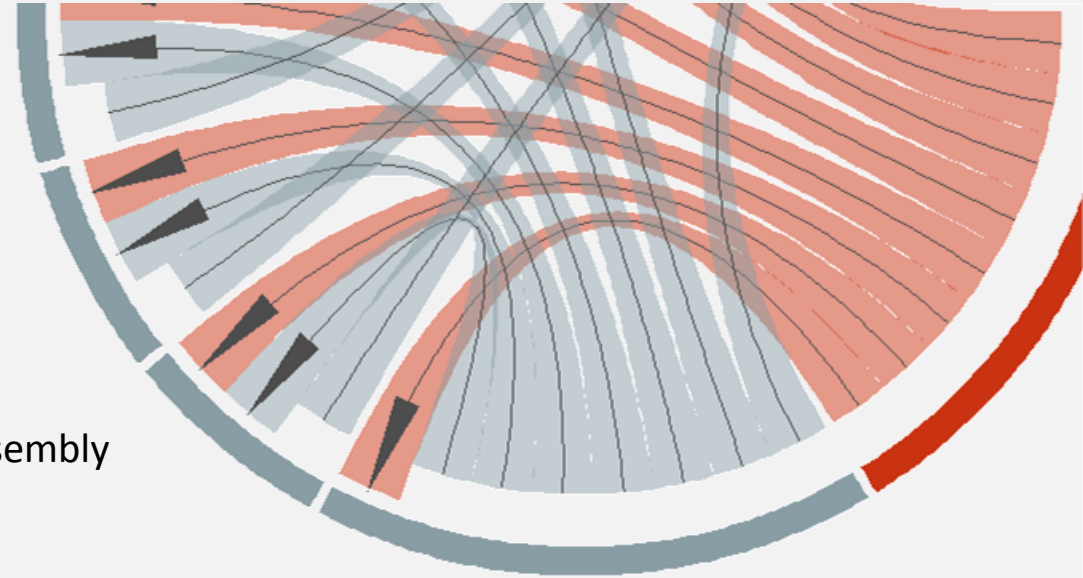
EGU General Assembly 2020



European Geosciences Union General Assembly
4-8 May 2020 (virtual meeting)

Traceability in isotope ratio measurements: the role of data analysis

JURIS MEIJA ◦ NRC Metrology

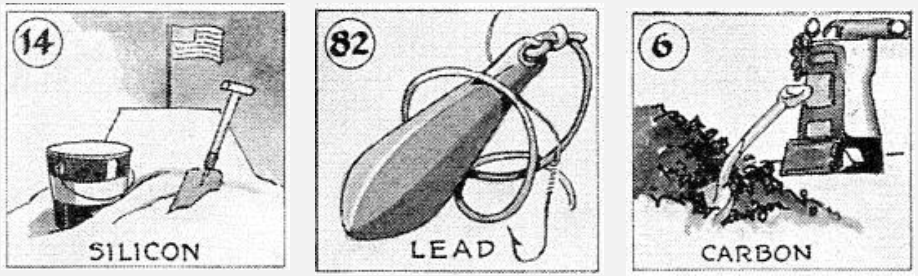
National Research Council Canada
Conseil national de recherches Canada

Canada

Four recent examples

2 Effect of measurement models

Importance of data disclosure and transparency 1



Traceability networks of reference materials 4

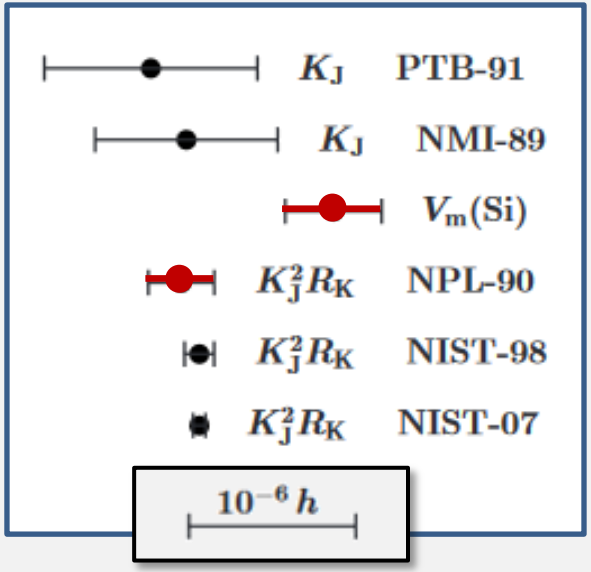
3 Coherence of isotope ratio measurements

Popular Science (1931)

The redefinition of the International System of Units required that an agreement between the **Avogadro** and **Planck** constants is in the order of 20 µg/kg ($2\times10^{-8}\,h$).

