



# Standard Practice for Establishing and Controlling Spectrochemical Analytical Curves<sup>1</sup>

This standard is issued under the fixed designation E 305; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>e1</sup> NOTE—Section 9 was added editorially in January 1995.

## 1. Scope

1.1 This practice provides guidance for establishing and controlling spectrochemical analytical curves. The preparation of analytical curves and their routine control are considered as separate although interrelated operations. This practice is applicable to optical emission spectrographs, optical emission spectrometers, or X-ray emission spectrometers with linear or logarithmic readouts.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

- E 116 Practice for Photographic Photometry in Spectrochemical Analysis<sup>2</sup>
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials<sup>2</sup>
- E 178 Practice for Dealing with Outlying Observations<sup>3</sup>
- E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data<sup>4</sup>

## 3. Terminology

3.1 For definitions of terms used in this practice, refer to Terminology E 135.

## 4. Summary of Practice

4.1 Systematic and random errors that occur in obtaining data are reviewed. Background corrections are considered for linear and logarithmic readout systems. Calibration procedures

are given, including the reference materials to be used and the generation of data. Procedures are provided for constructing the analytical curve, fitting a regression curve and evaluating curve fit. Control of curve shift and rotation is described.

## 5. Significance and Use

5.1 This practice is intended as a fundamental guide for the calibration, standardization, and daily control of the analytical curves on optical emission spectrographs and spectrometers, and X-ray spectrometers.

## 6. Precautions

### 6.1 Systematic Errors:

6.1.1 *Systematic Errors Due to Incorrect Calibration*—In the procedure for quantitative spectrochemical analysis, the initial construction of the analytical curve relates element concentration and spectral intensity or intensity ratio. The accuracy of the calibration may be affected by a number of factors, such as incorrect element concentrations, heterogeneity of the reference materials, spectral interferences, and matrix effects. Such errors may cause a rotation or bodily displacement of the analytical curve, thereby leading to systematic errors in the analytical data generated.

6.1.1.1 Calibration errors due to incorrect element concentrations may be minimized by the use of certified reference materials. When these are used, one or more other reference materials for which the chemical compositions have been carefully determined by approved methods of analysis, such as ASTM or BSI (British Standards Institute), may be included to detect whether systematic errors exist because of differences in the metallurgical condition of the certified reference materials and the specimens. In the absence of certified reference materials, it is helpful to use several reference materials from a variety of sources to detect systematic differences in these materials. In general, the use of a large number of reference materials will aid in the detection and rejection of those which are obviously inaccurate. In cases where it is necessary to synthesize reference materials, the synthesis of each one

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.20 on Fundamental Practices and Measurement Traceability.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 03.05.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 03.06.

should be independent of the remainder, thereby avoiding an accumulation of errors arising from a series of successive dilutions.

NOTE 1—Errors in determining the average intensity or intensity ratio from reference materials occur because of statistical variations, excitation parameters, and specimen inhomogeneity. In optical emission spectrometry, increasing the number of replicate determinations will reduce the effect of statistical variation and specimen inhomogeneity. The use of optimum excitation conditions, including sufficient preburn and exposure times, will also reduce statistical variations and increase accuracy. In X-ray spectrometry, increasing the exposure area will reduce the effect of inhomogeneity; increasing the counting time will reduce relative statistical variation; and the use of optimum excitation voltage will produce the best measurement.

6.1.2 *Systematic Errors Due to Experimental Variations*—Systematic errors may arise from experimental variations occurring within the operational procedure (for example, change in optics, source parameters, etc.). Such changes may result in displacement of the analytical curve which, if undetected, will introduce systematic errors. This practice is based on the assumption that such errors are negligible during the initial calibration procedure but can be detected, when they do occur, during subsequent operations, as described in 8.1.

#### 6.2 *Random Errors:*

6.2.1 *Measurement of Random Errors*—In addition to the normal variation of reading in any measurement system, randomness occurring in the excitation process causes variation in the intensities obtained from excitation of the same specimen. The best numerical measure of such variability is given by the standard deviation,  $\sigma$ . With a normal distribution, 68.3 % of the values will fall within  $\pm 1\sigma$  of the mean, 95.4 % will fall within  $\pm 2\sigma$  and 99.7 % within  $\pm 3\sigma$  of the mean. While the “true” standard deviation is designated  $\sigma$ , an estimate of standard deviation calculated from a limited number of values is designated by the symbol  $s$ . Equations for calculating the value of  $s$  are given in Practice E 876.

#### 6.2.2 *Constancy of Random Error:*

6.2.2.1 In photographic photometry, the standard deviation of the logarithm of the intensity ratio is constant (within the limits of random statistical variations) over the normally employed intensity ratio range. This constancy is affected adversely by increased microphotometer reading errors introduced by the measurement of very high and very low optical densities, and also by the variability of spectral background. The standard deviation is large when measurements fall outside the range of 60 to 20 %  $T$  (optical densities of 0.2 to 0.7).

