



Instrument Calibration Training

Presented By The
Arizona Department of Health Services
January 2007



New Rules at ADHS website:



Instrument Calibration Training

Part 1

Calibration Models



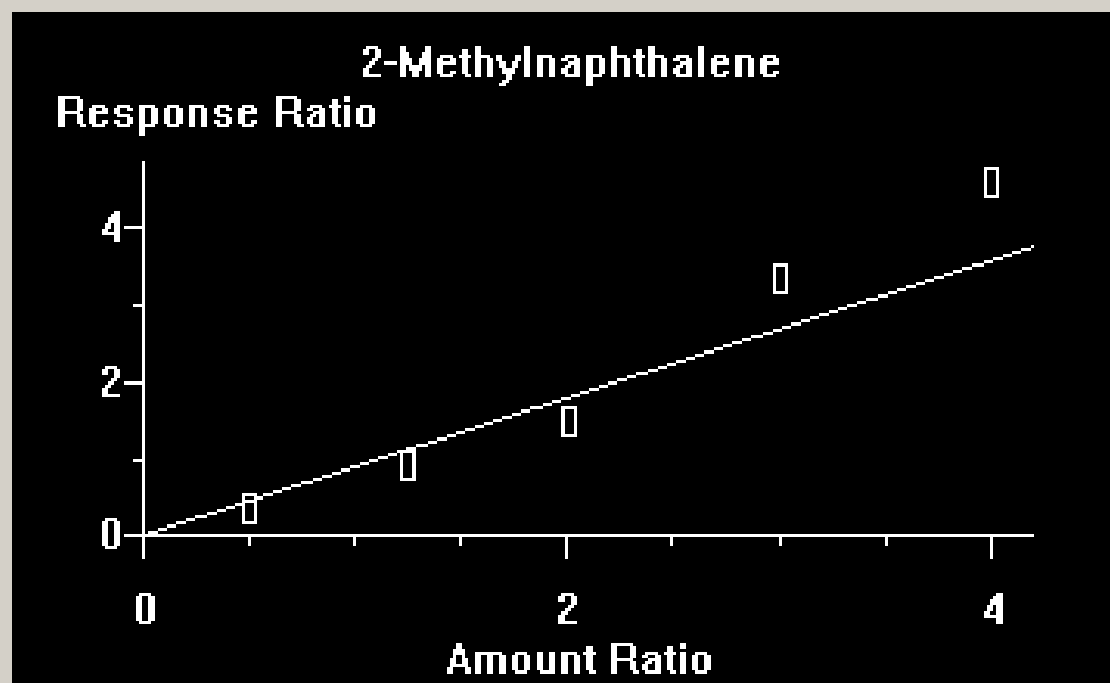


Instrument Calibration Training

Part 2

Possible Calibration Compromisers





Amount Ratio	Response Ratio
2.00000000	1.49796804
4.00000000	4.60049585
0.50000000	0.36029521
3.00000000	3.33926785
1.25000000	0.92751615

