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Abstract

The double isotope dilution is a powerful methodology to measure accurately the ratio between two isotopes of two different elements (*e.g.* $^{238}Pu/^{238}U$, $^{148}Nd/^{238}U$ or $^{230}Th/^{238}U$ ratios). To obtain the lowest possible uncertainty, some parameters must be optimized: the elaboration of the spike and the proportion of the spike in the sample - spike mixture. A piece of code is also provided to easily calculate the optimal parameters. As an example, the application of the code to $^{238}Pu/^{238}U$ and $^{148}Nd/^{238}U$ ratios determination in irradiated sample will be discussed.

Keywords

Mass spectrometry; double isotope dilution, isotope dilution

1. Introduction

Determining the ratio between two isotopes of two elements (*e.g.* $^{238}Pu/^{238}U$, $^{148}Nd/^{238}U$ or $^{230}Th/^{238}U$ ratios) is of prime interest in the nuclear and the geochemistry fields. One of the main application in the nuclear field is the burnup monitoring of irradiated samples using the $^{148}Nd/^{238}U$ ratio [1–3]. The ^{148}Nd isotope have the suitable properties for burnup level examination: it is a stable fission product and requires no decay correction, it is not volatile and has no volatile precursors, it is formed exclusively by fission as it has a low neutron capture cross section and is not present in non-irradiated samples. Other applications can be the transmutation yield determination for analytical irradiation examination or to determine the capture integral cross section of different isotopes [4–6]. In geochemistry, isotopes ratios like $^{230}Th/^{238}U$ or $^{226}Ra/^{238}U$ help identifying and characterize the contamination sources [7–9]. It can also be useful to date geological objects [10–13]. These applications require measuring these ratios with the best possible accuracy (*i.e.* measurement trueness and precision).

Isotope dilution (ID) is the main methodology used in mass spectrometry to determine accurately the mass fraction determination of an analyte in a sample, as it is a reference calibration method [14–17]. The ID principle is to mix a known amount of a sample, with a known isotope composition, with a spike solution containing the same analyte as the sample but with a different isotope composition. This solution is called the (sample–spike) mixture and its isotope ratio reflects the sample analyte mass fraction. To obtain the best performance (*i.e.* the minimum mass fraction uncertainty), the mixture between the sample and the spike must be prepared carefully. The ID-TIMS require an optimal mixture isotope ratio which can be determined theoretically [15]. The mixture is then prepared to obtain a mixture isotope ratio as close as possible to the theoretical one. The ratio between two isotopes of two elements is then calculated using the mass fraction of the two elements determined with the ID methodology, the isotope abundances and the molar masses. This method requires several gravimetric preparations which can increase the uncertainties. Moreover, it can be tedious when working in glove boxes or in hot cell laboratories.

Another existing method is the double isotope dilution (DID) method: it is used to directly determine the ratio between two isotopes of two elements present in a sample,

with one of them used as a reference [6]. Similarly to the ID, the DID is based on the addition of a spike to the sample. The spike solution must contain the same two analytes as the sample with a different isotope composition. The spike can be homemade and prepared from two Certified Reference Material (CRM) or a well-recognized CRM provided by an official supplier (NIST, JRC-Geel or CETAMA for example) can be used. The mixture isotope ratios are then measured using an accurate technique such as Thermal Ionization Mass Spectrometry (TIMS) or Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS). The mixture isotope ratios measurements helped to calculate the ratio between two isotopes of two elements in the sample. The benefit of the DID compared to the ID is that it is only based on the isotope ratio determination. Separation yields and weights uncertainties are not to be considered. The mixture or sample dilutions can be perform volumetrically without uncertainty degradation. Thus, implementing the DID is easier compared to the ID, especially when the experiments are performed in glove boxes or in hot-cells. To obtain the best performances for DID, some parameters like the spike solution preparation or the (sample - spike) mixture must be optimized.

Note that the DID must not be mistaken for reverse (or two-step) ID that is used when the spike is not certified. The spike material is calibrated against a well-characterized assay material with natural isotope abundance [18]. The DID must not be mistaken for the double spike technique. The double spike technique is a powerful method for correcting the instrumental mass fractionation in mass spectrometry. It is the most reliable method to obtain accurate isotope ratios of a single element [19].

This study aims at discussing and finding the optimal parameters for the DID. First, the DID will be summarized. Then, the theoretical calculations performed to find the optimal parameters will be discussed. Finally, different examples, coming from samples analyzed in the laboratory, will be evaluated. To make it as easy as possible for experimenters using the DID, a script written with open source software Octave is provided to easily determine the optimal parameters.

2. Materials and methods

2.1. Overview of the double isotope dilution methodology

2.1.1. Glossary

A schematic of the DID is presented in Fig. 1. The goal of the DID is to measure the ratio between two isotopes of two elements. Element 1 (noted E) is the reference element. Isotopes of element E are ^{A}E and ^{B}E. The reference isotope of E for the sample is the ^{B}E isotope (*e.g.* ^{238}U). The major isotope of the CRM used in the spike for element E is ^{A}E (*e.g.* ^{233}U or ^{235}U). The second element (noted element Z) can be any element of the periodic table with at least 2 isotopes. The isotopes of interest for element Z are ^{X}Z and ^{Y}Z. ^{X}Z is the major isotope of the CRM (*e.g.* ^{242}Pu or ^{150}Nd). ^{Y}Z is the isotope of interest for the sample (*e.g.* ^{238}Pu or ^{148}Nd). The "spike" term refers to the solution containing E and Z elements with a known $^{Y}Z/^{A}E$ ratio. The spike can be obtained from a CRM containing both elements or manufactured using two CRMs. For better clarity and concision, the following nomenclature was used in the manuscript:

- *T* refers to the spike (or tracer). It contains both elements E and Z
- *M* refers to the (sample – spike) mixture
- *S* refers to the sample
- CRM_E refer to the CRM containing only element E
- CRM_Z refer to the CRM containing only element Z
- *n* is the amount in mol
- *C* is the amount concentration in mol g^{-1}
- *(%A)* refers to the ^{A}E isotope abundance of element E (A being the major isotope of the CRM or spike)
- *(%B)* refers to the ^{B}E isotope abundance of element E (B being the reference isotope of the sample)
- *(%X)* refers to the ^{X}Z isotope abundance of element Z (X being the major isotope of the CRM or spike)

- *(%Y)* refers to the ^{Y}Z isotope abundance of element Z (Y being the reference isotope of the sample)
- u is the uncertainty with a coverage factor at k = 1
- u_r is the relative uncertainty with a coverage factor at k = 1
- κ is the proportion of element E in the spike solution (T)
- *(1- κ)* is the proportion of element Z in the spike solution (T)
- λ is the proportion of the spike solution (T) in the mixture (M)

2.1.2. Double isotope dilution formula

The $(^{B}E/^{A}E)_M$ ratio can be calculated from the E element sample and spike amount and the E element isotope abundances (Eq. (1), Fig. 1).

$$\left(\frac{^{B}E}{^{A}E}\right)_M = \frac{n(E)_S \cdot (\%B)_S + n(E)_T \cdot (\%B)_T}{n(E)_S \cdot (\%A)_S + n(E)_T \cdot (\%A)_T} \tag{1}$$

$$(\%A)_S = (\%B)_S \cdot \left(\frac{^{A}E}{^{B}E}\right)_S \tag{2}$$

$$(\%B)_T = (\%A)_T \cdot \left(\frac{^{B}E}{^{A}E}\right)_T \tag{3}$$

Combining Eq. (1), (2) and (3) leads to Eq. (4).

$$\left(\frac{^{B}E}{^{A}E}\right)_M = \frac{n(E)_S \cdot (\%B)_S + n(E)_T \cdot \left(\frac{^{B}E}{^{A}E}\right)_T \cdot (\%A)_T}{n(E)_S \cdot (\%B)_S \cdot \left(\frac{^{A}E}{^{B}E}\right)_S + n(E)_T \cdot (\%A)_T} \tag{4}$$

Rearranging Eq. (4) leads to Eq. (5).

$$n(E)_S \cdot (\%B)_S = n(E)_T \cdot (\%A)_T \cdot \frac{\left(\left(\frac{^{B}E}{^{A}E}\right)_M - \left(\frac{^{B}E}{^{A}E}\right)_T\right)}{\left(1 - \left(\frac{^{B}E}{^{A}E}\right)_M \cdot \left(\frac{^{A}E}{^{B}E}\right)_S\right)} \tag{5}$$

The same equation as Eq. (5) can be obtained for element Z (Eq. (6)).

$$n(Z)_S \cdot (\%Y)_S = n(Z)_T \cdot (\%X)_T \cdot \frac{\left(\left(\frac{^{Y}Z}{^{X}Z}\right)_M - \left(\frac{^{Y}Z}{^{X}Z}\right)_T\right)}{\left(1 - \left(\frac{^{Y}Z}{^{X}Z}\right)_M \cdot \left(\frac{^{X}Z}{^{Y}Z}\right)_S\right)} \tag{6}$$

Dividing Eq. (6) by Eq. (5) leads to the $(^{Y}Z/^{B}E)_s$ ratio and the DID formula (Eq. (7)).

$$\left(\frac{^{Y}Z}{^{B}E}\right)_S = \left(\frac{^{X}Z}{^{A}E}\right)_T \cdot \frac{\left(\left(\frac{^{Y}Z}{^{X}Z}\right)_M - \left(\frac{^{Y}Z}{^{X}Z}\right)_T\right) \cdot \left(1 - \left(\frac{^{B}E}{^{A}E}\right)_M \cdot \left(\frac{^{A}E}{^{B}E}\right)_S\right)}{\left(\left(\frac{^{B}E}{^{A}E}\right)_M - \left(\frac{^{B}E}{^{A}E}\right)_T\right) \cdot \left(1 - \left(\frac{^{Y}Z}{^{X}Z}\right)_M \cdot \left(\frac{^{X}Z}{^{Y}Z}\right)_S\right)} \tag{7}$$

2.1.3. Uncertainty estimation

The $(^{Y}Z/^{B}E)_S$ ratio uncertainty ($u[(^{Y}Z/^{B}E)_S]$, k = 1, Eq. (8)) was estimated by combining the uncertainties from each term of the DID equation (Eq. (7)) [20]. The terms of Eq. (7) were considered as not correlated, so no covariance terms are needed.

