemental analysis, isotope dilution is based on the intended alteration of isotopic abundances of the analyte element by the addition of a known amount of enriched isotope of the same element (tracer) to the sample. So, the analysed element must have, at least, two stable isotopes or one stable and a long-lived radioactive isotope, and they must be free of spectral interferences. In Table 2, several elements and their number of stable isotopes are shown.

Table 2. Number of stable isotopes of several elements.

Number of stable isotopes	Elements
10	Sn
9	Xe
8	Cd, Te
7	Mo, Ru, Ba, Nd, Sm, Gd, Dy, Yb, Os, Hg
6	Ca, Se, Kr, Pd, Er, Hf, Pt
5	Ti, Ni, Zn, Ge, Zr, W
4	S, Cr, Fe, Sr, Ce, Pb
3	O, Ne, Mg, Si, Ar, K
2	H, He, Li, B, C, N, Cl, V, Cu, Ga, Br, Rb, Ag, In, Sb, La, Eu, Lu, Ta, Re, Ir, Tl
1	Be, F, Na, Al, P, Sc, Mn, Co, As, Y, Nb, Tc, Rh, I, Cs, Pr, Tb, Ho, Tm, Au, Bi

As can be seen, most of the elements have more than one stable isotope and, therefore, measurable by isotope dilution. Only the elements in the last row require an alternative analysis method.

FUNDAMENTAL EQUATION

The basic concept of isotope dilution analysis is represented in Fig. 14 in the case of an element with two isotopes, *A* and *B*. As can be seen, isotope *A* is more abundant in the sample, while the tracer is enriched with isotope *B*. Thereby, isotopic abundances in the mix (and, therefore, the isotope ratio) will be at a middle point between the sample and the tracer.

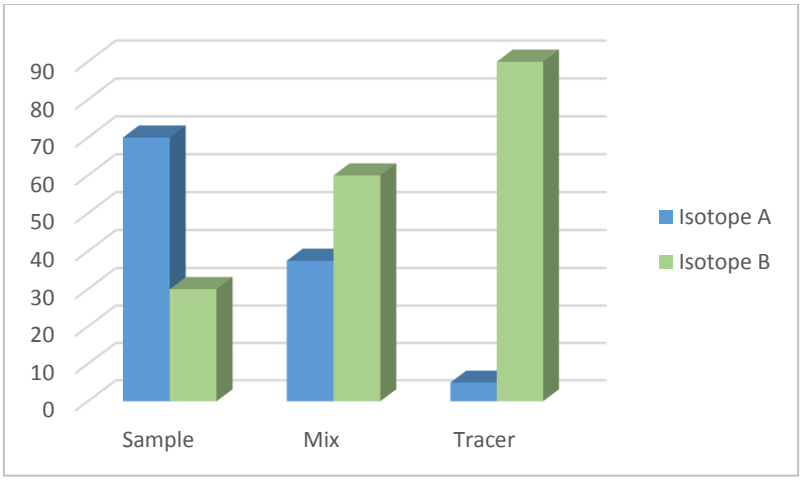

Fig. 14. Representation of Isotope Dilution Analysis fundamentals for an element with 2 stable isotopes, *A* and *B*.

This concept can be mathematically demonstrated developing the fundamental Isotope Dilution Analysis equation, allowing to calculate the original concentration of the analyte element in the sample from the measure of the isotope ratio in the mix.

Taking N_s as the number of moles of a poly-isotopic element in the sample and N_i as the number of moles of the same element in the tracer, we have that the number of moles in the mix N_m will be:

$$N_m = N_s + N_t \quad [1]$$

Applying similar mass balances for isotopes A and B:

$$N_m^a = N_s^a + N_t^a \quad [2]$$

$$N_m^b = N_s^b + N_t^b \quad [3]$$

Then, the ratio between equations [2] and [3] yields the isotopic ratio of both isotopes in the mix R_m:

$$R_m = \frac{N_m^a}{N_m^b} = \frac{N_s^a + N_t^a}{N_s^b + N_t^b} = \frac{N_s A_s^a + N_t A_t^a}{N_s A_s^b + N_t A_t^b} \quad [4]$$

Where $N_s^a = N_s A_s^a$, $N_t^a = N_t A_t^a$, $N_s^b = N_s A_s^b$, $N_t^b = N_t A_t^b$ given the abundances of isotopes *A* and *B* in the sample (A_s^a and A_s^b) and in the tracer (A_t^a and A_t^b), respectively.

Finally, solving for N_s:

$$N_s = N_t \frac{R_m A_t^b - A_t^a}{A_s^a - R_m A_s^b} \quad [5]$$

This last equation is the simplest form of the isotope dilution equation, with it the number of moles of the analyte element in the sample can be calculated by knowing the isotopic composition of the tracer and the sample, the added number of moles of tracer and the measure of the isotopic ratio of the mix.

This can be adapted for concentrations instead of moles defining $R_s = \frac{A_s^b}{A_s^a}$ as the isotopic ratio (b/a) in the sample and $R_t = \frac{A_t^a}{A_t^b}$ as the isotopic ratio (a/b) in the tracer, as follows:

$$N_s = N_t \cdot \frac{A_t^b}{A_s^a} \cdot \left(\frac{R_m - R_t}{1 - R_m \cdot R_s} \right) \quad [6]$$

Then, substituting $N_s = \frac{C_s \cdot m_s}{M_s}$ and $N_t = \frac{C_t \cdot m_t}{M_t}$ in it (where *C* is the concentration in the sample or tracer, *m* is the mass of sample or added tracer and *M* is the atomic weight of the element of the sample or tracer), the final isotope dilution equation is obtained:

$$C_s = C_t \cdot \frac{m_t}{m_s} \cdot \frac{M_s}{M_t} \cdot \frac{A_t^b}{A_s^a} \cdot \left(\frac{R_m - R_t}{1 - R_m \cdot R_s} \right) \quad [7]$$

As all of the parameters except R_m are known, a single measure of the isotopic ratio of the mix provides enough information to calculate the original concentration of analyte in the sample. This method lacks of parameters related to instrumental sensitivity as in the case of most quantification methods (such as standard additions and external calibration), so the isotope dilution analysis is free of the effect of instrumental instabilities or signal drift and they do not have impact over the final concentration value C_s.

