

019600-736

High Accuracy Determination of Trace Elements in NIST Standard Reference Materials by Isotope Dilution ICP-MS

Paul J. Paulsen and Ellyn S. Beary
Inorganic Analytical Research Division
Chemical Science and Technology Laboratory
National Institute of Standards and Technology, Gaithersburg, MD, 20899

Introduction

Isotope dilution mass spectrometry (IDMS) has been used for the certification of Standard Reference Materials (SRMs) at the National Institute of Standards and Technology (NIST) for more than 25 years. Since 1986, ICP-MS isotope dilution has had a dominant role in the certification process. The new generation of ICP mass spectrometers is capable of ratio measurement precisions of about 0.1% rsd.

Optimization of Ratio Measurements

Accuracy in ICP-MS ID equal to the precision of ratio measurement requires attention to the ion multiplier setup, calibration and use; mass bias drift correction; minimization of memory from previous samples; and most critically, the removal of interferences caused by molecular ions.

A generic plot for a continuous dynode multiplier in the ion count mode indicates a constant gain versus input signal to 10^5 cps, but shows progressive loss in gain by input signals of 10^6 and higher. Even in the pulse counting mode, when the gain drops, counts will be lost due to the change in efficiency of the detector. In addition, counts are lost to detector deadtime (ion count overlap). Historically, we have used the Nd 144/145 ratio (approximately 3/1) over a range of count rates (concentrations) to assess the linearity of corrected data. Figure 1 shows the degree of match when 1, 7 and 20 ns deadtimes are used. We select the deadtime that gives the most constant ratio across the count range. The maximum count rate is kept below 3×10^5 cps for the most accurate ID ratio measurements.

$^{144}/^{145}$ Nd Ratio

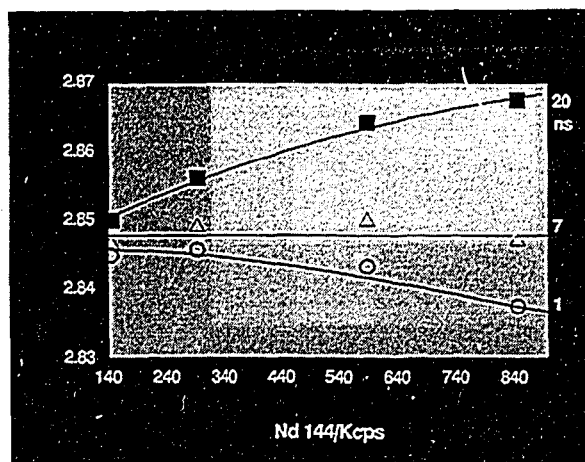


Figure 1: $^{144}/^{145}$ ratio vs count rate.

Drift in the instrument mass bias occurs during instrument "warm up" and throughout the day. Low mass elements are affected more than high mass elements. In the recent certification of Mg in Estuarine Sediment, for example, the mass bias correction for Mg 24/26 drifted from 1.0830 to 1.0923 in sixty minutes (0.85%).

Mass bias correction requires a dynamic measurement system with the "isotopic control samples" run at specific time intervals. This imposes a requirement that the memory from a previous sample be washed down 1000 fold within 3 to 4 minutes. Certain elements have notoriously long washout times under routine instrumental conditions due to adsorption/absorption to plastic, glass or other hardware, in addition to element volatility in the spray chamber. Figure 2 shows a washout study for boron using a combination of solvents. The mannitol/ NH_4OH mixture minimizes the boron memory, which is predominantly due to volatility.

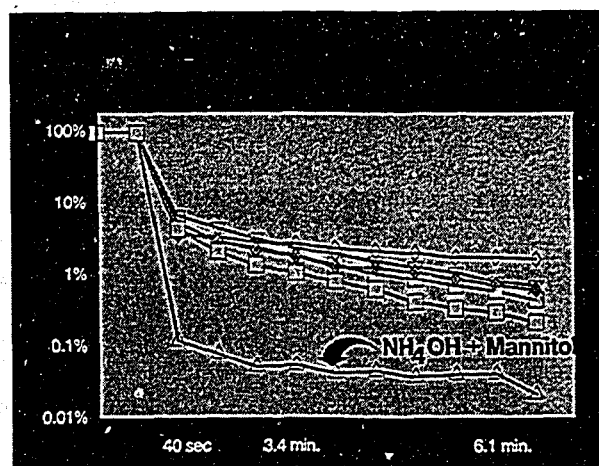


Figure 2: Washout time for boron using HNO_3 , HCl , NH_4OH with or without Mannitol.

Using a "natural" isotopic standard as a control to correct "spiked" samples for mass bias, drift suffers from a second type of memory problem which applies to all elements. A "spiked" sample has an isotope ratio significantly different from "natural". For example, for indium determinations, a "natural" indium control would have 3×10^5 cps for ^{115}In , and 1.5×10^4 cps for ^{113}In , while a properly spiked sample would have 3×10^5 cps for both isotopes. The problem arises when measuring a natural control following a spiked sample where a 0.1% memory at ^{113}In would be 15 cps. This represents a memory washdown of 20,000 fold from the spiked sample. Ideally, the isotopic control sample should have the same ratio as the spiked samples. For convenience, we use a spike calibration solution as the analysis control. The value for the control is determined by measuring a natural isotope ratio standard several times (to establish mass bias drift), followed by the isotopic control. This establishes the ratio of the working standard used to correct for the mass bias drift for the remaining spike calibrations, samples and blanks.

