Linear Calibration Using A Least Square Regression

According to NIST, Linear least squares regression has earned its place as the primary tool for process modeling because of its effectiveness and completeness.

Ref:
http://www.itl.nist.gov/div898/handbook/index.htm
Section 4.1.4.1

DEFINITION

A method of determining the curve that best describes the relationship between expected and observed sets of data by minimizing the sums of the squares of deviation between observed and expected values.

Ref: The American Heritage® Dictionary of the English Language, Fourth Edition Copyright © 2004, 2000 by Houghton Mifflin Company. Published by Houghton Mifflin Company. http://www.answers.com/topic/least-squares

The regression calculations attempt to minimize this sum of the squares, hence the name "least squares regression."

Ref: SW846, 8000C, Section 11.5.2

A linear calibration model based on a least squares regression may be employed based on past experience or *a priori* knowledge of the instrument response and at the discretion of the analyst. This approach may be used for analytes that do meet the RSD Limits.

The linear calibration model is most easily achieved by performing a linear least squares regression of the instrument response versus the mass of the analyte.

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Correlation Coefficient Definition: A measure of the interdependence of two random variables that ranges in value from −1 to +1, indicating perfect negative correlation at −1, absence of correlation at zero, and perfect positive correlation at +1. Also called *coefficient of correlation*

Ref: *http://www.answers.com/correlation+coefficient&r=67*

According to NIST Linear least squares regression is by far the most widely used modeling method. It is what most people mean when they say they have used "regression", "linear regression" or "least squares" to fit a model to their data.

Ref: NIST Section 4.1.4.1

Not only is linear least squares regression the most widely used modeling method, but it has been adapted to a broad range of situations that are outside its direct scope.

Ref: NIST Section 4.1.4.1

Linear Equation

$$y = mx + b$$

Where: y = Response A_x for External Standard

or A_x/A_{is} for Internal Standard

x = Concentration C_x for External Standard

or

C_x/C_{is} for Internal Standard

m = Slope

b = Intercept

Linear Regression Statistical Equations

Slope (m)

$$m = \frac{[(Swx_i y_i * Sw) - (Swx_i * Swy_i)]}{[(Sw * Swx_i^2) - (Swx_i * Swx_i)]}$$

Intercept (b)

$$b = y_{AVE} - (m * (x_{AVE}))$$

Linear Regression Statistical Equations

Correlation Coefficient (r)

$$r = \frac{[(Sw * Swx_iy_i) - (Swx_i * Swy_i)]}{\sqrt{\{[(Sw * Swx_i^2) - (Swx * Swx_i)] * [(Sw * Swy_i^2) - (Swy_i * Swy_i)]\}}}$$

Coefficient of Determination (r^2)

$$r^2 = r * r$$

Linear Regression Statistical Equations

Where: n = number of x, y pairs

x_i = individual values for the independent variable

y_i = individual values for the dependent variable

w = weighting factor, for equal or no weighting $w = 1$

x_{AVE} = average of the x values

y_{AVE} = average of the y values

S = the sum of all the individual values

Equations for Concentration

External Standard Equation

$$C_x = \{A_x - b\} / m$$

or

Internal Standard Equation

$$C_x = [\{(A_x)/(A_{is})\} - b] / m * C_{is}$$

Benefits

- This technique is the simplest and most commonly applied form of Linear Curve
- Computation of coefficients and standard deviations is easy