ERROR SOURCES

In the measurement of intensities, and therefore in the measurement of isotopic ratios, there are several factors that affect the precision and accuracy of a measurement and they and their correction methods will be discussed here.

Spectral interferences

The elemental isotopic dilution analysis can only be carried out if at least two isotopes of the considered element are free of spectral interferences. So, in order to achieve an exact measure of the isotopic ratios, the presence of poly and monoatomic ions of the same mass to charge ratio than that of the monitored isotopes must be avoided. But, this interferences are common in ICP-MS analyses due to the plasma gas and the elements present in the matrix.

In the case of Fe analysis using ICP-MS, depending on the chosen isotopes, different spectral interferences may appear. The possible interferences for the most widely used Fe isotopes for its determination are listed below.

Table 3. Spectral interferences of Fe isotopes.

Isotope	Abundance	Interference
^{54}Fe	5.845%	$^{54}Cr^{+}$, $^{40}Ar^{14}N^{+}$
^{56}Fe	91.754%	$^{40}Ar^{16}O^{+}$, $^{40}Ca^{16}O^{+}$
^{57}Fe	2.119%	$^{40}Ar^{16}O^{1}H^{+}$, $^{40}Ca^{16}O^{1}H^{+}$
^{58}Fe	0.282%	$^{58}Ni^{+}$, $^{23}Na^{35}Cl^{+}$, $^{42}Ca^{16}O^{+}$

As explained before, polyatomic interferences are readily avoided using CRC systems, but these do not eliminate the isobaric interferences, that is, atomic ions of the same mass. In the case that those interferers are in sufficient amount to lead to wrong measures, two procedures can be performed:

- Chromatographic separation: when the ICP-MS analysis is used as a detection method after a chromatography technique, most of the isobaric elements and polyatomic ions from the matrix are readily removed since in most cases this possible interfering species appear at retention times different from that of the analyte.

- Mathematical correction: in some cases, chromatographic separation is not capable of removing the interference so in this cases, and when chromatography is not used at all, measures of additional isotopes are required to apply correction equations. In this method, the calculated contribution of the interferer to the measured intensity is subtracted to obtain the contribution of the analyte alone. To do this, m/z of another isotope of the interfering element is measured and then, knowing the relative abundance of the interfering isotope, its intensity is calculated and subtracted from the measure.

$$I_{corrected} = I_{measured} - \frac{A_X}{A_Y} \cdot {}^{Y}I \quad [8]$$

Where *X* is the m/z of the interfering isotope and *Y* is the m/z of a non-interfering isotope of the same element.

Detector dead time

As seen before, the most common detector used in ICP-MS is the electron multiplier. In this pulse counting systems, when high counting speeds are produced (more than 10^6 counts per second, cps from here on), the detector dead time effect determines that the measured counts are less than the real counts. This problem worsens when measuring isotopic ratios in which the relative isotopic abundances between isotopes differ considerably, in this cases instrumental sensitivity is usually improved for the least abundant isotope to obtain good counting statistics, but this makes the measure of the other isotope more affected by the detector dead time.

Because of this, dead time correction is needed to correct the obtained intensities. The correction is applied as follows, knowing the detector dead time τ. The detector dead time is determined by plotting the measured isotopic ratio for different concentrations against arbitrary τ values and calculating the intersection point of the different obtained straight lines (this will be further explained in the experimental section).

$$I_{corrected} = \frac{I_{measured}(cps)}{1 - I_{measured}(cps) \cdot \tau(s)} \quad [9]$$

Mass discrimination

The mass discrimination effect is produced by a preferential transmission through the extraction interface and the mass spectrometer of heavier ions over lighter ones. If not corrected, an experimentally measured isotopic ratio R_m will carry an associated systematic error respect the real or theoretical isotopic ratio. The mass discrimination in ICP-MS comes from both the extraction interface (orifice effect) and the ion lenses system (space-charge effect), and it affect the measured intensity up to percentages.

The space-charge effect is the mutual repulsion suffered by the ions in the ion beam when they leave the skimmer cone. So, the number of ions transmitted by the ionic optics diminishes because lighter ions are deflected in greater degree while heavier ions tend to stay in the ion beam's centre.

The mass discrimination effect can be corrected using a certified standard of known or certified isotopic composition (isotopic reference material), but this factor can be calculated using an element with similar m/z ratio if a reference material is not available. In any case, this correction implies the mathematical calculation of what is known as the mass discrimination factor, the most used expression is an exponential equation:

$$R_{corrected} = R_{measured} exp(F\Delta m) \qquad [\,10\,]$$

Where R is the isotopic ratio, F is the mass discrimination factor per mass unit and Δm is the difference between the mass of isotopes. The calculation procedure will be explained later on, in the experimental section.

