Primary Standards, Reference Materials, and Uncertainty Analysis for the Measurement of Greenhouse Gases

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NIST has developed methods to characterize contributions of uncertainty from "unknown" sources that we do not fully understand yet, and to better represent such uncertainties in our data reductions for gas analysis.

"Historical" Uncertainty

Deriving from lack of reproducibility in the long term, historical uncertainty is included in the certification of gas mixture Standard Reference Materials (SRMs), to account for long-term changes in a gas mixture over time

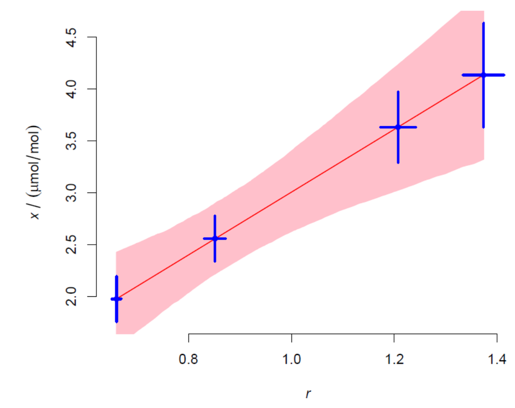
SRM Overview

- Produced by a specialty gas supplier and certified by NIST
- Dynamically blended in homogeneous batches ("lots")
- One cylinder is selected by NIST as the SRM lot standard (LS)
- The LS serves as analytical control, against which all other cylinders are analyzed, automatically correcting for instrument drift
- Resulting measurements are ***ratios*** of instrumental indications:

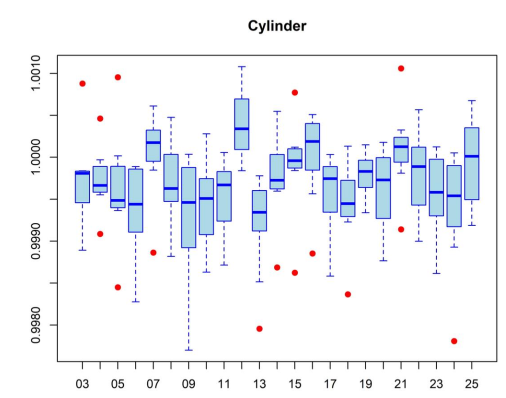
$$r_{CYL} = \frac{i_{CYL}}{i_{LS}}$$

Certification of the Lot

1. *Construction of the analysis function*
   - Based on measurements of gravimetric primary standard mixtures (PSMs)
   - Maps measured ratios into amount fraction values, consistent with ISO 6143



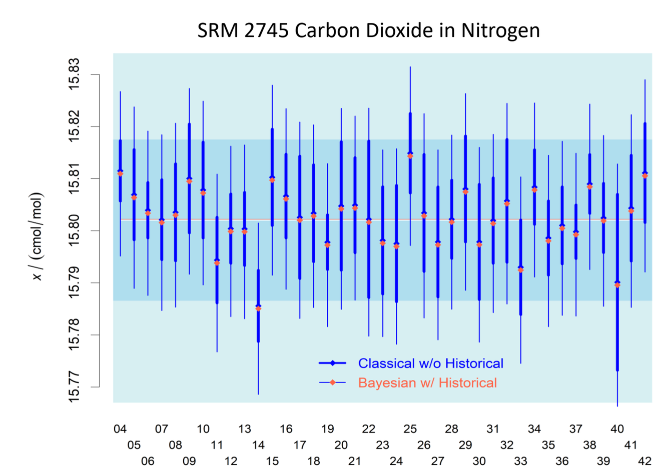
2. *Assessment of lot homogeneity*
   - Dispersion of amount fractions between cylinders
   - If sufficiently homogeneous, SRM lot is assigned one amount fraction value and uncertainty



3. *Evaluation of uncertainty*
   - Based on statistical models involving Monte Carlo methods
   - Includes contributions from: lack of repeatability of ratios, uncertainties of PSMs, construction of analysis function, and heterogeneity of cylinder compositions

Historical Uncertainty

- Lot standards from previous SRM lots are analyzed along with the current lot
- Differences between the original certified and analyzed values of these "historical" LSs are incorporated into the overall uncertainty of the new SRM lot
- Enables informed estimation of long-term behavior of an SRM over time
- Resulting uncertainties are more robust, realistic, and ultimately more reliable



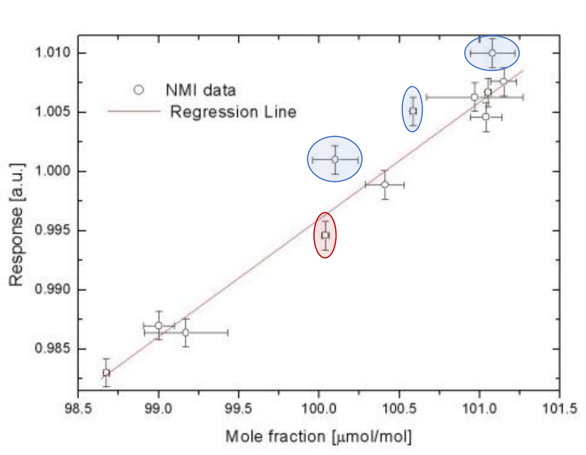
References: Certification of NIST Gas SRMs

