LGC

Estimation of Measurement Uncertainty of Stable Isotope Ratio Delta Values

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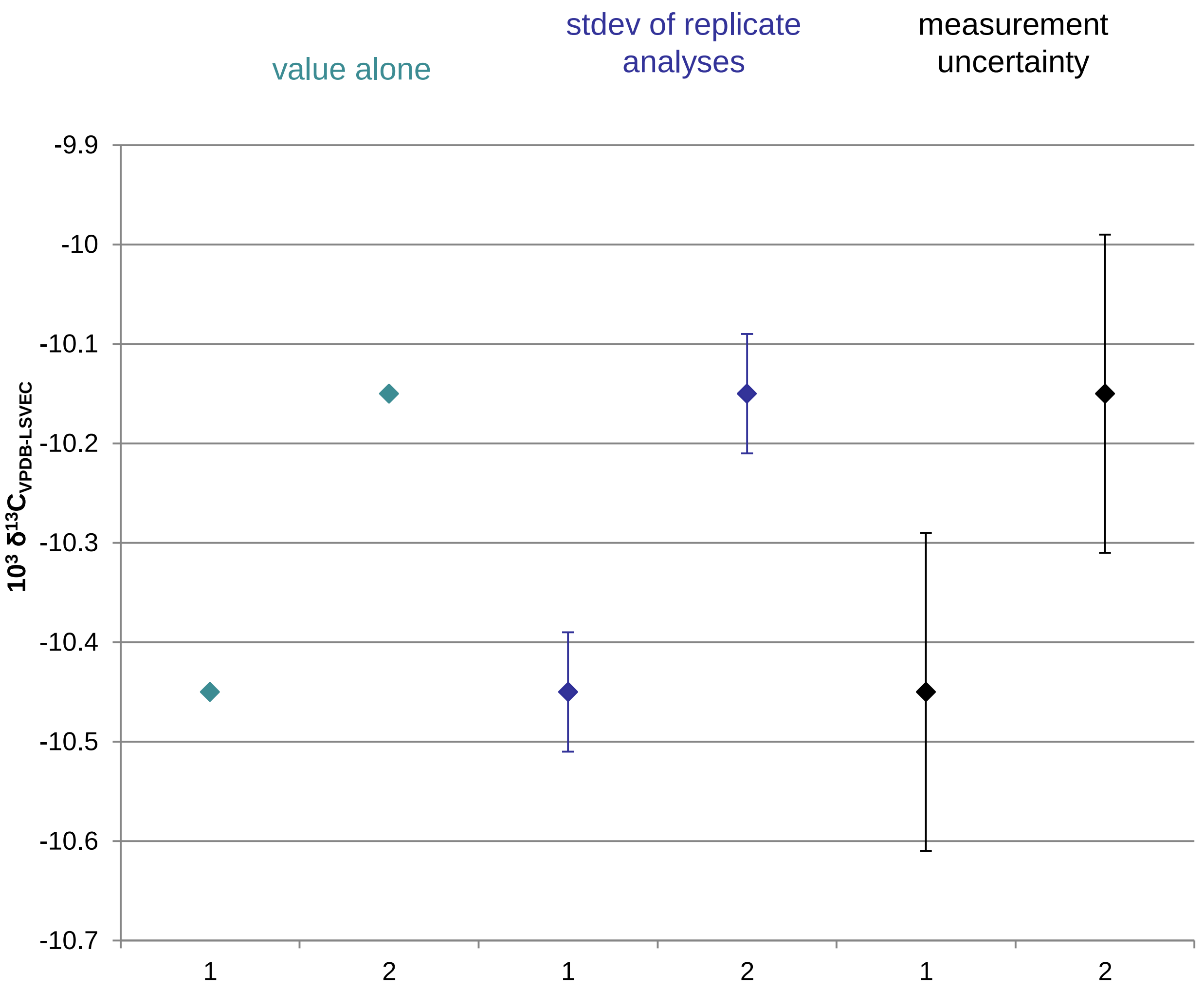
What is measurement uncertainty?

