What is measurement uncertainty?

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Introduction

Whenever a measurement is made, the result obtained is only an estimate of the true value of the property being measured. Many factors will cause measurement results to vary from the true value:

- uncontrollable random variations in the measurement process;
- limitations in the measuring equipment used;
- the presence of bias (i.e. results being consistently higher or lower than they should be).

An uncertainty estimate tells you about the doubt in a measurement result. The ISO definition of uncertainty[1] is:

> *"A parameter associated with the result of a measurement, that characterises the dispersion of results that could reasonably be attributed to the measurand."*

The uncertainty is a range, associated with the measurement result, which contains the true value. For example, the concentration of lead in a sample of soil is reported as 95 ± 14 mg kg^{-1}. This should be interpreted as, 'The true value for the amount of lead present in the soil sample is somewhere between 81 mg kg^{-1} and 109 mg kg^{-1}' (at a given level of confidence).

In the past, analysts have used confidence intervals obtained from precision data (i.e. the spread of results obtained from repeated measurements on a sample) to give an indication of the reliability of the result. However, a confidence interval only takes account of random variation in results and makes no allowance for non-random (systematic) effects. An estimate of measurement uncertainty includes the effect of all significant factors that cause results to vary, both random and systematic. Compared to a confidence interval, measurement uncertainty is a more robust indicator of the reliability of measurement results.

Why is measurement uncertainty important?

Without knowledge of measurement uncertainty it is difficult to make a meaningful interpretation of a measurement result. If you do not know the reliability of results, how can you tell whether the results produced by different laboratories are genuinely different or whether a legislative limit has definitely been exceeded? Measurement uncertainty allows us to judge whether results are likely to be fit for a particular purpose. In some cases a relatively large uncertainty may be acceptable, whilst in others this would be totally unacceptable. Although uncertainty means 'doubt', having knowledge of the measurement uncertainty means that we actually know more about the result as it allows us to quantify the doubt.

Sources of uncertainty: Random and systematic effects

Consider the preparation of a calibration solution. This typically involves weighing out the required amount of a substance, dissolving it in a suitable solvent and making the solution up to volume in a volumetric flask. The concentration of the solution is calculated from the known mass and purity of the material used and the final volume. There will be an uncertainty in the concentration of the solution due to the uncertainties associated with the operations carried out to prepare the solution, as shown in Figure 1.

Measurement uncertainty must take account of both random and systematic effects. Random errors cause variation in results from one measurement to the next in an unpredictable way. The size of the random errors will determine the precision of results. Random errors are always present and cannot be corrected for. They can, however, be reduced by increasing the number of measurements made and reporting the average, or by using a better piece of equipment which gives results that are more precise. Systematic errors cause results to differ from the true value by a constant amount, and in the same direction, each time

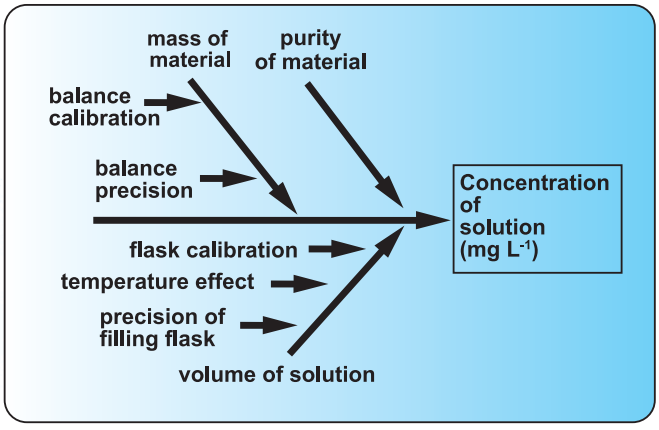


Figure 1: Factors contributing to the uncertainty in the concentration of a standard solution

[1]Guide to the Expression of Uncertainty in Measurement, 1st edition, ISO (1995) (ISBN 92 67 10188 9)

a measurement is made. If the size of a systematic error is known, it can be corrected for. Systematic errors cause results to be biased.