$$
\begin{aligned}
u^2\left(\left(\frac{{}^{Y}Z}{{}^{B}E}\right)_S\right) = {} & \left(\frac{\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M - \left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_T\right)\cdot\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M\cdot\left(\frac{{}^{A}E}{{}^{B}E}\right)_S - 1\right)}{\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M - \left(\frac{{}^{B}E}{{}^{A}E}\right)_T\right)\cdot\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M\cdot\left(\frac{{}^{X}Z}{{}^{Y}Z}\right)_S - 1\right)}\right)^2 \cdot u^2\left(\left(\frac{{}^{X}Z}{{}^{A}E}\right)_T\right) \\
& + \left(-\left(\frac{{}^{X}Z}{{}^{A}E}\right)_T \cdot \frac{\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M\cdot\left(\frac{{}^{A}E}{{}^{B}E}\right)_S - 1\right)}{\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M - \left(\frac{{}^{B}E}{{}^{A}E}\right)_T\right)\cdot\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M\cdot\left(\frac{{}^{X}Z}{{}^{Y}Z}\right)_S - 1\right)}\right)^2 \cdot u^2\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_T\right) \\
& + \left(\left(\frac{{}^{X}Z}{{}^{A}E}\right)_T \cdot \frac{\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M - \left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_T\right)\cdot\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M\cdot\left(\frac{{}^{A}E}{{}^{B}E}\right)_S - 1\right)}{\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M - \left(\frac{{}^{B}E}{{}^{A}E}\right)_T\right)^2\cdot\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M\cdot\left(\frac{{}^{X}Z}{{}^{Y}Z}\right)_S - 1\right)}\right)^2 \cdot u^2\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_T\right) \\
& + \left(-\left(\frac{{}^{X}Z}{{}^{A}E}\right)_T \cdot \left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M \cdot \frac{\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M - \left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_T\right)\cdot\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M\cdot\left(\frac{{}^{A}E}{{}^{B}E}\right)_S - 1\right)}{\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M - \left(\frac{{}^{B}E}{{}^{A}E}\right)_T\right)^2\cdot\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M\cdot\left(\frac{{}^{X}Z}{{}^{Y}Z}\right)_S - 1\right)}\right)^2 \\
& \cdot u^2\left(\left(\frac{{}^{X}Z}{{}^{Y}Z}\right)_S\right) \\
& + \left(\left(\frac{{}^{X}Z}{{}^{A}E}\right)_T \cdot \left(\frac{{}^{B}E}{{}^{A}E}\right)_M \cdot \frac{\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M - \left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_T\right)}{\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M - \left(\frac{{}^{B}E}{{}^{A}E}\right)_T\right)\cdot\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M\cdot\left(\frac{{}^{X}Z}{{}^{Y}Z}\right)_S - 1\right)}\right)^2 \\
& \cdot u^2\left(\left(\frac{{}^{A}E}{{}^{B}E}\right)_S\right) + \left(-\left(\frac{{}^{X}Z}{{}^{A}E}\right)_T \cdot \frac{\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M - \left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_T\right)\cdot\left(1 - \left(\frac{{}^{B}E}{{}^{A}E}\right)_T\cdot\left(\frac{{}^{A}E}{{}^{B}E}\right)_S\right)}{\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M - \left(\frac{{}^{B}E}{{}^{A}E}\right)_T\right)^2\cdot\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M\cdot\left(\frac{{}^{X}Z}{{}^{Y}Z}\right)_S - 1\right)}\right)^2 \\
& \cdot u^2\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M\right) + \left(\left(\frac{{}^{X}Z}{{}^{A}E}\right)_T \cdot \frac{\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_T\cdot\left(\frac{{}^{X}Z}{{}^{Y}Z}\right)_S - 1\right)\cdot\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M\cdot\left(\frac{{}^{A}E}{{}^{B}E}\right)_S - 1\right)}{\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M - \left(\frac{{}^{B}E}{{}^{A}E}\right)_T\right)\cdot\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M\cdot\left(\frac{{}^{X}Z}{{}^{Y}Z}\right)_S - 1\right)^2}\right)^2 \\
& \cdot u^2\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M\right)
\end{aligned}
\tag{8}
$$

2.2. Optimization of the double isotope dilution methodology

The DID methodology requires a parameters optimization to obtain the most accurate results: *i.e.* the minimal $({}^{Y}Z/{}^{B}E)_S$ relative uncertainty. Two different optimizations can be performed. The first optimization is needed if the spike solution (T) must be prepared using 2 CRMs. In this case, it is possible to optimize the proportion of each element in the spike solution (T) (κ parameter for element E and (1- κ) for element Z) and the proportion of the spike solution (T) in the mixture (M) (λ parameter). The second one is if the spike solution (T) containing both elements is already prepared or using a CRM solution commercially available. In this case the only parameter which can be optimized is the proportion of the spike solution (T) in the mixture (λ parameter).

2.2.1. Simultaneous optimization of λ and κ parameters for a spike solution prepared from two CRMs

The $(^{X}Z/^{A}E)_T$ ratio can be calculated as a function of the proportion of E and Z CRM in the spike (κ and (1-κ) parameters), amount concentrations and isotope abundances (Eq. (9)). Please note *(%A)*, *(%B)*, *(%X)* and *(%Y)* are the same in the CRM and in the spike, and will referred to as $(\%A)_T$, $(\%B)_T$, $(\%X)_T$ and $(\%Y)_T$, respectively.

$$\left(\frac{^{X}Z}{^{A}E}\right)_T = \frac{(1-\kappa)\cdot C(Z)_{CRM_Z}\cdot(\%X)_T}{\kappa\cdot C(E)_{CRM_E}\cdot(\%A)_T} \tag{9}$$

The $(^{B}E/^{A}E)_M$ ratio can be calculated as a function the proportion of E CRM in the spike (κ parameter), the proportion of spike in the mixture (λ parameter), amount concentrations and isotope abundances (Eq. (10)).

$$\left(\frac{^{B}E}{^{A}E}\right)_M = \frac{\lambda\cdot\kappa\cdot C(E)_{CRM_E}\cdot(\%B)_T + (1-\lambda)\cdot C(E)_S\cdot(\%B)_S}{\lambda\cdot\kappa\cdot C(E)_{CRM_E}\cdot(\%A)_T + (1-\lambda)\cdot n(E)_S\cdot(\%A)_S} \tag{10}$$

The $(^{Y}Z/^{X}Z)_M$ ratio can be calculated by the same way using Eq. (11).

