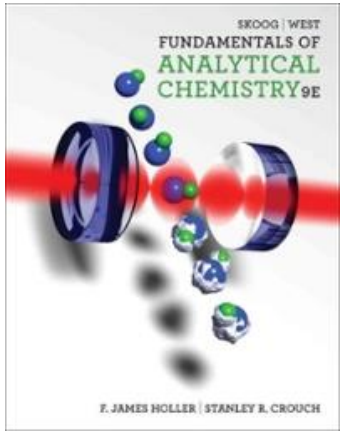
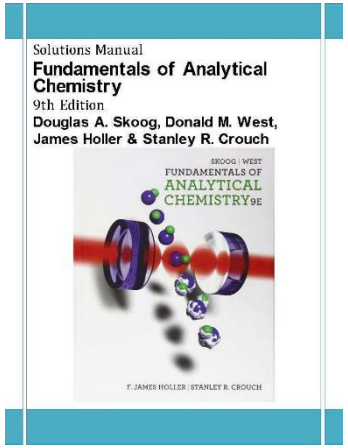
STATISTICS IN CHEMISTRY

1.



2.



1. Skoog DA, West DM, Holler FJ, Crouch SR. Fundamentals of Analytical Chemistry. Nelson Education; 2013.
2. Skoog DA, West DM, Holler FJ, Crouch SR. Solutions Manual of Fundamentals of Analytical Chemistry. Nelson Education; 2013.

Systematic Errors and Random Errors in Analysis

Errors in Chemical Analysis

The error is the difference between the measurement obtained from an analysis operation and the actual value of the measured quantity. The term error is also used to express the predicted uncertainty of an analytical process.

A single analysis result is never sufficient to determine the error in an analytical method and to obtain information about the validity of the results. An analytical method always uses analysis of at least two or more repeat samples. The mean or median value of the analysis results of repeat samples must be given as a result. The average value (mean) is represented by $\bar{x}$ ve and is calculated using the following equation.

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N}$$

The median is the average of the two results in the middle, or even in the case of an even number, when the analytical results are ordered from small to large.

There are two commonly used concepts about the reliability of the results of an analytical method. These are concepts of precision and accuracy.

Precision

Precision is a measure of the closeness of measurement results obtained in exactly the same way. The terms standard deviation, variance, and coefficient of variation are used to express the precision of a dataset and refer to how much each deviation of the measurement result deviates from the mean. The deviation from the mean is expressed in d_i.

$$d_i = |x_i - \bar{x}|$$

Accuracy

Accuracy is a measure of the proximity of each result (x_i) obtained from the analytical method to the correct value (x_t) and the correct accepted value. Accuracy is expressed in terms of absolute error (E) or relative error (E_r).

$$E = x_i - x_t$$

$$E_r = \frac{x_i - x_t}{x_t} \times 100$$

Types of errors affecting the test results

It is assumed that three types of errors affect the test results. These are systematic error (source specific error), random error (source uncertain error) and rough error. Coarse errors are errors that require the discovery of the test result and are caused by spillage, splashing, impurity contamination, power failure and the resulting calibration deterioration during application of the test method.

Systematic errors

The source of the systematic error can be identified and lead to a deviation in the results of the analytical method. The magnitude of systematic error in repeated measurements in the same way is the same.

There are three different sources that cause a systematic error. These; tool errors, method errors and personal errors. The effect of systematic errors on analytical results can be constant or proportional. Fixed errors are errors that are independent of the sample quantity and are relatively more important as the sample quantity decreases. Proportional errors are errors that increase or decrease in proportion to the sample quantity. The relative error in proportional errors can be fixed.

Instrument errors are the errors that result from the deterioration of the calibration of instruments such as pipettes, burettes, scales, metered balloons, electronic instruments used in the analytical method. Calibration of these instruments can be suggested to prevent such errors.

Method errors, reagents used in the analytical method and the reactions on which the method is based, slowness, incompleteness and so on. reasons are the errors that occur as a result of non-ideal behavior. In addition, impurities in the sample that show similar reactions with the analyte or disturb the reaction of the analyte are sources of method error. In determining the method errors, methods such as standard sample analyzes similar to the analyzed sample composition, analysis of the sample by a completely different method and witness determinations are used. In addition, the amount of the sample is changed to determine whether the error is fixed or proportional.

Personal errors are those that arise from the physical defects of the practitioner, prejudice, sloppy work, and most of these errors can be eliminated with careful and regular work. Errors caused by physical defects can be eliminated using a method that is not affected by this physical defect.

Detection of systematic method errors

- Analysis of standard samples
- Alternative method analysis with confirmed accuracy
- Blanck experiments,
- Sample quantities.