

A PRACTICAL APPROACH TO THE ESTIMATION OF MEASUREMENT UNCERTAINTY AND ITS ASSESSMENT

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By

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Estimation of Measurement Uncertainty Approaches

- 1) The metrological technique using the error budget approach (“Type B”)
- 2) The analytical chemistry approach using method validation and control sample data (“Type A”)

Type A & Type B Evaluations Of Standard Uncertainty

- Type A is based on an estimate of the uncertainty from repeated independent measurements
- Type B is based on scientific judgment using a pool of information (previous measurements, certificates, etc.)

Guide to the Expression of Uncertainty in Measurement 1993 ISO Geneva

Presentation Philosophy

- The uncertainty considerations have been known to fill people with dread – especially academic statisticians
- The aim of this presentation is to give us tools we can use in an operating laboratory to measure our uncertainty with a minimum of effort

Adapted From

EURACHEM CITAC Guide - Quantifying
Uncertainty In Analytical Measurements
and

VAM Project 3.2.1 Development And
Harmonization Of Measurement
Uncertainty Principals - Part (d): Protocol
for uncertainty evaluation from
validation data

Rationale For This Approach (1)

THE EURACHEM Guide says “Where a factor has been representatively varied during the course of a precision experiment... that factor needs no additional study.”

Rationale For This Approach (2)

The VAM Protocol states “...key studies routinely undertaken for validation purposes..... provide much of the data required to produce an estimate of measurement uncertainty.”

Error & Uncertainty (2)

- **Uncertainty** is “a parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand”

Uncertainty Comments

- Uncertainty is a range and, in general, it cannot be used to correct a measurement result
- Knowledge of the uncertainty implies “increased confidence” , it does not imply doubt about the validity of a measurement

Estimation Of Measurement Uncertainty

- Specify the measurand
- Identify uncertainty sources
- Quantify uncertainty components (using replicate data to include as many sources as possible)
- Calculate combined uncertainty

Specify The Measurand

- Identify what is measured
- Establish its relationship to parameters such as constants, calibration standards, weights etc. through the equation used to calculate the final measurand result.

Uncertainty Sources (1)

- Identify dependence of measurand on constants, calibration standards, measured quantities etc.
- Correct for known systematic effects
- Provide for sampling uncertainty
- Such info should be in SOP's

Uncertainty Sources (2)

- List possible sources (include those contributing to parameters mentioned above)
- Must include those arising from chemical assumptions (such as extraction efficiency)

Example 1: Ca in Water

- Measureand: Ca in water (by ICP/ES)
- The data available is from >30 results obtained on a reference sample over a period of 11 months
- List the sources of uncertainty for such a situation

Sources of Uncertainty

- Analyst
- Instrument (calibration, noise, drift, other?)
- Bias (uncertainty in reference value, samples different matrix from reference)
- Volumetric and other analytical manipulations
- Laboratory environment
- Sampling
- Others???

Laboratory Data

- Number of results - 31
- Mean of the results - 68 mg/L
- Standard deviation – 3.0 mg/L
- No bias reported or correction made
- Blanks low and SD small (<1 mg/L)
- Sampling uncertainty assumed low

Estimation of Measurement Uncertainty

- What possible sources were not varied over the many months the data was collected?
- If none, the MU can be estimated as the SD of the reference data (3.0 mg/L) at this concentration range (say 20 – 100 mg/L).

Reporting the MU Estimate and the Result

- The uncertainty $u_c = 3.0$ mg/L
- $N > 30$ so the expansion factor is 2
- The expanded uncertainty is $U_c = 2 \times 3.0 = 6.0$ mg/L
- The result would be reported as xx mg/L with an expanded uncertainty of 6 mg/L for a 95% level of confidence using an expansion factor of 2.

Example 2: Pb in Soil

- Pb in soils/silts by acid digestion and ICP/ES
- The data available is sample duplicate and reference sample data collected over several months.
- List the sources of uncertainty

Sources of Uncertainty

- Analyst
- Instrument (calibration, noise, drift, other?)
- Bias (uncertainty in reference value, samples different matrix from reference)
- Volumetric, weighing and other analytical manipulations
- Extraction efficiency in digestion step
- Laboratory environment
- Sampling: both from raw sample and in taking the analytical portion from the dried and screened sample
- Others???