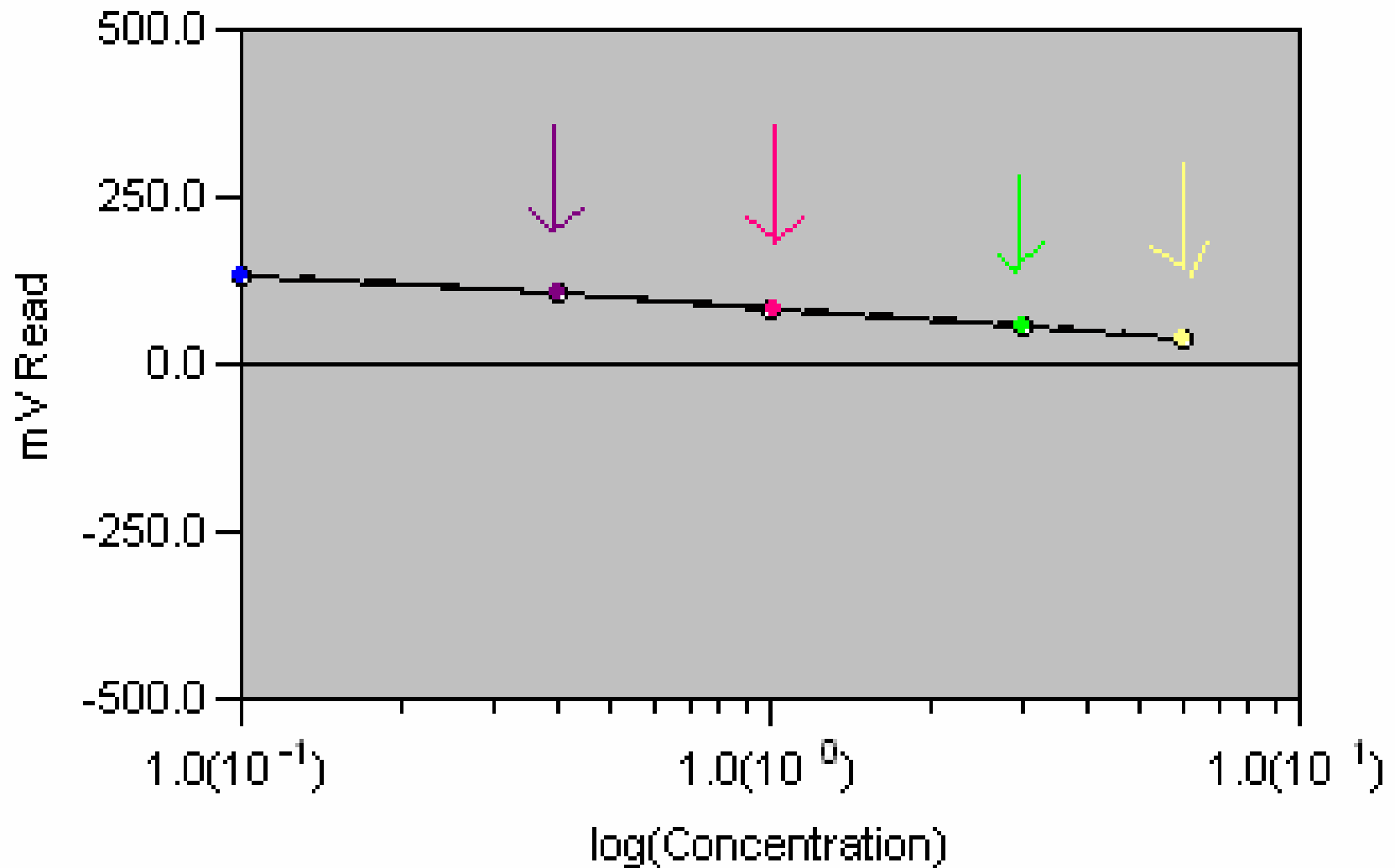
Resp Ratio = 8.95e-001 * Amt

RF Rel Std Dev = 24.2% Curve Fit: Avg RF

OK

Print



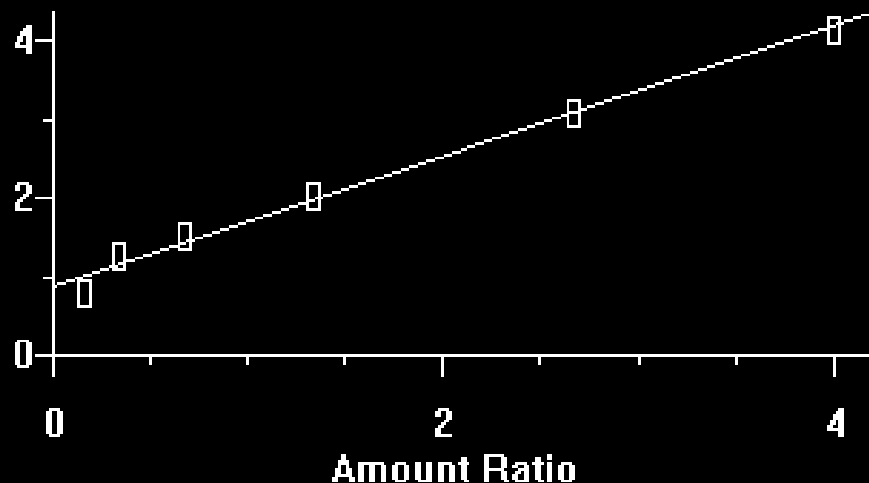


Point to Point Example From a Fluoride Analysis



Calibration Curve

Response Ratio

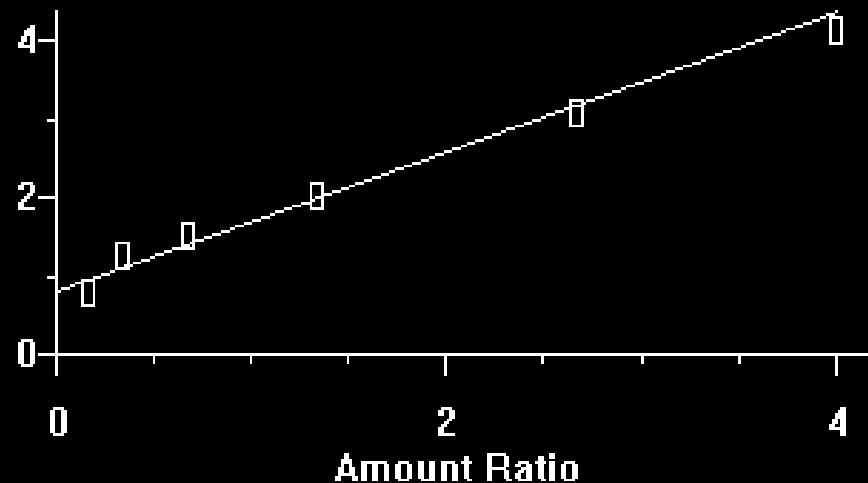


Amount Ratio	Response Ratio
0.16666667	0.80000000
0.33333333	1.26666667
0.66666667	1.53333333
1.33333333	2.03333333
2.66666667	3.06666667
4.00000000	4.13333333

Resp Ratio = $8.19\text{e-}001 \cdot \text{Amt} + 8.87\text{e-}001$
 Coef of Det (r^2) = 0.990 Curve Fit: Linear