Added tracer amount optimization

The amount of tracer that is added to the sample in order to perform the Isotope Dilution Analysis is one of the parameters that affect more significantly the final result. Its optimization can be mathematically demonstrated by calculating the optimal range of the sample/tracer ratio in which the statistical error are minimised. The error propagation theory says that, for the concentration in the sample C_s (see equation [7]), its variance $s(C_s)^2$ is:

$$s(C_s)^2 = \left[\frac{\partial C_s}{\partial m_t}\right]^2 s(m_t)^2 + \left[\frac{\partial C_s}{\partial m_s}\right]^2 s(m_s)^2 + \left[\frac{\partial C_s}{\partial M_t}\right]^2 s(M_t)^2 + \left[\frac{\partial C_s}{\partial M_s}\right]^2 s(M_s)^2 + \left[\frac{\partial C_s}{\partial A_t^b}\right]^2 s\left(A_t^b\right)^2 + \left[\frac{\partial C_s}{\partial A_s^a}\right]^2 s(A_s^a)^2 + \left[\frac{\partial C_s}{\partial R_s}\right]^2 s(R_s)^2 + \left[\frac{\partial C_s}{\partial R_t}\right]^2 s(R_t)^2 + \left[\frac{\partial C_s}{\partial R_m}\right]^2 s(R_m)^2 \quad [11]$$

Taking partial derivatives and grouping:

$$\left[\frac{s(C_s)^2}{C_s}\right] = \left[\frac{s(m_t)}{m_t}\right]^2 + \left[\frac{s(m_s)}{m_s}\right]^2 + \left[\frac{s(M_t)}{M_t}\right]^2 + \left[\frac{s(M_s)}{M_s}\right]^2 + \left[\frac{s\left(A_t^b\right)}{A_t^b}\right]^2 + \left[\frac{s(A_s^a)}{A_s^a}\right]^2 + \left[\frac{R_m R_s}{1 - R_m R_s}\right]^2 \left[\frac{s(R_s)}{R_s}\right]^2 + \left[\frac{-R_t}{R_m - R_t}\right]^2 \left[\frac{s(R_t)}{R_t}\right]^2 + \left[\frac{R_m(1 - R_t R_s)}{(R_m - R_t)(1 - R_m R_s)}\right]^2 \left[\frac{s(R_m)}{R_m}\right]^2 \quad [12]$$

As can be seen, the last three factors contain the R_m parameter, the only experimental measurement with significant uncertainty. Assuming that the value of the isotopic ratio in the sample and in the tracer (certified or tabulated, known with negligible uncertainty) do not affect significantly the final result, the error magnification factor *f(R)* can be defined as:

$$f(R) = \left[\frac{R_m(1 - R_t R_s)}{(R_m - R_t)(1 - R_m R_s)}\right] \quad [13]$$

Which depends on R_m, R_t and R_s. As R_t and R_s are known, as the natural isotopic abundances and the tracer composition are known, *f(R)* can be plotted against R_m to obtain the optimal added tracer amount range.

EXPERIMENTAL

MATERIALS

Instrumentation

- ICP-(ORS)-MS Agilent 7500c equipped with an Octopole Reaction System (ORS) for the intensity measurements at selected mass to charge ratios in Selected Ion Monitoring (SIM) mode.
- Milli-Q Gradient A10, Millipore, for obtaining de-ionised water (18 MΩ), used for dilutions and labware cleaning.
- Mettler-Toledo AE-200 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.

Reagents and Solutions

- TM-24.3 Certified Reference Material with $[Fe] = (15.4 \pm 4.2)\ ppb$ (Environment Canada).
- TMDA-51.4 Certified Reference Material with $[Fe] = (116 \pm 14.9)\ ppb$ (Environment Canada).
- 41.96 ppm Fe (natural abundances) stock solution prepared from a 1000 ppm Fe solution (Merck, Darmstad, Germany).

- 406.36 ppm ^{57}Fe stock tracer solution prepared from a solid iron oxide certified material purchased on May 29, 2012 to Isoflex USA:

Table 4. ^{57}Fe enriched tracer material information data.

Description	
Isotope	Fe-57
Enrichment	(96.60 ± 0.40) %
Element weight	100 mg
Form	Oxide (Fe_2O_3)

Isotopic Distribution	
Isotope	**Content (%)**
Fe-54	0.03
Fe-56	1.49 ± 0.20
Fe-57	96.60 ± 0.40
Fe-58	1.88 ± 0.20

Chemical Admixtures								
Element	Al	Cr	Cu	Mg	Ni	Si	Zn	C
Content (ppm)	<10	<10	<10	<10	<10	30	<10	45

- HNO_3 solutions: 1% for acidification of metal solutions and 5% for ICP-MS cleaning program and material cleaning.

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 (for $^{140}Ce^{2+}$ ions), ^{140}Ce, ^{156}CeO and optionally ^{56}Fe and ^{57}Fe.

With no-gas tuning configuration, sensibility for Li, Y and Tl is checked and compared with the values established by the manufacturer. $^{70}Ce/^{140}Ce$ for double charged species formation and $^{156}CeO/^{140}Ce$ for oxide formation ratios are monitored and checked as well. Then, another tune configuration is loaded, with He in the CRC as collision gas, and the same parameters are monitored.

Observed effects of collision gas are:

- Sensitivity suffers a drop of one order of magnitude when He is used, but in both cases is beyond the minimum established for each case.
- Oxide formation is below the limit in both cases.
- Double charged species ratio seemed to be too high, but this could be caused by ^{70}Zn contamination in the instrument, thus increasing the $^{70}Ce/^{140}Ce$ ratio. This fact had no further effect in the measurements.
- The intensities for typical iron ions (which is not present in the tune solution) were very high (more than 10^5 cps) when no gas was used, especially at m/z = 56. This intensities dropped drastically when collision gas was used, demonstrating the plasma interference elimination efficiency of the CRC system.

The measurements were taken using a previously configured settings for Fe determination in water, using He as collision gas, creating a method in the ICP-MS software to measure the 54, 56, 57, 58 and 60 m/z values and a sequence to analyse each solution (including calibration points, samples, spiked samples and blanks) three times.

EXTERNAL CALIBRATION

In order to assess the advantages of the Isotope Dilution Analysis, which is one of the most important topics of this project, an analysis using a more conventional type of analysis and most commonly applied as it is the external calibration will be applied as well.

To analyse the provided Certified Reference Materials with a single calibration curve, it had to comprise an enough wide concentration rage to include both concentrations, 15.4 and 116 ppb, respectively. The calibration curve was constructed by measuring the response of the instrument (intensity) at m/z = 56 for 7 solutions of different concentration from 5 to 200 ppb approximately, prepared from a stock solution of 41.96 ppm Fe, plus a blank solution. All of these solutions were acidified with 5% HNO_3 (to approximately 1% HNO_3 in the final solutions).

