Uncertainty Measurement and its Incorporation in Water Quality

Dr. Dinesh Mohan
Associate Professor
School of Environmental Sciences
Jawaharlal Nehru University
New Delhi – 110 067
Email: dm_1967@hotmail.com

Measurement uncertainty is one of the key issues in quality assurance. It became very important for analytical/water chemistry laboratories to have to ISO/IEC 17025 accreditation. The uncertainty measurement is the most important criterion for the decision whether a measurement result is fit for purpose. It also delivers help for the decision whether a specification limit is exceeded or not. Measurement uncertainty estimation is not trivial. Several strategies have been developed for this purpose.

The uncertainty characterizes the dispersion of the value, i.e. the expected spread of the data, which can be attributed to the measure and taking into account all reasonable effects.

"**Uncertainty**" is an unfortunate wording since for non-experts it implies doubts on the validity of results.

- Measurement Uncertainty does not imply doubt about the measurement validity
- On the contrary, Uncertainty knowledge implies increased confidence in the validity of a measurement result.

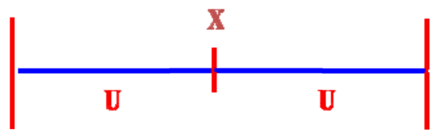
Many important decisions are based on the chemical quantitative analysis results. These include:

- To estimate yields
- To check materials against specifications or statutory limits
- To estimate monetary value

Thus, it is important to have some indication of the quality of the results, i.e. the extent to which they can be relied on for the purpose in hand.

One could think that the measurement uncertainty is a perfect quality indicator for any laboratory. The lower the reported uncertainty the better is the laboratory. As a consequence customers may commission these laboratories just because of the low reported uncertainties. It has to be clearly stated, that this is a misuse of uncertainty statements. As a result this would lead to unrealistic reported uncertainties by some laboratories just to get the contract. At the end of such an uncertainty-based battle all reported uncertainties are completely useless. Customers have to be educated to know that there is no need to have lower uncertainties than required from the purpose of the analysis.

Measurement Uncertainty (MU) is a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand (A quantity that is being determined by measurement).



A range containing the TRUE value

Uncertainty – Doubt?

- Uncertainty of measurement does not imply doubt about the validity of a measurement
- On the contrary, knowledge of the uncertainty implies increased confidence in the validity of a measurement result.

Requirements for evaluating uncertainty measurement:

Following are the requirements for evaluating uncertainty measurement.

- Knowledge and understanding of basic statistics.
- Good knowledge of the method and an ability to deconstruct the factors that influence the results.
- Knowledge of Measurement Uncertainty Principles and evaluation strategies.
- Raw data from Method Validation, Quality Control, Standards, Manufacturer's certificates, etc.
- Some experience

Error and Uncertainty

- ERROR is a DIFFERENCE
    - True value – Measured value
    - ☞ Need to know the true value

- UNCERTAINTY is a RANGE
    - ☞ TRUE value need not be known

Information it gives

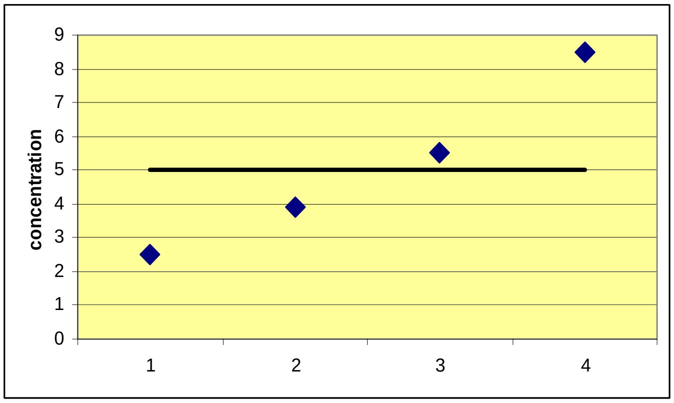
It defines a RANGE that could reasonably be attributed to the measurement result.
For example: 35.5 ± 2.8 mg.l^{-1}