Calibration Curve

Response Ratio

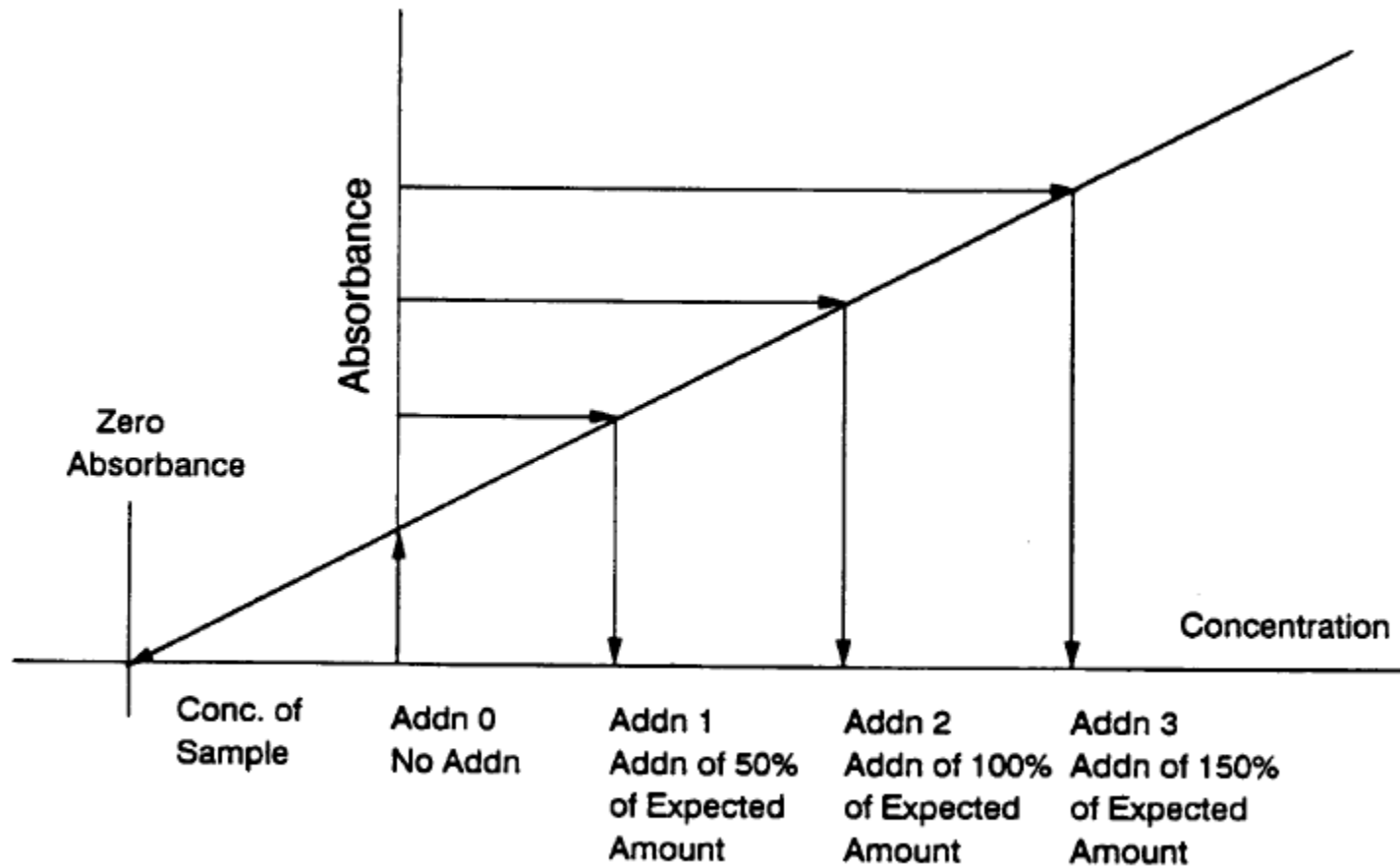


Amount Ratio	Response Ratio
0.16666667	0.80000000
0.33333333	1.26666667
0.66666667	1.53333333
1.33333333	2.03333333
2.66666667	3.06666667
4.00000000	4.13333333

Resp Ratio = $8.89\text{e-}001 \cdot \text{Amt} + 7.81\text{e-}001$
 Coef of Det (r^2) = 0.949 Curve Fit: wlr[1/a]