6.2.2.2 With optical emission spectrometers, the random error is constant from the point at which the background is small compared to the line signal up to the point where the analytical curve begins to deviate from linearity such as can occur from self-absorption.

6.2.2.3 In linear readout systems, the constancy of random error is expressed in terms of relative standard deviation rather than standard deviation.

## 7. Calibration

7.1 *Spectral Background*—Background intensities vary throughout the spectral region. Including the background in measurements of spectral line intensities can introduce signifi-

cant analytical error, especially when reading a weak line which is only slightly more intense than the background.

NOTE 2—The need for background correction varies with the type of material being analyzed. Make sure that background correction is necessary and can be accomplished accurately before proceeding with the correction.

NOTE 3—The procedure for background correction varies with different instrumentation. This section is intended to be representative, but not necessarily inclusive, of the types available. The user should evaluate his system in regard to its limitations and his particular application before attempting to apply background correction.

7.1.1 *Background Correction with Photographic Systems*—Refer to Practice E 116 for background correction methods.

7.1.2 *Background Correction with Linear Systems*—Three methods of background correction are available in linear systems, two of which are normally used in optical emission spectrometry and the other in X-ray spectrometry:

7.1.2.1 Bias control is a static baseline compensation used to subtract a background from readings, making zero concentration read zero (See Note 4). It is applicable only when excitation conditions are nearly constant and may be used to provide a convenient display in which readings have a simple proportion to concentration. In such cases, multiplying readings by some simple factor will result in a “direct reading” of the concentration.

NOTE 4—Bias in a linear readout system is a counter voltage applied to either the reference of a capacitor used to integrate a signal or to a final reading so as to suppress the portion of signal attributable to background. Bias can also be used to suppress readings from concentrations that are below the level of interest.

7.1.2.2 In dynamic background correction, a selected portion of the background of a spectrum is integrated simultaneously with analytical signals. When this integrated measurement is large enough, a proportion of it can be used to bias the measurement of an analytical line, effectively subtracting out the background which can be presumed to have been part of the measurement of the analytical line. Background may be made to have a strong signal by using a wide exit slit for the background reading, increasing the dynode voltage on the photomultiplier tube used for background, using an extra-sensitive photomultiplier tube for the measurement, or by a combination of these. The dynamic approach is difficult to control since it depends on maintaining consistent responses on the photomultiplier tubes used for the analytical lines as well as for the background. Changing a dynode setting on either the background or analytical line photomultiplier tube affects the correction. If a specimen is available which has none of the elements being measured, such as a piece of the pure matrix element, this may be run and the background control adjusted, after the integration, to make the element reading be zero.

NOTE 5—A pure piece of the matrix element is applicable only if the excitation of such a specimen is consistent with the type of excitation obtained when a normal specimen is run. This is a direct step in systems that bias the voltage on the element integrators so that changes in gain will not affect the correction. If matrix materials with “zero” concentrations of the elements of interest are not available, trial and error excitations may have to be made until the analytical curve shows zero concentration reading zero. In systems that bias the final reading rather than the integrated voltage, dynamic background corrections are generally not applicable.

7.1.2.3 In X-ray spectrometry, background is determined directly by making a measurement at a point near the analytical line which is free of any other lines. This measurement, corrected for any slope in the background, is subtracted from the measured intensity of the analytical line. The measurement time for the background should be of sufficient length so as not to adversely affect the statistics of net intensity of the analytical line. See 7.2.2.1.

7.1.3 *Background Correction with a Logarithmic Readout System*—With a logarithmic readout system, correct for background as follows:

7.1.3.1 Position an exit slit at a location where no spectral line is expected. Position a photomultiplier tube to receive the image from the exit slit.

7.1.3.2 Adjust the dynode voltage of the photomultiplier tube to integrate 2.0 V on a capacitor. Use the capacitor voltage as the input of a high-impedance voltage follower. Connect the output of the voltage follower to a series of potentiometer controls, one for each element channel to be corrected.

7.1.3.3 With the background correction system disabled, ensure that there are no elemental spectrum lines passing through the background exit slit. To do this, excite a pure specimen of the matrix material and a normal alloyed specimen, and compare the two readings to confirm that there is no significant contribution from elemental spectrum lines to the background reading. The use of a highly alloyed sample, in which the matrix element is significantly reduced in concentration, will verify that the background slit is not on a matrix line.

7.1.3.4 With the background correction system disabled, excite reference materials to calibrate the element of interest. Draw a line tangent to the straight line portion of the curve down to the lower end of the useful analytical range.

7.1.3.5 Enable the background correction system. Excite a typical specimen in which the element to be corrected is near the detection limit. Adjust the element potentiometer to obtain a reading midway between the uncorrected position and the straight line extension of the curve as shown in Fig. 1. Repeat as required, until all desired elements are corrected.

NOTE 6—**Caution:** Do not overcorrect. Approaching a straight line can result in inaccuracy for specimens which have background greater than the typical specimen used to adjust the element potentiometer.