Calibration curve

To prepare all the points in the calibration curve, an intermediate solution had to be prepared to go from a concentration of ppm to the ppb scale. To do this, a weighted amount of 41.96 ppm Fe stock solution was diluted with Milli-Q water until approximately 1000 ppb.

Table 5. Fe intermediate solution preparation for calibration curve.

Intermediate Solution		
$m_{stock\ sol.}$	m_{final}	$[Fe]_{intermediate\ sol.}$
1.214 g	50.4374 g	1.009954 ppm

Where the final Fe concentration is calculated as follows:

$$[Fe]_{intermediate\ sol.} = \frac{m_{stock\ sol.} \cdot [Fe]_{stock\ sol.}}{m_{final}} = \frac{(1.214\ g \cdot 41.96\ ppm)}{50.4374\ g} = 1.009954\ ppm \quad [14]$$

Solutions of different concentration along the desired concentration range were prepared from this intermediate solution by weighing in the same way as explained above. These solutions, labelled from 1 to 7, were analysed in the ICP-MS and the measured intensities at m/z = 56 were plotted against the concentration to obtain the calibration curve. The following chart shows the weighed amounts of intermediate solution and final weight for each solution, as well as the exact Fe concentration and the corresponding measured intensity. Calibration graph is plotted in Fig. 15.

Table 6. Calibration points and measures.

Calibration curve				
Solution	$m_{intermediate\ sol.}$	m_{final}	**[Fe]**	$I_{measured}$ **(cps)**
B	-	-	0 ppb	19070.9
1	0.1081 g	20.0895 g	5.43 ppb	81130.5
2	0.2047 g	19.9477 g	10.36 ppb	139466.5
3	0.4941 g	19.9321 g	25.04 ppb	315768.9
4	0.9889 g	20.3482 g	49.08 ppb	597654.8
5	1.9628 g	20.2562 g	97.86 ppb	1359241.4
6	2.9496 g	20.1686 g	147.70 ppb	2023405.4
7	3.8374 g	19.9961 g	193.82 ppb	2612914.7

Where the exact concentrations are calculated for each solution using equation [15].

$$[Fe] = \frac{m_{intermediate\ sol.} \cdot [Fe]_{intermediate\ sol.}}{m_{final}} \qquad [\ 15\ ]$$

For example, in the case of solution 1, including the unit conversion factor:

$$[Fe]_1 = \frac{0.1081\ g \cdot 1.00994\ ppm}{20.0895\ g} \cdot \frac{1000\ ppb}{1\ ppm} = 5.434481\ ppb$$

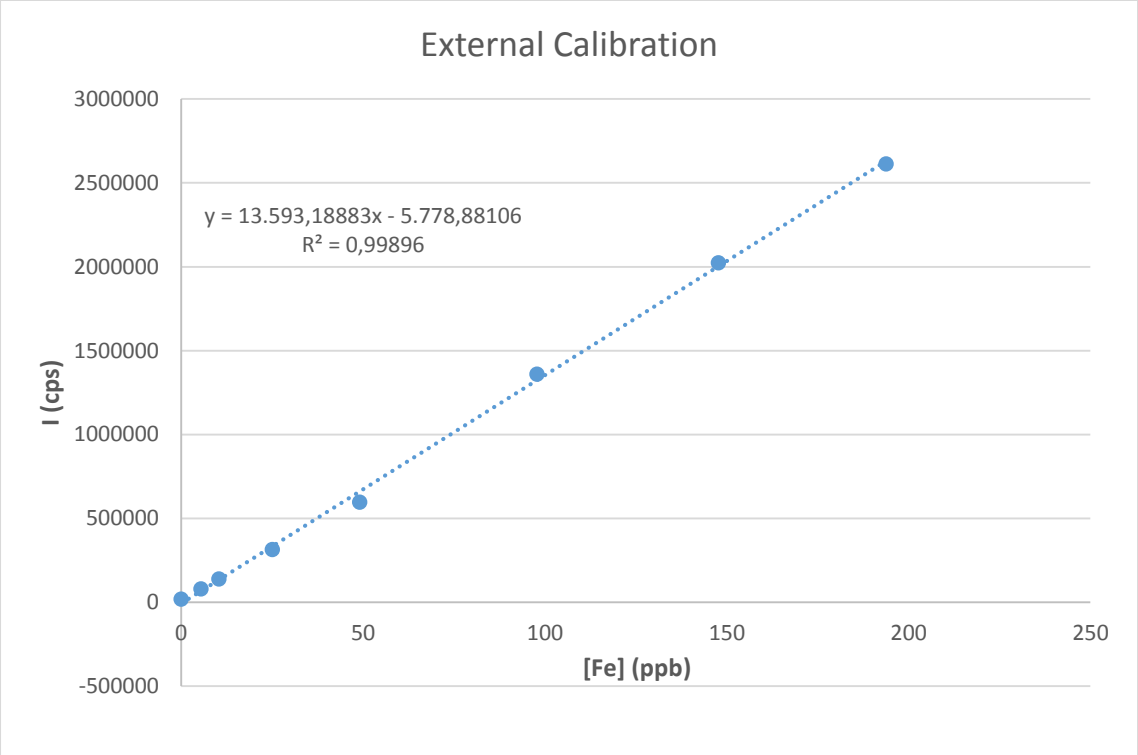

Fig. 15. Calibration curve plot.

CRM Analysis

Once the calibration curve has been plotted, the Fe concentration of the two Certified Reference Materials can be determined substituting the intensities obtained in the equation of the linear fit. Both CRM were analysed in triplicate (Table 7) and each intensity was used to obtain three Fe concentrations for each CRM with equation [16].

Table 7. CRM measurements for calibration curve determination.

