How good are my stable isotope data? Implications on using an in-house QC system for stable isotope measurements

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Stable isotope measurements

- Stable isotopes are widely used with applications in forensics, ecology, biogeochemistry, atmospheric sciences, and hydrology.
- Isotope data in the recent years has increased considerably and a demand of high-quality isotope data is required.
- It is difficult to compare different isotope datasets, which might have been produced using different protocols, and even different calibration and normalization approaches.

Photo credit: H.Roop, NSF
Data comparability

• For example, global water isoscapes, ice cores, materials with exchangeable H, and many more...

Isoscapes (e.g. GNIP)
- Standardized methods for representative sample
- Data quality tools – [see D497 - EGU2020-22653]

Organic materials with exchangeable H
- Differential protocols and calibration approaches [see D493 - EGU2020-9674]
- NMR vs. IRMS – [see D494 - EGU2020-11630]
Quality Management System

Internal Quality Control tools are needed in research and service laboratories to support isotope data quality (e.g. ISO 17025)

• Metrological traceability [see D499 - EGU2020-22382]

• Uncertainty estimation (incl. operator errors)

• Quality control tools
Uncertainty estimation

- Uncertainty calculations may be complicated by various and not well-controlled factors, including sample matrix effects, incomplete reactions and by-products formed etc. (external precision).
- The use of data scatter (e.g. SD of Reference Materials (RMs) and in-house working standards) as a measure of uncertainty is obviously insufficient.
- When establishing target uncertainty values, standard specifications should be considered.

Samples & RMs → Analyte gas \( (H_2, CO, N_2) \) → IRMS or optical

“External” vs. “Internal”
Uncertainty estimation

1. Uncertainty due to preparation steps:
   - Samples & RMs
   - Analyte gas (H₂, CO, N₂)
   - IRMS or optical

2. Uncertainty components shall include:
   - Uncertainty assigned to QC (either RM or lab-standard)
   - Analytical uncertainty
     - data scatter observed on replicates
     - uncertainty of the calibration line
   - Correlation between U components shall be considered

3. Uncertainty estimation
   - Specify measurand:
     - Stable isotope measurements:
       - Standard Operating Procedures (SOPs)
       - Identical Treatment (IT) principle
       - Matrix specific

   - Sources of uncertainty
     - 1) Uncertainty of RMs (storage, homogeneity)
     - 2) Analytical uncertainty (internal vs. external)
     - 3) Uncertainty of the calibration (one vs. two point calibration)

   - Quantify components
     - Sample preparation
     - Operator effects
     - Random effects

   - Combined uncertainty
     \[ U = \sqrt{(U_1)^2 + (U_2)^2 + \ldots + (U_n)^2} \]
Uncertainty vs. “fit-for-purpose”

- Any isotope laboratory shall establish “target” uncertainty as based on intended data use.
- However, correctly estimated uncertainties can reduce the probability of obtaining significant differences between groups of unknowns, which the purpose of the analysis could not fit. ➔ e.g. low uncertainty for carbonate RMs [see D506 - EGU2020-11525]

Reduce uncertainty: e.g.
- Improved instrumentation
- Enhanced calibration

Specific protocol: e.g.
- matrix specific
- needed uncertainty for application
Quality Control tools

- Performance based on QC materials can be estimated by using the z-score criteria developed for proficiency tests (z-score <2):

\[
z\text{-}score = \left[ \delta^15N_{QM\text{-}\text{assigned}} - \delta^15N_{QM\text{-}\text{observed}} \right] / U_{QC\text{-}\text{combined}}
\]

Data from Assonov et al (2019) - EGU2019-16776
Quality Control tools

- Control charts:
  - the criteria to revise limits of QC standards in an objective manner including the removal of outliers.
  - Warning and action limits depend on isotopic composition, homogeneity, and statistical approach → uncertainty estimation

Criteria to revise limits of QC standards
- Outlier removal?
- Which period of data?
- long-term data vs. one calibration data with U propagation?
Conclusions

• Establishing target-uncertainty, as related to intended data use (applications) is required.

• As QC, one shall take a similar-to-samples material, available in large amounts. One may suggest to run it regularly, in particular after changing (major) operational parameters gas flow, O₂ flow, etc.

• When results on QC materials are outside warning limits and action limits, this shall trigger the need of further investigation and remedial actions.

• For example, material heterogeneity or difficulty of combustion for complex materials can cause data to be outside limits. Realistic uncertainty estimation of the method to be used in accordance of the established target uncertainty must be determined.

• When stable isotope measurements are used, implementation of these protocols are of great relevance for a well-balanced decision making based on the use of isotope results.
Thank you

Any questions?

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