

Pharmaceutical Analysis . Unit 1

ERRORS

Error is defined as the numerical difference between a measured value and a true value of an analytical determination. It can be classified as 1

1, Determinate Error (Systemic Error)

Depending upon the way of occurring

1. Operational error and personal error
2. Instrument and reagent error
3. Method Error
3. Unknown Source

Depending upon the magnitude

1. Constant error
2. Proportional error

2. Indeterminate Error

(accidental error)

1. Physical error
2. Chemical error

1., DETERMINATE ERROR- those errors which can be avoided or whose magnitude can be determined.

a. Operational And Personal Error

Due to the factor for which the experimenter is personally responsible and do not depend on method or procedure

- They arise from erratic personal judgement, prejudice or biased, inability
 1. Eg- judgement of a colour of the solution at the end point
 2. Estimation of position of pointer in balance.
 3. Level of meniscus on a burette/pipette.
 4. Insufficient cooling of a crucible before weighing
 5. Allowing hygroscopic material to absorb moisture before /during weighing

Such errors can be varied from person to person and can be minimized by experienced and careful physical manipulation.

b. Instrumental And Reagent Error

These arise from the imperfections in measuring devices. Electronic devices are much prone to this because of voltage fluctuations

1. Eg. Unadjusted chemical balance

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2. Uncalibrated weight's usage
3. Usage of uncalibrated glasswares
4. Reactions between chemicals and porcelain resulting in introduction of new undesirable material.
5. Usage of low grade chemicals.

c. Method Error

These errors arise from incorrect sampling and incomplete reactions involved in the determination

1. Eg .In volumetric analysis, errors arise due to failure of reaction to proceed to completion, occurrence of side reactions etc
2. In iodometric, determination of Cu, I gets adsorbed on starch which is difficult to remove completely

The determinate errors are further classified into constant errors and proportional errors

A, Constant error (Depends on Magnitude) – Independent of magnitude of measured quantity and becomes less significant as magnitude increases, also independent on concentration.

Error value remains same, its magnitude changes.

For example- In a number of titration if there is a constant error of 0.10 ml, then this indicates 1 % of 10 ml titrant and 0.2% of a 50 ml of titrant .

Ie, Constant Error decreases with increases in a measured quantity.

B, Proportional Error – Most common errors, because of presence of interfering impurities in sample. Here its magnitude will remain constant with the change in concentration.

Eg- In Iodometric titration of copper, if the sample is contaminated with Fe(III) impurity, it will also liberate I_2 from KI along with copper; hence resulting in a false result of high copper concentration. And if the concentration of sample is doubled, the error will also get doubled.

INDETERMINATE ERROR

Random errors arises from uncertainties which are associated with physical or chemical measurements. Such errors cannot be attributed to any known source or cause.

- They are random or accidental in nature .
- Lead to both high and low results with equal probability
- Cannot be eliminated or corrected
- And are the ultimate limitation on the measurement.

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Minimization of errors –

They can be minimized by

- Calibration of apparatus and application of corrections.
- Analysis of standard samples.
- Running a blank determination
- Independent analysis- ie strength of HCl can be determined by titration with Na OH and again it can be determined by gravimetric precipitation with AgNO₃ as AgCl. If the 2 results obtained are concordant, high propability of correct values.

ACCURACY AND PRECISION

- There are certain basic concepts in analytical chemistry that are helpful to the analyst when treating analytical data. This section will address accuracy, precision, mean, and deviation as related to chemical measurements in the general field of analytical chemistry.

ACCURACY

- In analytical chemistry, the term 'accuracy' is used in relation to a chemical measurement. It can be defined as "closeness of the agreement between the result of a measurement and a true value." In theory, true value is that value that would be obtained by a perfect measurement.
- Accuracy is how close a measurement is to its desired or theoretical value.
- For example, if we need to dispense 25.0 mL of dilute HCl, then dispensing 24.9 mL is more accurate than dispensing 25.7 mL.
- Accuracy usually is reported as a percent error

$$\% \text{Error} = \frac{\text{actual value} - \text{expected value}}{\text{expected value}} \times 100$$

For analytical methods there are two methods for determining accuracy.

1. **ABSOLUTE METHOD** – In this Sample containing known amount is used. Various concentration of known amount is made and proceeded according to specified instructions

The amount of constituent should be varied, because the determinate error is considered as a function

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Eg 1, 100% known + 5% added ----- 105%	}	Accurate
2, 100% known + 6% added ----- 106%		
1, 100% known + 5% added ----- 105%	}	Not Accurate
2, 100% known + 6% added ----- 105%		

2. **COMPARATIVE METHOD** – sometimes when primary samples unavailable and are impossible to prepare it for analyst. In those cases a secondary standard is used in a same method. But this method is not usefull in analytical purpose.

PRECISION

Precision is the reproducibility of a set of measurements. For example, Three identically prepared solutions with pH values of **6.76, 6.73, and 6.78** are more precise than a duplicate set with pH values of **6.76, 6.54, and 6.92**.

Precision usually is reported as a standard deviation, s ,

which we define as
$$S = \frac{\sqrt{\sum(x_i - \bar{x})^2}}{2n-1}$$

Where ‘ \bar{x} ’ is the average, or mean result, and ‘ x_i ’ is one of the ‘ n ’ different results.

Another example - 2 analyst performing analysis for an accurate value 70%.

Analyst 1

70.07	}	NOT PRECISE
70.18		
70.14		
70.08		
70.02		

Analyst 2

70.20	}	MORE PRECISE
70.21		
70.23		

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70.21
70.20

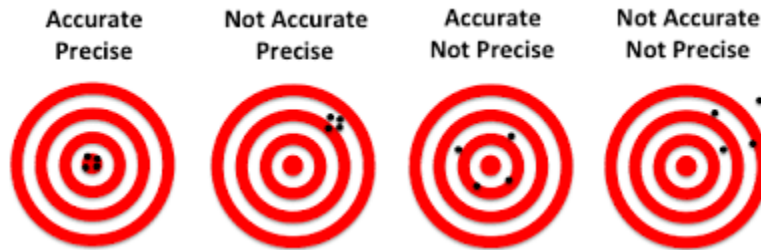


Figure 2: Clusters of five rifle shots illustrating the difference between accuracy and precision

SNSCPHS

