CALCULATION OF UNCERTAINTY IN CHEMICAL ANALYSIS

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UNCERTAINTY (U)

- Every measurement has error which is unknown and unknowable. This unknown error is called "measurement uncertainty".

Types of Error

Type I Error (false detection): Probability of deciding a constituent is present, when it is actually absent.

Type II error (false non-detection): Probability of not detecting a constituent, when it is actually present.

Systematic error: For these errors definite cause can be assigned and can be corrected. The term "Accuracy" is related to systematic error. Thus a method showing good accuracy will bear less systematic error.

Random error: Scatter of repeated measurements about their mean value. The sign and magnitude of the error varies at random and cannot be known exactly. Normally they are easy to recognise and are always present in a measurement.

Other important terms:

- **Precision**: Precision is closeness of agreement between repeated measurements.
- **Accuracy**: Accuracy is the closeness of measured value to the true value.
- **Bias**: Consistent deviation of measured value from the true value, caused by systematic error.

Error Vs Uncertainty

- Error is a difference between true value and measured value. Whereas, uncertainty is a range.
- Any parameter which cannot be expressed with certainty is associated with uncertainty. It exists in all quantitative measurements.
- Uncertainty is quantitative indication of the quality of the result.
- It is the interval around the estimated value between which the true value of the measured parameter is expected to lie.

ISO / IEC 17025

- During the year 1993, ISO prepared and published the document **“Guide to the expression of uncertainty in measurement “**which is abbreviated as GUM.
- Clause 5.4.6: Estimation of uncertainty of measurement:
- A calibration laboratory, or a testing laboratory performing its own calibrations, shall have and shall apply a procedure to estimate the uncertainty of measurement for all calibrations and types of calibrations.
- Clause 5.4.6.2: The laboratory shall at least attempt to identify all the components of uncertainty.
- Clause 5.4.6.3: All important uncertainty components shall be taken into account using appropriate methods of analysis.

Importance of uncertainty

- It is the quantitative indication of quality of result.
- Information on uncertainty can often avoid unnecessary repeatation of analysis.
- Consideration of all uncertainty components provides scope for improvement.
- It provides valuable information about the quality and reliability of result.
- Avoids unwarranted or risky decisions taken based on only measurement.

Sources of uncertainty

- Sampling (stability, contamination etc)
- Storage conditions
- Sample preparation (weighing, sub-sampling, extraction, etc)
- Instrument effects (analytical balance etc)
- Reagent purity
- Environmental conditions (dust, humidity, temperature)
- Calibration effect (Linearity of calibration, weighing, temperature, etc)
- Blank correction
- Analyst effect (Minor variations in applying method, lack of knowledge)

How to minimize the uncertainty

- Use of superior grade chemicals.
- Use of high end model of the equipment.
- Improving the knowledge of analyst.
- Better method / technique.
- Better control of environmental conditions

Procedure for uncertainty evaluation

- Define the measurand and select the appropriate procedure.
- Identify the factors that will influence the result.
- Evaluate standard uncertainty. Type A and Type B evaluation.
- Evaluate combined uncertainty.
- Determine the effective degree of freedom.
- Determine expanded uncertainty.

Categories of uncertainty

- Type A: Based on any valid statistical method – Average, std. Deviation
- Type B: Based on scientific judgment using all information available, which may include, previous measurement data, manufacturer's specifications, data provided in calibration certificates etc.

- Linearity,Glassware,Certified reference material Purity,Temperature,Instrument

Reporting of result

- Report results in the units of measured quantity or in %.
- It is always reported at 95% confidence level unless otherwise specified

Uncertainty distributions

Distribution	Factor	Applied for
Normal	1 or 2	CRM
Rectangular	√3	Balance , temperature etc
Triangular	√6	Glassware
U Shaped	√2	-----

Example

- **Calibration of weighing balance:**
- **Procedure:**
- Weigh at least three weights, minimum 5 times, keeping at the centre of pan and 4 corners of the pan. The average values for the five measurements are as follows:

  0.9989, 0.9988, 0.9991, 0.9989, 0.9987

- Calculation of Type A uncertainty: Calculate mean and standard deviation.
- Calculation of Type B uncertainty: Select the components