In 2000s, there was a two-order of magnitude larger discrepancy between N_A and h due to silicon isotope ratio measurements.

See Mohr et al et al (2008) *Rev. Mod. Phys.* 80, 633-730

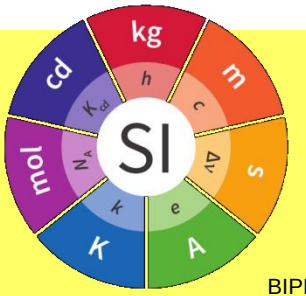


Least Squares Adjustment of Fundamental Constants (CODATA 2006)

1

SILICON: THE REDEFINITION OF THE KILOGRAM

Disclosure of data and transparency

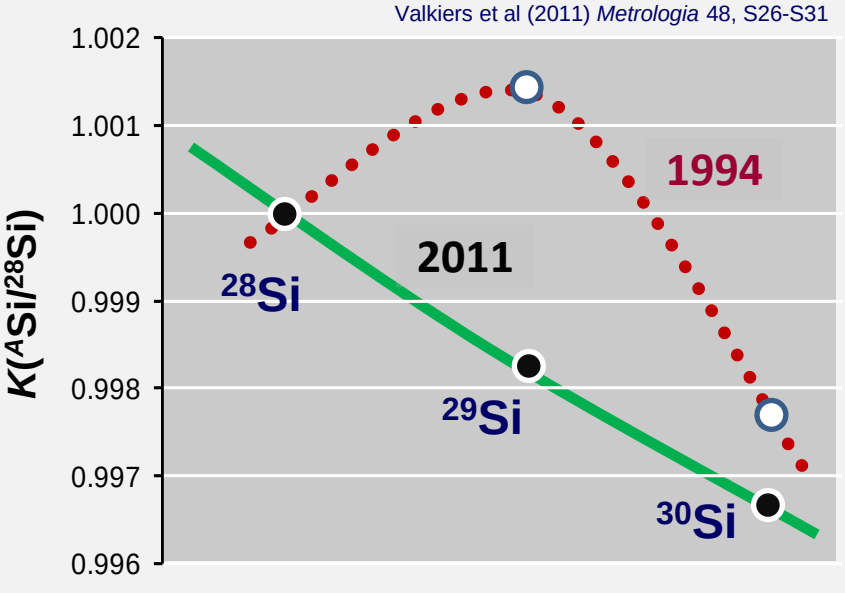


BIPM

In isotope ratio measurements, the calibration is usually a monotonic function of the mass difference between the isotopes, for example

$$\ln K(^{A}\mathrm{Si}/^{28}\mathrm{Si}) \sim m_a(^{A}\mathrm{Si}) - m_a(^{28}\mathrm{Si})$$

The lack of disclosure of the raw data delayed the understanding of the errors inherent in these early results.



Early silicon isotope ratio measurements in support of the redefinition of the kilogram

1

SILICON ISOTOPE MEASUREMENTS AND THE REDEFINITION OF THE KILOGRAM

Correction of instrumental fractionation

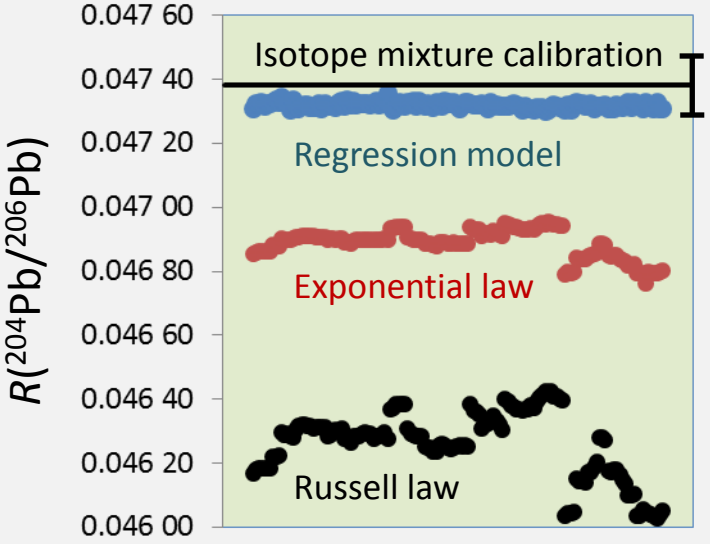
Exponential models are applied to nearly all ICP-MS isotope ratio measurements of heavy elements, and they are embedded into double spike calibration.

