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Value Assignment of Isotopic Reference Materials – Approaches, Pitfalls and Workarounds based on Experiences from the Avogadro Project

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Isotope ratio measurements and their application to the natural world have undergone profound changes in the past decade. These changes have arisen due to improvements in measurement precision by modern multi-collector instrumentation and also the maturation of powerful ionization sources, specifically those employing inductively coupled plasma (ICP) torches. The latter development has made the entire periodic table a fertile hunting ground for small but significant natural isotopic variations produced by new and novel processes as well as the older and well studied mechanisms.

Unfortunately, Isotopic Reference Material (IRM) production by National Metrology Institutes (NMI) has not kept up this these advances. This has necessitated the production and value assignment of working IRMs by the researchers pioneering these advances. This sort of distribution and characterization system leads to problems with long-term availability to the research community as the pioneers move onto other elements and isotopic systems, losing interest in the "old" when tempted by "new" and therefore fundable research opportunities. Furthermore, most value assignments of such IRMs are based on "best measurements" by the original groups and thus represent mass discrimination dependent models of the materials' isotopic signature, a situation that often leads to a proliferation of different values depending on research group or philosophy, a highly confusing and potentially non-constructive situation!

We have been working closely with other NMIs (PTB, NRC and NIM) to produce accurate molar mass determinations of the highly pure 28Si being used in the Avogadro Project (an international effort to replace the original kilogram artifact with a procedure and measurement protocol that any technologically advanced nation can use to realize this fundamental SI unit). The basis for the approach was conceived and developed at the PTB (e.g. [1]). Its applicability to accurate and non-mass discrimination model dependent measurements of other isotopic systems offers a potential work around of some of the fundamental limitations of the old Atomic Weight approach for accurate isotopic measurements pioneered by NBS nearly 50 years ago. The accurate characterization of isotopic systems using this method, building on insights gained from the Avogadro Project, will be discussed. We will be looking at elements having 2, 3 and 4 isotopes and comparing its efficacies with other methodologies currently being used to correct for mass discrimination (e.g. Sample-Standard-Bracketing, Surrogate Elements, etc.)

[1] Pramann et al. (2011) Int. J. Mass Spectrom. 299,78