

CLIL - Errors and statistics

The function of the analyst is to obtain a result as near to the true value as possible by the correct application of the analytical procedure employed. The level of confidence that the analyst may enjoy in his results will be very small unless he has knowledge of the accuracy and precision of the method used as well as being aware of the sources of error which may be introduced. Before we start with the study of errors and statistics we must give the definitions of accuracy and precision. **Accuracy** is how close a given set of measurements (observations or readings) are to their true value. The accuracy of a determination may be defined as the concordance between it and the true or most probable value. It follows, therefore, that systematic errors cause a constant error (either too high or too low) and thus affect the accuracy of a result. For analytical methods there are two possible ways of determining the accuracy; the so-called absolute method and the comparative method. Precision may be defined as the concordance of a series of measurements of the same quantity. Accuracy expresses the correctness of a measurement, and precision the 'reproducibility' of a measurement (the latter definition will be modified later). **Precision** is how close the measurements are to each other. Precision always accompanies accuracy, but a high degree of precision does not imply accuracy. This may be illustrated by the following example. A substance was known to contain 49.10 ± 0.02 per cent of a constituent A. The results obtained by two analysts using the same substance and the same analytical method were as follows. Quantitative analysis is not simple, the errors which affect an experimental result may conveniently be divided into "systematic" and "random" errors. **Systematic** (determinate) **errors**. These are errors which can be avoided, or whose magnitude can be determined. The most important of them are:

1. Operational and personal errors;
2. Instrumental and reagent errors;
3. Errors of method;
4. Additive and proportional errors.

Random (indeterminate) **errors**. These errors manifest themselves by the slight variations that occur in successive measurements made by the same observer with the greatest care under as nearly identical conditions as possible. They are due to causes over which the analyst has no control, and which, in general, are so intangible that they are incapable of analysis.

The **absolute error** of a determination is the difference between the observed or measured value and the true value of the quantity measured. It is a measure of the accuracy of the measurement. The true or absolute value of a quantity cannot be established experimentally, so that the observed result must be compared with the most probable value. If several analysts determine the same constituent in the same sample by different methods, the most probable value, which is usually the average, can be deduced from their results. In both cases, the establishment of the most probable value involves the application of statistical methods and the concept of precision. The **relative error** is the absolute error divided by the true value; it is usually expressed in terms of percentage or in parts per thousand. In analytical chemistry one of the most common statistical terms employed is the **standard deviation** of a population of observations. This is also called the root mean square deviation as it is the square root of the mean of the sum of the squares of the differences between the values and the mean of those values and is of particular value in connection with the normal distribution.

Adapted from: Vogel

■ TEACHING AIMS:

- Understanding the meaning of errors in the Analytical Chemistry;
- Understanding the differences between accuracy and precision;
- Understanding the differences between systematic errors and random errors;
- Understanding the classification of systematic errors;
- Understanding the differences between absolute error, relative error and standard deviation.

EXERCISES (read the text and the maps)

1 Match the word in the right spaces (use dictionary if needed): relative error, random errors, accuracy, standard deviation, systematic errors, absolute error, precision.

