ESTIMATION OF MEASUREMENT UNCERTAINTY

The new accreditation standard ISO/IEC 17025: 1999 requires laboratories to estimate the uncertainty of measurement.

"I used to be uncertain – now I'm not so sure"

Uncertainty does not inspire confidence, but from an analytical laboratory perspective, uncertainty defines the range of the values that could reasonably be attributed to an analytical result. Uncertainty arises as a result of random effects, such as short-term fluctuations in temperature, relative humidity and power source variations or a result of systematic effects, such as instrumental drift between calibrations. When laboratories report uncertainty it gives a quantitative indication of the quality of the analytical results, and it allows the user of the result to:

- Assess its reliability
- Assess the confidence that can be placed on a result, when comparing it with a limiting value defined in a specification or regulation
- Compare analytical results e.g., from different laboratories
- Assess the "fitness for purpose" of the result

The complexity involved in estimation of uncertainty of measurement in the case of testing varies considerably from one test field to another and also within one field itself. A less metrologically rigorous process than that which can be followed for calibration can also often be used. Clause 5.4.6.2 of ISO/IEC 17025 allows for these factors. The degree of rigor needed in an estimation of uncertainty of measurement depends on factors such as:

- Requirement of the test method
- Requirement of the client
- There are narrow limits on which decisions conformance to a specification are based

If the test method is well recognized (ASTM, ISO) and specifies limits to the values of the major sources of uncertainty of measurement, and specifies the form of presentation of calculated results, the laboratory is considered to have satisfied this clause by following the test method and reporting instructions. Clause 5.4.6.3 states that uncertainty components/budgets are a combination of many factors that may include, but are not limited to:

- Sampling – where in-house or field sampling form part of the specified procedure, effects such as random variations between different samples and any potential for bias in the sampling procedure
- Storage conditions – where test sample is stored prior to analysis, the storage conditions may affect the analytical result
- Properties and condition of item being tested
- Equipment used – limits of accuracy of instruments used in the measurement process i.e., analytical balance
- Analytical method used – assumed stoichiometry, reagent purity, instrument settings, blank correction
- Reference standards
- Reference materials
- Environmental conditions
- Calibration
- Operator effects
- Known physical characteristics of components such as, coefficient of thermal expansion. These often can be looked up in engineering and scientific handbooks.
- Data processing

The Process of Measurement Uncertainty Estimation

Uncertainty of measurement comprises, in general, many components. Some of these components may be estimated on the basis of the statistical distribution of the results of series of measurements and can be characterized by experimental standard deviations, and are called Type A evaluation. The Type A can be applied when several independent observations have been made for one of the input quantities under the