Exponential law $\ln K_{1/2} \sim m_1 - m_2$

Russell law $\ln K_{1/2} \sim m_1/m_2$

Most of us use the exponential or Russell law but just how good are these models?

Yang et al (2011) *Anal. Chem.* 83, 8999-9004
Tong et al (2019) *Anal. Chem.* 91, 4164-4171



Percent-level biases can be obtained when $^{206}Pb/^{208}Pb$ ratio is used to correct for $^{204}Pb/^{206}Pb$ in MC-ICP-MS with exponential models

2

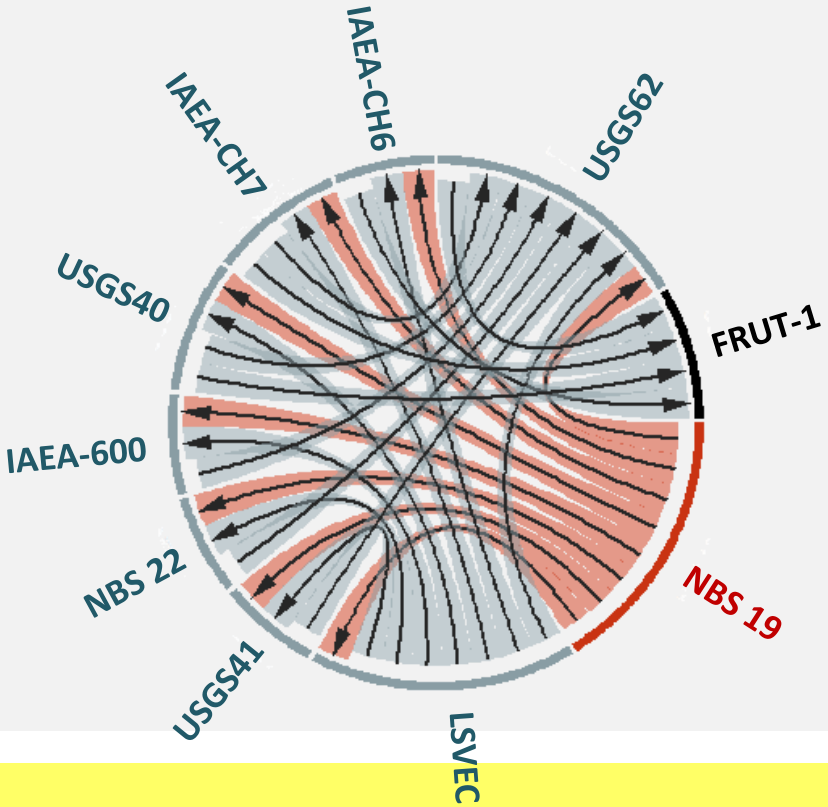
MANY ISOTOPES DO NOT FOLLOW EXPONENTIAL FRACTIONATION LAW

Correction of instrumental fractionation

The NRC Canada recently produced carbon isotope delta standard FRUT-1 (fructose). Although it is on the VPDB scale, defined by NBS 19, the assigned isotope delta values depend on many other standards.

What happens when we find problems with some of these standards? LSVEC and USGS41 are now known to be isotopically unstable – what implications does that have to the existing pool of international CRMs?

See also Dunn et al (2020) *Rapid Commun. Mass. Spectrom.* (10.1002/rcm.8711)



3

TRACEABILITY NETWORK OF CARBON ISOTOPE DELTA STANDARDS

Isotope standards are not independent

Consider the NRC FRUT-1 reference material certified for carbon isotope delta from an inter-laboratory study using multivariate random effects statistical model that takes into account correlations between the laboratories (as many of them use the same calibrators). What isotope delta value would NRC have assigned if

A *the correlations were to be ignored?*
B *simple arithmetic mean was used?*

Meija and Chartrand (2018) *Anal .Bioanal. Chem.* 410, 1061-1069

NRC FRUT-1 fructose

Method	$\delta_{VPDB}(^{13}C)$
A	–10.99(2) ‰
B	–11.00(1) ‰
Certified	–10.98(4) ‰

10.4224/crm.2018.frut-1

3

CARBON ISOTOPE DELTA MEASUREMENTS

Uncertainty evaluation differs among experts

Before the 1960s, atomic weight measurements of many elements were related because of the network of inter-comparisons to Ag, Cl, Br, and I for which T. W. Richards received the 1914 Nobel Prize in Chemistry. This allowed to assess the coherence of atomic weight measurements.

