10.3.3 Data interpretation

For the terms and concepts of this subsection also the corresponding general analytical terms and concepts in Chapter 18 and 2 should be consulted.

10.3.3.1 General concepts

10.3.3.1.1 Measures of concentration and quantity

In all fields of spectrochemical analysis, a quantitative *measure*, x, of some characteristic spectral feature (e.g. a spectral band, edge, etc.) of the *analyte*, i.e. the analysis element, is observed. The *concentration*, c, or the *quantity*, q, of a substance contained in a sample must be derived from the observed measure. Random and systematic uncertainties in the value of x itself and in its relationship to c or q determine the precision and accuracy of the analysis.

10.3.3.1.2 Sensitivity

A method is said to be sensitive if a small change in concentration, c, or quantity, q, causes a large change in the measure, x; ie when the derivative $\mathrm{d}x/\mathrm{d}c$ or $\mathrm{d}x/\mathrm{d}q$ is large. The *sensitivity*, S_i, for element i is defined as the slope of the analytical calibration curve (see Section 10.3.3.2). Although sensitivity may vary with the magnitude of c_i or q_i, it is usually constant at low values of c_i or q_i. Sensivity may also be a function of the c or q of other analytes present in the sample. The use of *characteristic concenctration* and *characteristic mass* as a measure of (inverse) sensitivity in atomic absorption spectrometry is dealt with in Section 10.3.4.5.4.

10.3.3.1.3 Relative standard deviation

If the same measurement is repeated n times, the values observed for x will not be exactly the same each time. A useful term describing the random variation in x is the *standard deviation* s. The value of s is given by the expression

$$s = [\sum_{\mathrm{i}=1}^{\mathrm{n}} (x_\mathrm{i} - \bar{x})^2 / (\mathrm{n}-1)]^{1/2}$$

where x_i is an individual measurement and $\bar{x}$ the mean. In a precise sense, the equation gives the correct value, σ, of the standard deviation of the whole population only if n is an infinitely large number. When n is a small number, say 10, the symbol s should be used instead of σ to indicate that the value of standard deviation is only an estimate obtained from a small number of measurements.

Relative standard deviation s_r, is simply s divided by $\bar{x}$. It is preferably expressed as a decimal fraction but may be expressed in per cent.

10.3.3.1.4 Variance

Several factors contribute to the random uncertainty in any measurement or determination, e.g. random variations in the number of photons emitted or absorbed, variations in setting the instrument at the desired position, errors in measuring time, and contamination by reagents. Each of these factors contribute to the standard deviation of the final result according to the rules of *variance*. The total variance is given by the expression

$$s_T^2 = s_1^2 + s_1^2 + s_3^2 + \ldots s_m^2$$

where the subscripts refer to statistically independent factors contributing to the uncertainty.

In particular, background or blank corrections must be made for most spectrochemical procedures and the *background*, s_b, or *blank*, s_{b1} , standard deviations, are some of the terms contributing to s_T.

10.3.3.1.5 Precision

The random uncertainty in the value for the measure, x, or the corresponding uncertainty in the estimate of concentration, c, or quantity, q, is represented by *precision*, which is conveniently expressed by the term standard deviation or relative standard deviation.

10.3.3.1.6 Counting precision in X-ray measurement

X-ray measurements are very easy to estimate because the photons are counted individually and photon emission is a random-time process for which a Poisson distribution can be assumed. Therefore, the *standard deviation for counting*, $s(N)$, for a single measurement of N counts, where N is large, is simply $s(N) = \sqrt{N} = \sqrt{I_t}$, where I is the intensity in counts per second, and t is the counting interval in seconds. The rules for adding variance apply to the effects of other random errors introduced by subtracting background or taking ratios of intensities. For example, when the signal N_p in total counts at the line-peak position and N_B at the background position are both measured, the value of $s(N)$ for the characteristic line above background becomes

$$s(N) = \sqrt{N_P + N_B} = \sqrt{(I_P + I_B)t}$$

In as much as N_P and N_B are usually large numbers (greater than 1000) the standard deviation for a single measurement is a good approximation of the true standard deviation, σ. The relative standard deviation, s_r, can be written as

$$s_r = \sqrt{N_P + N_B} / \sqrt{N_P - N_B}$$

10.3.3.1.7 Accuracy

Accuracy expresses the extent of the agreement between the measured concentration and the '*true value*'. The principal limitations on accuracy are: (a) *random errors* and (b) systematic errors due to *bias* in a given analytical procedure. Bias represents the positive or negative deviation of the mean analytical result from the known or assumed true value. In addition, in multicomponent systems of elements, the treatment of interelement effects may involve some degree of approximation that leads to reproducible but incorrect estimates of concentrations.