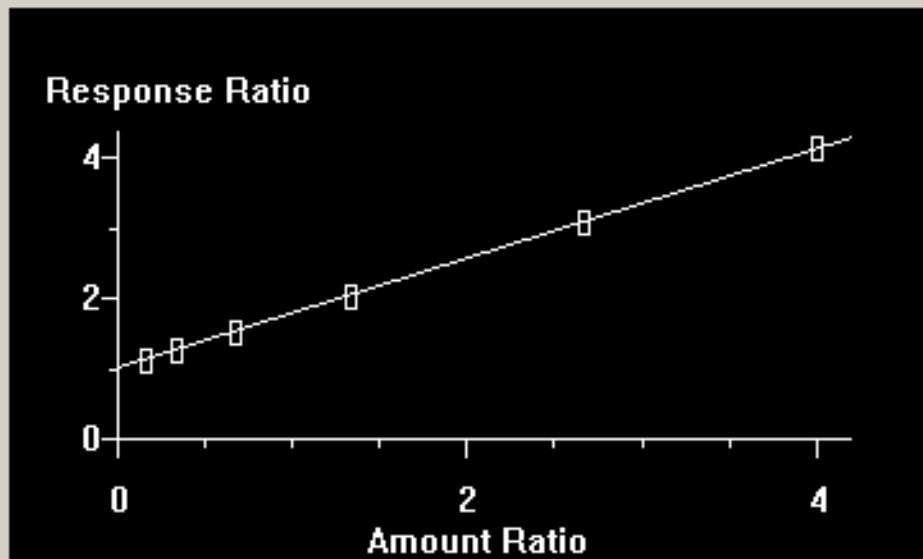


Unweighted vs. Weighted



SW-846 7000B/7010 Section 9.7

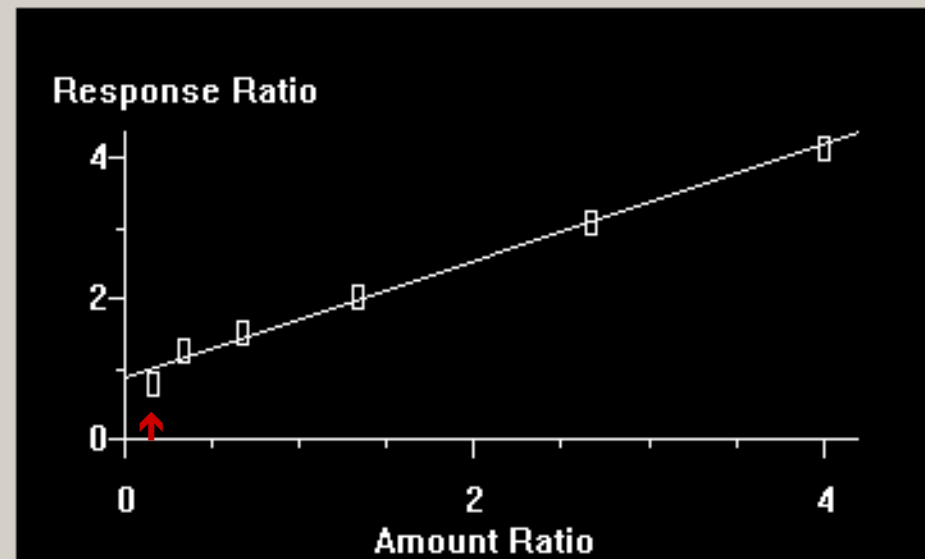
t Calibration Curve



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 = $7.80\text{e-}001 \cdot \text{Amt} + 1.00\text{e+}000$
 Coef of Det (r^2) = 1.000 Curve Fit: Linear

t Calibration Curve

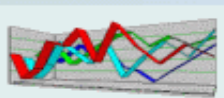


Amount Ratio	Response Ratio
0.16666667	0.80000000
0.33333333	1.26666667
0.66666667	1.53333333