$$\left(\frac{^{Y}Z}{^{X}Z}\right)_M = \frac{\lambda\cdot(1-\kappa)\cdot C(Z)_{CRM_Z}\cdot(\%Y)_T + (1-\lambda)\cdot C(Z)_S\cdot(\%Y)_S}{\lambda\cdot(1-\kappa)\cdot C(Z)_{CRM_Z}\cdot(\%X)_T + (1-\lambda)\cdot C(Z)_S\cdot(\%X)_S} \tag{11}$$

By introducing Eqs. (9), (10) and (11) in Eqs. (7) and (8), the $(^{Y}Z/^{B}E)_S$ ratio relative uncertainty ($u_r[(^{Y}Z/^{B}E)_S]$) can be expressed as a function of λ and κ (Eq. (12)).

$$u_r\left(\left(\frac{^{Y}Z}{^{B}E}\right)_S\right) = f(\lambda,\kappa) \tag{12}$$

Finding the λ and κ optimal parameters is simply a matter of locating the minimal relative uncertainty of the $(^{Y}Z/^{B}E)_S$ ratio. It helps obtaining the most accurate result. The $(^{B}E/^{A}E)_M$ and $(^{Y}Z/^{X}Z)_M$ optimal mixture isotope ratios are then calculated by introducing optimal λ and κ parameters in Eqs. (10) and (11).

It is possible to plot the function described in Eq. (12) to study the variation of the relative uncertainty as a function of λ and κ. An example of this plot, hereafter referred to as a contour plot, is showed in Fig. 2. The contours are spaced out with intervals of

1 % of the optimal relative uncertainty. The plot is cut off so that only contours within 20 % of the minimal error are shown. The contour plot is useful to show how robust the optimal parameters are. In fact, the sample amount concentration ($c(E)_S$) and $c(Z)_S$) are generally not accurately known. It can be provided by different sources: neutronic simulation code, fast analytical technic like UV/Vis spectrometry or L-line X-ray fluorescence or estimated using the results from previous experiments. It is difficult to mix the sample and the spike with the exact and optimal proportions. So, it is important to understand how the error of the relative uncertainty varies around the λ and κ optimal parameters.

2.2.2. Optimization of the λ parameter for a spike solution already prepared or commercially available

If the homemade spike is already prepared or if using a commercially available spike, the κ parameter is a fixed characteristic of the spike and does not need to be optimized: in others words the $({}^{X}Z/{}^{A}E)_T$ ratio is known. The λ parameter can only be optimized to obtain the minimal $({}^{Y}Z/{}^{B}E)_S$ ratio relative uncertainty.

The $({}^{B}E/{}^{A}E)_M$ ratio can be calculated depending on E and Z element amount concentration in the spike, the proportion of spike in the mixture (λ parameter), sample amount and isotope abundances (Eq. (13)).

$$\left(\frac{{}^{B}E}{{}^{A}E}\right)_M = \frac{\lambda \cdot C(E)_T \cdot (\%B)_T + (1-\lambda) \cdot C(E)_S \cdot (\%B)_S}{\lambda \cdot C(E)_T \cdot (\%A)_T + (1-\lambda) \cdot C(E)_S \cdot (\%A)_S} \tag{13}$$

In the same way, the $({}^{Y}Z/{}^{X}Z)_M$ ratio can be calculated (Eq. (14)).

$$\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M = \frac{\lambda \cdot C(Z)_T \cdot (\%Y)_T + (1-\lambda) \cdot C(Z)_S \cdot (Y)_S}{\lambda \cdot C(Z)_T \cdot (\%X)_T + (1-\lambda) \cdot n(Z)_S \cdot (\%X)_S} \tag{14}$$

By introducing Eq. (13) and (14) in Eq. (7) and (8), the $({}^{Y}Z/{}^{B}E)_S$ ratio relative uncertainty as a function of λ is calculated (Eq. (15)).

$$u_r\left(\left(\frac{{}^{Y}Z}{{}^{B}E}\right)_S\right) = f(\lambda) \tag{15}$$

Finding the λ optimal value is simply a matter of locating the minimal relative uncertainty of the sample $^{Y}Z/^{B}E$ ratio. The $(^{B}E/^{A}E)_M$ and $(^{Y}Z/^{X}Z)_M$ optimal ratio are then calculated by introducing the optimal λ in Eq. (13) and (14). To understand how the error varies around the λ optimal value, the error of the relative uncertainty as a function of λ can be drawn.

2.3. Script

All the calculation were implemented in a script written with the open source software Octave [21], version 5.1.0. To start the script, unzip the "double_ID_optimization.zip" file available in the supplementary materials. Start Octave software and set the browser directory to the appropriate folder where the unzipped folder is located. Starting the script is performed by typing "startup_DID" in the Octave command window. Then, the script allows to select which parameters need to optimized: simultaneous optimization of λ and κ parameters or optimization of the λ parameter. Then, all parameters, including the choice of elements and isotopes, must be selected. The default parameters can be modified in the "private\default_value_data_double_ID.m" file. Once the calculation is complete, the optimal parameters, including the optimal mixture isotope ratios, are displayed in the Octave command windows. The plot are also displayed. The plot can be saved as a 8 cm × 8 cm ".png" file. The results and the raw data can be saved in a ".txt" file.

