2. PRESENTATION OF THE RESULTS OF CHEMICAL ANALYSIS

2.1 Introduction

The scope of Chapter 2 encompasses three primary topics: (1) general terminology relating to the precision and accuracy of experimental results; (2) descriptive statistics appropriate for univariate analysis of chemical measurements, such as various measures of central value and dispersion, and formulae for calculating confidence intervals; (3) quantities employed in the estimation and application of linear calibration functions. The third topic depends on the first two for its logical development; and it provides terminology and expressions suitable for the reporting of calibration function parameters and their uncertainties, plus estimates and confidence intervals for both dependent and independent variables.

The text that follows is designed to provide the necessary means for reporting results in a standardized form with the intention that, by using recommended terms and symbols, data may be reported unambiguously, without further explanation of terminology or method of computation. Only if other terms were used would it be necessary to define them.

The list of terms includes both standard statistical terms like "median" and less standardized terms, like "percentage relative error", which are useful to the analytical chemist. Such non-standardized terms, despite common use, frequently cause confusion because differing meanings are attributed to them. The statistical terms in this document have been selected and defined according to the practical needs of the laboratory analyst. Those unfamiliar with elementary statistics may find it useful to consult the relevant papers (Section 2.7) and references cited therein.

Assumptions and Caveats. It is extremely important to realize that assumptions play a central role in the validity of the conclusions resulting from statistical operations on experimental data. Since such assumptions are frequently implicit, it is appropriate at the beginning to call attention to their existence and importance. The principal assumptions of concern relate to the model employed. For example, if the observations $\boldsymbol{y}$ are represented by the following relation:

$$y = f(x) + e_y \qquad (1)$$

we must be aware of assumptions connected with the functional relation $\boldsymbol{f(x)}$, as well as those connected with the error structure $\boldsymbol{e_y}$. In section 2.3, $\boldsymbol{f(x)}$ is taken as the population mean of $\boldsymbol{x}$ -- i.e. the expected value of the observations equals a constant; in section 2.4, $\boldsymbol{f(x)}$ is taken as $\boldsymbol{a + bx}$ --i.e., the straight line ("linear") calibration curve. Deviations from these assumed functional relations **will** result in erroneous conclusions. There are, fortunately, test statistics such as $\boldsymbol{t}$ and $\boldsymbol{x^2}$ and $\boldsymbol{F}$, plus methods such as residual analysis and control charts to aid in detecting model errors, but these must not be blindly relied upon. That is because all statistical tests have two fundamental limitations:

(1) they themselves rest on assumptions, and

(2) their statistical power to detect erroneous models (or alternative hypotheses) is always limited -- i.e. non-detectable model error may nevertheless cause important conclusion errors.

Assumptions related to e_y include: randomness, independence, homogeneity of variance (homoscedasticity), and the form of the error distribution (***cdf*** = cumulative distribution function). For most of the discussion, we assume a normal distribution of errors.

It should be noted that the scientific user of statistical measures must bear full responsibility for the validity of the assumptions made, making appropriate statistical tests of the more crucial assumptions, but realizing that passing such tests does not **prove** assumption validity. When the functional relation (model) is wrong, estimates of means and calibration parameters will be biased; when the error model is wrong, presumed confidence intervals and tests of significance may be misleading. The **only** route to the correct model is through sound, scientific knowledge of the measurement process.

This chapter is prepared using the paper "Nomenclature for the presentation of results of chemical analysis" (PAC 66 595-608 (1994)). The text therefore has been fully rewritten compared to Chapter 2 of the Compendium of Analytical Nomenclature, 2nd Edition 1987. In the text some terms and definitions have been taken partly or wholly from the ISO Standard 3534 (1993) document on Statistics - Vocabulary and Symbols.

This chapter does not include the terms and definitions concerning performance characteristics of analytical processes, and the evaluation procedures of analytical methods for validation or qualification. These terms and definitions are dealt with in Chapter 18.