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# Guideline on Isotope Dilution Mass Spectrometry

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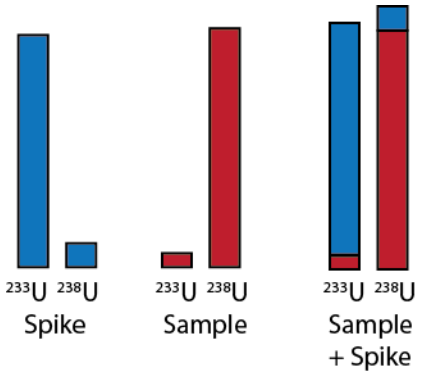
## Executive Summary

Isotope dilution mass spectrometry is used to determine the concentration of an element of interest in a bulk sample. It is a destructive analysis technique that is applicable to a wide range of analytes and bulk sample types. With this method, a known amount of a rare isotope, or 'spike', of the element of interest is added to a known amount of sample. The element of interest is chemically purified from the bulk sample, the isotope ratio of the spiked sample is measured by mass spectrometry, and the concentration of the element of interest is calculated from this result. This method is widely used, although a mass spectrometer required for this analysis may be fairly expensive.

## Introduction

Isotope dilution mass spectrometry is a destructive analysis method for the concentration determination of an element of interest in a bulk sample. In this method, a precisely known amount of a rare isotope of the element of interest, commonly called a 'spike' or 'tracer', is added to the bulk sample. The spiked sample is homogenized, and for most applications, the element of interest is chemically purified from the bulk sample. The isotope ratio of the spiked sample is measured by mass spectrometry, and the analyte concentration is calculated from this isotope ratio. Although it optimal to use a spike that is highly pure, with a spike isotope abundance > 99%, in practice many isotope spikes are less pure. Conversely, the spike isotope may also be present in the sample.

For example, with an isotope dilution assay of U using a $^{233}$U spike, the measured $^{233}$U/$^{238}$U (at./at.) of the spiked sample will reflect a mixture of the $^{233}$U/$^{238}$U (at./at.) of the spike with the $^{233}$U/$^{238}$U (at./at.) of the sample:




$$\left(\frac{^{233}U}{^{238}U}\right)_{measured} = \frac{^{233}U_{sample} + ^{233}U_{spike}}{^{238}U_{sample} + ^{238}U_{spike}} \qquad (1)$$

**Figure 1.** Illustration of the principle of isotope dilution: the measured isotope ratio of the spiked sample is a combination of the isotope ratio of the spike and the isotope ratio of the sample. $^{233}U$ and $^{238}U$ are the numbers of atoms.

The concentration of U in the bulk sample is then calculated from the measured $^{233}U/^{238}U$ atom ratio, and the known amounts of isotope tracer, the amount of bulk sample used, and the independently measured isotopic composition of U in the bulk sample. In this example, the concentration of U in the bulk sample is given with the following expression.

$$^{total}U_{sample} = {}^{total}U_{spike} \frac{X^{233}_{spike} - \left(\frac{^{233}U}{^{238}U}\right)_{measured} \left(X^{238}_{spike}\right)}{\left(\frac{^{233}U}{^{238}U}\right)_{measured} \left(X^{238}_{sample}\right) - X^{233}_{sample}} \qquad (2)$$

where $^{233}U$ and $^{238}U$ are numbers of atoms in the spike or sample aliquots used for analysis, X represents the atom fraction of a given U isotope in the sample or spike, and $^{total}U$ represents the total number of atoms of U in the sample or spike aliquot used for the analysis. The total number of U atoms in the sample aliquot is converted to the U assay of the sample using the weight of the sample solution taken for analysis, and the g sample/g solution determined from sample and serial dilution weights.

**Use for Nuclear Forensics**

The assay of U or Pu in a bulk material, or the concentration of trace constituents in a bulk material, are important characteristics of a material. For example, the U assay of a material reveals whether the material is pure U-metal, $UO_2$, $U_3O_8$ or some other U compound. Isotope dilution mass spectrometry may also be used to quantify the impurity levels of trace actinides (e.g., Th, Pa, Pu, U) that are present in a sample of bulk U or Pu. These impurity concentrations may be a signature of the material. Impurities determined by IDMS may also be used to calculate daughter/parent ratios of radionuclides, which, in turn, may be used to calculate a radiochronometric model age, which is also an important forensic signature of a material.

**Sample Requirements**

This method is applicable to assay of U in bulk U metal, oxide, ore concentrate, or other U compound, and assay of Pu in bulk Pu metal, oxide, or other Pu compound. It is also applicable to the assay of trace constituents (e.g., Th, Am, Pa, etc..) in bulk U or Pu. After addition of the spike to the sample, complete equilibration and homogenization of the spike with sample is essential. Chemical purification of the element of interest prior to analysis is necessary for any application other than U assay in high-purity U metal or U oxide. Quantitative recovery of the element if interest is not required.

Initial dissolution of >250 mg of bulk sample is recommended to minimize uncertainty associated with sample weighing. Less than 10 ng of the element of interest are required for IDMS analysis; therefore bulk samples may require serial gravimetric dilution to achieve a reasonable sample solution concentration. For other materials where the analyte is a trace constituent, larger amounts of bulk sample, on the order of several mg, may be processed for analysis. The optimal spike-sample ratio may be calculated to minimize the error magnification factor for the measurement; uncertainty is maximized when the isotope ratio of the sample-spike mixture approaches the isotope ratio of either the pure spike or the pure sample

**Pros and Cons of the Technique**

Pros:

- A small amount of sample is consumed relative to titration assay methods
- The method offers the most precise assay results for elements that are minor or trace constituents of the bulk sample.
- Because the concentration is calculated from an isotope ratio, the method does not rely upon quantitative recovery of the analyte from chemical purification or other chemical processing.
- IDMS is applicable to analytes of a wide range of concentrations in the bulk sample; it may be used for assay of bulk U or Pu materials, and also for concentration analysis of ultra-trace impurities, present in the bulk material at parts per billion or lower concentrations.

Cons:

- Requires calibrated spikes for all elements to be measured
- Chemical purification is required for most applications
- A large quantity of sample (> 250 mg) is required for initial dissolution in order to minimize uncertainty associated with weighing.

**FAQ**

- This analysis technique requires a mass spectrometer, and the precision of this method is directly related to the precision of the isotope ratio measurement. Therefore, a

magnetic-sector single-collector or multi-collector instrument is necessary for optimal precision. Instrument cost ranges from ~$550k for a SC-ICPMS to ~$1M for a MC-ICP-MS or MC-TIMS.

- This method requires calibrated isotope tracers; these may be purchased from a metrology institute, or calibrated 'in-house' using a traceable concentration standard material. The calibration data for the isotope spike must include the atoms of spike isotope per gram of spike solution, and the isotopic composition of the spike. The precision of the assay result reflects the precision of the spike calibration.

- Independent measurement of the isotopic composition of the element of interest in the sample is necessary. Generally this measurement is made on an unspiked aliquot of the sample.

- A high-precision analytical balance is required for obtaining weights of sample and spikes.

- Routine analysis of quality control material is recommended.

**Useful References**

De Bièvre, P. and Peiser, H. S. (1997) Basic equations and uncertainties in isotope-dilution mass spectrometry for traceability to SI of values obtained by this primary method. *Fresenius J Anal Chem* v. 359, P. 523-525.

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