Why it is important:

It enables us to:

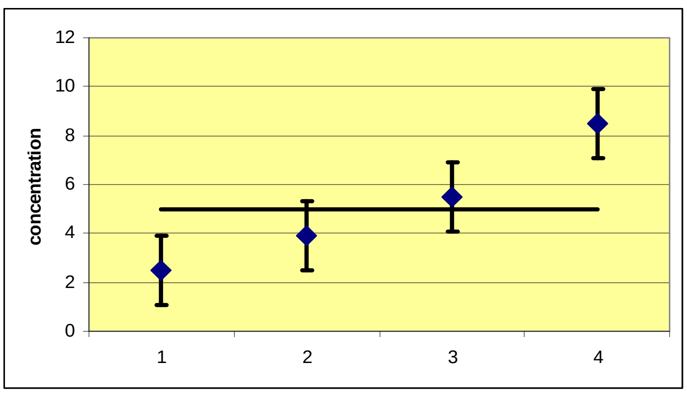
- Describe the reality of the result
- Compare measurement results
- Assess the confidence that can be placed in a decision based on the result e.g. Compliance judgment

Uncertainty and Limits



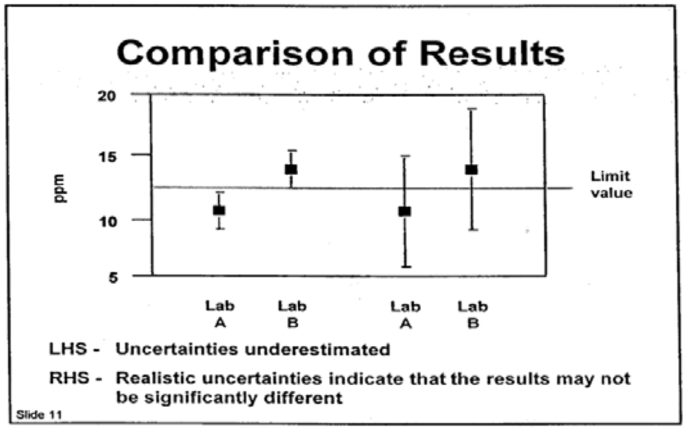
In the above figure

- We have four different results and a limit
- The situation seems to be clear



In the above figure

- we have results with uncertainty
- Is the situation different now?



Measurement Uncertainty in ISO/IEC 17025

- *5.4.6.2 Testing laboratories shall have and shall apply procedures for estimating uncertainty of measurement*
- *... Reasonable estimation shall be based on knowledge of the performance of the method and on the measurement scope and shall make use of, for example, previous experience and validation data*
- *5.4.6.3 When estimating the uncertainty of measurement, all uncertainty components which are of importance in the given situation shall be taken into account using appropriate methods of analysis*
- *Test reports, 5.10.3.1:*
  ... tests reports shall, where necessary for the interpretation of the test results, include the following:
  ...
  c) where applicable, a statement on the estimated uncertainty of measurement; information on uncertainty is needed in test reports when it is relevant to the validity or application of the test results, when a client's instruction so requires, or when the uncertainty affects compliance to a specification limit;

Mathematical Form of Uncertainty

If $y = f(x_{i,j})$, where i and j =1→n, then

$$U_c^2(y) = \Sigma(\partial y/\partial x)^2 . u^2(x_i) + 2\,\Sigma\,\Sigma(\partial y/\partial x_i).(\partial y/\partial x_j).s(x,ij)$$

This term is zero where xi and xj are independent

$$S(x,ij) = u(x_i).u(x_j).r(x_i, x_j)$$

Where r_{ij} is the correlation coefficient

Sensitivity Coefficients, ($\partial y/\partial x$)