7.2 *Preparation of the Analytical Curve:*

7.2.1 *Reference Materials*—Reference materials, preferably certified reference materials as described in 6.1.1.1, should span the concentration ranges expected. Extrapolation should be avoided. It is recommended that at least four reference materials shall be used for each curve. If the concentration range exceeds one decade or if several reference materials are close to each other in concentration, the use of more than four reference materials is recommended. See also 8.2.1.

7.2.2 *Number of Replications for Each Reference Material*—If  $n$  replications are to be made for each specimen in an analysis, at least  $4n$  replications should be made for each reference material to establish each analytical curve. Thus, if only one specimen analysis is to be made, the minimum number of replications is four for each reference material for each element; for duplicate analyses, eight replications of reference materials, etc. These replications for each reference material should be divided into subsets run in random order so that all replications for a given reference material are not run together. When more than four reference materials are used, the number of replications may be less than  $4n$  provided that the total number of all replications exceeds  $16n$ .

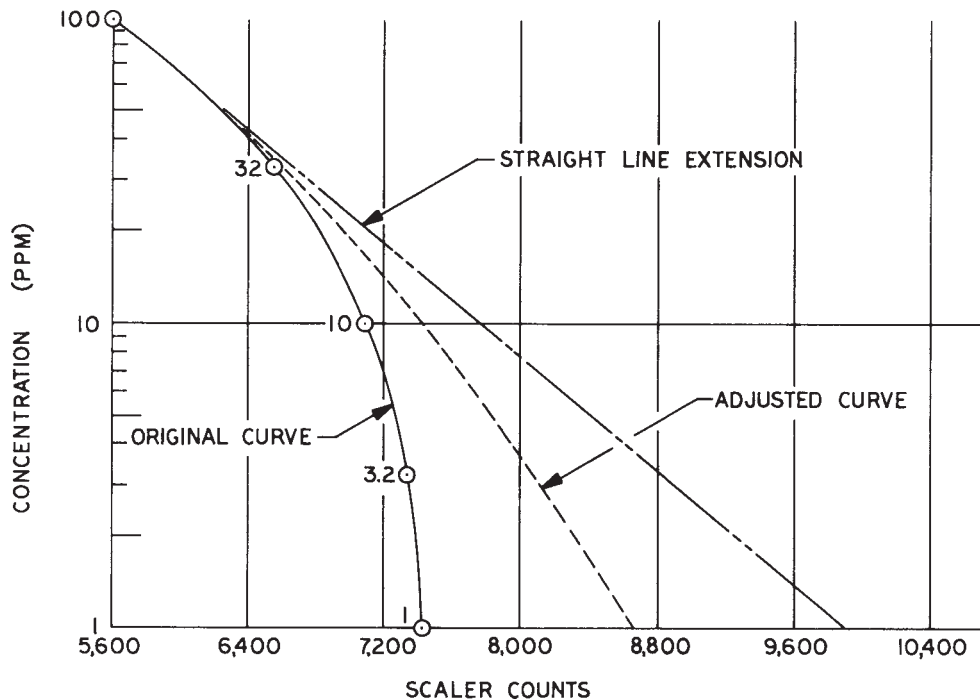


FIG. 1 Background Correction with Logarithmic Readout System

7.2.2.1 In X-ray spectrometry, where single measurements are made, calculate the counting time,  $T$ , as follows:

$$T = \frac{100}{\sigma} \cdot \frac{1}{\sqrt{R_p} - \sqrt{R_b}} \quad (1)$$

where:

$\sigma$  = the desired relative standard deviation, and  
 $R_p$  and  $R_b$  = the count rates on the peak and background.

The time is divided between the peak measurement time,  $T_p$ , and background measurement time,  $T_b$ , as follows:

$$T_p/T_b = \sqrt{R_p/R_b} \text{ and } T_p + T_b = T \quad (2)$$

7.2.3 Construction of the Analytical Curve:

7.2.3.1 For the purposes of this section, the term “concentration function” will be used to denote either concentration, concentration ratio, or logarithm of concentration and “intensity function” will be used to denote intensity, intensity ratio, or logarithm of intensity ratio. The user shall select the appropriate form applicable to his situation.

7.2.3.2 Plot the concentration function versus the intensity function for each reference material (Note 7). Suspected outliers should be examined using the procedures described in Practice E 178. Determine whether the plot is linear or curved (Note 8). On logarithmic and semilogarithmic coordinates, the instrumental response function will curve near the background (that is, signal:background of 2:1 or below) and may also show curvature at high concentrations which is due to nonlinear response or self-absorption, or both, depending on the type of excitation. Once the decision is made, proceed to 7.2.3.3.

NOTE 7—When making logarithmic or semilogarithmic plots, the logarithmic cycles should be of sufficient size to make plotting and reading errors negligible. Graph papers having a 10-in. (25.4-cm) scale with either one or two cycles are commercially available.

NOTE 8—Whether a plot is curved or straight is sometimes a subjective determination. The analyst must keep in mind such factors as spectral background, tendency of the analytical line to exhibit self-absorption, and reliability of the reference materials.