- ISO definition:
  - "a parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand."
- More simply:
  - The bit of the result after the ± sign
- Not the same thing as error
  - Error is difference between measured and true result
  - Uncertainty is a range that does not require knowledge of the true result
- Required for accreditation to ISO/IEC 17025

$10^3\ \delta^{13}C_{VPDB\text{-}LSVEC} = -30.03 \pm 0.09$
(expanded uncertainty, k=2)

Why is uncertainty important?



<u>Why</u> uncertainty and not simply stdev of replicate analyses?

- Drift/linearity correction from Anders Ohlsson, Analyst, 1999

$$\delta_{corr} = \delta_r + k_{\delta A} + k_{\delta t}$$

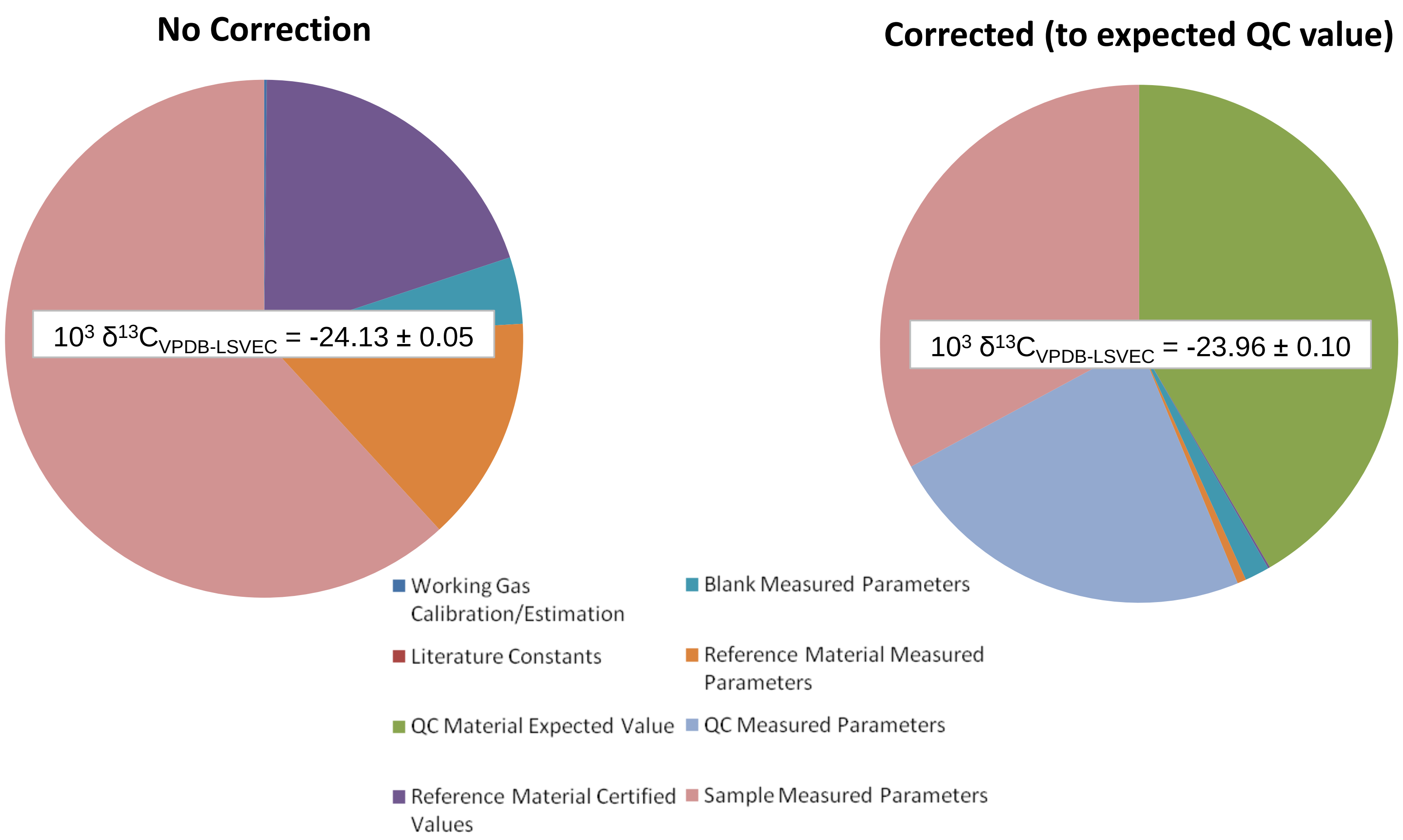
- correction factors are polynomials (linear) determined from QC materials.
- minimise QC sd. and set QC mean to expected value to determine correction factors.