CRM Analysis			
CRM	**Measure**	**$I_{measured}$ (cps)**	**[Fe]**
TM-24.3	1	212996.1	16.0945 ppb
	2	211453.3	15.9810 ppb
	3	212889.5	16.0866 ppb
TMDA-51.4	1	1710166.1	126.2356 ppb
	2	1799953.3	132.8410 ppb
	3	1684128.9	124.3202 ppb

Where the concentration is calculated substituting in the calibration equation:

$$y = 13593.18883 \cdot x - 5778.88106 \quad \leftrightarrow \quad I_{measured} = 13593.18883 \cdot [Fe] - 5778.88106$$

$$[Fe] = \frac{I_{measured} + 5778.88106}{13593.18883} \qquad [\,16\,]$$

For example, in the case of Replica 1 of TM-24.3:

$$[Fe] = \frac{212996.1 + 5778.88106}{13593.18883} = 16.0945\ ppb$$

From the obtained results of the three replicates, the concentration, standard deviation, relative standard deviation and relative error are readily calculated (Table 8):

Table 8. Fe determination in CRMs using external calibration.

TM-24.3				
$[Fe]_{average}$	**s**	**RSD**	**ε**	**RESULT**
16.0540 ppb	0.0634	0.39%	4.25%	**(16.05 ± 0.06) ppb**

TMDA-51.4				
$[Fe]_{average}$	**s**	**RSD**	**ε**	**RESULT**
127.7989 ppb	4.4703	3.50%	10.17%	**(128 ± 4) ppb**

ISOTOPE DILUTION ANALYSIS

In order to apply the IDA method, several mass to charge ratios have been measured for each fortified samples and also for the solutions used in the calibration curve construction, not all of these measures will be used, but several of them will be necessary to make the appropriate corrections. Remember that each measurement has been performed in triplicate. **Table 9** shows the average of these three measures of each solution and m/z value.

Table 9. Averaged intensities measured for IDA method.

Averaged Measures					
Solution	**^{54}Fe**	**^{56}Fe**	**^{57}Fe**	**^{58}Fe**	**^{60}Ni**
5ppb	4499,4178	81130,534	1947,667267	1375,503733	455,8136967
10ppb	7813,767433	139466,4767	3335,057367	1711,710333	533,7182433
25ppb	17635,268	315768,8733	7656,146167	2649,372133	679,2807
50ppb	33424,896	597654,8133	14655,20467	3565,728267	655,3289
100ppb	66022,883	1359241,4*	28932,403	5633,847333	664,0950733
150ppb	98451,15367	2023405,4*	43521,95333	7606,2526	640,1429233
200ppb	128350,0433	2612914,7*	56384,406	9336,532867	553,4719033
Blank	1246,3286	19070,877	534,0916833	2922,510667	1234,009433
M. Fort. 1	13431,832	209026,63	209518,39	69356,531	27745,873
M. Fort. 1	13961,898	217255,06	217195,5	71887,914	28653,355
M. Fort. 1	13339,163	206407,78	206311,36	68254,984	26970,131
M. Fort. 2	98924,422	1597256,1*	1735131,1*	800501,63	331343,69
M. Fort. 2	101890,96	1642529,3*	1794725,4*	825745,13	341233,13
M. Fort. 2	98581,336	1599549,3*	1725281*	795877,44	329276,09

***Measured in analogic mode.**

Spectral interferences

As explained before, spectral interferences can cause an overestimation of a measure in ICP-MS. The main interferences in Fe analysis, that is mass to charge ratios of 56 and 57, are caused by polyatomic species such as $^{40}Ar^{16}O^{+}$ and $^{40}Ar^{16}O^{1}H^{+}$ produced by the plasma itself. This type of interference is eliminated by using, optimising and checking the Collision/Reaction Cell with He as collision gas.

On the other hand, isobaric interferences may appear, as it is in the case of m/z = 58. Unexpectedly high measures for this m/z were notice, so nickel could be interfering. To make the mathematical correction, the less abundant but non-interfered ^{60}Ni was measured and then the correction shown in equation [8] was applied knowing the natural relative abundances of ^{58}Ni (68.077%) and ^{60}Ni (26.223%). These abnormally high values at m/z = 58 only appeared in the calibration solutions, so correction only was applied in those cases as these measurements for different concentrations are needed for the next correction.

Table 10. Isobaric spectral interference correction.

Spectral Interference Correction			
Solution	**^{58}Fe$_{measured}$**	**^{60}Ni**	**^{58}Fe$_{corrected}$**
5 ppb	1375.5	455.8	192.2
10 ppb	1711.7	533.7	326.1
25 ppb	2649.4	679.3	885.9
50 ppb	3565.7	655.3	1864.4
100 ppb	5633.8	664.1	3909.8
150 ppb	7606.3	640.1	5944.4
200 ppb	9336.5	553.5	7899.7

Correction was made applying the equation [8], using the measure of m/z = 60 to correct the intensity at m/z = 58:

$$I_{corrected} = I_{measured} - \frac{A_{58}}{A_{60}} \cdot {}^{60}I$$

For example, in the case of 5 ppb solution:

$$I_{corrected} = 1375.5 - \frac{68.077}{26.223} \cdot 455.8 = 192.2$$

Detector dead time

Previously, the correction needed to compensate the detector dead time has been presented, but in order to apply that correction, the dead time has to be found. The most used method to calculate the detector dead time is the measure of the isotopic ratios of the element at different concentrations. To do so, the equation [9] is applied for different values of τ and the normalised isotopic ratio R_n is calculated with equation [17].

$$R_n = \frac{R_{corrected}}{R_{theoretical}} \qquad [\,17\,]$$

Where $R_{theoretical} = \frac{A(^{57}Fe)}{A(^{56}Fe)} = \frac{2.119}{91.75} = 0.023095$ and $R_{corrected}$ is:

$$R_{corr} = \frac{I_{corr}^{57}}{I_{corr}^{56}} = \frac{\frac{I^{57}}{1 - I^{57} \cdot \tau}}{\frac{I^{56}}{1 - I^{56} \cdot \tau}} = \frac{I^{57}(1 - I^{56} \cdot \tau)}{I^{56}(1 - I^{57} \cdot \tau)} = R_{measured} \cdot \frac{1 - I^{56} \cdot \tau}{1 - I^{57} \cdot \tau}$$

$$= R_{measured} \cdot \frac{1 - I^{56} \cdot \tau}{1 - R_{measured} \cdot I^{56} \cdot \tau} \qquad [18]$$

Then, the obtained R_n are plotted against τ for each concentration and the value of the detector dead time is obtained for the intersection between the lines. In this case 5, 10, 25 and 50 ppb solutions were used:

Table 11. Normalised isotopic ratios of masses 57/56 for detector dead time determination.