2.4. Experimental

As concrete examples, experiments performed on samples from the DIAMINO irradiation were considered in details [4, 22]. The DIAMINO irradiation was an analytical irradiation experiment performed on $UAmO_2$ discs to study their behaviors under irradiation, to determine the americium transmutation yield and to study the influence of the microstructure on the gas release as a function of temperature. Among the determinations, $^{238}Pu/^{238}U$, $^{241}Am/^{238}U$ and $^{148}Nd/^{238}U$ ratios were of prime interest. In these examples, $^{238}Pu/^{238}U$ and $^{148}Nd/^{238}U$ ratios were investigated in more details. Thus, element Z can be Pu and Nd alternatively. The first element E was chosen as

uranium as it is usually used as reference in the nuclear field. Its reference isotope is $^{B}E = {}^{238}U$.

All theoretical investigations were performed on the same sample (DIAMINO sample [4, 22]). The characteristics of the sample have been summarized in Table 1. The isotope ratios, abundances and uncertainties of the sample were determined in previous studies [4, 22]. The U and Pu amount concentration of the sample were estimated using a L-line X-ray fluorescence analysis located in a shielded line [23]. It is a non-destructive, non-invasive and relatively fast technique giving the actinide amount concentration with an uncertainty of about 10 %. This measurement is important to obtain a reliable estimation of the U and Pu amount concentration in the sample before implementing the DID. The Nd amount concentration was estimated using a neutronic simulation code as Nd cannot be measure using L-line X-ray fluorescence analysis.

The mixture isotope ratios relative uncertainties ($u_r[({}^{B}E/{}^{A}E)_M]$ *and* $u_r[({}^{Y}Z/{}^{X}Z)_M]$) were set at 0.07% (k = 1), corresponding to the International Target Value (ITV) for a $^{238}U/^{235}U$ isotope ratio of about 1 [24].

3. Results and discussion

3.1. Simultaneous optimization of λ and κ parameters

For such case, κ is plotted versus λ, and a contour plot is presented with each line representing a 1 % variation of the minimal relative uncertainty.

3.1.1. $^{238}Pu/^{238}U$ ratio determination

In the first case, the spike is manufactured from two uranium and plutonium CRM. The reference uranium and plutonium isotope of the sample is ^{238}U (*i.e.* $^{B}E = {}^{238}U$) and ^{238}Pu (*i.e.* $^{Y}Z = {}^{238}Pu$), respectively. The natural choice to prepare the uranium spike is a CRM enriched with ^{233}U or ^{235}U isotope (*i.e.* $^{A}E = {}^{235}U$ or ^{233}U). For plutonium, a CRM enriched with ^{242}Pu isotope is a good choice to prepare the spike (*i.e.* $^{X}Z = {}^{242}Pu$).

3.1.1.1. Solutions enriched with ^{235}U and ^{242}Pu isotopes

In this first example, the U CRM, enriched in ^{235}U (*i.e.* $^{A}E = {}^{235}U$), was the IRMM 054 CRM provided by the Joint Research Centre of the European Commission (EC-JRC). This U CRM was diluted gravimetrically to obtain a uranium mass fraction near 10 µg g^{-1}. The Pu CRM, enriched in ^{242}Pu isotope (*i.e.* $^{X}Z = {}^{242}Pu$), was the IRMM 049d CRM provided by EC-JRC. This Pu material was diluted gravimetrically to obtain a plutonium mass fraction near 5 µg g^{-1}. The characteristics of the CRM, with the appropriate notation, are summarized by example 1 in Table 1. The optimal λ and κ parameters were 0.84 and 0.30, respectively. This corresponds to $(^{B}E/^{A}E)_{M}$ and $(^{Y}Z/^{X}Z)_{M}$) ratios measured at 3.49 and 0.0769, respectively. The contour plot is represented in Fig. 2. In this example, the optimal parameters are quite robust as the relative uncertainty surface is flat: there are a wide range of λ and κ values that are within 1 % of the minimal relative uncertainty. It is easy to manufacture the spike and the mixture without the risk to lose the measurement accuracy. The minimal relative uncertainty was estimated to 0.17 % (k = 1). This uncertainty corresponds to the uncertainty linked to the DID uncertainty (Eq. (8)) and does not take into account the repeatability.

3.1.1.2. Solutions enriched with ^{233}U and ^{242}Pu isotopes

As second example the uranium CRM used was a CRM enriched in ^{233}U isotope (*i.e.* $^{A}E = {}^{233}U$): the IRMM-051 CRM. The CRM characteristics for example 2 are summarized in Table 1. All the other parameters are the same as in example 1 (Pu CRM and sample characteristics). Using a uranium CRM enriched in ^{233}U isotope is interesting as the sample generally contains no ^{233}U isotope: $(\%A)_s = 0$ and $u(AB_S) = 0$. The optimal λ and κ parameters were calculated using the data in example 2 in Table 1. However, in such case, the simultaneous optimization of λ and κ cannot work for mathematical reasons. Indeed, the κ parameter approaches 0, which makes no sense: it is impossible to compute the $(^{Y}Z/^{B}E)_{S}$ ratio with a spike containing no U element. However, the plot in Fig. 3, helps finding the optimal λ and κ parameters. The surface where the relative uncertainty is within 1 % of the minimal relative uncertainty is relatively flat: in this central surface, the relative uncertainty is between 0.1380 % and 0.1394 % (k = 1). Graphically, it exists a lot of λ and κ parameters pairs for the best conditions: one pair, presented in Fig. 3, could be λ = 0.8 and κ = 0.2. Thus, when the

major isotope of a spike is not present in the sample, the λ and κ optimal parameters can be determined graphically.