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2.66666667	3.06666667
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Resp Ratio = $8.19\text{e-}001 \cdot \text{Amt} + 8.87\text{e-}001$
 Coef of Det (r^2) = 0.990 Curve Fit: Linear

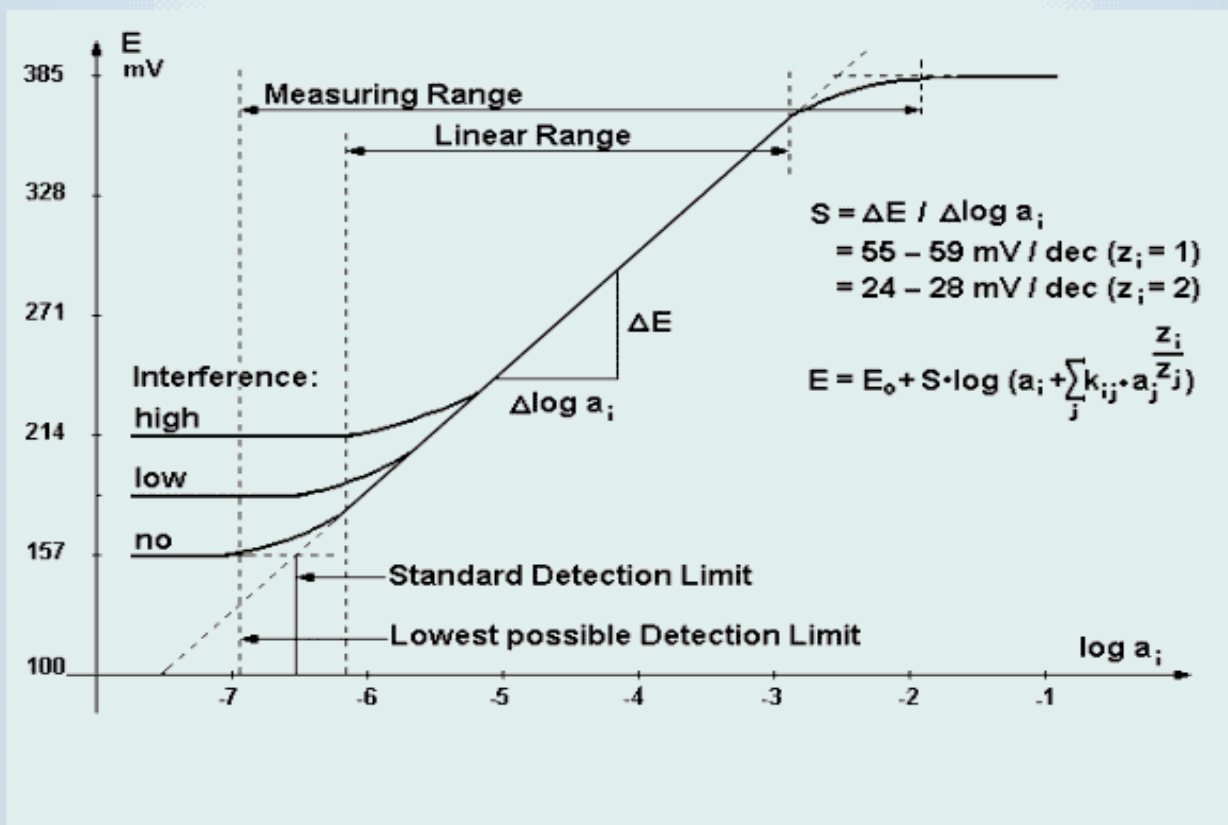
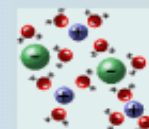
Disadvantage of Linear (Least Square) Calibration





Typical ISE Calibration Graph

NB: X-axis units are the logarithm of the Molar Activity of the Ion



NICO 2000 LTD.