Detector dead time plot				
τ (s)	**R_n (5ppb)**	**R_n (10ppb)**	**R_n (25ppb)**	**R_n (50ppb)**
0	1,039455	1,035401036	1,049822835	1,061736097
1,00E-08	1,038632	1,033991483	1,046587949	1,055545272
2,00E-08	1,037808	1,032581836	1,043352568	1,049352632
3,00E-08	1,036985	1,031172095	1,040116692	1,043158177
4,00E-08	1,036162	1,02976226	1,03688032	1,036961905
5,00E-08	1,035339	1,02835233	1,033643452	1,030763815

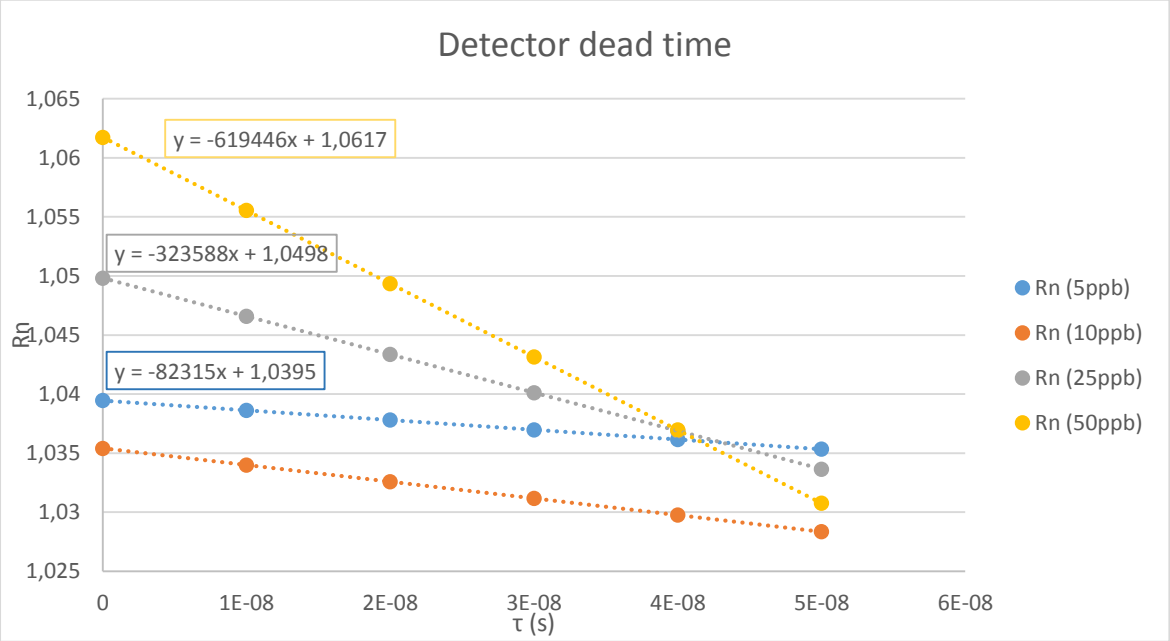

Fig. 16. Detector dead time plot. As the line for 10 ppb does not intersect with the rest, it will be not used for the calculations.

Combining the equations of the three possible intersections of linear fits:

Table 12. Dead time results for each intersection.

Intersections			
	50ppb and 5ppb	**5ppb and 25ppb**	**25ppb and 50ppb**
τ (s)	4,133E-08	4,26902E-08	4,0222E-08

$$\tau_{average} = 4.14143 \cdot 10^{-8} s \equiv 41.413\ ns$$

For example, in the case of the first intersection:

$$-82315x + 1.0395 = -619446x + 1.0617$$

$$x = \tau(s) = \frac{1.0617 - 1.0395}{619446 - 82315} = 4.133 \cdot 10^{-8} s$$

Mass discrimination factor

The mass discrimination factor F is calculated by plotting the natural logarithm of $R_{corr}/R_{theoretical}$ ratio against the mass increment (equation [19]), using different isotopic ratios. This representation can be deducted from the correction equation [10]:

$$R_{corr} = R_{theor}\exp(F\Delta m)$$

$$\frac{R_{corr}}{R_{theor}} = \exp(F\Delta m)$$

$$\ln\frac{R_{corr}}{R_{theor}} = F\Delta m \qquad [\ 19\ ]$$

So, using the measured intensities of 200 ppb solution to calculate the corrected ratios R_{corr} (with detector dead time and spectral interference corrections):

Table 13. Calculations for mass discrimination factor determination.