- sequence position and peak area as drift/linearity proxies.
- What about the uncertainty budgets?

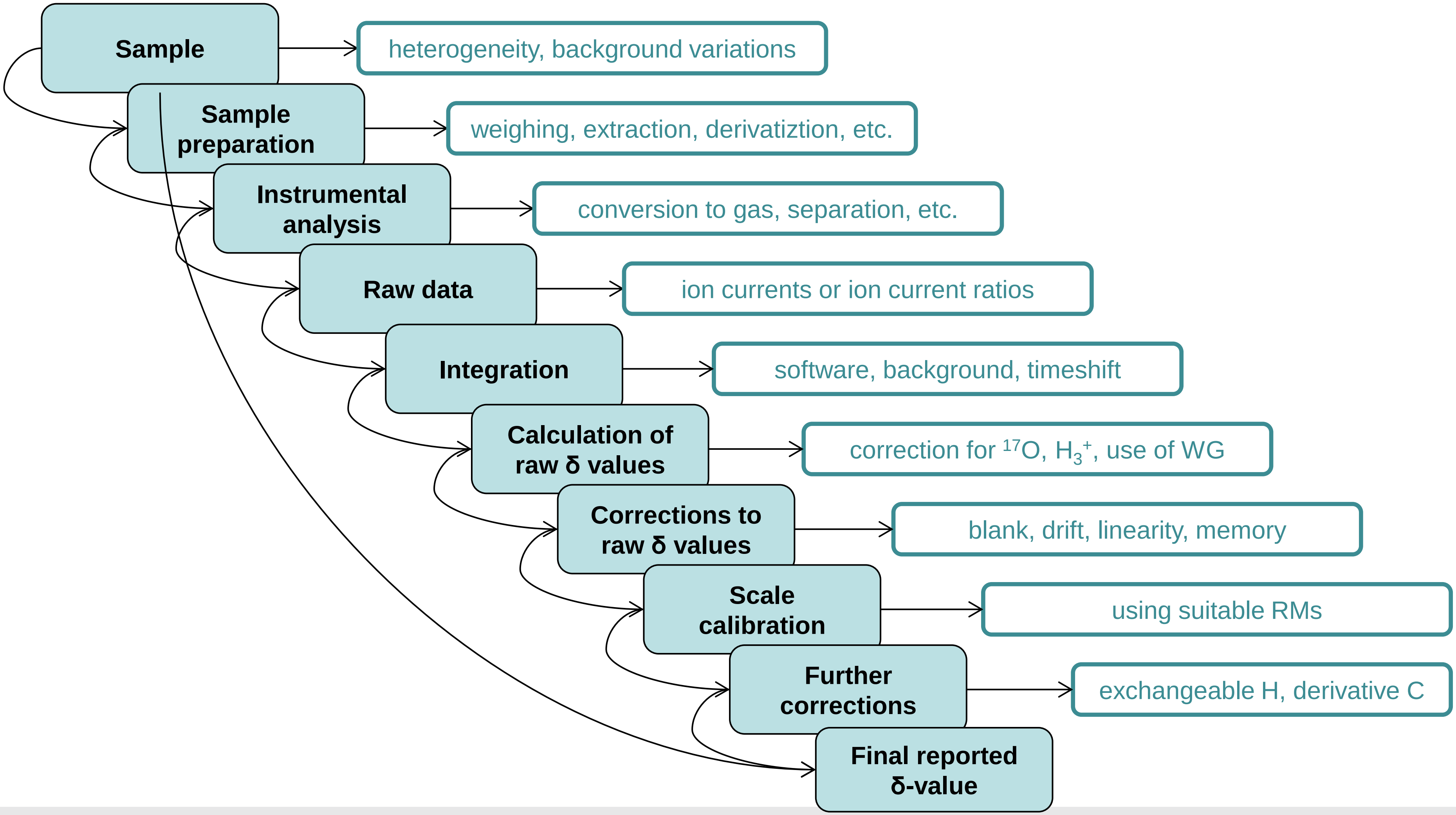
Why uncertainty and not stdev?

