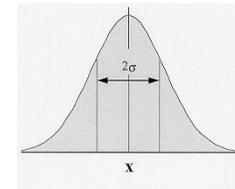


Measurement Uncertainty

-a quantitative concept of accuracy

-defined as “a parameter, associated with the result of a measurement that characterises the dispersion of values that could reasonably attributed to the measurand” [NPL, 2006]



-**random error** causes data to be scattered more or less symmetrically around a mean value and affects measurement precision (rel. stand. dev. (RSD) $\times 100\% = s_y/y \times 100\%$)

-**systematic error**, or bias, causes the mean of a data set to differ from the accepted values and affects the accuracy of results

-**error propagation** - total uncertainty s_y/y for $y = a \times b/c$ can be estimated as:

$$s_y/y = \sqrt{(s_a/a)^2 + (s_b/b)^2 + (s_c/c)^2}$$

In some cases, both constant and proportional effects on the uncertainty are important.

Calculating standard deviation of results from slope of a calibration curve:

Most often, calibrations are analysed using un-weighted least squares regression on a set of n pairs of values (x_i, y_i) , assuming no errors in x_i .

The parameters usually of interest are the average of a result (uncertainty calculated by %RSD) or the slope, i.e. PA/g (or mol)

Least squares method minimizes sum of squares of the residuals

$$SS_{\text{resid}} = \sum_{i=1}^N [y_i - (b + mx_i)]^2$$

Standard deviation of slope, s_m :

$$s_m = \sqrt{\frac{SS_{\text{resid}}}{S_{xx} (N - 2)}} \quad N \text{ is number of points used}$$

$$S_{xx} = \sum (x_i - \bar{x})^2$$

Measurement Uncertainties in VSLH measurements

Uncertainty associated with gas-phase sampling

Line losses (bias)

Sample flow rate (bias)

Atmospheric artefacts (e.g. humidity, co-elutions) (bias)

Analytical precision/reproducibility of gas phase standards (noise) – takes into account noise on integrations, detector

Uncertainty associated with water sampling

Losses or production in water sample during storage (bias)

Losses or production in water sample during purging or equilibration (bias)

Sample flow rate (bias)

Reproducibility of water standards (noise), or

Reproducibility purge efficiencies (noise) + purge volume (noise), or Reproducibility of equilibrated samples

Uncertainty associated with calibration

- (1) Gas standards
- (2) Liquid standards
- (3) Permeation tube approach

$$\text{Total Uncertainty } U \sim \sqrt{u_{\text{sampling/meas}}^2 + u_{\text{calibration}}^2}$$

Participant responses:

Analytical precision – (replicates)

- a few to 10% - 15% or so...dependent on compound and absolute amount of analyte
- 2-5% range (but not near LODs)
- 3-5% range
- approximately 5% for all compounds taking into account sampling, standard and analytical errors
- 0.9-3%
- 0.6-6.6% (10-15% at atmospheric levels?)
- 2-4%
- 4-8%
- 1-5%
- 5% (CH_3I) - 15% CH_2I_2

Analytical precision cont.

- 1-10% (dependant on particular instrument being used and compound being analysed)
- 2-15% depending on compound and instrument condition
- 1.9 to 4.2 % (of the average concentration)
- Air: ~5-10%, depending of the compound and its ambient mixing ratio. Water: ~5-20%, again, compound and concentration dependant
- 0.1% at the higher concentrations to order 1 or 2% for concentrations in the 1 ppt range
- Typically 1-5 % for air

Sampling precision

- ? x 5
- 2% air, 12% water (from RSD of purge efficiencies)
- 3-15% water (equilibrator), estimated from cruise data during non-varying periods
- limited by the analytical precision x 5
- 5%
- For most compounds sampled from whole air by continuous pumping in the field, sampling errors are negligible. For some compounds there are concerns of contamination by elastomers used in the sampling system.

Sampling precision cont.

- derived from taking an entire series of calibrations (air) for a field campaign. For each sequence of three calibrations, the first and last are interpolated to derive a value for the middle calibration. The derived value is compared to the expected value and the deviation used as the measurement uncertainty. Result 2-25%.

Participant responses:

Calibration uncertainty

Gas standards:

- NOAA-CMDL/ESRL x 4, overall accuracy (incl. drift) over a 3-5 year period estimated to be 10-15%
- AGAGE scale x 2. Between 1 - 2%.
- NCAR x 3 (Elliot Atlas). Better than 10% for most compounds (working std related to Scott Marrin ppbv gas standard) x 2
- UCI (Don Blake) x 2, ~5-10%, compound and mixing ratio dependant
- Compounds which are stable in 100-ppt standard gas cylinders : ~1% (commercially prepared Japan)

Calibration uncertainty cont.

Permeation tubes:

- Hard to tell, perm tube and gravimetric stds for CH_3I seem to be in good agreement (10%). Probably not better than 20% for CH_2I_2 .
- mean of 12%

Liquid standards:

- 2%
- few % (scale accuracy, purity of pure stock solutions and the last dilution)
- 2-3%
- 3-10%

Summary:

Analytical precision

- typically <5% in air for ppt range
- higher for water
- much higher nearer to LODs

Sampling precision

- limited by analytical precision for air samples
- 10-15% for water

Calibration uncertainty

- large range for gravimetrically prepared air standards (1-10%). Depends on drift and on concentration
- permeation tubes – little information but ~10-15%
- liquid standards –few % (?)