7.2.3.3 If a straight line is assumed, locate the point whose coordinates are  $X$  = the average of the intensity functions and  $Y$  = the average of the concentration functions (Note 9). With a straight edge, draw a line through this point with a slope such that all other average points deviate a minimum from the line. Fig. 2 shows a curve applying this technique to the data in Table 1. When a large number of reference materials has been used and it is difficult to estimate the slope, the method of least squares described in 7.3 can be used.

NOTE 9—If the intensity or the concentration functions, or both, are logarithmic, the average of the logarithms shall be used rather than the logarithm of the average of the original quantities. For a rigorous computation, this practice should be extended to averaging the logarithms of the original replicate data for each specimen.

7.2.3.4 If a straight line cannot be assumed, draw the curve of best fit using appropriate drafting tools. When a mathematical function of concentration versus intensity is desired, proceed as in 7.3.3.

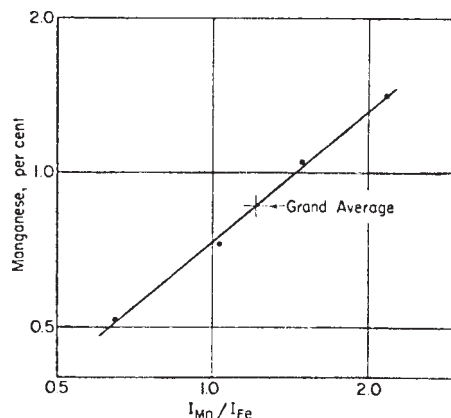


FIG. 2 Curve Drawn from Data in Table 1 with the Technique Described in 7.2.3.3

TABLE 1 Data and Computations for a Straight Line Analytical Curve

Reference Material	Manganese, %	log <sub>10</sub> % Mn	I <sub>Mn</sub> /I <sub>Fe</sub>	log <sub>10</sub> I <sub>Mn</sub> /I <sub>Fe</sub>
1	1.41	+0.149	2.15	+0.342
			2.30	
			2.12	
			2.23	
			2.20 <sup>A</sup>	
3	1.05	+0.021	1.40	+0.161
			1.52	
			1.38	
			1.50	
			1.45 <sup>A</sup>	
5	0.725	-0.140	0.95	+0.013
			1.07	
			1.01	
			1.09	
			1.03 <sup>A</sup>	
7	0.515	-0.288	0.61	-0.187
			0.70	
			0.66	
			0.63	
			0.65 <sup>A</sup>	
	0.86 <sup>B</sup>	-0.065 <sup>C</sup>	1.21 <sup>D</sup>	+0.082 <sup>E</sup>

<sup>A</sup> Average intensity ratio for each reference material.

<sup>B</sup> Grand average of log percent Mn converted into percent Mn.

<sup>C</sup> Grand average of log percent Mn.

<sup>D</sup> Grand average of log I<sub>Mn</sub>/I<sub>Fe</sub> converted into I<sub>Mn</sub>/I<sub>Fe</sub>.

<sup>E</sup> Grand average of log I<sub>Mn</sub>/I<sub>Fe</sub>.

7.3 Fitting a Regression Line—The technique for fitting a regression line may be found in statistical texts.<sup>5, 6, 7, 8</sup> Many desk calculators are equipped to perform linear regression

<sup>5</sup> Wallis, W. A., and Roberts, H. V., *Statistics, A New Approach*, The Free Press, Glencoe, IL, 1956.

<sup>6</sup> Youden, W. J., *Statistical Methods for Chemists*, John Wiley and Sons, Inc., New York, NY, 1951.

<sup>7</sup> Berl, W. G., *Physical Methods in Chemical Analysis II*, Academic Press, Inc., New York, NY, 1951 (Section on “Statistical Analysis” by J. Sherman).

<sup>8</sup> Box, G. E. P., Hunter, W. G., and Hunter, J. S., *Statistics for Experimenters*, John Wiley and Sons, Inc., New York, NY, 1978.

analyses. Computer programs can achieve second, third and higher degrees of regression. In using equations greater than first order, caution must be exercised to ensure that no maxima or minima occur in the analytical range of the equation.

7.3.1 A linear regression line, as determined below by the method of least squares, goes through the grand average of all points.

7.3.1.1 Assume the analytical curve to be a straight line described by the equation:

$$Y = a + bX \quad (3)$$

where:

$X$  = the intensity function, and

$Y$  = the concentration function.

Then the slope,  $b$ , and intercept,  $a$ , of the curve, as estimated by the method of least squares, are given as follows:

$$b = \frac{\Sigma(xy)}{\Sigma(x)^2} \quad (4)$$

$$a = \bar{y} - b\bar{x} \quad (5)$$

where:

$$x = X - \bar{x}$$

$$y = Y - \bar{y}$$

$\bar{x}$  and  $\bar{y}$  = average values (that is,  $\bar{x} = \frac{\Sigma X}{n}$ ), and

$n$  = number of points.