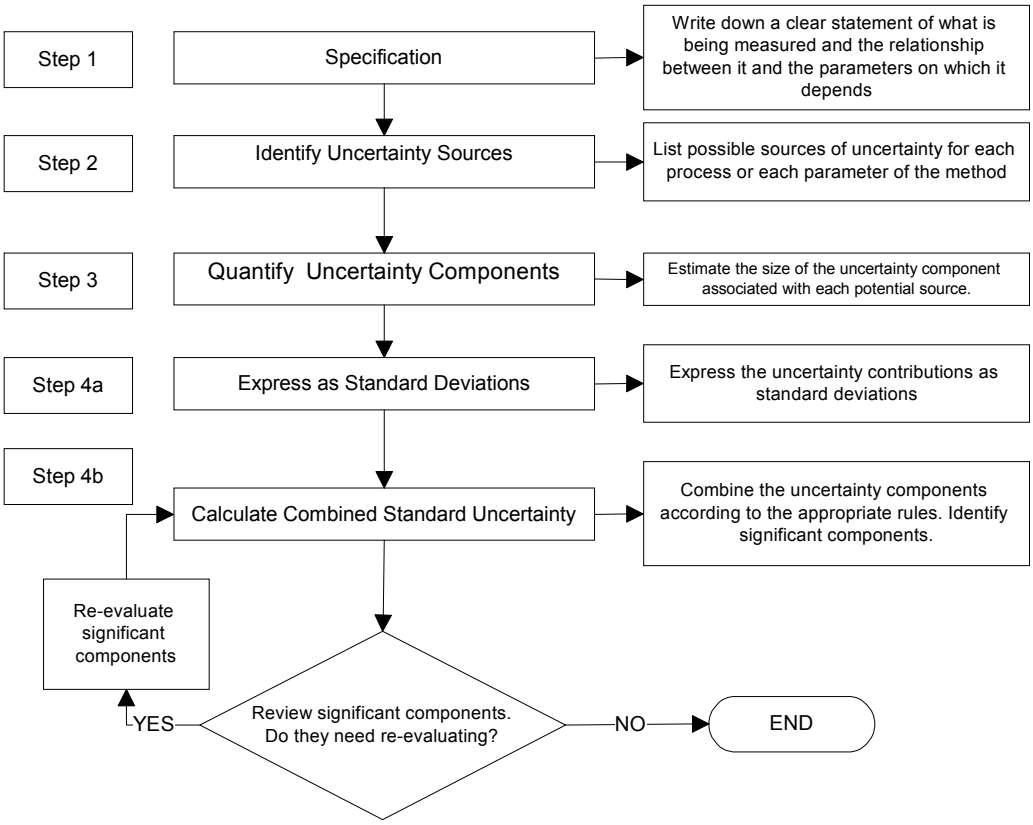
same conditions of measurement. If there is sufficient resolution in the measurement process, there will be an observable scatter or spread in the values obtained. In this case, the standard uncertainty is the experimental standard deviation of the mean that follows from an averaging procedure or an appropriate regression analysis.

Estimates of other components can only be based on experience or other information, and are called Type B evaluation. Values belonging in this category may be derived from:

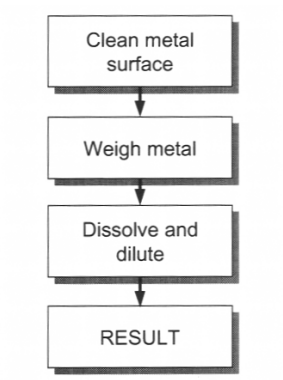
- Previous measurement data
- Experience with or general knowledge of the behaviour and properties of relevant materials and instruments
- Manufacturer's specifications
- Data provided in calibration and other certificates
- Uncertainties assigned to reference data taken from handbooks

The measurement uncertainty for a given calibration is the combination of all the type A and type B components of the uncertainty budget.

Uncertainty estimation is a simple process in principle. The following flow chart summarises the steps that need to be performed in order to obtain an estimate of the uncertainty associated with a measurement result.



The following example of quantifying uncertainty is taken from EURACHEM/CITAC Guide[1], preparation of a 1000mgL^{-1} Cd calibration standard from high purity metal. The stages of the procedure are shown in the following flow chart, Figure 1.



where

c_{Cd} :concentration of the calibration standard [mg l^{-1}]

1000 :conversion factor from [ml] to [l]

m :mass of the high purity metal [mg]

P :purity of the metal given as mass fraction

V :volume of the liquid of the calibration standard [ml]

$$c_{Cd} = \frac{1000 \cdot m \cdot P}{V} \text{ [mg l}^{-1}\text{]}$$

Figure 1. Steps involved in preparing a 1000mgL^{-1} Cd calibration standard.

Identification of the uncertainty sources

For each stage of the analytical procedure list the sources of uncertainty. This can conveniently be done using a cause and effect diagram, showing how the sources of uncertainty relate to each other and indicating their influence on the uncertainty of the result. Cause and effect diagrams, were the brainchild of Professor Kaoru Ishikawa of Tokyo University who pioneered quality management processes in the Kawasaki Steel Works, also help to avoid double counting of sources.

