Geophysical Research Abstracts, Vol. 9, 04448, 2007
SRef-ID: 1607-7962/gra/EGU2007-A-04448

Can isotopic Certified Reference Materials be made to meet the capabilities of modern isotope ratio instrumentation?

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Recent developments in thermal ionization and inductively coupled plasma multi-collector mass spectrometers have lead to isotope ratio measurements with uncertainties approaching 10 to 100 ppm. Such measurements would normally be benchmarked by Certified Reference Materials (CRMs). However, the currently available isotopic CRMs distributed by various National Metrological Institutes have total uncertainties for their absolute isotopic ratios that are no better than a few parts in 10,000. Can isotopic CRMs be produced to meet the capabilities of modern isotope ratio instrumentation?

The “classical” approach for producing an isotopic CRM requires considerable effort and is, in fact, an atomic weight determination. A pure, stoichiometrically definable form of the element under study must be selected, and pure separated isotopes of known assay of the same element must be found. Accurately known isotopic mixtures of the separated isotopes are gravimetrically prepared. These mixtures become the accuracy base for the mass spectrometric measurements and are the principal limit to the overall accuracy of the absolute values. At present, isotopic mixtures can be prepared on an absolute basis with an accuracy of few parts in 10,000. Synthetic mixtures of the enriched isotopes are made to bracket the range of ratios in the candidate CRM and are used to correct the measured ratios to an absolute value. These samples are measured following a rigidly defined protocol specifying the sample form, amount, and loading parameters among other factors. From these measurements, simple correction

factors (e.g. T/E or True/Experimental) for the measured isotope ratios are obtained. The absolute isotopic ratios and their uncertainties are derived from the corrected ratio data together with the contributing sources of error or bias occurring during the certification process. The resulting CRM, while accurately characterized at the 1 to 0.5 permil level, is clearly not suited to the current generation of instrumentation.

With modern isotopic ratio measurement precisions now firmly in the ppm range, the certified values for the aforementioned CRMs clearly do not meet current measurement needs and may also be biased. Because the chemistry portion of the value assignment process is the limiting step in reducing the uncertainty and at present intractable, other approaches must be utilized or developed to bring the certified values into alignment with current analytical capabilities. The advent of the multi-collector inductively coupled plasma mass spectrometers (MC-ICPMS) has enabled new approaches to standardizing isotope ratio measurements. For example, mass bias corrections to isotope systems with only two isotopes can be applied on a standard-sample-standard bracketing basis, whether the data is from a thermal ionization or an ICP source. MC-ICPMS data can also be corrected using a surrogate element for internal standardization. Additionally, elements with more than two isotopes also open up the possibility of using double and triple spikes as internal correctors for instrumental biases. However, while these standardization methods offer potential improvements for value assignment to such CRMs, there are a host of issues (exacerbated when measurement precisions are in the ppm range) which can only be addressed through careful experimental design and statistical control. Even though absolute values in the "classical" sense may remain elusive, a new generation of isotopic CRMs, with consistent certified uncertainties in the ppm range, would significantly aid ongoing research utilizing these isotope systems.

We will discuss a new initiative underway at NIST to provide such CRMs and present the results of a careful metrological/statistical analysis of high precision Pb isotopic measurements on SRM 981 in the context of possible new certified values. Such an analysis encompasses published data from different double spikes, thallium internal standards and statistical analysis aimed at augmenting the signal to noise ratio.