7.3.1.2 Since the line passes through the point  $\bar{x}$ ,  $\bar{y}$ , it is easily drawn once  $b$  is calculated. An example of a regression calculation is shown in Table 2 and Fig. 3.

7.3.2 Alternatively, the regression line can be calculated using individual points, rather than the differences from the average. An example of this calculation is shown in Table 3.

7.3.3 Analytical curves will not always be straight lines, but sometimes can be fitted to a quadratic equation. By describing the analytical curve mathematically, its curvature can be drawn more accurately. If a quadratic equation has been defined, any number of points can be calculated for the analytical curve. It is not valid, however, to use the equation to extrapolate beyond the limit of the data. Making regression fits to equations higher than second order requires a computer. However, a least squares fit to a quadratic equation can be done with the aid of a small calculator.

7.3.3.1 An example of data that does not fit a straight line is given in Table 4 which covers a range of nickel concentrations in a two-component cupro-nickel system. Ignoring that the standard deviations of the higher readings are a little greater than the standard deviations of the lower readings, a simple fit of the data can be made as follows: Calculate the sums of  $X$ , the powers of  $X$ , and the sums of the products of  $X$  and  $Y$  terms as shown in Table 4. Set up three equations of three unknowns to determine the coefficients  $a$ ,  $b$ , and  $c$  in the general quadratic equation:

$$Y = a + bX + cX^2 \quad (6)$$

The equations are:

$$a\Sigma X^2 + b\Sigma X^3 + c\Sigma X^4 = \Sigma X^2 Y \quad (7)$$

TABLE 2 Data and Computations for Fitting a Regression Line Using Differences from the Average<sup>A</sup>

Concentration % Mn	(Y) $\log_{10}(\% \text{ Mn})$	$I_{\text{Mn}}/I_{\text{Fe}}$	(X) $\log_{10}(I_{\text{Mn}}/I_{\text{Fe}})$	(x) $X - \bar{x}$	(y) $Y - \bar{y}$
1.41	0.1492	2.15	0.3324	0.2505	0.2136
	0.1492	2.30	0.3617	0.2798	0.2136
	0.1492	2.12	0.3263	0.2444	0.2136
	0.1492	2.23	0.3483	0.2664	0.2136
1.05	0.0212	1.40	0.1461	0.0642	0.0856
	0.0212	1.52	0.1818	0.0999	0.0856
	0.0212	1.38	0.1399	0.0579	0.0856
	0.0212	1.50	0.1761	0.0942	0.0856
0.725	-0.1397	0.95	-0.0223	-0.1042	-0.0753
	-0.1397	1.07	0.0294	-0.0525	-0.0753
	-0.1397	1.01	0.0043	-0.0776	-0.0753
	-0.1397	1.09	0.0374	-0.0445	-0.0753
0.515	-0.2882	0.61	-0.2147	-0.2966	-0.2238
	-0.2882	0.70	-0.1549	-0.2368	-0.2238
	-0.2882	0.66	-0.1805	-0.2624	-0.2238
	-0.2882	0.63	-0.2007	-0.2826	-0.2238

Computation:

$$n = 16$$

$$\bar{x} = 0.0819323$$

$$\bar{y} = -0.064362$$

$$\Sigma x^2 = 0.6124477$$

$$\Sigma y^2 = 0.4348249$$

$$\Sigma xy = 0.5117891$$

$$b = \Sigma xy / \Sigma x^2$$

$$= 0.5117891 / 0.6124477$$

$$= 0.8356 \text{ (0.8356453)}$$

$$a = \bar{y} - b\bar{x}$$

$$= -0.064362 - 0.8356453 (0.0819323)$$

$$= -0.1328 \text{ (-0.132828)}$$

$$r^2 = (\Sigma xy)^2 / \Sigma x^2 \Sigma y^2$$

$$= (0.5117891)^2 / 0.612447 (0.4348249)$$

$$= 0.9836$$

<sup>A</sup> Computations in Table 2, Table 3, and Table 5 were done in a computer with no rounding. Rounding was done after all calculations were completed. Therefore, if the calculations are repeated using the logarithms tabulated, there may be minor differences in the results obtained.

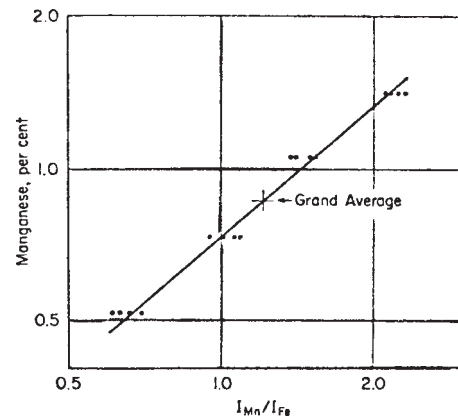


FIG. 3 Curve Drawn by the Regression Technique from Data in Table 2

$$a\Sigma X + b\Sigma X^2 + c\Sigma X^3 = \Sigma XY \quad (8)$$

$$an + b\Sigma X + c\Sigma X^2 = \Sigma Y \quad (9)$$



**TABLE 3 Computations for Fitting a Regression Line Using Y and X Values from Table 2<sup>A</sup>**

Y	X
0.1492	0.3324
0.1492	0.3617
0.1492	0.3263
0.1492	0.3483
0.0212	0.1461
0.0212	0.1818
0.0212	0.1399
0.0212	0.1761
-0.1397	-0.0223
-0.1397	0.0294
-0.1397	0.0043
-0.1397	0.0374
-0.2882	-0.2147
-0.2882	-0.1549
-0.2882	-0.1805
-0.2882	-0.2007