- Write the calculation equation, the parameters form the main branches of the diagram
- Consider each step in the analytical method and add contributing factors to the diagram
- Smaller branches (contributing factors) are added to the main branches, each representing an effect on the previous branch
- The diagram is "simplified" by:
  - Eliminating canceling effects – no net effect on result
  - 'Same effect – same time' are combined as a net effect
  - Restructure to group similar effects

The relevant uncertainty sources are shown in the cause and effect diagram below, Figure 2:

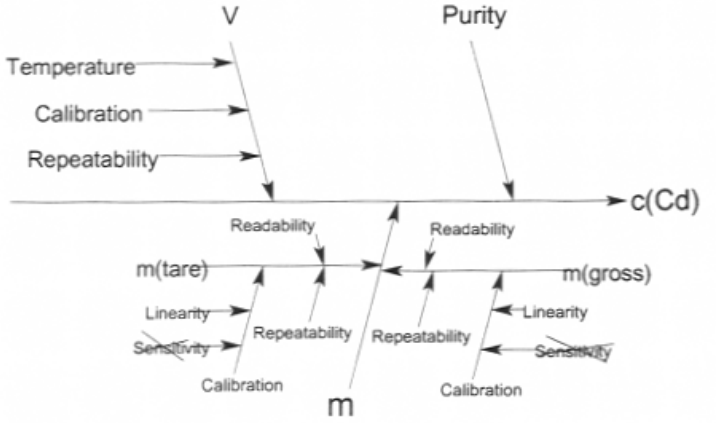


Figure 2. Sources of uncertainty in preparing a 1000mgL^{-1} Cd calibration standard shown in a cause and effect diagram

Quantitation of the uncertainty components

Measure or estimate the size of the uncertainty component associated with each potential source of uncertainty defined. Much of the data for this step can be obtained from method validation data, calibration certificates, certified reference material certificates and proficiency testing data. It is important to consider whether available data account sufficiently for all sources of uncertainty, and plan additional experiments and studies to ensure all sources of uncertainty are adequately accounted for.

Uncertainty estimation relies on the use of statistical methods and therefore some knowledge of basic statistical parameters. The following table shows chemists how to calculate a standard uncertainty from the parameters of the two most important distribution functions.

Distribution	Use when	Uncertainty
Rectangular	A certificate that specifies a range (±a) without confidence level	$u(x) = \frac{a}{\sqrt{3}}$
Triangular	A range value (±a) is more likely to be near the centre of the range	$u(x) = \frac{a}{\sqrt{6}}$

The values and their uncertainty are shown in the table below.

Combined Standard Uncertainty:

The combined standard uncertainty for the preparation of a 1002.7mgL^{-1} Cd calibration standard is 0.9mgL^{-1}.

Individual contributions to the uncertainty should be given in terms of a standard deviation. Uncertainties expressed as standard deviations are **standard uncertainties**. Standard deviation is a measure of the spread of data around the sample mean – a measure of precision. The standard deviation is considered an estimate of the population standard deviation from a sample of results. The relative standard deviation is a measure of the spread of the data in comparison to the mean. It is simply the standard deviation divided by the mean. Relative standard deviations are combined to calculate the total uncertainty. Variance also describes the spread of data, and is the square of the standard deviation.

There are two basic rules for combining standard uncertainties:

Rule 1

For models involving only a sum or difference of quantities e.g., combining the three contributions for the standard uncertainty *(uV)* of the volume use

$$u_c(y(p,q..)) = \sqrt{u(p)^2 + u(q)^2 + ...}$$

Rule 2

For models involving only a product or quotient e.g., combining standard uncertainties to calculate the uncertainty of the concentration of the cadmium calibration solution use

$$u_c(y) = y\sqrt{\left(\frac{u(p)}{p}\right)^2 + \left(\frac{u(q)}{q}\right)^2 + ...}$$

	Description	Value	Standard uncertainty	Relative standard uncertainty *u(x)/x*
P	Purity of the metal	0.9999	0.000058	0.000058
M	Mass of the metal	100.28mg	0.05mg	0.0005
V	Volume of the flask	100.0mL	0.07mL	0.0007
c_{Cd}	Concentration of the calibration standard	1002.7mgL^{-1}	0.9mgL^{-1}	0.0009

This example deals with the very simple case of preparing a calibration standard for trace metal AAS or ICP analysis and shows how to evaluate the components of uncertainty arising from the basic operations of volume measurement and weighing and how these components are combined to determine the overall uncertainty.

References

1. EURACHEM/CITAC Guide, Quantifying Uncertainty in Analytical Measurement, Second Edition, 2000