Parameter	Normalised		Corrected to expected QC	
	value	uncertainty	value	uncertainty
Sample mean	-24.13	0.05	-23.96	0.10
QC mean	-28.93	0.06	-28.82	0.11
QC stdev	0.13	0.07	0.04	0.05

Why uncertainty and not stdev?



Where might uncertainty arise in IRMS?



How to estimate measurement uncertainty

- General information
  - ISO/IEC Guide to the expression of uncertainty in measurement (GUM) – freely available from www.bipm.org
  - Eurachem CITAC guide to “Quantifying uncertainty in analytical measurement” – freely available from www.eurachem.org
  - Training (e.g. www.lgcgroup.com/services/training)
- Various approaches possible:
  - Cause and effect diagram, measurement equation
  - Identify contributing factors, determine standard uncertainties and combine using the standard rules (e.g.)

$$u_c(y) = \sqrt{u(x_1)^2 + u(x_2)^2 + \ldots u(x_n)^2}$$

  - Partial derivatives
  - Monte Carlo simulations
  - Kragten spreadsheet approach

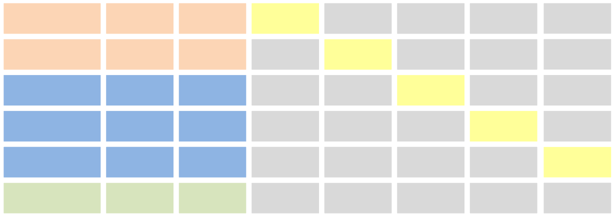
How does the Kragten approach work?

- Determines effect of uncertainty in each parameter on final value.
  - Example provided in current FIRMS Good Practice Guide for IRMS:

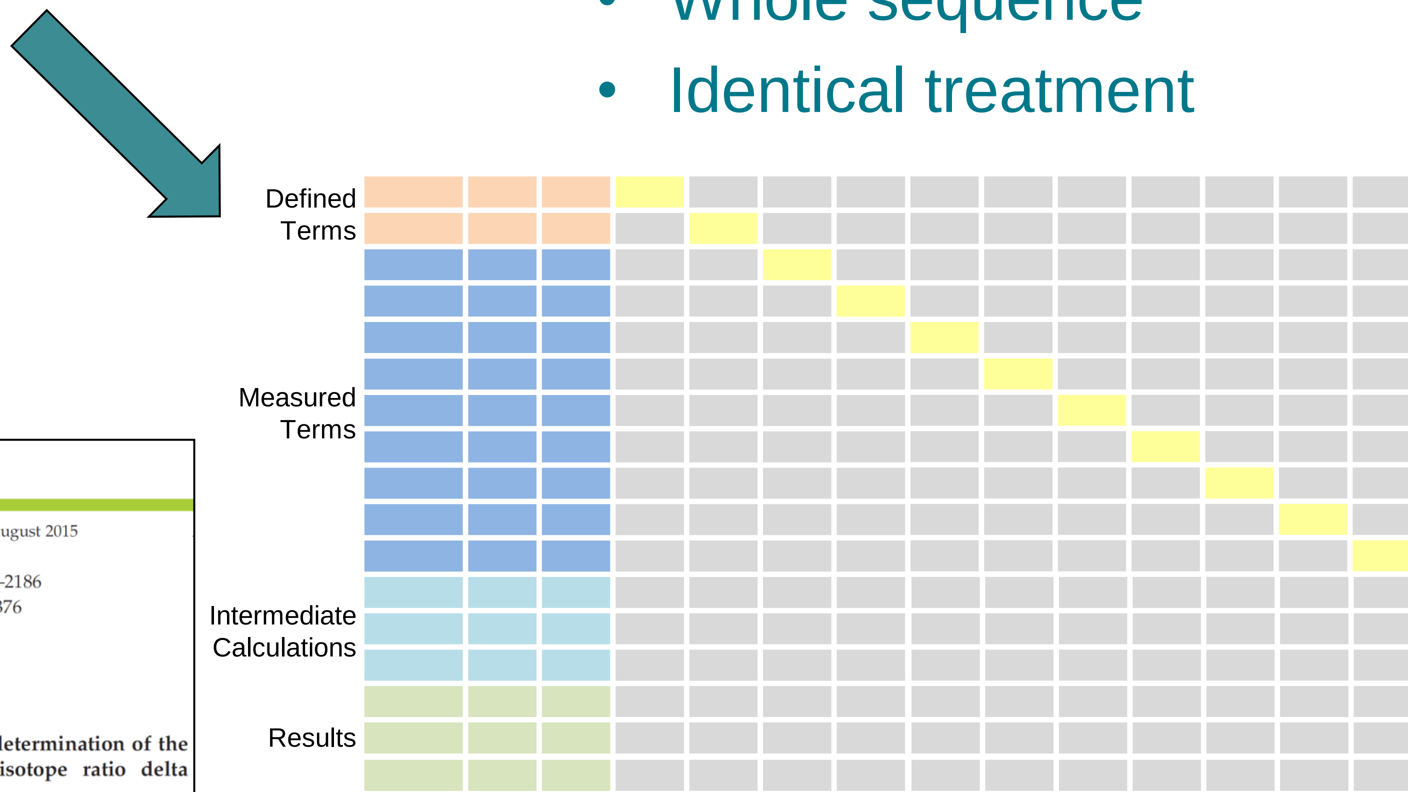
	A	B	C	D	E	F	G	H
1								
2	**Parameter**	**value (δ^2H, ‰)**	**uncertainty (δ^2H, ‰)**					
3	$\delta_{true(VSMOW2)}$	0.0	0.3	0.3	0.0	0.0	0.0	0.0
4	$\delta_{true(SLAP2)}$	-427.5	0.3	-427.5	-427.2	-427.5	-427.5	-427.5
5	$\delta_{raw(VSMOW2)}$	0.3	1.2	0.3	0.3	1.5	0.3	0.3
6	$\delta_{raw(SLAP2)}$	-420.7	1.2	-420.7	-420.7	-420.7	-419.5	-420.7
7	$\delta_{raw(sample)}$	-189.0	1.5	-189.0	-189.0	-189.0	-189.0	-187.5
8	$\delta_{true(sample)}$	**-192.2**	**1.8**	-192.06	-192.09	-192.89	-192.77	-190.70
9			Difference	0.1651	0.1349	-0.6687	-0.5495	1.5232

- Pros
  - simple and transparent
  - can handle same input term more than once in measurement equation
- Cons
  - limited to calibration
  - one sample at a time
  - care over correlation between input parameters