10.3.3.2 Analytical functions and curves

10.3.3.2.1 Systems without interelement effects

In general, the relation of the measure x to concentration c or quantity q is called the *analytical function*. A graphical plot of the analytical function, whatever the coordinate axes used, is called the *analytical curve*.

For one-component systems or multicomponent systems for which interelement effects can be neglected, the measure x_i of element i can be expressed as a function of concentration c_i or quantity q_i, i.e. $x_i = g_I(c_i)$ or $x_i = g_I(q_i)$. These functions are called the *analytical calibration functions*; the graphs corresponding to these functions are called *analytical calibration curves* and are determined by observations on reference samples of known concentrations.

The *analytical evaluation functions*, $c_i = f_i(x_i)$ or $q_i = f_i(x_i)$ are often used; their corresponding graphs are called *analytical evaluation curves*. These curves are derived from analytical calibration curves by interchanging the x and the c or q axes. The distinction between analytical evaluation and analytical calibration functions may at first seem superfluous. This distinction my be trivial in the case of analysis for one-component systems, but assumes importance for multicomponent systems when the measures for the individual component are interdependent because of various interelement effects.

10.3.3.2.2 Systems with interelement effects

The measure x_i for the element i may depend not only on the concentration c_i (or quantity q_i) but also on the concentration or quantities of other elements present. The analytical calibration functions then take the form

$$x_i = g_i(c_1, c_2, c_3, \ldots c_n)$$

and the analytical evaluation functions take the form

$$c_i = f_i(x_1, x_2, x_3, \ldots x_n).$$

These functional relationships can be expressed in various approximate forms. In the simplest approximation, the effect of element j on element i may be expressed as a constant multiplier α_{ij} to give a set of linear equations

$$c_i = \sum_j \alpha_{ij} x_j.$$

This approximation may be valid only over a small range of variation of the values of c. In special cases, nonlinear analytical functions may be linearized, in good approximation, by introducing new sets of variables which are suitable functions of c_i or x_i.

10.3.3.3 Terms related to small concentrations

10.3.3.3.1 Limit of detection

The *limit of detection*, expressed as the concentration, c_L, or the quantify, q_L, is derived from the smallest measure, x_L, that can be detected with reasonable certainty for a given analytical procedure. The value of x_L is given by the equation

$$x_L = \bar{x}_{b1} + k s_{b1}$$

where $\bar{x}_{b1}$ is the mean of the blank measures and s_{b1} the standard deviation of the blank measures and k is a numerical factor chosen according to the confidence level desired. In this context, blank measures x_{b1} refer to the measures observed on a sample that does not intentionally contain the analyte and has essentially the same composition as the material under study. The value of s_{b1} must be determined from the measuring conditions to be used for evaluation x_L and $\bar{x}_{b1}$. The minimum concentration or quantity detectable is, therefore, the concentration or quantity corresponding to

$$c_L = (x_L - \bar{x}_{b1})/S$$

$$q_L = (x_L - \bar{x}_{b1})/S$$

where S, (sensitivity) is assumed to be constant for low values of c or q. The values for $\bar{x}_{b1}$ and s_{b1} cannot usually be determined from theory but must be found experimentally by making a sufficiently large number of measurements, say 20. (When counting statistics are involved, as in X-ray spectroscopy, s_{b1} is often estimated directly from a single measurement of s_b because $x_b \approx N_b$, the number of photons, and $s_b \approx \sqrt{N_b}$, if Poisson statistics are followed).

A value of 3 for k in equation 5 is strongly recommended; for this value, a 99.6% confidence level applies only for a strictly one-sided Gaussian distribution. At low concentrations, non-Gaussian distributions are more likely.

Moreover, the values of $\bar{x}_{b1}$ and s_{b1} are themselves only estimates based on limited measurements. Therefore, in a practical sense, the $3s_b$ value usually corresponds to a confidence level of about 90%.