Example of a Curve Using Logarithmic Concentration

Ref: *Beginners Guide to ISE Measurement. Chapter 7: Calibration Theory.*
 Retrieved September 12, 2006 from <http://www.nico2000.net/Book/Guide8.html>



Instrument Calibration Training

Part 1

Calibration Models





General Calibration Models

- External Standard Calibration
- Internal Standard Calibration





- **Power and Exponential Calibration**
- Point to Point Calibration
- Linear Calibrations
 - Response/Calibration Factor
 - Linear Calibration Using A Least Square Regression
 - Linear Forced through Zero
 - Method of Standard Additions
 - Weighted Least Square Regression
- Non-Linear/Quadratic





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Calibration Definition

Reference standards with known values for selected points covering the chosen concentration range are measured with the instrument. A functional relationship is then established between the values of the standards and the corresponding measurements.

Ref: NIST Engineering Statistics Handbook, Section 2.3.6, Purpose of instrument calibration. Retrieved on January 2007 from <http://www.itl.nist.gov/div898/handbook/mpc/section3/mpc36.htm>





Calibration Definition

Calibration: set of operations that establish, under specific conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realized by standards (VIM: 6.11).

*Ref: 2003 NELAC Standards, Appendix A: Glossary, page 42,
Retrieved on January 2007 from
<http://74.52.133.66/%7Enelac/2003standards.html>*





Purpose of Instrument Calibration

Instrument calibration is intended to eliminate or reduce bias in an instrument's readings over a range for all continuous values.

Ref: NIST Engineering Statistics Handbook, Section 2.3.6, Purpose of instrument calibration. Retrieved on January 2007 from

<http://www.itl.nist.gov/div898/handbook/mpc/section3/mpc36.htm>





Precision and Bias

Precision is a measure of the degree of agreement among replicate analyses of a sample, usually expressed as a standard deviation

Bias is consistent deviation of measured values from the true value, caused by systematic errors in a procedure

Ref: Standard Methods for the Examination of Water and Wastewater, 20th edition, Section 1010 C





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Accuracy

Accuracy is the combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to a true value

Ref: Standard Methods for the Examination of Water and Wastewater, 20th edition, Section 1010 C





Types of Calibration

Multiple curve fits are available for use including:

- Linear
- Logarithmic (Log)
- Power
- Exponent
- Second Order (Quadratic)
- Point to Point
- And others

*Ref: Hewlett Packard Reference Manual, Volume II, HP
3365 Series II, Chemstation, Page 15-26,27*





Types of Calibration

- There are three ways to treat the origin:
 - Ignore
 - Include
 - Force
- A single level calibration is always calculated with linear forced through zero.

Ref: Hewlett Packard Reference Manual, Volume II, HP 3365 Series II, Chemstation, Page 15-28





Initial Calibration

Perform initial calibration with a minimum of three concentrations of standards for linear curve, a minimum of five concentrations for nonlinear curves, or as specified by the method of choice.

The reporting limit is included in the calibration range.

Ref: Standard Methods for the Examination of Water and Wastewater, 20th edition, Sections 1020 B, 4020 B





Initial Calibration Cont.

At the beginning of each day that samples are to be analyzed, a calibration curve covering the sample concentration range and all target analytes should be generated according to the approved SOP.

Depending on concentration ranges, the curve should be composed of three or more points.

Ref: EPA Manual for the Certification of Laboratories Analyzing Drinking Water, 5th edition, Chapter IV, Section 7.2.3





Daily Verification Standard

Where the determinative time is extensive and the instrument is very stable, the calibration curve should be initially developed as specified in 7.2.3.

Thereafter, each day analyses are performed, this curve should be verified by analysis of at least one standard for each of the target analytes at the expected concentration range. This verification should be done at both the beginning and end of the analyses.