- **Components are:**
- Std. weight uncertainty
- Uncertainty due to resolution
- Uncertainty due to e centric loading
- Uncertainty due to air buoyancy
- Uncertainty due to linearity
- Type A: Average: 0.9989. Std. Deviation: 0.15
- Type A uncertainty (Ua) = SD / √ n = 0.15 / √ 5 = 0.067

For type B:

Component	Available data	Formula	Result
1	Uncertainty of weight – 0.05mg	Certificate uncertainty / 2	0.025
2	Least count – 0.1 mg	(Least count) / (2 x √ 3)	0.0288
3	Max and min values	(Max – Min) / (2 x √ 3)	0.115
4	Air density -0.011 Density of steel – 8	(0.011 x Avg wt) / (2 x 8 x √ 3)	0.396
5	Linearity – 0.12	Linearity / √ 3	0.069

Combined uncertainty (Uc) : $\sqrt{(\text{Type A})^2 + (\text{Type B})^2}$

$$= \sqrt{(0.067)^2 + (0.025)^2 + (0.0288)^2 + (0.115)^2 + (0.396)^2 + (0.069)^2}$$

$$= \sqrt{(0.004) + 0.000625 + 0.000829 + 0.013225 + 0.156816 + 0.004761)}$$

$$= \sqrt{0.180} = 0.42 \text{ mg}$$

Degree of freedom: $(Uc)^{4} / ((Ua)^{4} / (n-1)$

$= (0.42)^4 / ((0.067)^4 / 4 =$ **6176**

Expanded uncertainty = K value x Uc = 1.96 x 0.42 = 0.86 mg

(where K is coverage factor obtained from student T table)

Expanded uncertainty = 1 ± 0.86 mg at 95% confidence level

UNCERTAINTY CALCULATION FOR PREPARATION OF STANDARD SOLUTION

- **Example:**
- Preparation of 0.1 N FAS solution.
- Mol.wt of FAS: $Fe(NH_4)_2 (SO_4)_2 . 6 H_2O$ = 391.99
- Wt. of FAS for preparation of 0.1 N FAS = 39.199 gm
- Type A uncertainty: nil

- Type B uncertainty:
- **Components are:**

1. Mol.wt
2. Balance
3. Volume
4. Purity of substance

Molecular weight

- $\sqrt{(\text{no.of atoms x at.wt uncer})^2} / \sqrt{3}$

Atoms	No. of atoms	At.wt uncertainty	Total	U mol
Fe	01	0.002	0.002	
H	20	0.00007	0.0014	
N	02	0.00007	0.00014	0.009
O	14	0.00017	0.00238	
S	02	0.006	0.012	

Balance

As per certificate, balance uncertainty is: 0.1 mg

$Ub = (0.1 / 39199) / \sqrt{3} = 0.00000147$

Volume uncertainty

- Three major sources are: Calibration, Repeatability, Temperature

a. Calibration: 1000 ± 0.1 mL at 20° C.

Standard uncertainty = 0.1 / √6 = 0.04 mL

b. Repeatability: Standard uncertainty = 0.02 mL

c. Temperature: Calibration is done at 20° C. Whereas, laboratory temperature varies between the limits ± 4°C

Ut = $2.1 \times 10^{-4} \times 1000 \times 4$

(2.1×10^{-4} is coefficient of expansion of water)

= ± 0.84 mL

0.84 / √3 = 0.48 mL

Total uncertainty due to volume is:

$\sqrt{(0.04)^2 + (0.02)^2 + (0.48)^2}$

= 0.48 mL / 1000 = 0.00048mL

Purity

- 99.25% purity. i.e,. 0.75% impurity is there.
  $(0.75 / 100) / \sqrt{3} = 0.0043$

$Uc = \sqrt{(Umol.wt)^2 + (Ubal)^2 + (Uvol)^2 + (U\ pur)^2}$
$= \sqrt{(0.009)^2 + (0.00000147)^2 + (0.00048)^2 + (0.0043)^2}$
$= 0.009$

Expanded uncertainty = 2 x 0.009 = 0.018
U = 0.018 x 39.199 = 0.705 gm/L

Uncertainty in terms of normality:
0.705 x 0.1 / 39.199 = 0.0017 N

Hence normality of standard solution: 0.1 ± 0.0017 N

THANK YOU