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Advances in the Metrology of Absolute Value Assignments to Isotopic Reference Materials: Consequences from the Avogadro Project

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All isotope amount ratios (hereafter referred to as isotope ratios) produced and measured on any mass spectrometer are biased. This unfortunate situation results mainly from the physical processes in the source area where ions are produced. Because the ionized atoms in poly-isotopic elements have different masses, such processes are typically mass dependent and lead to what is commonly referred to as mass fractionation (for thermal ionization and electron impact sources) and mass bias (for inductively coupled plasma sources.) This biasing process produces a measured isotope ratio that is either larger or smaller than the "true" ratio in the sample. This has led to the development of numerous fractionation "laws" that seek to correct for these effects, many of which are not based on the physical processes giving rise to the biases. The search for tighter and reproducible precisions has led to two isotope ratio measurement systems that exist side-by-side. One still seeks to measure "absolute" isotope ratios while the other utilizes an artifact based measurement system called a delta-scale. The common element between these two measurement systems is the utilization of isotope reference materials (iRMs). These iRMs are used to validate a fractionation "law" in the former case and function as a scale anchor in the latter.

Many value assignments of iRMs are based on “best measurements” by the original groups producing the reference material, a not entirely satisfactory approach. Other iRMs, with absolute isotope ratio values, have been produced by calibrated measurements following the Atomic Weight approach (AW) pioneered by NBS nearly 50 years ago. Unfortunately, the AW is not capable of calibrating the new generation of iRMs to sufficient precision.

So how do we get iRMs with isotope ratios of sufficient precision and without bias? Such a focus is not to denigrate the extremely precise delta-scale measurements presently being made on non-traditional and tradition stable isotope systems. But even absolute isotope ratio measurements have an important role to play in delta-scale schemes.

Highly precise and unbiased measurements of the artifact anchor for any scale facilitates the replacement of that scale’s anchor once the initial supply of the iRM is exhausted. Absolute isotope ratio measurements of artifacts at the positive and negative extremes of a delta-scale will allow the appropriate assignment of delta-values to these normalizing iRMs, thereby minimizing any scale contractions or expansions to either side of the anchor artifact. And finally, absolute values for critical iRMs with also allow delta-scale results to be used in other scientific disciplines that employ other units of measure.

Precise absolute isotope ratios of Si has been one of the consequences of the Avogadro Project (an international effort to replace the original kilogram artifact with a natural constant, the Planck constant.) We will present the results of applying such measurements to the principal iRMs for the Si isotope system (SRM 990, Big Batch and Diatomite) and its consequences for their delta-Si29 and delta-Si30 values.