"Dark" Uncertainty

Emerging from mutually inconsistent measurement results, dark uncertainty is applied to errors-in-variables (EIV) regression analysis, to account for excess dispersion of participants' results in a GAWG key comparison

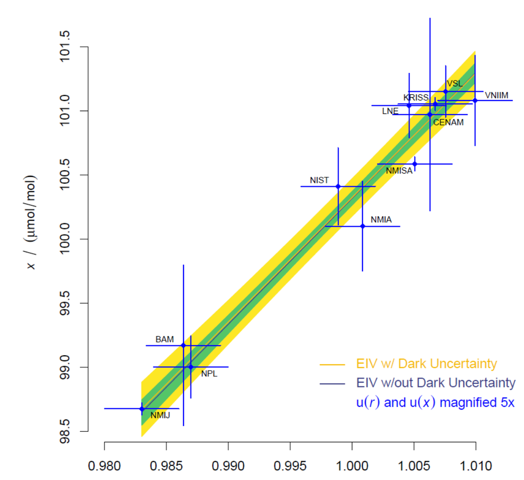
CCQM-K53 Oxygen in Nitrogen

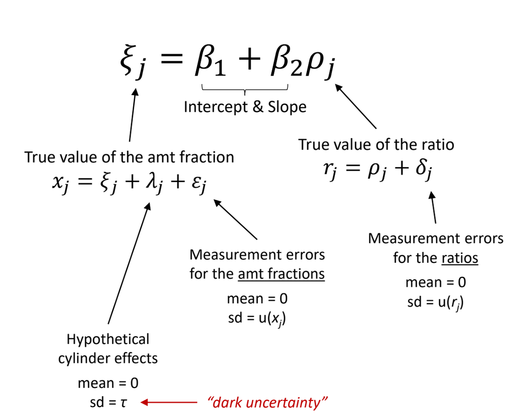
- Key comparison reference function (KCRF): ISO 6143 regression using participants' mixtures as calibrants
- Participants' results found to be mutually inconsistent, i.e., more dispersed around the regression line than expected given the reported uncertainties
- As a result, 3 results were excluded (blue), owing to some "unknown" uncertainty, possibly related to impurities in the gas mixture
- One result (red) also excluded due to self-reported error by the participant

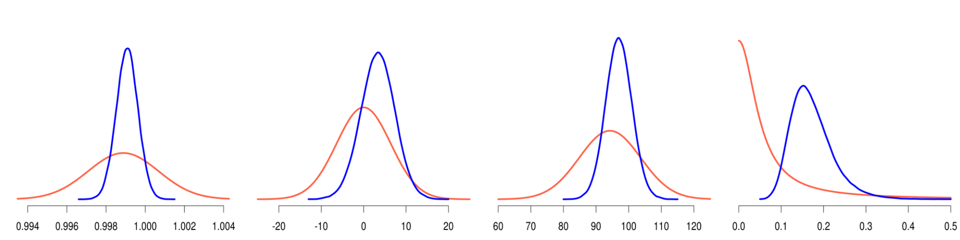


EIV Regression with Dark Uncertainty

- Includes ALL valid participant measurements
- Accommodates "dark uncertainty" for the amount fractions (τ), which reveals itself only after a line has been fitted to all the measurement results together
- Evaluated using a Bayesian procedure: produces samples of the probability distribution of the parameters using Markov Chain Monte Carlo (MCMC) sampling
- Prior distributions (red) reflect initial best guesses of the true values
- Posterior distributions (blue) are results of updating those guesses taking into account the information in the data

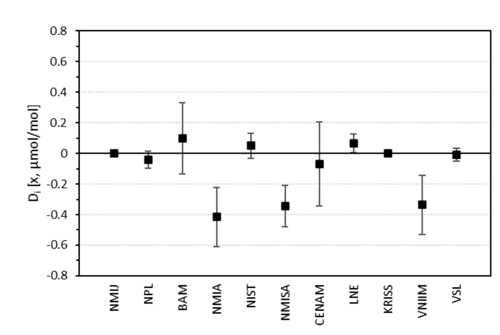




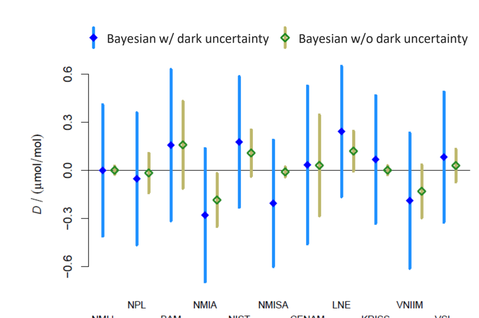


Degrees of Equivalence

- Original results: classical linear regression model; some results excluded to achieve mutual consistency



- NIST reanalysis: Bayesian model with and without dark uncertainty; all results included



- The model including dark uncertainty is more inclusive than the conventional model, in that it easily accommodates measurement results that are mutually inconsistent

References: Dark Uncertainty; CCQM-K53 Final Report; EIV Calibration with Dark Uncertainty