3.1.2. $^{148}Nd/^{238}U$ ratio determination

In this example, the optimal parameters for the determination of the $^{148}Nd/^{238}U$ ratio were studied (example 3 in Table 1). The laboratory has already prepared a homemade characterized Nd material [4]: this Nd material solution was prepared by dissolving a ^{150}Nd enriched (95%) non-radioactive neodymium oxide powder in 3 mol L^{-1} HNO_3. The Nd mass fraction of the Nd material is about 7.5 µg g^{-1} ($c(Z_T) = 0.0499\times10^{-6}$ mol g^{-1}). The U CRM, enriched in ^{235}U isotope, is the IRMM 054 CRM. The characteristics of the material and the sample are summarized in example 3 in Table 1.

The optimal λ and κ parameters were 0.59 and 0.994, respectively. The optimal parameters indicates that the spike must contain mostly U (only 0.06 % of Nd material in the spike). The contour plot is represented in Fig. 4.a. In this example, the optimal values is not robust as the relative uncertainty surface is not flat. It exist a small region around the κ and λ values to obtain the minimal uncertainty. A small error on the spike preparation will have a large impact on the relative uncertainty. In this case, diluting the Nd material would help obtaining more robust parameters.

So, the λ and κ parameters were optimized again using a Nd material diluted 100-fold: the Nd mass fraction is about 0.075 µg g^{-1} ($c(Z_T) = 0.0499\times10^{-8}$ mol g^{-1}). All of the other parameters were unchanged (example 3 in Table 1). The optimal λ and κ parameters were calculated and are 0.69 and 0.61, respectively. The contour plot is represented in Fig. 4.b. The optimum is now robust as the relative uncertainty surface is flat: there are a wide range of λ and κ values that are within 1 % of the minimal relative uncertainty. It is now easier to mix the U and Nd materials to obtain the appropriate spike. With these optimal parameters, the $(^{B}E/^{A}E)_M$ and $(^{Y}Z/^{X}Z)_M$ mixture ratio were 4.10 and 0.0117, respectively. The minimal uncertainty was estimated to 0.30 % (k = 1).

3.2. Optimization of the λ parameter

In this example a spike enriched in both elements that was already prepared or using a CRM is used (example 4 in Table 1). The IRMM 046c CRM, provided by EC-JRC was used in this example. It is a spike solution enriched in both ^{233}U and ^{242}Pu isotopes. Uranium and plutonium amount concentrations and isotope abundances of the spike are certified (see Table 1): that means the κ parameter cannot be optimize and only the λ parameter can in such case. Thus, the error for the $^{238}Pu/^{238}U$ ratio relative uncertainty as a function of λ is plotted.

In this example, the minimal relative uncertainty was found for λ = 0.14. The minimal uncertainty was estimated to 0.11 % (k = 1). This corresponds to $(^{B}E/^{A}E)_M$ and $(^{X}Z/^{Y}Z)_M$ ratios measured at 0.288 and 0.180, respectively. The error for the $^{238}Pu/^{238}U$ ratio relative uncertainty as a function of λ is shown in Fig. 5.a. In this theoretical study, the relative uncertainty is almost stable around the optimal λ parameter but only for λ values higher than the λ optimal parameter. For λ values lower than the optimal λ parameter, the relative uncertainty increases rapidly. As the uranium and plutonium amount concentration is generally not known accurately, there is a high risk to degrade the accuracy measurement when performing the sample spike mixture. As the dilution have no impact on the $(^{X}Z/^{A}E)_T$ ratio uncertainty, it will be interesting to dilute the spike to obtain a more robust optimal λ parameter.

The λ parameter was optimized using the IRMM-046c CRM diluted 10-fold: $c(E_T) = 4.4742\times10^{-7}$ mol g^{-1} and $c(Z_T) = 0.37519\times10^{-7}$ mol g^{-1}. All the others parameters were the same as example 4 in Table 1: similarly, the $^{Y}Z/^{A}E$ ratio of the spike remains constant whatever the dilution factor. The optimal λ parameter is now equal to 0.62. As expected, the minimal relative uncertainty remains constant (0.11 %, k = 1) as the dilution does not affect the isotope ratio. The error for the relative uncertainty as a function of λ is shown in Fig. 5.b. The λ parameter is now more robust: the relative uncertainty is stable around the optimal λ parameter. There are a wide range of λ values corresponding to the minimal relative uncertainty.

4. Conclusion

The DID is a powerful method to determine two isotopes ratio of two elements present in a sample, with one of them used as a reference. As it is only based on isotope ratio

measurement, accurate measurements can be obtained. To obtain the best performance, the parameters must be set carefully, especially the spike production and the (sample – spike) mixture. This work comes along whit a piece of code that can be found in the supplementary material, to easily calculate the optimal parameters. The source code is freely available and can be modified if needed by individual users.

Table

Table 1: Parameters used for the theoretical study to find the optimal parameters of the DID. The relative uncertainty are expressed with a coverage factor at k = 1