Mass discrimination plot					
Ratio	**R_{med}**	**R_{corr}**	**R_{theor}**	**$\ln(R_{corr}/R_{teor})$**	**Mass increment**
54/56	0,049121	0,049383907	0,063705722	-0,25464978	2
57/56	0,021579	0,02162963	0,023095368	-0,06556793	-1
58/56	0,003023	0,003024309	0,003073569	-0,01615701	-2

And plotting:

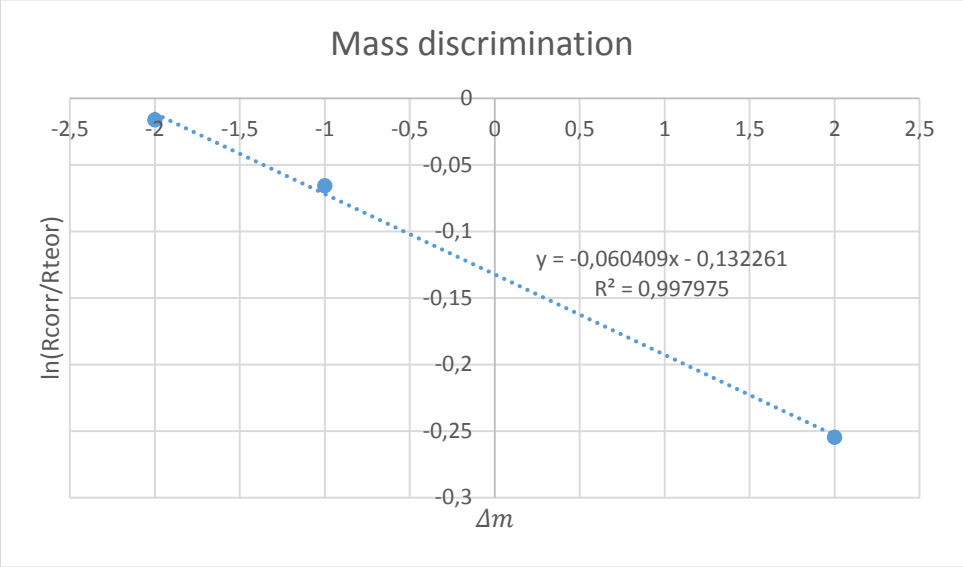

Fig. 17. Mass discrimination plot.

From the slope of the linear fit, following the expression [19], we have that:

$$F = -0.060409$$

This obtained mass discrimination factor will be used for corrections later on.

Added tracer amount

From the expression of added tracer amount optimisation exposed previously (equation [13]), substituting with the abundance values of natural Fe and tracer Fe, an error magnification curve can be plotted.

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

$$R_t = \frac{1.49}{96.60} = 0.01542; \qquad R_s = \frac{2.119}{91.75} = 0.023095$$

$$f(R) = \left[\frac{0.99964 \cdot R_m}{(R_m - 0.01542)(1 - 0.023095 \cdot R_m)}\right] \qquad [\ 20\ ]$$

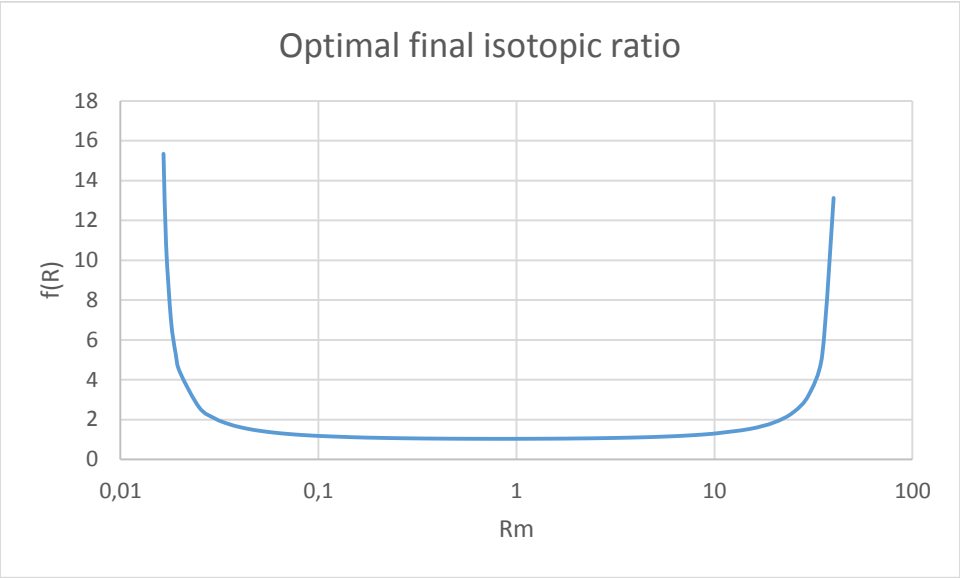

Fig. 18. Optimum range of added tracer amount, from the equation [20] plot.

From the plot it can be deduced that the optimum range for the isotopic ratio in the final spiked sample must be between 0.1 and 10, approximately. Based on that and the fact that isotopic ratios are very similar in tracer and sample, it is decided to add the same amount of tracer Fe that Fe present in the sample to achieve a $R_{measured} \approx 1$.

Fe determination in Certified Reference Materials

The two selected CRMs were spiked with a similar amount of ^{57}Fe than total Fe in them (the concentrations are known since they are Certified Materials), which is a good error-optimised amount as seen previously, and then measured in triplicate. The original Fe concentration was calculated for each sample and measurement with the fundamental IDA equation.

The use of the available 406. 63 ppm ^{57}Fe tracer solution, already prepared from a solid ^{57}Fe-enriched Fe_2O_3 material, would imply too small amounts of solution to be added to the CRM samples, since they contain a Fe concentration in the ppb range. So, an intermediate solution must be prepared diluting a weighted amount of solution with de-ionised water to approximately 2 ppm.

Table 14. Intermediate ^{57}Fe tracer solution preparation for IDA.

Intermediate Solution		
$m_{stock\ sol.}$	m_{final}	$[Fe]_{intermediate\ sol.}$
0.1043 g	20.4841 g	2.069085 ppm

Where the final Fe concentration is calculated as follows, analogously to equation [14]:

$$[Fe]_{intermediate\ tracer\ sol.} = \frac{m_{stock\ sol.} \cdot [Fe]_{stock\ sol.}}{m_{final}} = \frac{(0.1043\ g \cdot 406.36\ ppm)}{20.4841\ g}$$
$$= 2.069085\ ppm$$

This intermediate tracer solution is the one used for spiking the samples. This spiking has to be about the same amount of Fe present in the sample so an estimation of the amount to be added to each CRM can be calculated, taking account that about 20 mL of sample will be used:

$$15.4\ ppm\ Fe * 20 \cdot 10^{-3} L \cdot \frac{1}{2.069085\ ppm} = 0.14886\ g\ of\ tracer \text{ for TM-24.3}$$

$$116\ ppm\ Fe * 20 \cdot 10^{-3} L \cdot \frac{1}{2.069085\ ppm} = 1.12127\ g\ of\ tracer \text{ for TMDA-51.4}$$

The actual amounts of added tracer, final weight and measured intensities are shown in the following charts.

