M.Sc. (Semester-II) Forensic Science, FS-201 Forensic Analytical Chemistry

Absolute and comparative methods of analysis:

Absolute method:

It involves in substituting all the constants involved in the equation together with the measured response to obtain the concentration of an analyte.

Consider the equation 1 (Beer-Lambert law) used for the calculation of the concentration of an analyte based on the absorbance measurements,

$$A = \varepsilon bc$$
 1

where A is the absorbance, ϵ is the molar extinction coefficient, b is the path length and c is the concentration of the analyte.

In the absolute method, one has to substitute the values of ϵ and b to calculate the concentration of the analyte. This may lead to considerable errors since the value of constants may not be known exactly.

Consider the equation 2 (Ilkovic equation) used for the calculation of the concentration of an analyte based on the polarographic current measurements.

$$(I_d)_{average} = 607n D^{1/2} m^{2/3} t^{1/6} c$$
2

where $(I_d)_{average}$ is the diffusion current, n is the number of electrons, D is the diffusion coefficient, m is the mass flow rate of mercury, t is the drop time and c is the concentration of the analyte.

In the absolute method, one has to substitute the values of n, D, m and t to calculate the concentration of the analyte. This may lead to considerable errors since the value of constants may not be known exactly.

Comparative method:

It involves in carrying out a determination of standard of the same analyte under exactly similar experimental conditions as that of the unknown analyte. Then the following relation (equation 3) can be used to determine the concentration of the analyte.

$$\frac{\textit{Result found for standard analyte}}{\textit{Result found for unkown analyte}} = \frac{\textit{weight of standard analyte}}{\textit{weight of unknown analyte}} \qquad3$$

The comparative method removes any errors associated with the constants involved in the equation relating to the concentration of the analyte (for example equations 1 and 2 above). Therefore, comparative method is considered to be more accurate than the absolute methods.