Example	1	2	3	4
Ratio of interest	$^{238}Pu/^{238}U$	$^{238}Pu/^{238}U$	$^{148}Nd/^{238}U$	$^{238}Pu/^{238}U$
Element 1 (E)	U	U	U	U
Element 2 (Z)	Pu	Pu	Nd	Pu
^{A}E isotope (spike major isotope)	^{235}U	^{233}U	^{235}U	^{233}U
^{B}E isotope (sample reference isotope)	^{238}U	^{238}U	^{238}U	^{238}U
^{X}Z isotope (spike major isotope)	^{242}Pu	^{242}Pu	^{150}Nd	^{242}Pu
^{Y}Z isotope (sample reference isotope)	^{238}Pu	^{238}Pu	^{148}Nd	^{238}Pu
CRM	U: IRMM 054 Pu: IRMM 49d	U: IRMM 051 Pu: IRMM 49d	U: IRMM 054 Nd: ^{150}Nd material	IRMM 46c
$(\%B)_T$	5.4102 %	0.8042 %	5.4102 %	0.2099 %
$(\%A)_T$	93.176 %	98.0430 %	93.176 %	99.763 %
$C(E)_{CRM\ or\ T}$	0.0404×10^{-6}	0.10303×10^{-6}	0.0404×10^{-6}	4.4742×10^{-6}
$u_r\left(\left(\frac{^{B}E}{^{A}E}\right)_T\right)$	0.0300 %	0.122 %	0.0300 %	0.000927 %
$(\%Y)_T$	0.50446 %	0.50446 %	0.93850 %	0.50446 %
$(\%X)_T$	94.622 %	94.622 %	94.745 %	94.622 %
$C(Z)_{CRM\ or\ T}$	0.0183×10^{-6}	0.0183×10^{-6}	0.0499×10^{-6}	0.37519×10^{-6}
$u_r\left(\left(\frac{^{Y}Z}{^{X}Z}\right)_T\right)$	0.0646 %	0.0646 %	0.170 %	0.00204 %
$u_r\left(\left(\frac{^{X}Z}{^{A}E}\right)_T\right)$	0.136 %	0.0924 %	0.282 %	0.0227 %
$(\%B)_S$	99.310 %	99.310 %	99.310 %	99.310 %
$(\%A)_S$	0.45640 %	0	0.45640 %	0
$C(E)_S$	0.209×10^{-6}	0.209×10^{-6}	0.209×10^{-6}	0.209×10^{-6}
$u_r\left(\left(\frac{^{A}E}{^{B}E}\right)_S\right)$	0.138 %	0	0.138 %	0
$(\%Y)_S$	74.010 %	74.010 %	10.447 %	74.010 %
$(\%X)_S$	15.745 %	15.745 %	6.308 %	15.745 %
$C(Z)_S$	0.0141×10^{-6}	0.0141×10^{-6}	0.000569×10^{-6}	0.0141×10^{-6}
$u_r\left(\left(\frac{^{X}Z}{^{Y}Z}\right)_S\right)$	0.0994 %	0.0994 %	0.261 %	0.0994 %

$u_r\left(\left(\frac{{}^{B}E}{{}^{A}E}\right)_M\right)$	0.07 %	0.07 %	0.07 %	0.07 %
$u_r\left(\left(\frac{{}^{Y}Z}{{}^{X}Z}\right)_M\right)$	0.07 %	0.07 %	0.07 %	0.07 %

Figure

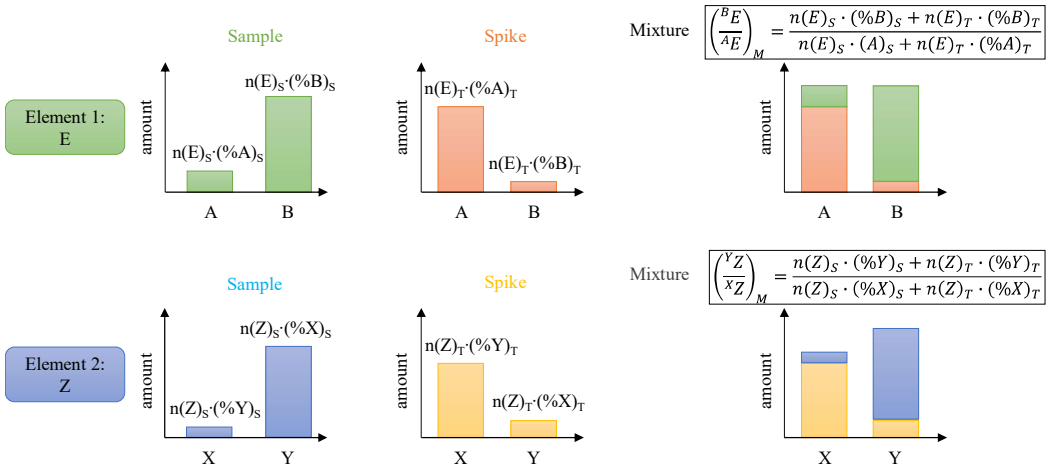

Fig. 1: Schematics of the DID methodology

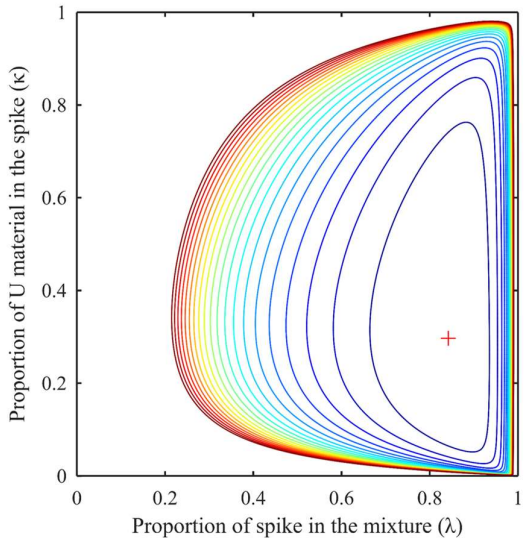

Fig. 2: Contour plot of error for the relative uncertainty of the sample $^{238}Pu/^{238}U$ ratio using U (IRMM-054) and Pu (IRMM-049d) CRM (example 1 in Table 1). The optimum is marked by the cross. The plot is cut off so that only contours within 20 % of the minimal error are shown. The contours are spaced out with intervals of 1 % of the minimal error

