PART II: DATA INTERPRETATION
(Recommendations 1975))

1. INTRODUCTION

The previous document in this series and others which will follow are concerned with specific fields of spectrochemical analysis. The other documents are primarily concerned with the instrumentation and techniques for obtaining the data. The present document is concerned with the nomenclature and symbols related to data interpretation common to all of the specific fields of spectrochemical analysis. Therefore this document is not intended to stand by itself but rather to be used along with the other documents.

One purpose of this document is to provide the simplest format for describing quantitative results with carefully defined limits of uncertainty. Another purpose is to standardize terms and symbols which will allow easy exchange of information and analytical procedures.

2. GENERAL CONCEPTS

2.1 Measure 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.

2.2 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; that is, 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 3). S_i may vary with the magnitude of c_i or q_i; at low values of c_i or q_i, S_i is usually constant. S_i may also be a function of the c or q of other analytes present in the sample.[1]

2.3 Standard deviation[2,3]

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

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[1] *Note*: The term sensitivity has occasionally been misused in atomic absorption spectroscopy to denote the concentration required to cause 1% absorption. The term sensitivity has also been misused to denote the limit of detection. All such misuses are discouraged because they only make communication between analysts more difficult (see III 4.2).

[2] The number of observations on which the reported standard deviation and/or relative standard deviations were calculated should always be given. Furthermore, the procedures followed in obtaining the standard deviations should be described.

[3] By analogy, it is understood that the general Eq. (I) for the calculation of a, s, or s_r can be applied to determined concentrations, c, or quantities, q. The values of a, s, or s_r calculated for c or q generally will not agree with the corresponding value for the analyte measures.

$$s = \left[\sum_{j=1}^{n} \left(x_j - \bar{x} \right)^2 \Big/ (n-1) \right]^{1/2}$$

(1)

where x_j is an individual measurement. In a precise sense, Eq. 1 gives the correct value, $\boldsymbol{s}$, of the standard deviation of the whole population only if n is an infinitely large number. When n is a small number, say l0, the symbol s should be used instead of $\boldsymbol{s}$ to indicate that the value of standard deviation is only an estimate obtained from a small number of measurements.

2.4 Relative standard deviation

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 (by multiplying by 100) in those cases where possible confusion with per cent concentration does not arise.

2.5 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

$$s_T^2 = s_1^2 + s_2^2 + s_3^2 + \cdots s_m^2$$

(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_{bl}, standard deviations, are some of the terms contributing to s_T (The limitations introduced by s_b are treated more fully in Section 4.1)

2.6 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 as discussed in previous Sections 2.3 or 2.4. For multicomponent systems, the precision in c_i or q_i for element i may depend not only on the precision of x_i but also on the precision of x_i for each of the other elements present.

2.7 Accuracy

Accuracy relates the agreement between the measured concentration and the *'true value'*. The principal limitations on accuracy are; (a) random errors (see Section 2.6); (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; and (c) 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.

3. ANALYTICAL FUNCTIONS AND CURVES

3.1 Systems without interelement effects[4]

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 may 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.

3.2. 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

$$x_i = g_i(c_1, c_2, c_3, \ldots c_n) \tag{3}$$

and the analytical evaluation functions take the form

$$c_i = f_i(x_1, x_2, x_3, \ldots x_n) \tag{4}$$

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 a_{ij} to give a set of linear equations

$$c_i = \sum_j a_{ij} x_j$$

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.

4. TERMS RELATED TO SMALL CONCENTRATIONS

4.1 Limit of detection

The *limit of detection,* expressed as the concentration, c_L, or the quantity, 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

$$x_L = x_{bl} + k\, s_{bl} \tag{5}$$

where x_{bl} is the mean of the blank measures, s_{bl} the standard deviation of the blank measures and k is a numerical factor chosen according to the confidence level desired. In this context,

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[4] Although the term "interelement" refers to atomic species, the concepts are applicable to molecules as well.

blank measures x_{bl} 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_{bl} must be determined from the measuring conditions to be used for evaluating x_L and x_{bl}. The minimum concentration or quantity detectable is, therefore, the concentration or quantity corresponding to

$$c_L = (x_L - \bar{x}_{bl})/S \tag{6}$$

$$q_L = (x_L - \bar{x}_{bl})/S \tag{7}$$

where S (sensitivity) is assumed to be constant for low values of c or q. The values for x_{bl} and s_{bl} 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_{bl} is often estimated directly from a single measurement of s_b because x_b Å N_b, the number of photons and s_b Å $\sqrt{N_b}$, if Poisson statistics are followed.)

A value of 3 for k in Eq. 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 x_{bl} and s_{bl} 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%.