ERRORS

ERROR

- An error can be defined as a deviation of the observed value from the most probable value.

- Refers to the difference between a measured value and the true or known value.

- The deviation may be positive or negative

- Measurements or analytical results involve errors.

May be due to :

- the mistakes of the analyst
- wrong calibration or standardization
- random variation

It is impossible to perform a chemical analysis that is absolutely free of error.

But it can be minimized & estimated their size with acceptable accuracy.

Example:

Quantitative determination of iron in a sample of known concentration (20 ppm).

The solution is divided into 6 equal parts & analysed in the same way.

6 Different results ranging from 19.4 ppm to 20.3 ppm.

The results are as follows

19.4, 19.5, 19.6,19.8, 20.1,20.3 ppm.

The average value of data is 19.8 ppm.

I.e., Very close to the true value.

Types of errors in experimental data

A. Systematic or Determinate or Constant

B. Random or Indeterminate or Accidental

C. Gross errors

A. Systematic errors

- **Systematic (or determinate) errors are reproducible and** Magnitude can be determined Errors which can be avoided
- systematic errors are relatively constant errors
- Systematic error can be corrected.

Systematic errors are again classified as

1. Instrumental errors
2. Method errors
3. Personal error
4. Operational errors
5. Reagent errors
6. Environmental errors

1. Instrumental errors

Instrument errors can occur due to the use of instruments

Caused by

- Non ideal instrument behaviour
- Faulty calibration - Not calibrated properly
  Not calibrated recently
- Use under inappropriate condition

Measuring devices (Burette, Pipette, Standard flask) may hold or deliver volumes slightly different from their graduations.

-May be due to their use at a temp.slightly different from their calibration temp.(Depending upon the temp. glass apparatus may expand and their volume changes.)

-May be from contaminants on the inner surface of the glassware

- Calibration eliminates this type of instrument error

- Electronic instruments show instrument error. Eg: voltage of a battery operated power supply decreases with use.

- Use of a pH meter not calibrated properly will give wrong results.

Errors of this type are detectable & correctable.

Remedy

- Selecting a suitable instruments for the particular measurements according to applications
- Applying correction factors after determining the amount of error.
- Calibrating the instruments against a known standard

2) Method errors

- Due to the incompleteness of a reactions and incorrect sampling
- Due to the nonideal physical/chemical behaviour of reagents or reactions.
- Most serious and important as they are difficult to detect.

Examples:

- Decomposition/Volatilization of the weighing form on ignition, in gravimetry.

- Solubility of precipitates in titration
- Slowness/Incompleteness of some reactions
- Nonspecific reaction of the reagent
- Titration error due to the use of more amount of titrant for the indicator to undergo colour change

3) Personal errors

For those measurements which need personal judgment.

Examples:

- Estimating the position of the pointer between two scale divisions
- Color of solution at the end of titration
- Level of the liquid with respect to graduations in the pipette/ burette

- In making calculations.
- Incomplete drying of sample before weighing

Remedy

- *Take care in reading and recording measured data*
- *Take at least three separate readings*

(preferably under conditions in which instruments are switched off-on).

- *Needs good practice*

4. Operational errors

- These are physical in nature and arises when proper analytical technique is not followed.
- Ex: Mechanical loss of materials in various steps of analysis i.e, underwashing or over washing of precipitates
- Absorption of moisture by the hygroscopic materials before weighing

5. Reagent errors

- Use of reagents containing impurities
- Attack of reagents on glassware, porcelain, etc.

- *Remedy*

  By using pure reagents and pyrex glassware.

6. Environmental errors

Environmental errors are due to surroundings

Eg. Noise from electrical machine. Magnetic field, temperature.

- Remedy

By providing proper shielding.

Methods to reduce systematic error

- *Calibration of apparatus and application of correction*
- *Running a blank determination*

Separate analysis using the same amount and number of reagents in the same solvents omitting the sample

Helps when errors are due to impurities in the reagents and vessels.

Running control determination

Separate analysis using same amount of a standard substance

Result for std/result for unknown = wt of std/x

X= Weight of sample

Isotopic dilution :

- Known amt of comp R isotope is mixed with sample and component is isolated in pure form.
- The radioactivity of the isolated is measured and compared with the added component from which the wt of component in unknown sample can be obtained.