Computation:

$$\begin{aligned}
 n &= 16 \\
 \Sigma X &= 1.3109166 \\
 \Sigma Y &= -1.0297850 \\
 \Sigma XY &= 0.4274164 \\
 \Sigma X^2 &= 0.7198541 \\
 \Sigma Y^2 &= 0.5011035 \\
 b &= \frac{\Sigma X \Sigma Y - n \Sigma XY}{(\Sigma X)^2 - n \Sigma X^2} \\
 &= 0.8356 (0.8356453) \\
 a &= (\Sigma Y - b \Sigma X) / n \\
 &= -0.1328 (-0.132828) \\
 r^2 &= \frac{\Sigma XY - \Sigma X \Sigma Y / n}{(\Sigma X^2 - (\Sigma X)^2 / n)(\Sigma Y^2 - (\Sigma Y)^2 / n)} \\
 &= 0.9836
 \end{aligned}$$

<sup>A</sup> Computations in Table 2, Table 3, and Table 5 were done in a computer with no rounding. Rounding was done after all calculations were completed. Therefore, if the calculations are repeated using the logarithms tabulated, there may be minor differences in the results obtained.

**TABLE 4 Data and Computations for a Least Squares Fit for a Quadratic Equation<sup>A</sup>**

y = % Ni	x = Reading	Sums of x and y Terms	
19.77	55.5	$\Sigma X = 294.0$	$\Sigma Y = 104.26$
10.21	32.6	$\Sigma X^2 = 16\ 075.82$	$\Sigma XY = 5903.358$
6.51	25.1	$\Sigma X^3 = 948\ 610.446$	$\Sigma X^2 Y = 356\ 797.7488$
29.06	70.6	$\Sigma X^4 = 58\ 812\ 032.443$	$n = 6$
25.0	66.2		
13.71	44.0		

<sup>A</sup> Data for nickel in a set of six cupro-nickels from a linear read-out.

where:

$n$  = number of observations.

These equations may be easily solved by using the method of determinants. The solution can also be made with less computation by solving the simultaneous equations by the method of successive elimination.

7.3.3.2 Successive elimination of variables to determine the quadratic coefficients of the data in Table 4 is accomplished as follows:

$$16\ 075.82 a + 948\ 610.466 b + 58\ 812\ 032.443 c = 356\ 797.7488 \quad (10)$$

$$294.0 a + 16\ 075.82 b + 948\ 610.446 c = 5903.358 \quad (11)$$

$$6.0 a + 294.0 b + 16\ 075.82 c = 104.26 \quad (12)$$

Multiplying (Eq 11) by (16 075.82/294.0) and subtracting from (Eq 10):

$$6\ 942\ 335.912 c + 69\ 590.09637 b = 34\ 004.1414131 \quad (13)$$

Multiplying (Eq 12) by (294.049/6.0) and subtracting from (Eq 11):

$$160\ 895.266 c + 1669.82 b = 794.618 \quad (14)$$

Multiplying (Eq 14) by (69 590.09637/1669.82) and subtracting from (Eq 13):

$$236\ 992.1825 c = 888.2707221 c = 0.0037481 \quad (15)$$

Substituting the value for  $c$  in (Eq 14):

$$1669.82 b = 191.56623 b = 0.114722685 \quad (16)$$

Substituting the values for  $b$  and  $c$  in (Eq 10):

$$16\ 075.82 a = 27\ 37.1502 a = 1.71295 \quad (17)$$

Substituting the values for  $a$ ,  $b$ , and  $c$  in (Eq 6) yields:

$$Y = 1.71295 + 0.11472 X + 0.0037481 X^2 \quad (18)$$

Then (Eq 18) can be solved for  $Y$ , the concentration of nickel, to plot the curve shown in Fig. 4.

7.3.3.3 The determination of confidence limits described in 7.3.5 is not applicable to the curved relationship as there is no longer a single slope.

7.3.4 *Coefficient of Correlation*—The coefficient of correlation is an index which indicates how well the regression line represents the actual data. The equation is as follows:

$$r = \frac{\Sigma(xy)}{\sqrt{\Sigma(x^2)\Sigma(y^2)}} \quad (19)$$

where  $r^2$  is less than or equal to unity. A perfect fit will have a coefficient of correlation  $r = \pm 1.0$ . Generally for spectrochemical data, an  $r$  value of greater than 0.98 indicates a good fit and less than 0.90 a poor fit.