Ref:
http://www.itl.nist.gov/div898/handbook/index.htm
Section 4.1.4.1

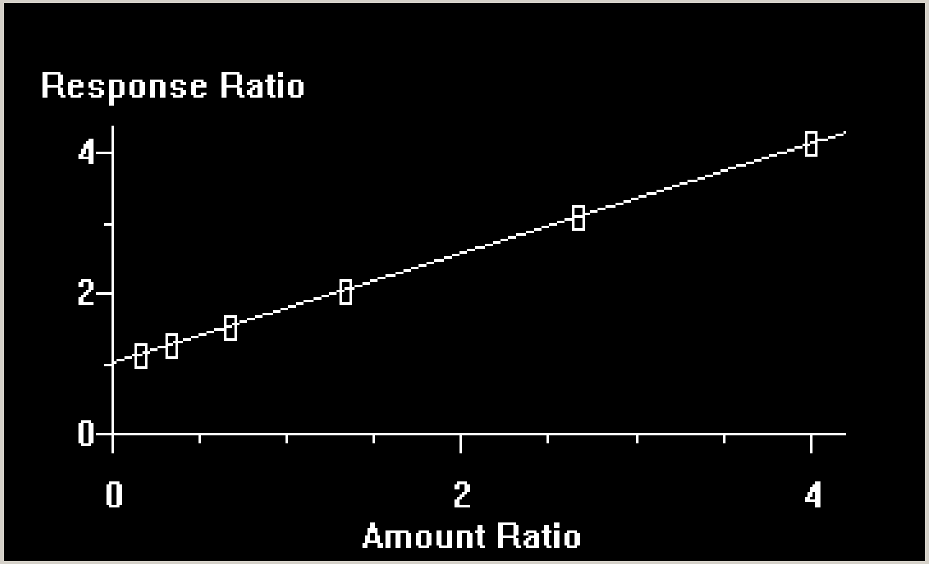
Disadvantages

- If least squares regression (linear and non-linear) is used for curve construction it is usually noticed that the lower levels of the calibration may fail the re-fit criteria (<20% D) even when the r/COD/r2 criteria have been met.

- Analysts that use least squares regression and rely only on the r/COD/r2 criteria for curve acceptance may not be aware of this potential problem at the lower calibration levels.

Ref: SW846 8000C, Section 11.5.5.2

t Calibration Curve

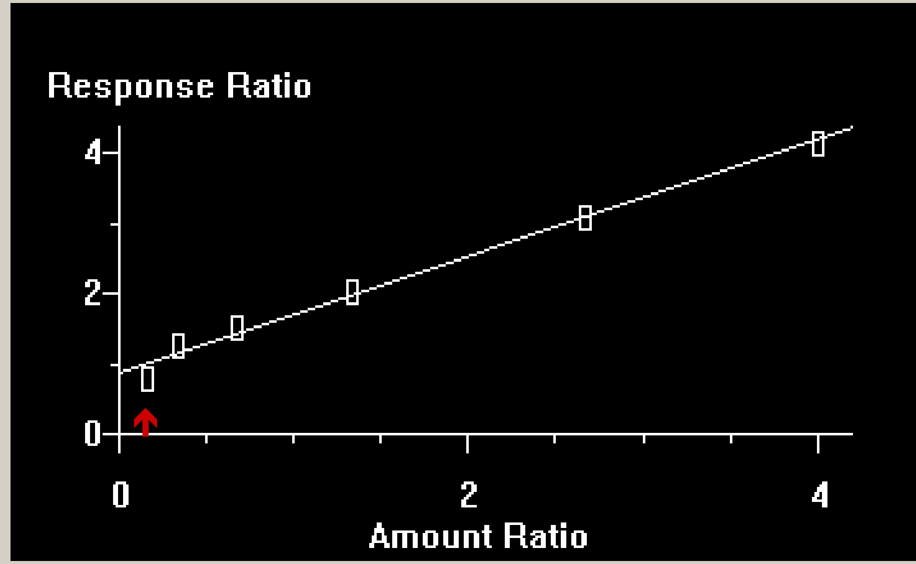


Amount Ratio	Response Ratio
0.16666667	1.13333333
0.33333333	1.26666667
0.66666667	1.53333333
1.33333333	2.03333333
2.66666667	3.06666667
4.00000000	4.13333333

Resp Ratio = 7.80e-001 * Amt + 1.00e+000

Coef of Det (r^2) = 1.000 Curve Fit: Linear

t Calibration Curve



Amount Ratio	Response Ratio
0.16666667	0.80000000
0.33333333	1.26666667
0.66666667	1.53333333
1.33333333	2.03333333
2.66666667	3.06666667
4.00000000	4.13333333

Resp Ratio = 8.19e-001 * Amt + 8.87e-001

Coef of Det (r^2) = 0.990 Curve Fit: Linear

Disadvantage of Linear (Least Square) Calibration