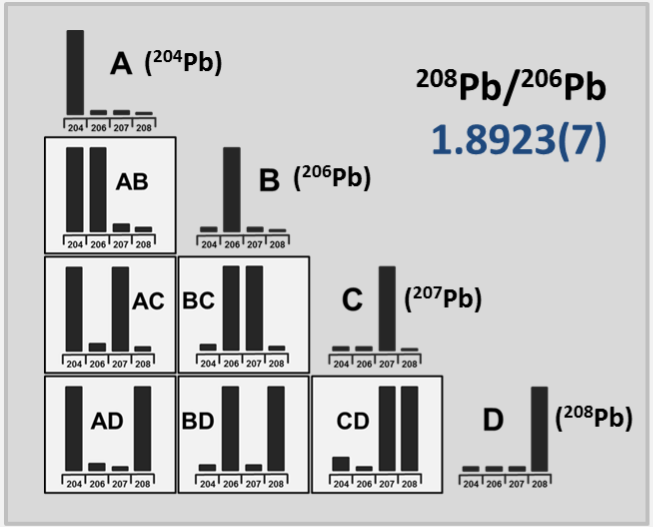
Today, most isotope ratio measurements of the elements do not benefit from such inter-connectivity. Hence, efforts to evaluate the coherence of isotope reference materials remain as important as ever, especially given the scarcity of *independent* isotope ratio measurements for many elements.

4

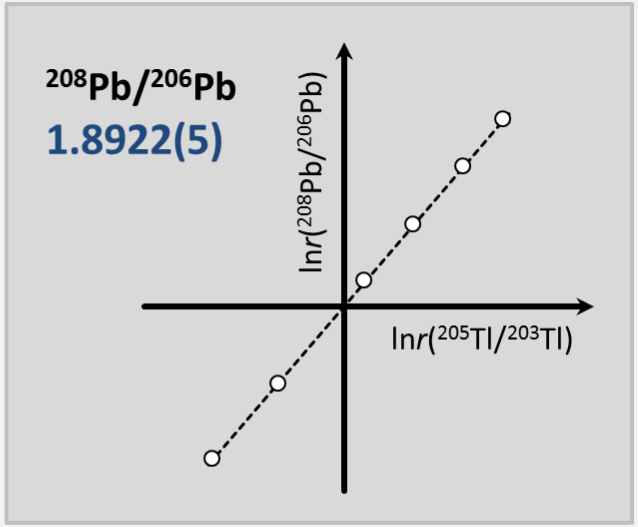
Coherence of isotope reference materials

Tong et al (2019) *Anal. Chem.* 91, 4164-4171

Comparison of lead isotope ratios in NRC HIPB-1 and thallium isotope ratios in NIST SRM 997



Full gravimetric calibration using pure lead isotopes



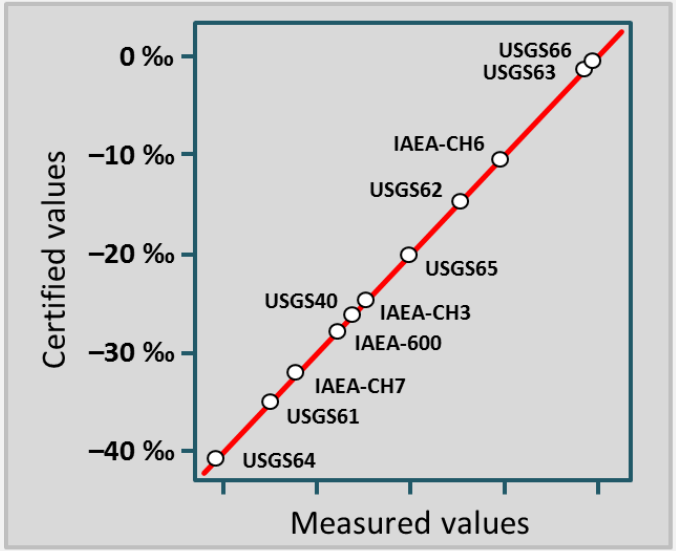
Independent calibration using regression method via thallium isotopic standard