In Figure 1, both systematic and random effects are shown. An example of a systematic effect is the calibration of the balance used to weigh out the material. An example of a random effect is the precision of filling the volumetric flask to the calibration line – each time the flask is filled to the line there will be a slight variation in judging the position of the meniscus. Although it is important to remember that both systematic and random effects must be accounted for when evaluating measurement uncertainty, when it comes to combining different uncertainty estimates, they are both treated in the same way.

Note that measurement uncertainty is intended to represent the expected variation in results obtained when the test method is being carried out correctly and is under statistical control. Uncertainty does not, therefore, include the effect of gross errors (or mistakes!).

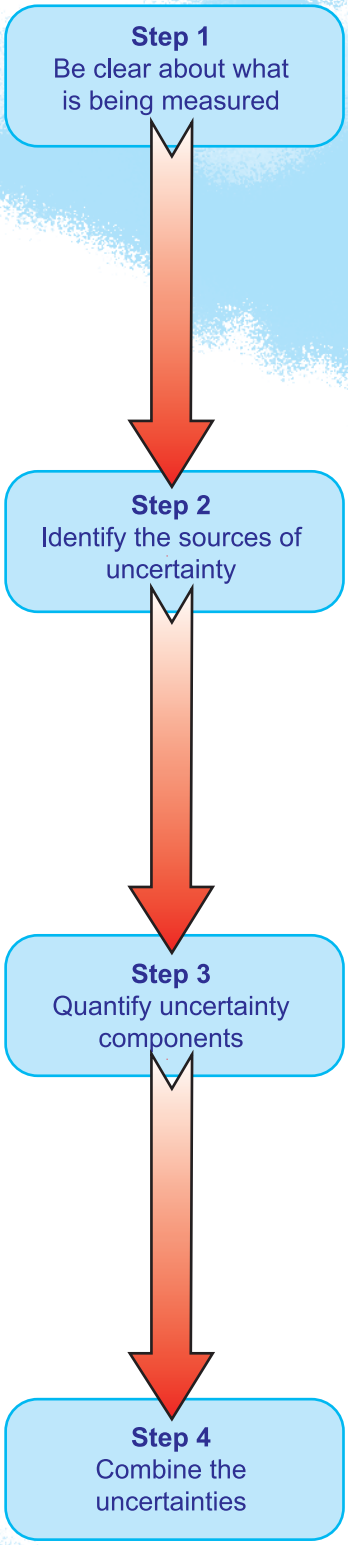
Examples of sources of uncertainty in chemical test methods

General categories of sources of uncertainty are shown in Table 1.

Table 1: Typical sources of uncertainty

Source	Examples
Analyst	Small differences in application of the method.
Sample	Homogeneity and stability. Matrix – interferences and influence on analyte recovery.
Test method	Sample pre-treatment – drying, grinding, blending. Analyte extraction from sample – extraction conditions, incomplete recovery. Sample clean-up – possible loss of analyte. Measurement of the analyte concentration – instrument effects and calibration.
Laboratory	Environmental conditions.
Computational effects	Calibration model – uncertainty associated with predicted values obtained from a calibration curve.
Random effects	Always present for all stages of the method – variation in extraction efficiency, variation in filling volumetric glassware to the calibration mark, variation in instrument response.

The uncertainty evaluation process



At the beginning of the process of evaluating uncertainty it is important to be clear about what is being measured (e.g. total lead vs. extractable lead). Write down the equation that will be used to calculate the result. The parameters in the equation (masses, volumes, instrument response, etc) will contribute to the uncertainty in the measurement result.

A critical step in evaluating uncertainty is compiling a list of all the possible sources of uncertainty. This will include the sources that contribute to the parameters identified in step 1, but there are likely to be other sources of uncertainty as well. It is useful to consider each stage of the test method in turn and think about the things which could cause results to vary.

The next step is to estimate the size of each uncertainty component identified in step 2. This can be done by using published data, or method performance data from validation studies or on-going quality control. Where such data are not available additional experimental studies will be required. It is often possible to plan experiments that can account for a number of different sources of uncertainty.