7.3.5 *Confidence Limits*—The confidence limits,  $\pm s_{yc}$ , are affected by two factors; the error in the slope, and the error in the intercept. This joint effect is recognized in the following equation:

$$s_{yc} = s_{y \cdot x} \sqrt{\frac{1}{n} + \frac{(X - \bar{x})^2}{\Sigma x^2}} \quad (20)$$

where:

$s_{y \cdot x}$  = the standard error of estimate which is defined in 7.3.5.1, and the other symbols are defined for (Eq 5).

7.3.5.1 The standard error of estimate,  $s_{y \cdot x}$ , is a measure of the scatter about the line of regression and is minimized in the regression process.  $s_{y \cdot x}$  may be calculated as follows:

$$s_{y \cdot x} = \sqrt{\frac{\Sigma y^2 - b \Sigma xy}{n - 2}} \quad (21)$$

7.3.5.2 The error in the slope,  $s_b$ , may be calculated as follows:

$$s_b = \frac{s_{y \cdot x}}{\sqrt{(X - \bar{x})^2}} = \frac{s_{y \cdot x}}{\sqrt{\Sigma x^2}} \quad (22)$$

where:

$s_{y \cdot x}$  is obtained from (Eq 21) and the other symbols are the

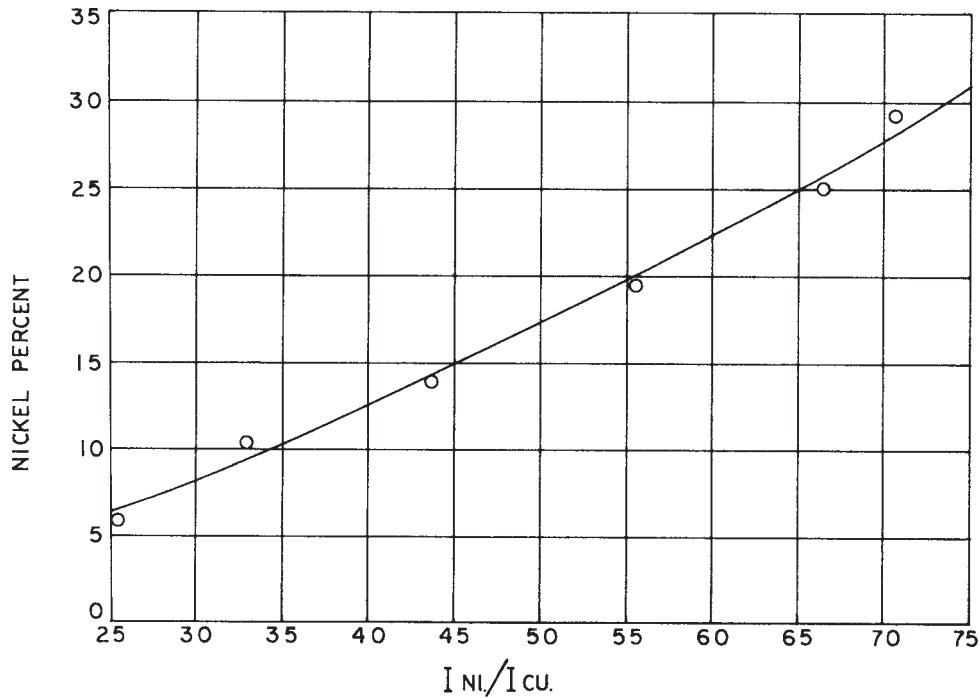


FIG. 4 Curve of a Quadratic Fit for Data in Table 3

same as for (Eq 21).  $s_b$  becomes smaller as  $\sum(X - \bar{x})^2$  is increased. This occurs if  $n$  is increased, or more significantly, if the spread in the standards is increased.

7.3.5.3 Using the data and computations given in Table 5, the 95 % confidence limit lines,  $\pm 2 s_{yc}$ , are shown in Fig. 5 (see Note 10). The confidence limit lines indicate the region within which there is a 95 % probability that the “true” value of  $Y$  occurs for a given value of  $X$ . It can be seen both from Fig. 5 and (Eq 20) that the calculation of  $Y$  gets less precise as  $X$

TABLE 5 Confidence Limits Computed from Data in Table 2<sup>A</sup>

$X - \bar{x}$	$S_{yc}^2$	$S_{yc}$	$2S_{yc}$
0	$3.192 \times 10^{-5}$	0.0057	0.011
$\pm 0.100$	$4.026 \times 10^{-5}$	0.0063	0.013
$\pm 0.200$	$6.528 \times 10^{-5}$	0.0081	0.016
$\pm 0.300$	$1.070 \times 10^{-4}$	0.0103	0.021

Computation:

$$S_{yx}^2 = (\sum Y^2 - b \sum XY) / (n - 2)$$

$$= 0.00051076723$$

$$S_{yx} = 0.0226$$

$$S_{yc}^2 = S_{yx}^2 \left( \frac{1}{n} + \frac{(X - \bar{x})^2}{\sum X^2} \right)$$

$$= 0.00051076723 \left( \frac{1}{16} + \frac{(X - \bar{x})^2}{0.6124477} \right)$$

$$S_b^2 = \frac{S_{yx}^2}{\sum X^2} = \frac{0.00051076723}{0.6124477}$$

$$= 0.000833977$$

$$S = 0.0289$$

<sup>A</sup> Computations in Table 2, Table 3, and Table 5 were done in a computer with no rounding. Rounding was done after all calculations were completed. Therefore, if the calculations are repeated using the logarithms tabulated, there may be minor differences in the results obtained.