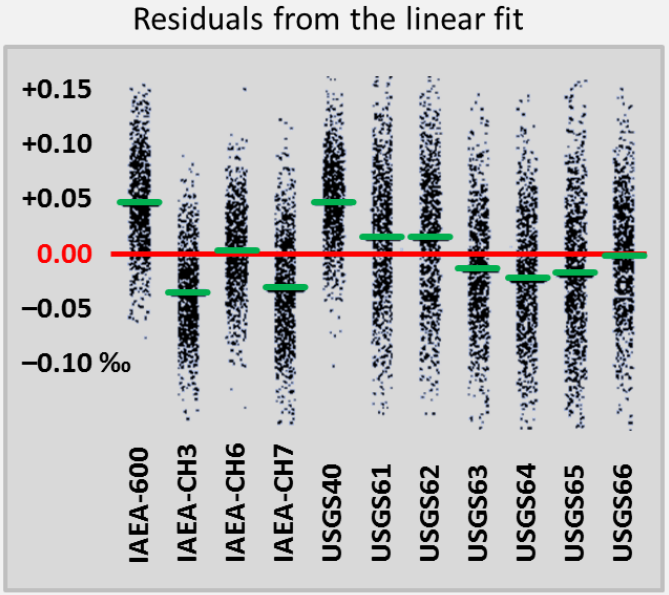
4

COMPARING THE ISOTOPE RATIOS OF LEAD AND THALLIUM

Coherence of isotope reference materials

Chartrand et al (2019) *Rapid Commun. Mass Spectrom.* 33, 272-280





Comparison of certified isotope delta values and raw measured values (against in-house reference gas).

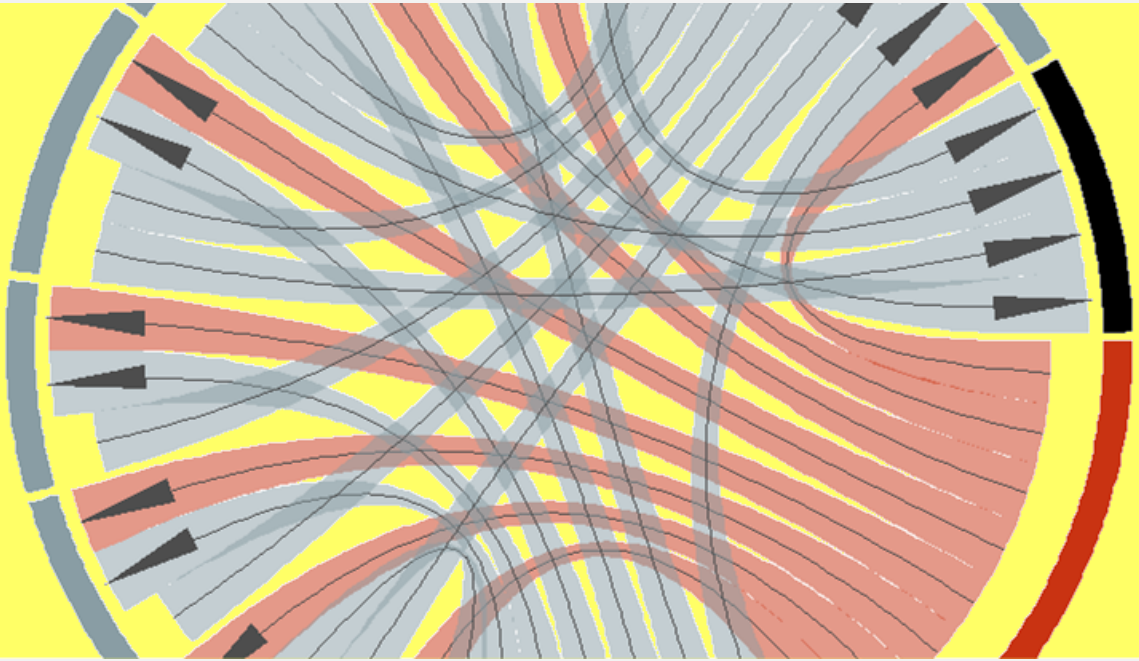
Coherence of the assigned $\delta_{VPDB}(^{13}C)$ values in the set of eleven international reference materials

4

HOW WELL CAN WE REALIZE THE VPDB SCALE?

Coherence of isotope reference materials

NRC.CANADA.CA



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