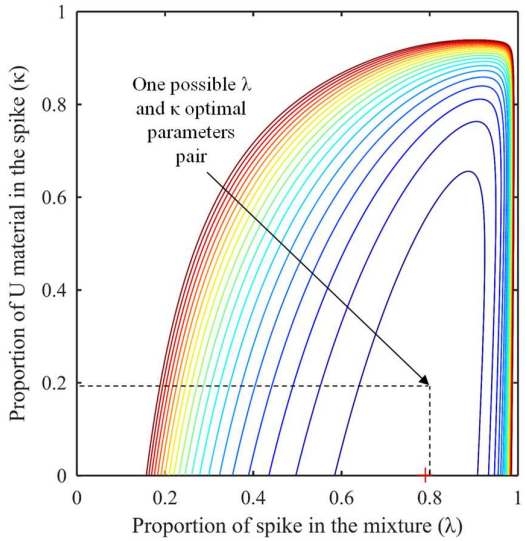

Fig. 3: Contour plot of error for the relative uncertainty of the sample $^{238}Pu/^{238}U$ ratio using U (IRMM-051) and Pu (IRMM-49d) CRM (example 2 in Table 1). The optimum is marked by the cross. The plot is cut off so that only contours within 20 % of the minimal error are shown. The contours are spaced out with intervals of 1 % of the minimal error

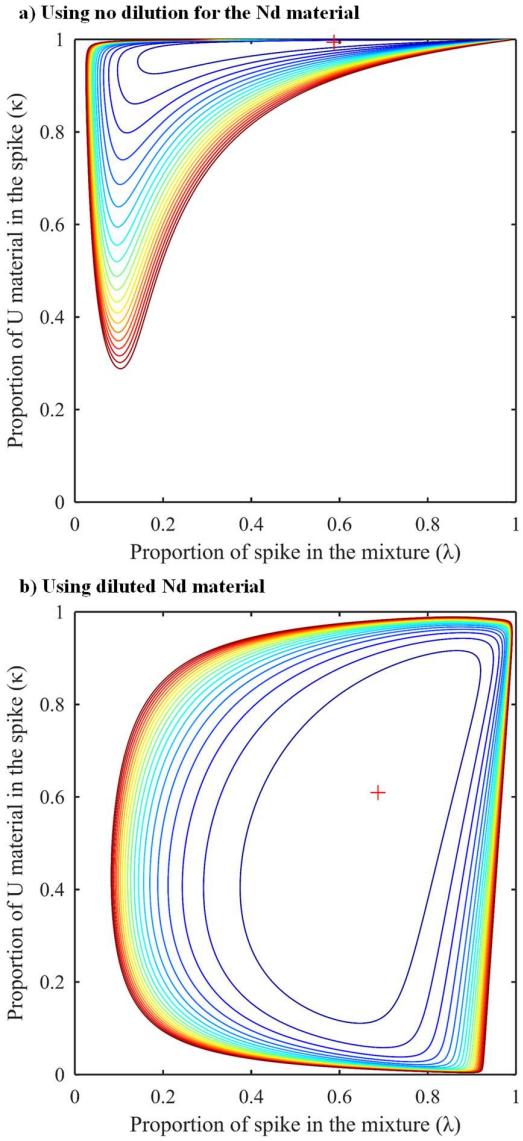

Fig. 4: Contour plot of error for the relative uncertainty of the sample $^{148}Nd/^{238}U$ ratio using U CRM (IRMM 054) and no diluted (a) and diluted (b) Nd material (example 3 in Table 1). The plot is cut off so that only contours within 20 % of the minimal error are shown. The contours are spaced out with intervals of 1 % of the minimal error

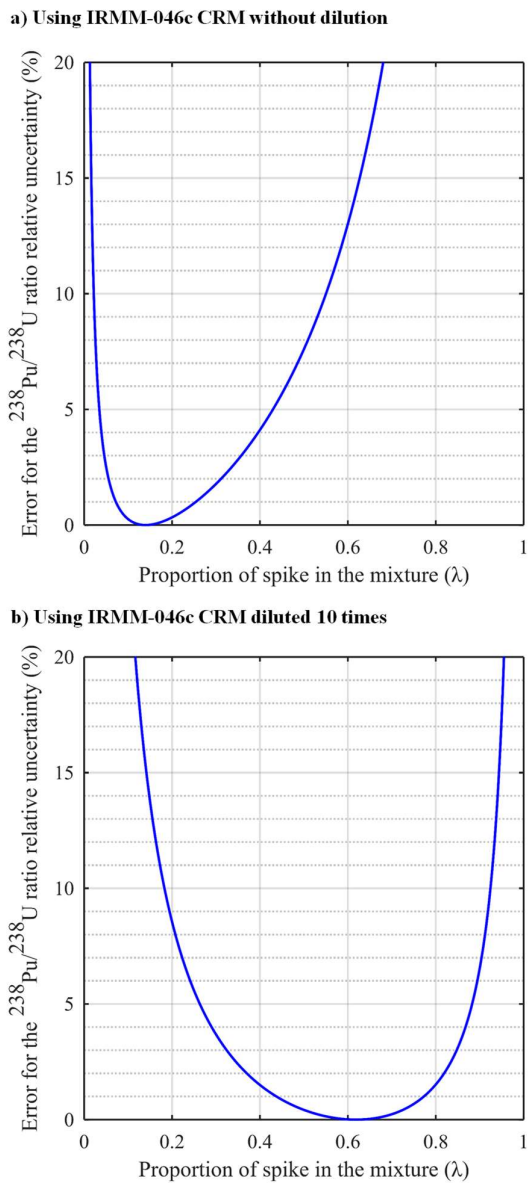

Fig. 5: Error for the $^{238}Pu/^{238}U$ ratio relative uncertainty (%, k = 1) as a function of λ parameter using the IRMM-046c CRM without dilution (a) and diluted 10-fold (b)

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