Laboratory Data – Reference Sample

- Number of results – 36 (over 8 months)
- Mean of the results – 32.7 mg/L
- Standard deviation – 3.22mg/L
- No bias reported or correction made
- Sampling uncertainty assumed low for the reference sample

Laboratory Data – Sample Duplicates Excel Format

Laboratory Data – Sample Duplicates

$$\text{Variance} = \Sigma R^2 / 2N$$

$$\Sigma R^2 \text{ (5 – 50 mg/g range)} = 15.2079$$

$$N=16$$

$$\text{Variance} = 15.2079 / 32 = .4572$$

$$\text{SD} = (.4572)^{-} = .6894 \text{ (.69)}$$

Sources Covered by Reference Sample Data

- ✓ Analyst
- ✓ Instrument (calibration, noise, drift, other?)
- ✓ Bias (uncertainty in reference value, samples different matrix from reference)
- ✓ Volumetric, weighing and other analytical manipulations
- ✓ Extraction efficiency in digestion step
- ✓ Laboratory environment
- Sampling: both from raw sample and in taking the analytical portion from the dried and screened sample
- Others???

Sources Covered by Duplicate Sample Data

- Analyst
- Instrument (calibration, noise, drift, other?)
- Bias (uncertainty in reference value, samples different matrix from reference)
- Volumetric, weighing and other analytical manipulations
- ❖ Extraction efficiency in digestion step
- Laboratory environment
- ✓ Sampling: in taking the analytical portion from the dried and screened sample, **not from sub-sampling raw sample**
- Others???

Combine Individual Uncertainties Using Variances

- Variance from reference sample data $(3.22)^2 = 10.368$
- Variance from duplicates data = 0.4572
- Combined uncertainty $u_c = (10.368 + 0.4572)^{1/2} = 3.29 \text{ mg/g}$
- Expanded combined uncertainty $U_c = 2 \times 3.29 = 6.58 \text{ mg/g}$

Reporting the MU Estimate and the Result

- Expanded combined uncertainty $U_c = 2 \times 3.29 = 6.58$ mg/g **for this concentration range (say 5 – 50 mg/g)**
- The results would be reported as xx mg/L with an expanded uncertainty of 7 mg/L for a 95% level of confidence using an expansion factor of 2.

Assessment of Estimates of Measurement Uncertainty (1)

Look for a definition of the measureand(s):

- o the analyte(s)
- o the measurement objectives for fit-for-purpose (LOD, precision, accuracy, analytical range, selectivity & etc. as should be found in the method SOP and validation files)

Assessment of Estimates of Measurement Uncertainty (2)

Look for a list of the anticipated sources of uncertainty (including the parameters found in the equation used to calculate the final result to be reported).

Assessment of Estimates of Measurement Uncertainty (3)

Ensure the repeated data sources are identified:

- o Spikes
- o Reference samples
- o Duplicates (at different sampling stages)
- o Method validation data
- o Round robin data (as a last resort)

Assessment of Estimates of Measurement Uncertainty (4)

Confirm the MU sources identified as being matched are indeed varied during the collection of the repeat data.

For those MU sources not covered, look for well documented estimates of their magnitudes.

Assessment of Estimates of Measurement Uncertainty (5)

Look for over-estimates of MU due to double-counting of sources.

Long-term spike and reference sample data sets for example, can both contain uncertainties introduced by different analysts, calibration solutions, drift, lab environment etc.

Assessment of Estimates of Measurement Uncertainty (6)

Possible table format to compile some of the information

Description of Uncertainty Source	Value of x	Uncertainty measured or found	u(x) as Standard Deviation	u(x) as Relative Standard Deviation	Source of u(x) information

Assessment of Estimates of Measurement Uncertainty (7)

Using the appropriate uncertainty estimates compiled (as in the table shown for example), ensure all identified sources have been estimated but not double counted.

Check that the individual estimates of MU are combined using their variances (squares of the individual SD's).

Assessment of Estimates of Measurement Uncertainty (8)

Ensure the appropriate coverage factor is applied to the combined MU estimate to get the Expanded Uncertainty.

Ensure this expanded uncertainty meets the specified requirements for the data to be fit-for-purpose.

Ensure reported data (where required) includes the expanded uncertainty, the expansion factor and the confidence level (eg 95%)