

MINIMISING SYSTEMATIC ERRORS

Systematic errors may be reduced substantially and significantly by adopting one of the following procedures rigidly, such as :

(i) Calibration of Instruments, Apparatus and Applying Necessary Corrections

Most of the instruments, commonly used in an analytical laboratory, such as : UV-Spectrophotometer, IR-Spectrophotometer, single—pan electric balance, pH-meter, turbidimeter and nephelometer, polarimeter, refractometer and the like must be calibrated duly, before use so as to eliminate any possible errors. In the same manner all apparatus, namely : pipettes, burettes, volu-metric flasks, thermometers, weights etc., must be calibrated duly, and the necessary corrections incorporated to the original measurements. In some specific instances where an error just cannot be avoided it may be convenient to enforce an appropriate correction for the effect that it ultimately causes ; for instance : the inherent impurity present in a weighed precipitate can be estimated first and then deducted duly from its weight.

(ii) Performing a Parallel Control Determination

It essentially comprises of performing an altogether separate estimation under almost identical experimental parameters with a quantity of a standard substance that consists of exactly the same weight of the component as is present in the unknown sample. Thus, the weight of the component present in the unknown sample may be calculated with the help of the following expression :

$$\frac{\text{Wt. of component in Standard Substance}}{X} = \frac{\text{Result obtained for Standard Substance}}{\text{Result obtained for Unknown Sample}}$$

where, X = Weight of the component present in the Unknown Sample.

Note : A good number of Standard Samples, including primary standards, such as : arsenic trioxide, benzoic acid, potassium hydrogen phthalate, sodium oxalate, are available as :

BPCRS = British Pharmacopoeia Chemical Reference Substance,

EPCRS = European Pharmacopoeia Chemical Reference Substance,

CRM = BCS—Certified Reference Materials,

ECRM = EURONORM—Certified Reference Materials.

(iii) Blank Determination :

In order to ascertain the effect of the impurities present in the reagents employed and reaction vessels used ; besides establishing exactly the extent to which an excess of standard solution required to locate the exact end-point under the prevailing experimental parameters of the unknown sample—a blank determination is an absolute necessity. It may be accomplished by performing a separate parallel estimation, without using the sample at all, and under identical experimental parameters as employed in the actual analysis of the given sample.

Note : Always avoid using an appreciably large blank correction which gives rise to a vague and uncertain 'exact value' thereby minimising the precision of the analysis.

(iv) Cross-checking Results by Different Methods of Analysis

In certain specific cases the accuracy of a result may be cross-checked by performing another analysis of the same substance by an altogether radically different method.

Examples :

(a) HCl-Solution : It may be assayed either by titration with a standard solution of a strong alkali (NaOH), or by precipitation and weighing as AgCl ; and

(b) Fe³⁺ : It may be assayed either by gravimetric method as Fe(III) hydroxide after getting rid of the interfering elements and igniting the precipitate to Fe(III) oxide, or by titrimetric method *i.e.*, first reducing to the Fe(II) state and then titrating with a suitable oxidizing agent, for instance Ce(IV) sulphate, K₂Cr₂O₇. In short, the results thus obtained by the two fundamentally different techniques must be concordant thereby justifying and ascertaining the fact that the values obtained are fairly small limits of error.

(v) Method of Standard Addition

Here, a small known quantity of the component under estimation is added to the sample, which is subsequently subjected to analysis for the total amount of component present. The actual difference in the quantity of components present in samples with or without the added component ultimately gives the recovery of the quantum added component. A good satisfactory recovery builds up the confidence in the accuracy of the method of analysis.

Note : The method of 'standard addition' is particularly useful to physicochemical techniques of analysis, for instance : spectrophotometry, turbidimetry.

(vi) Method of Internal Standards

The specific method is of immense value both in chromatographic as well as spectroscopic determinations. Here, a fixed quantity of a reference substance (*i.e.*, the 'internal standard') is added to a series of known concentrations of the material to be assayed.

A graph is plotted between the concentration values and the ratios obtained from the physical value (*i.e.*, peak area of absorption) of the 'internal standard' and the series of known concentrations, thereby producing a straight line. Any unknown concentration may be determined effectively by adding the same amount of 'internal standard' and locating exactly where the ratio obtained falls on the concentration scale.