How to improve the GPG approach



- Add intermediate calculations
- Whole sequence
- Identical treatment



Letter to the Editor

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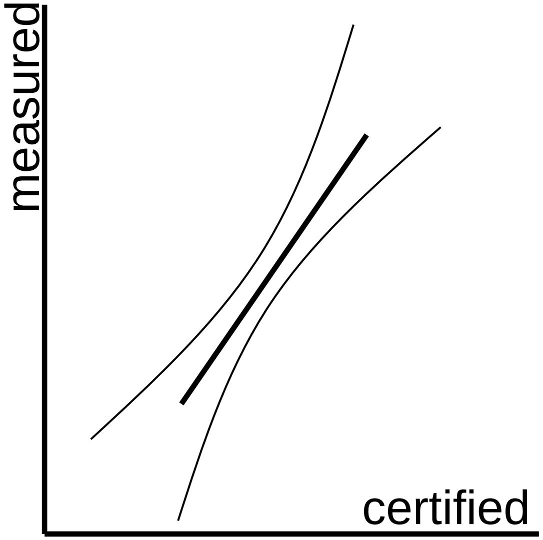
Dear Editor,

Simple spreadsheet templates for the determination of the measurement uncertainty of stable isotope ratio delta values

Kragten approach – thought experiment

- Compare interpolation with extrapolation
- 2 RMs for scale calibration at -10 ± 0.1 and -30 ± 0.1 ‰
- u in raw *δ* value measurement 0.15 ‰ (regardless of *δ*)

sample *δ* value	u in *δ* value
-20 ‰	0.20 ‰
-15 or -25 ‰	0.21 ‰
-10 or -30 ‰	0.24 ‰
-5 or -35 ‰	0.28 ‰
0 or -40 ‰	0.32 ‰
+30 or -70 ‰	0.67 ‰



How else might uncertainty be estimated?

- CCQM-K140 key comparison on stable carbon isotope ratio delta values in bulk honey.
  - 5 metrology institutes participated
  - no two used the same approach in terms of calculation sequence for data handling
  - all reported a measurement uncertainty and budget
- Same sample distributed to FIRMS laboratories
  - 6 laboratories
  - more consistent scale calibration approaches
  - only standard deviations of replicate analyses reported.

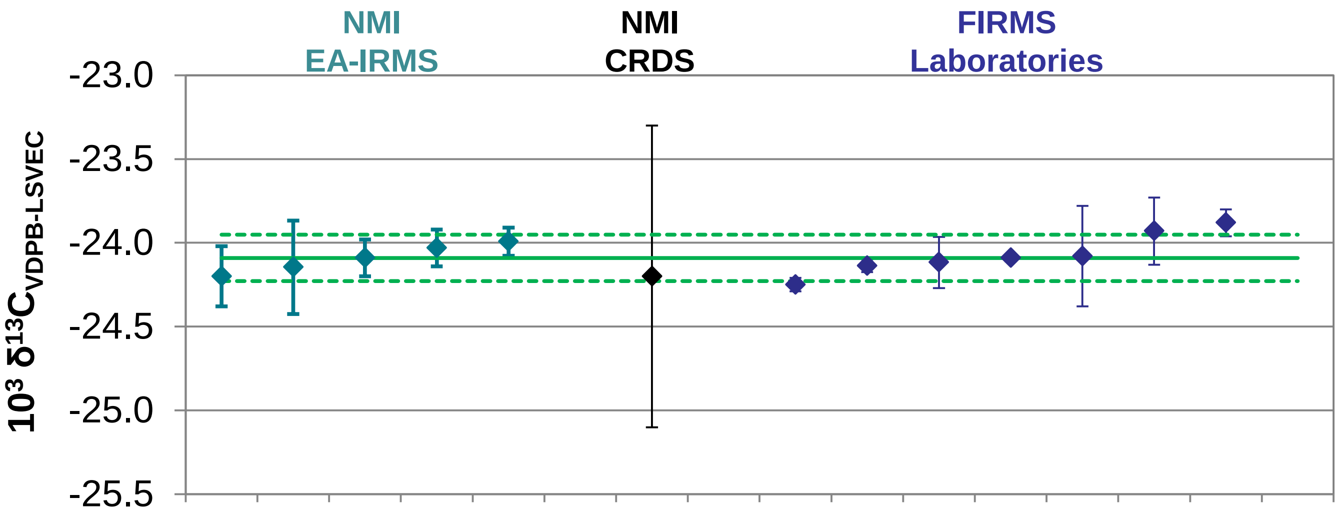
NMI approaches to estimate uncertainty

- Kragten spreadsheet for each sequence.
  - combined results from multiple sequences.
  - budget as average from sequences.
  - Ion current ratios/peak areas as input data
- All calculations using raw ^{13}R not δ-values
  - reproducibility, calibration, ^{17}O correction, bias and precision all combined