Ref: EPA Manual for the Certification of Laboratories Analyzing Drinking Water, 5th edition, Chapter IV, Section 7.2.4





Acceptable Calibration

An acceptable calibration assures that an instrument will produce results which meet or exceed some defined criteria with a specified degree of confidence.

Ref: Answers.com, Science and Technology Encyclopedia, Calibration. Retrieved on January 2007 from <http://www.answers.com/topic/calibration>





Calibration Plot

A working curve is a plot of the instrument response as a function of analyte concentration. The concentration of an unknown sample is determined by correlating its response to the mathematical relationship of concentration to the instrument response established by the curve.

Ref: University of Adelaide, Australia, Department of Chemistry. Working Curve or Calibration Curve. Retrieved on January 2007 from <http://www.chemistry.adelaide.edu.au/external/soc-rel/content/wcurve.htm>





Response Factor/Calibration Factor

Both calibration factors and response factors are measures of the slope of the calibration relationship. Each calibration or response factor represents the slope of the line between the response for a given standard and the origin. Under ideal conditions, the factors will not vary with the concentration of the standard. In practice, some variation is to be expected.

Ref: SW-846 8000 C, Section 11.5.1





Response Factor/Calibration Factor

If response factors or calibration factors are used, the calculated % RSD for each analyte of interest must be less than or equal the method-specified value. Refer to the applicable method for the calibration procedure and acceptance criteria on the response factors or calibration factors for each analyte.

Ref: Standard Methods for the Examination of Water and Wastewater, 20th edition, Sections 6020 B





Correlation Coefficient

The correlation coefficient is a measure of the degree with which the independent variable and its partner move either together or in opposition

A positive result indicates direct correlation and a negative result indicates an inverse correlation

Ref: Kelley, William D.; Ratliff, Jr., Thomas, A.; and Nenadic, Charles. (1992) Basic Statistics for Laboratorians: A Primer for Laboratory Workers, page 92-93. Published by John Wiley & Sons, Inc.





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Correlation Coefficient Criteria

If linear regression is used, use the minimum correlation coefficient specified in the method. If the minimum correlation coefficient is not specified then a minimum value of 0.995 is recommended.

The appropriate linear or nonlinear correlation coefficient for standard concentration to instrument response should be ≥ 0.995 .

If a linear regression is used, the correlation coefficient should be > 0.995 .

Ref: Standard Methods for the Examination of Water and Wastewater, 20th edition, Sections 1020B, 4020A, and SW-846 6020B





Correlation Coefficient

- It is not necessarily true that a relationship measured by r is meaningful.
- There must be a rational relationship of the two variables under investigation.
- The sample on which the data is based must be large enough to ensure that the influence of chance causes of variation is minimized.

Ref: Kelley, William D.; Ratliff, Jr., Thomas, A.; and Nenadic, Charles. (1992) Basic Statistics for Laboratorians: A Primer for Laboratory Workers, page 92-93. Published by John Wiley & Sons, Inc.





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Coefficient of Determination

In a correlation analysis, r^2 (occasionally called the “correlation index”) may be calculated most simply by squaring the correlation coefficient, r . It may be described as the amount of variability in one of the variables accounted for by correlating that variable with the second variable.

Ref: Zar, Jerrold H. 1996. Biostatistical Analysis: Third Edition. Chapter 18: Multiple Regression and Correlation, page 373. Published by Prentice Hall





Coefficient of Determination

As in regression analysis, r^2 may be considered to be a measure of the strength of the straight-line relationship.

Ref: Zar, Jerrold H. 1996. Biostatistical Analysis: Third Edition. Chapter 18: Multiple Regression and Correlation, page 373. Published by Prentice Hall





Coefficient of Determination Criteria

In order for the linear regression model to be used for quantitative purposes, r , COD, or r^2 must be greater than or equal to 0.99

Ref: SW-846 8000 C, Section 11.5.2.2





GENERAL CRITERIA FOR ALL CALIBRATION MODELS

Mid-points cannot be dropped to meet criteria

Points can be reanalyzed, original run must be discarded

Ref: SW846, Method 8000C, Section 11.5.5.2





GENERAL CRITERIA FOR ALL CALIBRATION MODELS

Analyzing additional standards and discarding some to achieve a better correlation coefficient value is prohibited

Narrowing of curve on either end is allowed

Ref: SW846, Method 8000C, Section 11.5.5.2