- *Use of independent method of analysis*

Carry out the analysis by some other methods and compare the results.

eg: Strength of HCl can be determined

- by titration with a std base (NaOH)
- by precipitation & weighing as AgCl

Running parallel determination

- Carry out the analysis 2 or 3 times and compare the results.
- Or by 2 or 3 analysts simultaneously
- A constant error may be present in all the results.
- Should not vary by more than 0.3 %

B. Indeterminate (or) Random errors

- Due to unknown reasons
- Cannot be determined (no control over)
- Magnitude and direction not known
- Measurements made by the same observer under same conditions may show variations.(+ve or –ve)
- Cannot be eliminated/corrected. Errors due to unknown Causes.
- Expressed as average deviation of probable errors or standard deviation

Random errors

a) Variable determinate errors :

Analyst may get different values without regular variation.

Ex : Ignition of the ppt Al(OH)3 to constant wt of Al2O3

Can be determined and corrected by careful analysis.

b) Erratic errors :

Measurement vary from one to another and analyst has no control over

Due to

- Accidental loss of material
- Variations during reading instruments

Remedy

Multiple trials help to minimize

Increase the no. of readings and using statistical methods.

- Statistical Analysis

Arithmetic Mean

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i = \frac{1}{n}(x_1 + \cdots + x_n)$$

Deviation from Mean

$$d_1 = x_1 - A.M.$$

$$d_2 = x_2 - A.M.$$

etc

Average Deviation

$$D = \sum |d| / n$$

Standard Deviation

$$\sigma = \text{sqrt}\left(\Sigma\ |d_i|^2 / n\right)$$

For finite observations

$$\sigma = \text{sqrt}\left(\Sigma\ |d_i|^2 / (n-1)\right)$$

Variance

$$v = \sigma^2$$

mean square deviation

Probable error

γ = +/- 0.6745 σ

(obtained from Gaussian error curve)

C. Gross errors

- Some gross error can be detected & some others cannot.
- Complete elimination is not possible.

Types of gross errors

Human Error

due to humans

a) may be due to misreading of instruments.

b) Incorrect adjustments

c) Improper application of instruments

d) Computational mistakes etc.

common in begineers

- ***Remedy***

take care in reading and recording measured data

Take at least three separate readings

needs good practice

Installation error

- Due to improper applications
- Faulty insulations are predominant if device used beyond limit Or if used in excess temp. , vibration, pressure Or poor impedance matching

Remedy

Use devices according to the specifications recommended by manufactures.

- Zero error :

  If the instrument is not set to zero before taking measurement.
- Due to variation in ambient conditions
- Due to ageing

Sources of Error

sampling

Representative sample

homogeneous vs. heterogeneous

preparation

Loss

Contamination (unwanted addition)

analysis

Measurement of Analyte

Calibration of Instrument or Standard solutions

Some statistical terms

<u>Why to analyze several samples with effort?</u>

Single analysis gives no information about the sample.

- Individual results may or may not be the same.

- Best estimate is the central value for 2 to 5 results.

Because central value of a set will be more reliable than individual result (Mean/Median)

Mean & Median

- Most widely used measures of central value
- Mean is also known as arithmetic mean or the average.
- Obtained by dividing the sum of measurements by the number of measurements in the set.

$$x = \Sigma x_i / N$$

x_i= Individual values of x

Σx_i= Sum of all the values of x_i

N= Number of measurements

Median

- Is the middle value in the set of data arranged in numerical order (increasing or decreasing value)

- For an odd number results it will be the middle value

- for an even number results it will be the mean of the middle pair

How to calculate Mean & Median

Analysis of the weight of iron in a sample is as follows:

19.6, 19.4, 19.8, 19.5, 20.3, 20.1

Mean = $\bar{x} = \sum x_i / N$

[19.4+ 19.5+19.6+ 19.8+ 20.1+ 20.3]/6 = 19.78

Arrange in numerical order

19.4, 19.5,19.6, 19.8, 20.1, 20.3. (Even number)

Median = [19.6+19.8]/2 = 19.7