Table 15. ^{57}Fe spiking of CRM for IDA.

Sample spiking and measure					
CRM	**m_{tracer}**	**m_{final}**	**Measure**	**$^{56}I_{measured}$**	**$^{57}I_{measured}$**
TM-24.3	0.1524 g	19.9474 g	1	209026.6	209518.4
			2	217255.1	217195.5
			3	206407.8	206311.4
TMDA-51.4	1.1374 g	19.9085 g	1	1597256.1*	1735131.1*
			2	1642529.3*	1794725.4*
			3	1599549.3*	1725281.0*

***Measured in analogic mode.**

With this measurements, isotopic ratio of the spiked samples can be calculated. As can be seen, all of them are very close to the selected optimum value ($R_{measured} \approx 1$). Then, corrections are applied and the concentration is calculated for each replicate.

Table 16. Corrected isotopic ratios and calculated original Fe concentration.

Ratio correction and Concentrations				
CRM	**$^{57/56}R_{med}$**	**$^{57/56}R_{corr}$ (τ)**	**$^{57/56}R_{corr}$ (K)**	**C_s (ppb)**
TM-24.3	1.002353	1,002373606	0,943614129	15,63500727
	0.999726	0,999723431	0,941119308	15,59206454
	0.999533	0,999528713	0,940936005	15,58890959
TMDA-51.4	1.08632	-	1,022639471	133,7792142
	1.09266		1,028607524	134,5908963
	1.078604		1,0153763	132,7916991

Where the $R_{measured} = \frac{^{56}I_{measured}}{^{57}I_{measured}}$, corrected with the detector dead time correction ([9]) for $\tau = 41.413\ ns$ and then with the mass discrimination correction ([10]) using $F = -0.060409$ (note that the detector dead time effect only affects measures in pulse counting, thus the correction is not applied in analogic measures).

The concentration is readily calculated using the IDA equation ([7]). For example, for measure 1 of TM-24.3:

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

$$= 2069.085\ ppb \cdot \frac{0.1524\ g}{(19.9474 - 0.1524)g} \cdot \frac{56}{58} \cdot \frac{96.60}{91.75}$$

$$\cdot \left(\frac{0.94361 - \frac{1.49}{96.60}}{1 - 0.94361 \cdot \frac{2.119}{91.75}}\right) = 15.63500727\ ppb$$

Finally, the results were:

Table 17. Fe determination in CRMs using IDA.

TM-24.3				
$[Fe]_{average}$	s	RSD	ε	RESULT
15,605327 ppb	0,025752	0,17%	1,3%	**(15.61 ± 0.03) ppb**

TMDA-51.4				
$[Fe]_{average}$	s	RSD	ε	RESULT
133,72060 ppb	0,901029	0,67%	15,3%	**(133.7 ± 0.9) ppb**

METHOD COMPARISON. DISCUSSION

At this point, when both elemental analysis methods have been performed over the same Certified Materials, comparisons can be made. To do so, the most typical figures of merit evaluated in Analytical Chemistry will be reviewed.

Accuracy

The results obtained by conventional external calibration show relative error values of 4.25% and 10.17% for TM-24.3 and TMDA-51.4, respectively. So the Fe amount measured has been overestimated respect to the certified value in both samples.

A similar behaviour occurred when analysing the CRMs using IDA, when relative errors resulted in 1.3% and 15.3%, respectively. Although in the TM-24.3 the relative error is less than in external calibration, it is larger for TMDA-51.4, so no improvement can be inferred.

It is well known that Isotope Dilution Analysis is more accurate than external calibration and this fact should have been demonstrated here, but since both CRMs were out of date, the ambiguous results obtained are not unusual. We can assume that the certified Fe concentration in the materials is no longer applicable for the moment of the analysis, so no further evaluations can be made in relation to the accuracy comparison. Moreover, measures for TMDA-51.4 were made in analogic mode, which is less accurate than pulse counting mode and this could also contribute to the deviation from the certified value.

Precision

Regarding to the precision, in external calibration we have relative standard deviations of 0.39% and 3.50%, which are reasonably good values in Analytical Chemistry since RSD values below 5% are taken as good precision for this concentration level and matrix.

But, in the other hand, when using IDA we have very lower RSD values, 0.17% and 0.67%, respectively. In this case, the superiority of IDA versus calibration-based methods are indeed demonstrated.

Analysis time

Another point in favour of IDA is the fact that it only requires a single measure, in contrast with the various measures required to plot a calibration curve, which can vary between 5 and 10 points of different concentration. This implies longer analysis times, for obvious reasons.

Conclusions

As we have seen, Isotope Dilution Analysis is a powerful tool in elemental Analytical Chemistry which usually provides better precision and accuracy in the determination of trace elements of simple matrixes within a single sample acquisition. This has already been exploited as a rapid and reliable method to validate other analytical methods, as well as for certification of various kinds of materials.

However, the method has two problems, one is the cost of the isotope-enriched materials required to perform the analysis, and the other is the fact that not all elements have available alternative stable isotopes to analyse their abundances.

The logical next step in the development of IDA could be the extension of its application to more complex matrixes and the development and research of methods to apply the concept to molecules as well, which is already been done as of today. With the development of the technique in the molecular analysis field and the availability of isotope-labelled standards, Isotope Dilution Analysis could become one of the most useful and reliable techniques not only in elemental analysis field, but in the whole trace analysis.

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