1. $\partial y/\partial x$ = 1 or 1/x, for uncertainties calculated from rules 1 to 4,
   OR
2. $\partial y/\partial x$ can be evaluated by experiment, OR
3. $\partial y/\partial x$ can be evaluated mathematically where a reliable description exists, OR
4. $\partial y/\partial x$ can be evaluated by the *Kragten* numerical method

The ISO Guide to the Expression of Uncertainty in Measurement (GUM Principles)
Principle 1

- Specify what is being measured (in detail)
- For each stage of the measurement procedure list sources of Uncertainty
  - Identify what causes the results to change
- Quantify the Uncertainty components

Principle 2

Type A: These uncertainties are evaluated by statistical analysis of a series of observations

Type B: These uncertainties are evaluated from any other information, such as information from past experience of the measurements, from calibration certificates, manufacturers specifications, etc.

Type A and B uncertainties are based upon probability distribution.

Type A uncertainties are estimated on the basis of repeat measurements, usually assuming the normal or "t" distribution for the variability in the mean of the values.

Type B uncertainty, by and large are obtained by assuming a particular probability distribution, such as normal, a rectangular or a triangular distribution.

Principle 3

- Convert data to standard uncertainties, u
- Combine uncertainties, u_c, as variances, u^2
- Express as 'expanded uncertainty', Uc, for additional confidence, where k is the 'coverage factor'

$$\mathbf{U_c = k.u_c}$$

Combining Uncertainties

Rule 1

y = f (a,b,c,….)

- **Addition or Subtraction**

Volume (y) = Volume (a) + Volume (b)

$$[u(y)]^2 = [u(a)]^2 + [u(b)]^2$$

Rule 2

- **Product or Quotient**

Concentration of a Solution, C ($g.l^{-1}$)

C = w/v

Where w is weight and v is the Volume

To combine uncertainties use:

$$\frac{u(C)}{C} = \sqrt{\left\{\frac{u(w)}{w}\right\}^2 + \left\{\frac{u(v)}{v}\right\}^2}$$

Rule 3

- Measured quantity multiplied by a constant

q = B.x

The uncertainty in q is: u(q) = B.u(x)

- Where there is a variable raised to a power, e.g.

$$q = x^n$$

Then uncertainty in q is computed from:

$$\frac{u(q)}{q} = \frac{n.u(x)}{x}$$

Rule 4

- Measured quantity has relation of type

$$y = \frac{(O+P)}{(Q+R)}$$

- Compute U_{op} and U_{qr} (rule 1) and then
- Compute $U_{op/qr}$ (rule 2)

Some Basic Statistical Methods for Uncertainty Evaluation
Measures of a Value

- **Mean**

For a set of 'n' observations, $x_1, x_2, x_3, \ldots x_n$, the mean, x

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Provides an estimate of the central or typical value

- **Standard Deviation :**

  For a set of 'n' observations, $x_1, x_2, x_3, \ldots x_n$, the sample standard deviation, s:

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

  - Provides an estimate of the spread

- **Standard Deviation of Means (SDM)**

$$SDM = \frac{s}{\sqrt{n}}$$

- **Variance, s^2** : Also describes the spread

Pooled Standard Deviation

$$s_{pool} = \sqrt{\frac{s_1^2(n_1-1)+s_2^2(n_2-1)+\ldots}{n_1+n_2+\ldots N}}$$

Where;

- N is the number of sets of data
- n_1, n_2 (to n_N) are the numbers of replicates and s_1, s_2 (to s_N) are the standard deviations of each of the sets of data.
- S can be a SD or a RSD

Relative Standard Deviation (RSD)

$$rsd = \frac{s}{x}$$

The Coefficient of Variation (CV)

$$CV = rsd\% = \frac{s}{x}.100$$

Confidence Interval

- The confidence interval (CI) is the range within which a stated percentage of values would be expected to lie.
  - For example

