Bowman Analytics: Basic Counting Statistics

The production of X-ray photons by electrons is a random process and heavily related to statistical methods. The ability to model errors and precision is a major advantage of XRF spectrometry

1. Statistical Terms
   a. True Result

      The thickness or concentration that actually exists in a representative sample, i.e. the right or correct concentration, which may be the accepted or most reliably known thickness or concentration

   b. Mean

      The average or arithmetic mean (x), defined as the arithmetic sum of a set of results divided by "n", the number of results.

   c. Standard Deviation

      (S), a measure of dispersion about the mean and defined a sthe root mean aquare deviation of a set of observation from the arithmetic mean

   d. Relative Standard Deviation

      Also known as Coefficient of Variation, s/x

      The COV is usually expressed as a percentage,

      i.e. E% = s/x x 100%

   e. Confidence interval

      The upper and lower values between which a measurement will fall with a certain probability. For an infinitely large number of readings having a Gaussian distribution, there is a 68% probability that a measurement will fall within +/- 1 sdv of mean; a 95.4% probability that it will fall within +/12 sdv of the mean, and a 99.7% probability that it will fall within +/13 sdv of the mean

   f. Random error

      An error in a measurement due to fluctuation which follow a predictable pattern. Most random errors follow a Gaussian distribution. Thus, the size and significance of a random error can be predicted in terms of the parameters of this distribution. The magnitude of random errors can be evaluated, minimized but not corrected for.

g. Systematic error

Also known as bias. The difference between the true and experimental results. The magnitude of systematic error or bias will include random errors. Systematic errors can be evaluated, avoided and corrected for.

h. Accuracy

The nearness of a result to the true result. The accuracy of a result is dependent both upon the precision of the measurement and on the difference between the true result and the experimental result

i. Precision

The reproducibility of, or closeness of agreement among, replicate results obtained under any definite set of experimental conditions, and usually expressed as relative error. An improvement in precision implies a decrease in its absolute numerical value, i.e. a decrease in the standard deviation or relative error of the set of results

2. Quantitative Analysis
The basic requirement of quantitative analysis is to measure the intensity of the analyte peak since this is related to thickness/concentration. If necessary, particular for trace element analysis, the analyte peal intensity must be corrected for background under thepeal and for spectal overlap. It is the net peak intensity, Peak-Background or ($I_{i,m}$-$I_{i,b}$), that is directly related to thickness/concentration.
By determining the net peak for standards it is possible to draw a calibration curve and to calculate the slope from the equation

A, = ($I_{i,m}$-$I_{i,b}$)/C_i

Where
$I_{i,m}$= measured (total) peak count rate
$I_{i,b}$= background count rate
C_i= concentration in % or um
A_i= slope of calibration curve for analyte i

The overall accuracy of the analysis depends on the accuracy of both peak and background measurement and on the accuracy of the calibration factor "a"

For the thickness determincation,
T_i = ecp B_0 (ln (1/(1-N_i)))B_1

Where

T i= Thickness of Analyte

Ni = Normalized intensity

3. Errors

Errors arise mainly from three sources

- The statistical nature of the emission and detetction of X-rays
- Variations in sample composition or physical state (matrix effects)
- Apparatus stability and reproducibility

Main source of random and systematic errors

E = sqrt (e2 counting + e2 generator+e2 equipment + e2 sample + e2 equipment + e2 sampling)

a. Random errors
    i. Counting statistics (function of time)
    ii. Generator and x-ray tube stability
    iii. Equipment error
b. Systematic errors
    i. Sample errors
        1. Absorption
        2. Enhancement
        3. Particle effects
        4. Chemical state
c. Standards deviation of measurement
    i. $\sigma2$ = sum of (individual measurement std)2
d. Sampling errors
    i. Dependant upon sample mass and particle size

Reference

Willims & Dunecan 2004

Jenkins and de Vries, 1967