Step 3 will result in a list of a number of sources of uncertainty together with an estimate of their magnitude. This is often referred to as the 'uncertainty budget'. The individual contributions must be expressed as standard deviations and are combined using mathematical rules for the combination of variances. This results in a combined uncertainty estimate for the result of the measurement. This is known as the combined standard uncertainty.

Standard and expanded uncertainties

There are many potential sources of information that can be used to help evaluate and quantify uncertainty components. Calculating the uncertainty for the results from a particular test method usually involves combining data from a number of different sources. One problem that frequently arises is that the data are not expressed in the same way (see Table 2). Before they can be combined, the data must be converted to the same mathematical form. The correct form is the standard deviation. When an uncertainty component is expressed in the form of a standard deviation it is known as a standard uncertainty. Standard uncertainties are denoted by the symbol u. When individual uncertainty estimates are combined, the result is the combined standard uncertainty. This is also equivalent to a standard deviation. For data following a normal distribution, approximately 68% of values are expected to lie within ±1 standard deviation of the mean as shown in Figure 2.

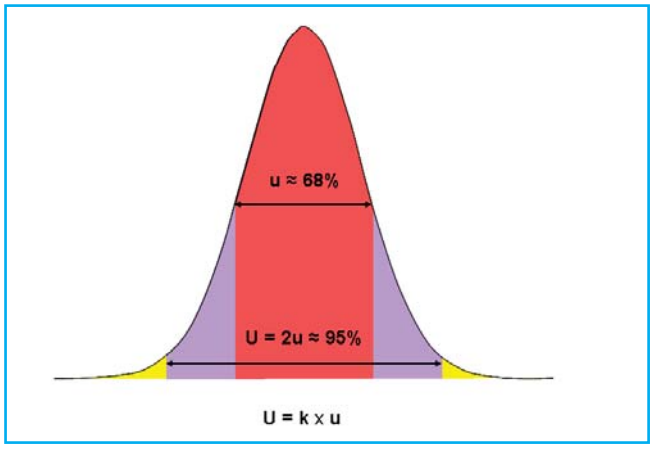


Figure 2: Calculating the expanded uncertainty

To increase the level of confidence that the uncertainty quoted includes the true value, the combined standard uncertainty is usually expanded to include 95% of values. This is achieved by multiplying the combined standard uncertainty by a coverage factor, k. To obtain a confidence level of approximately 95%, a coverage factor of 2 is generally used, as illustrated in Figure 2. Expanded uncertainties are denoted by the symbol U.

Some of the common forms of uncertainty data, and the rules for converting them to a standard uncertainty, are shown in Table 2.

Table 2: Forms of uncertainty data

Form of uncertainty data	Example	Conversion factor to obtain standard uncertainty
Standard deviation	The calculated standard deviation of results from the analysis of 10 portions of a reference material.	No conversion required.
Confidence interval	The concentration of a standard solution is quoted as 1000 ± 3 mg L^{-1} with a level of confidence of not less than 95%.	Divide the half-range (i.e. ± value) by 1.96.
Expanded uncertainty	Calibration certificate for a 25 mL pipette quotes an uncertainty of ± 0.03 mL where the reported uncertainty is an expanded uncertainty calculated using a coverage factor of 2 which gives a level of confidence of approximately 95%.	Divide quoted expanded uncertainty by the stated coverage factor.
Stated range – values equally likely across the range	The purity of a compound is quoted as (99.9 ± 0.1)%.	Divide ± value by 3.*
Stated range – values close to mean more likely than values at the extremes of the range	The manufacturer's tolerance for a Class A 100 mL volumetric flask is quoted as ± 0.08 mL.	Divide ± value by 6.**

*Assumes a *rectangular* distribution of data
**Assumes a *triangular* distribution of data