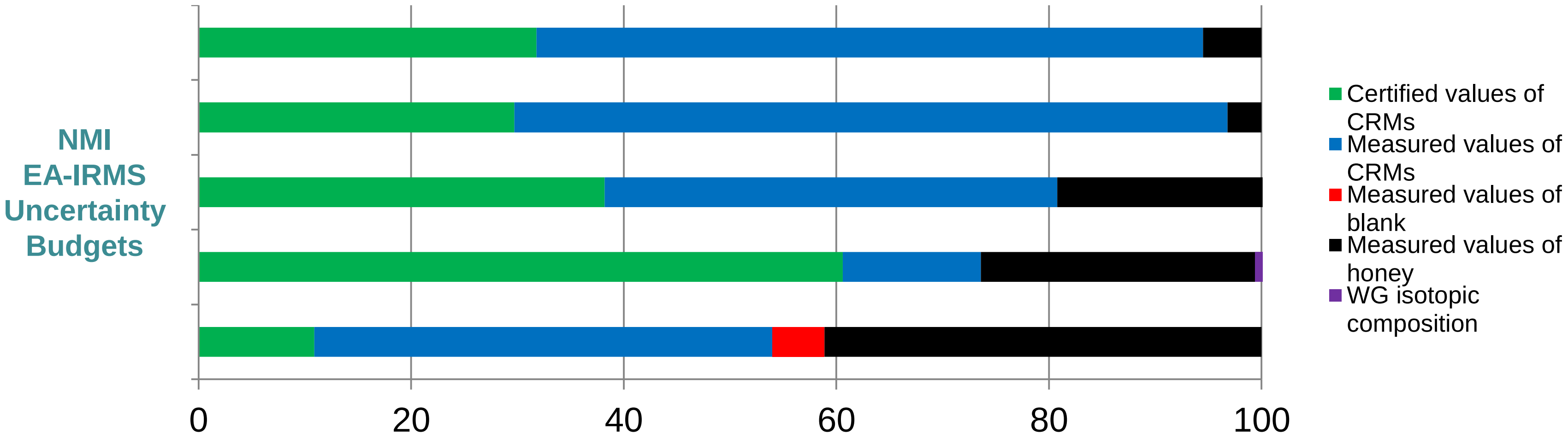
- Square root sum of the squares
  - Various factors considered including
    - certified values for RMs
    - u in calibration plot
    - repeatability (sample and RMs)
    - reproducibility
    - linearity
    - e.g.

$$u = \sqrt{u_{rep-rel}^2 + u_{linearity-rel}^2 + u_{8573-rel}^2}$$

Results



Error bars represent the expanded uncertainty (k=2) for metrology institutes and the standard deviation of replicate analyses for expert laboratories. The solid green line is the median of the NMI results while the two dashed green lines represent this median plus or minus its expanded uncertainty (k=2.776, u. in median =MAD_E).



Method Uncertainty from Validation data

- Best estimate of precision
  - long time periods
  - representative variation of experimental factors
  - i.e. intermediate precision
- Bias
  - Use CRMs
- Other factors investigated through ruggedness study.
  - Method specific

Accred Qual Assur (2000) 5:47–53

PRACTITIONER'S REPORT

Vicki J. Barwick
Stephen L.R. Ellison

The evaluation of measurement uncertainty from method validation studies

Part 1: Description of a laboratory protocol

Take home messages

- Measurement uncertainty is important.
- Can arise from all calculation stages from raw instrumental data onwards.
- Corrections to data can significantly impact the source and magnitude of the measurement uncertainty (even when standard deviations of replicates decrease).
- Kragten spreadsheet approach useful for IRMS data
  - But other approaches also offer similar estimates

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