Molecular ion interferences are potential problems for all elements except high concentration elements and elements at low (Li, B, and Mg) and high mass (Hg, Tl, Pb, Th, and U). Natural materials, such as the current SRMs produced at NIST, are most susceptible to these problems. Interferences exist if an element in an unspiked sample shows a different isotopic ratio than a reference solution containing only that element. The necessary chemical separations schemes for removing interferences can be rapidly tested with a full element semiquantitative scan on the ICP-MS. ICP-MS has the advantage that only the source of interference needs to be removed. Therefore, separations are flexible and can be specially designed based on the matrix composition and the elements of interest. It is not necessary to isolate the analyte as required for thermal ionization mass spectrometry.

Analyses by ICP-MS ID

ICP-MS ID has been used in the certification of NIST SRMs for eight years. A summary of materials analyzed and elements determined are shown in Table 1. Of these analyses more than half required chemical separations.

Table 1: ICP-MS ID SRM Certifications

Elements	B, Mg, Ti, Cr, Fe,Ni, Cu, Rb, Sr, Mn* Mo, Rh*, Pd, Ag, Cd, Sn, Ba, Nd, Pt, Hg, Pb, I, Th, U	24
Matrix Types	Alloys, Autocatalysts, Blood, Cokes, Filters, Flours, Fly Ash, Glass, Leaves, Oils, Ores, Paint, Sediment, Serum, Soils, Tissues, Water	32
Element Certifications	Material X Element	125

* Mononuclidic, internal standard quantification

One example of an SRM certification requiring no chemical separations is boron, as interferences are unlikely for low mass elements. Boron was determined in a number of NIST leaf SRMs (Apple, Spinach, Tomato and Peach Leaves). Table 2 lists the results from a recent certification of boron in SRM 1547, Peach Leaves. Because of the potential volatility problem during sample preparation, dissolution was accomplished in tall Teflon containers and harsh evaporations were avoided. The 0.8% rsd is typical, and reflects the heterogeneity of boron in the leaf materials analyzed to date. Natural samples often display different levels of homogeneity for different elements.

Table 2: Concentration of Boron in Peach Leaves, SRM 1547 ($\mu\text{g/g}$)

29.46	29.31	29.19	29.64	29.79	29.31
Grand Avg. 29.45 $\mu\text{g/g}$; 0.8% rsd					

Chemical separations were required for the analysis of SRM 2711, Montana II Soil. A semiquantitative analysis of this complex material confirmed the absence of only four elements. All of the elements determined by ICP-MS suffered from molecular ion interferences. Most, but not all, molecular ion interferences involve oxides generated from lower mass elements at higher concentrations than the analyte. The Ag was separated from its interference, ZrO^+ , by electrodeposition of Ag from a dilute acid solution. The Ni had interferences from oxides of both Ca and Ti. Potassium, Ca and Ar oxides fall in the Mo mass region, and the double oxides, as well as Mo oxide, interfere with Cd. A two stage chromatographic separation was used to remove these interferences. Chelation chromatography efficiently separates the alkali/alkaline earth elements from the transition metals. In this scheme, Mo was eluted with dilute NH_4OH , and the transition metals (including Ni and Cd) were stripped with dilute HNO_3 . Anion exchange chromatography was used to remove the Ti and to separate the Ni and Cd. All separated elements gave their true natural ratio indicating that all interferences had been removed. The Ni, Cd, Mo, and Ag concentrations as determined by ICP-MS isotope dilution with chemical separations are shown in Table 3. The certified values are based on a statistical combination of results from several techniques, according to NIST policy.

Table 3: ICP-MS ID and Certified Values for Ni, Cd, Mo, Ag in SRM 2711, soil

	Ni	Cd	Mo	Ag
ICPMS	20.33 \pm 0.06	41.74 \pm 0.10	1.596 \pm 0.025	4.683 \pm 0.075
Certified	20.6 \pm 1.1	41.70 \pm 0.25	(1.6)	4.63 \pm 0.39

Conclusions

ICP-MS ID has certified a wide range of elements in a variety of materials with high accuracy and precision. Both the chemical preparation and instrumental procedures are simplified over other ID mass spectrometric techniques. The ICP-MS has picogram/mL detection limits for most elements using fixed operating parameters. Chemical separations are required only to remove an interference or to preconcentrate the analyte. Since both aspects of the analysis are not as restrained as traditional mass spectrometry, their flexible integrator. results in high precision and accuracy, simplified chemical procedures, and lower blanks.

References

- [1] J.D. Fassett and P.J. Paulsen, *Anal. Chem.* 61, 643A (1989).
- [2] E.S. Beary and P.J. Paulsen, *Anal. Chem.* 65, 1602 (1993).
- [3] Galileo Electro-optics Corp., *Channeltron Electron Multiplier Handbook for Mass Spectrometry Applications*, Sturbridge, MA 01566.