Combining standard uncertainties

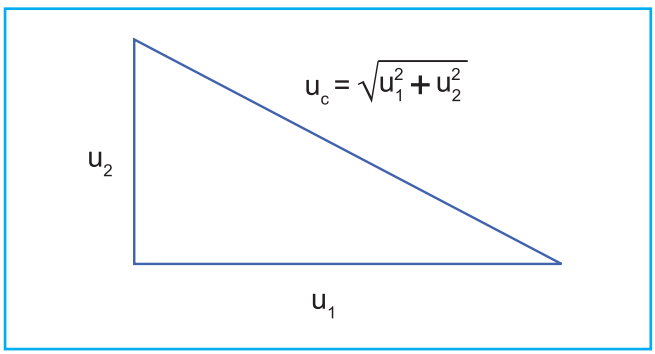


Figure 3: Combining standard uncertainties

Standard uncertainties are combined using the mathematical rule for combining variances. This is sometimes referred to as the 'root sum of squares' rule and is illustrated in Figure 3. u_1 and u_2 are independent uncertainty components, expressed as

standard deviations and u_c is the combined uncertainty. Due to the way the standard uncertainties are combined, if u_1 is much greater than u_2 then u_c will be approximately equal to u_1.

There are two 'rules' commonly used for combining standard uncertainties. Which rule is used depends on the form of the equation used to calculate the result.

Rule 1

Equation used to calculate the result involves only addition and/or subtraction, e.g. result *y* calculated from:

$$y = a + b - c$$

Uncertainty in *y*, $u_c(y)$ calculated from:

$$u_c(y) = \sqrt{u(a)^2 + u(b)^2 + u(c)^2}$$

u(*a*), u(*b*) and u(*c*) are the uncertainties associated with parameters *a*, *b* and *c*, expressed as standard uncertainties. This is the rule shown in Figure 3.

Rule 2

Equation used to calculate the result involves multiplication and/or division, e.g. result *y* calculated from:

$$y = \frac{d \times e}{f}$$

Uncertainty in *y*, $u_c(y)$ calculated from:

$$u_c(y) = y \times \sqrt{\left(\frac{u(d)}{d}\right)^2 + \left(\frac{u(e)}{e}\right)^2 + \left(\frac{u(f)}{f}\right)^2}$$

u(*d*), u(*e*) and u(*f*) are the uncertainties associated with parameters *d*, *e* and *f*, expressed as standard uncertainties. In this case the uncertainties are combined as relative standard deviations.

If the equation used to calculate the result involves a mixture of addition/subtraction and multiplication/division the uncertainty is calculated by breaking down the equation into components that can be handled using the rules given above.

Sources of information

There are a number of sources of information that can be used to obtain estimates of the magnitude of different uncertainty components.

Table 3: Sources of information for uncertainty estimation

Information	Examples
Data from method validation studies*	Estimates of method precision and bias obtained during in-house method validation studies. Data from ruggedness studies, used to confirm insignificant sources of uncertainty. Reproducibility data from a collaborative study of method performance.
Quality control data	Data from the analysis of quality control samples, data from balance log books.
Manufacturers' specifications for equipment	Tolerances for instruments and glassware.
Calibration certificates	Certificates for balances and thermometers, certificates accompanying certified reference materials.
Literature data	Published studies on method performance.
Analyst's experience	Knowledge of performance of similar methods.

* For more information on method validation please refer to the leaflet "Introduction to method validation" in this series.

Further help from VAM

Valid Analytical Measurement (VAM) is a DTI funded programme which aims to:

- Improve the reliability of analytical measurements made in the UK;
- Facilitate mutual recognition of analytical data across international boundaries;
- Develop a robust and transparent infrastructure aimed at achieving international comparability and traceability of chemical measurements.

Further information about this programme can be obtained from the VAM website www.vam.org.uk. The website will also provide you with up to date information on current publications, new resources and VAM events. Resources that are directly relevant to evaluating measurement uncertainty include:

- Quantifying Uncertainty in Analytical Measurement, 2nd edition, Eurachem (2000) (ISBN 0 948926 15 5)
- Introducing Measurement Uncertainty, LGC (2003) (ISBN 0 948926 19 8)
- VAMSTAT II (A computer-aided learning package for training in statistics for the analytical chemist), LGC (2000)

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