  For a Normal distribution, approximately 95% of the values lie between

  x ± 2s

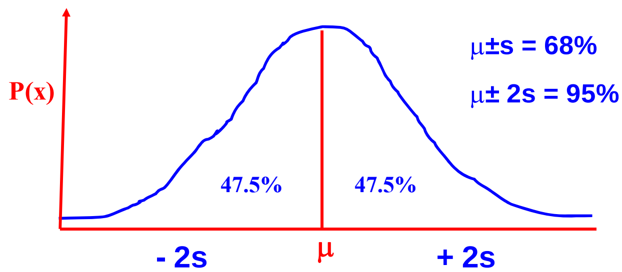
- In a more general form,

$$CI = \bar{x} \pm \frac{t.s}{\sqrt{n}}$$

Where t is the two-tailed Student ‘t’ distribution for a given probability, with a given number of repeat observations (n) and a specified degrees of freedom (n-1).

Probability Distributions

Normal Distribution:



Where "μ" is the mean and "s" is the standard deviation.

When to use normal distribution

a. In some situations, the quoted uncertainty in an input or output quantity is stated along with level of confidence. In such cases, one has to find the value of coverage factor by using the Table-1.

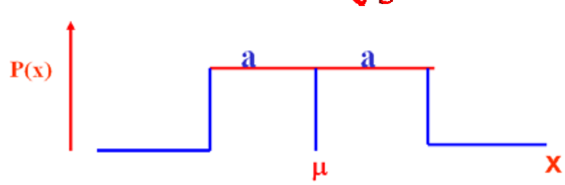
b. In the absence of any specific knowledge about the type of distribution, one may assume it to be normal distribution.

Confidence Level	68.27%	90%	95%	95.45%	99%	99.73%
Coverage factor (k)	1.000	1.645	1.960	2.000	2.576	3.000

Probability Distributions

Rectangular Distribution

$$u(x) = \frac{a}{\sqrt{3}}$$

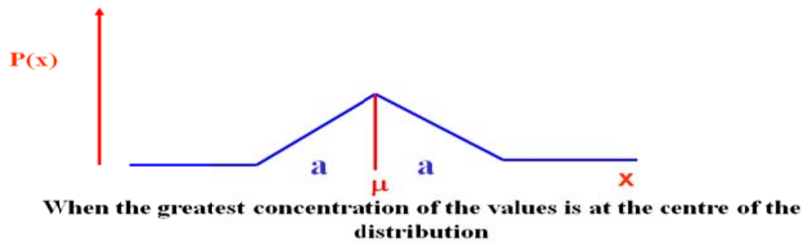


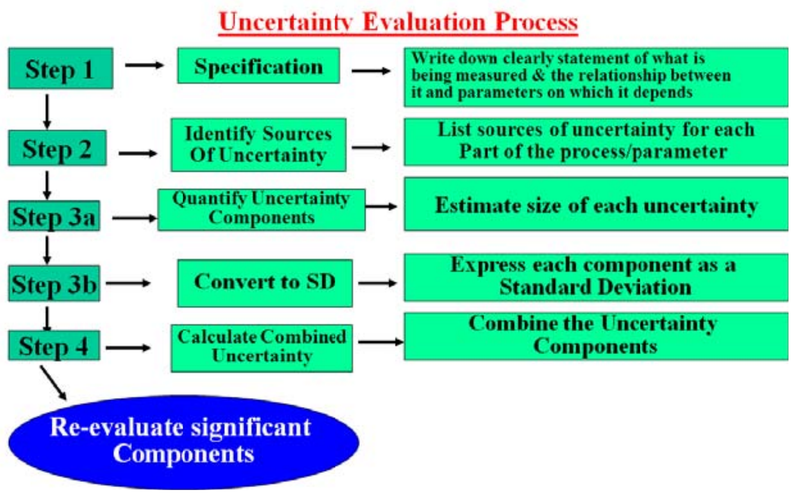
When to use rectangular distribution ?

