Multi-element Isotope Dilution Analyses Using ICP-MS

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Introduction

Since separated isotopes became commercially available nearly fifty years ago, isotope dilution (ID) mass spectroscopy has provided definitive chemical concentration analyses [1-3]. Compared with other standardization methods, ID achieves high analytical sensitivity, precision and accuracy. It is a critical methodology for research in biochemistry, nuclear physics and geochemistry. Traditionally, thermal ionization mass spectroscopy dominated inorganic ID analysis. The emergence of plasma source, quadrupole mass spectroscopy, ICP-MS, expands the application of isotope dilution methodology [4-6]. Versatile sample introduction, uniform degrees of ionization, and good precision isotope ratio data are key ICP-MS attributes.

Presently, thirty seven elements ranging from light elements (Li, B) through transition metals, noble, rare (REE) and heavy elements, to actinide and transuranic (Pu, Am, Cm) elements are measured by isotope dilution at LLNL. Projects range from geologic and hydrologic to biologic. The research goal is to measure accurately many elements present in diverse matrices at low abundance ($\leq$ppb) using isotope dilution methods instead of ion intensity calibration and aqueous dilution. This paper discusses technical issues and benefits associated with multi-element ID-ICP mass spectroscopic measurements.

Caveat

The success of multi-element isotope dilution ICP-MS depends on using mass spectrometric techniques that require more instrument set-up and calibration than routine ion intensity calibration. Important parameters include detector linearity and deadtime, mass resolution, mass bias, background, and data acquisition strategy. Thorough review is described elsewhere [7]. Also, available and affordable separated isotopes are essential and can be the major drawback. Often ID-ICP-MS is used to measure very low element abundances ($\leq$ppb) in complex matrices such as saline ocean water. In this instance, both separation chemistry and cleanroom facilities are necessary. Clearly, isotope dilution will not supplant other ICP-MS standardization methods, nor should it. ID-ICP-MS fills an important niche in inorganic mass spectrometry linking high precision mass spectrometry and bulk elemental analyses.

Advantages and Concerns

Major advantages of ID methods are accuracy, elimination of ion intensity calibration inaccuracy due to matrix effects and drift, and quantitation for samples that require chemical processing. Chemical pre-concentration removes interfering matrices and improves method detection levels. Isotope dilution reduces the need to quantify chemical yield. Accuracy of ID-ICP-MS methods depends on tracer isotope calibration, tracer-sample isotopic equilibration, and appropriate background, isobaric, and mass bias corrections. Propagation of isotope ratio error due to improper tracer isotope addition is a major concern with multi-element analyses when abundances vary widely. Optimization of the amount of tracer isotope requires estimating element abundance in the sample.

Mass Bias

Isotope ratios measured with ICP-MS deviate from absolute values. Mass bias varies with instrument type, operating conditions and element analyzed. In general, heavier isotopes are preferentially transmitted to the analyzer. Mass bias is due to plasma gas dynamics and sampling interface space charge effects [8]. Unlike thermal ionization mass fractionation, ICP-MS mass bias is time independent, provided gas dynamics and electronic settings are stable, and similar to precision of replicate measurements ($\leq$1-2 %/amu). Yet, for multi-element ID-ICP-MS, mass bias uncertainty can be a significant source of inaccuracy [9]. Figure 1 shows mass bias for solutions with known isotope abundance that were measured with the ICP-MS optimized for indium. Mass bias for multi-elements varies about 6% from preferential light isotope (i.e., Cu) to heavy isotope (Rb) bias.

Mass bias correction is possible during ICP-MS measurements using external or internal normalization. Mass bias can be determined using standards with known isotope abundance, such as NIST SRM's including the uranium isotopic standards. An example of routine mass bias determination and correction for U isotopes is shown in Figure 2. Here, mass bias during the analysis period is measured repeatedly using NIST U-500 standard. Mass bias corrected ratios for another standard, NIST U-005 validate accuracy of the approach (Figure 2).

Other correction methods include 1) internal normalization using two isotopes for elements having three or more stable isotopes (i.e., Zn, Ba), 2) internal normalization using double spiking techniques, and 3) internal normalization using a surrogate element with similar mass (i.e., Ga for Zn, and Tl for Pb). The latter correction can be misleading for quadrupole ICP-MS given mass bias results shown in Figure 1.

Figure 1: Mass bias for solutions with known isotope abundance; ●, NIST SRM; □, ORNL isotopes.

Figure 2: Yearly data for NIST uranium isotope standard, U-005. Data are corrected for mass bias using NIST U-500 measurements.

Applications

Though ID-ICP-MS plays a significant role in many fields, the clearest applications demonstrating the strength of the method are in marine chemistry (see [10] for review). Nearly fifty elements of interest are present at extremely low concentration, less than part-per-billion, in a saline matrix dominated by eleven elements. All saline water measurement techniques, AAS to TIMS, require pre-concentration and separation chemistry. The advantages of ID-ICP-MS compared with other techniques are precision, accuracy, method sensitivity, sample throughput and multi-element versatility.

We are pursuing active research studies using trace element and isotope characterization in various hydrologic and coastal ocean projects. Recently we developed a technique for separating and measuring simultaneously eight rare earth elements (REE) in natural waters using ID-ICP-MS [11]. Typically, REE in open ocean waters are less than one part-per-trillion. Results for triplicate measurement of saline waters shown in Figure 3 are similar to data using instrumental neutron activation analyses (INAA) and ID-TIMS. Precisions for REE abundances between 0.1-1.7 pg/g are 2-10% RSD.
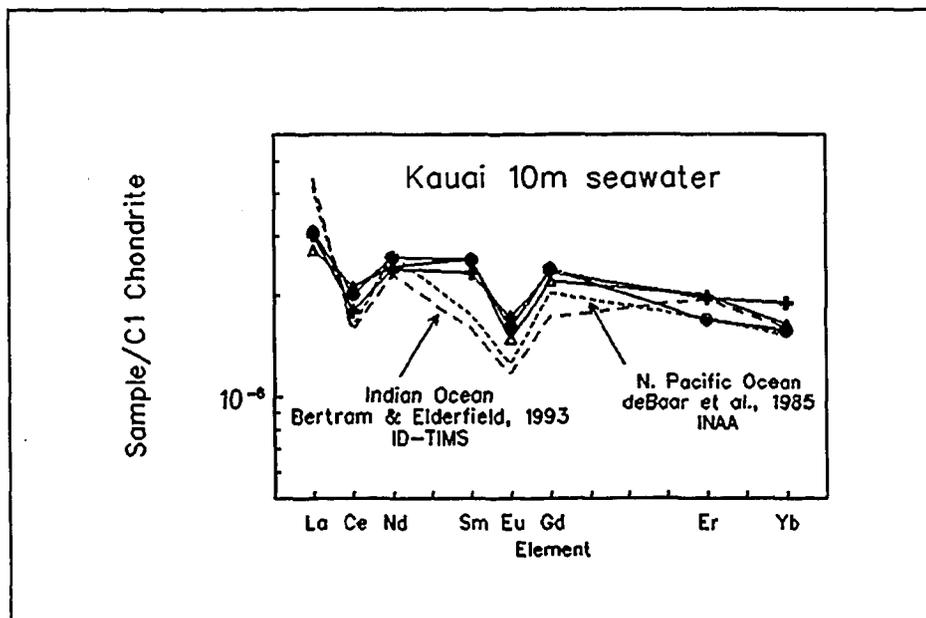

Figure 3:   Triplicate REE measurement of N. Pacific seawater compared with ID-TIMS and INAA.

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