In those cases, where it is possible to estimate only the upper and lower limits of an input quantity (X) and there is no specific knowledge about the concentration of values of (X) within the interval, one can only assume that it is equally probable for X to lie anywhere within this interval.

Triangular Distribution

$$u(x) = \frac{a}{\sqrt{6}}$$





Uncertainty Evaluation Process

1. Method Specifications

Write down clearly

- Statement of what is being measured and
- The relationship between the measurand and the parameters on which it depends.

Example:

To prepare a standard solution of Cadmium from its salt for calibration purpose. Detailed procedure: State weighing of known mass of Cd salt and dissolving in distilled water making up final volume (say 1000ml) in a volumetric flask.

$$C = \frac{1000\ .P.m}{V} \quad \text{mg/l}$$

Where,

C = Concn of substance in solution, mg/l
P = Purity of the Substance
M = mass of the substance, mg
V = Volume of the made up solution, ml

2. Sources of Uncertainty

List what affects the results

- Sampling
- Sample Preparation
- Calibration(s)
- Instrument measurement
- Laboratory effects
- Analyst effects
- Computational effects

Sampling

- Sample stability
- Sample Homogeneity
- Contamination

Sample Preparation

- Sub-sampling/Preparation
- Weighing
- Digestion, Dissolution, etc.
- Extraction, Separation, etc.
- Concentration
- Addition of Standards and spikes
- Making up Volume

Calibration/Bias/RMs

- Calibration with pure substances, RMs
  - Purity, Stability, Linearity of Calibration
- Bias / Recovery
  - Using matrix reference materials
    Certified value, match with sample
  - Using Recovery of Spike
    Recovery of spike vs recovery of analyte
- Weighing, volumetric, temperature, etc.

End Measurement

- Interferences leading to signal overlap

- Suppression or enhancement of signal due to matrix effects
- Instrumental effects
- Reagent impurities
- Memory of carry over effects

Laboratory Effects

- Chemical cross-contamination
- Laboratory and Equipment temperature changes
- Humidity
- Vibration
- Electromagnetic interferences
- Power supply instability

Analyst effects

- Reading scales consistently high or low
- Minor variations in applying method
- Monday morning effects

Computational effects

- Inappropriate calibration model
- Rounding errors
- Computer software / calibration errors
- Constants

3. Quantifying Sources of Uncertainty

- Data from method validation
  - Repeat experiments for random components
  - Bias evaluation using CRMs/ Spike recovery
  - Ruggedness testing
- Data from collaborative trials/proficiency testing/ QC
- Manufacturers' specifications and certificates
- Experience and /or literature data
- Calculation
- Uncertainty information obtained in different forms needs to be converted into a standard form – *A Standard Uncertainty*
- For data available as:

- Standard deviations	-	Use as it is
- RSD	-	Convert
- SD of Mean	-	Use as it is
- Confidence Intervals	-	Convert
- Stated Ranges	-	Convert

Convert Data to Standard Uncertainties

S N	Data as available	Expression	For Standard Uncertainty, u(x)
1	SD	s	u(x) = s
2	RSD	s/x	u(x) = RSD . x
3	C.V.	RSD% = (s/x).100	u(x) = CV.x./100
4	C.I.		Divide by 't' value of CL (1.96 or 2.58 or …)
5	SD of Means		$u(x) = s/\sqrt{n}$
6	Rect. Dist.		$u(x) = a/\sqrt{3}$
7	Triang. Dist.		$u(x) = a/\sqrt{6}$

4. Combining Uncertainties

Combining of uncertainties using Rule 1, 2, 3 and 4 is also important before reporting is done.

5. Reporting Uncertainty

- Compute Expanded Uncertainty, Uc (k=2)
- Report Result with Expanded Uncertainty as,

  $X \pm U_c(k=2)$

  where X is the measurement result and Uc is the Expanded Uncertainty with k=2.
  k is is the coverage factor for 95% Confidence level.