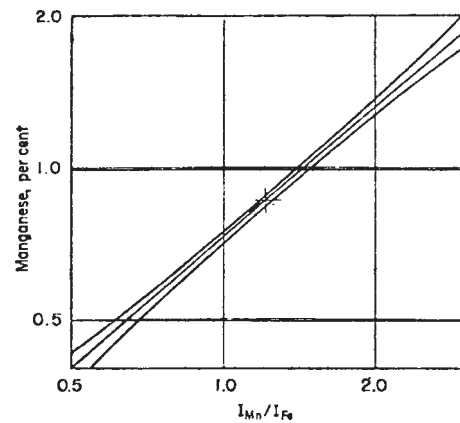


FIG. 5 Curve and 95 % Confidence Limits Drawn from Data in Table 4

gets farther from the mean,  $\bar{x}$ . At  $X = \bar{x}$ , the effect of the error of the slope is zero. This implies that the reference materials used for calibration, ideally, should be close in composition to the material being analyzed. The calculations to obtain  $s_{y,x}$  and  $s_b$  are also shown in Table 5.

NOTE 10—The students “ $t$ ” for 16 degrees of freedom is 2.12 and decreases to 1.96 for  $\infty$  degrees of freedom. An approximate value of 2 is used for this example.

## 8. Controlling Curve Shift and Rotation

8.1 *General Consideration*—Analytical curve shift and rotation can be caused by a change in such experimental variables as optics, excitation source, photographic material and processing, spectrometer electronics, or even ambient room conditions. The best way to prevent curve shift is by rigorous control of the experimental variables and by use of alternative means to check the equipment. Further control can

be achieved by frequent emulsion calibration or by monitoring excitation conditions. The use of drift tests described in Practice E 876 is also suggested.

8.1.1 Spectrometers in which readings are proportional to capacitor voltages provide a linear readout. They may include controls or adjusting readings after the integrated signals have been obtained. These controls can alter curve slope and are referred to as gain, sensitivity, or trimmer controls. They can provide a range in readings from a maximum value that is only 10 % greater than the minimum to a maximum that is ten times greater than the minimum. The term “trimmer” is preferred when it provides only the 10 % range. Provision is usually made for off-setting readings with a fixed bias, often called a “zero depress”, for curve intercept control. Linear systems can have subchannels displayed with different gain and bias controls without changing dynode voltages to permit dividing concentrations into smaller ranges.

8.1.2 Logarithmic readouts are based on the fixed discharge rate of a capacitor through a resistor. Only a change in excitation characteristics for different alloys or materials (influencing a change in spectral background or excitation temperature) will cause curve rotation and this may be avoided by making separate calibrations for different types of alloys or materials. Slight parallel curve shift may occur due to variations in photomultiplier tube or source efficiency, line voltage, etc. During calibration, include a reference material suitable for standardization and record elemental readings. During standardization compare current readings with those recorded during calibration and correct for any differences which are statistically significant prior to making routine analyses.

## 8.2 Standardization:

### 8.2.1 Reference Materials:

8.2.1.1 When using two-point standardization, the two reference materials employed should have sufficient difference in element concentrations to provide a set of readings at the high and low ends of each element’s range. In practice, it is usually not possible to have two reference materials that contain the highs and lows for all the elements of interest. Therefore, additional reference materials may be necessary. Reference materials should be as homogeneous as possible.

8.2.1.2 When using a single-point standardization, reference materials should have elemental concentrations within the central 50 % portion of the calibration range for each element being analyzed. If this is not possible with a single reference material, the use of more than one is permitted. Reference materials should be as homogeneous as possible.

8.2.1.3 Include all reference materials that will be used for controlling standardization when constructing the analytical curves. They may be excited both before and after the excitation of sets of the other reference materials to obtain more precise measurements and to serve as an indication of short-term drift, if any. Sufficient replication of the reference materials should be made to obtain estimates of standard deviation,  $s$ , and permit working within an acceptable confidence level with limits of  $\pm 2s/\sqrt{n_s}$ , where  $n_s$  is the number of times the reference material is run. Deviation measurements of other reference materials may be used to estimate the standard deviation by pooling estimates as recommended in

Practice E 876. Estimates of standard deviation from data having at least 16 degrees of freedom, as defined in Practice E 876, will effectively approach the value of  $\sigma$  within  $\pm 10\% \sigma$  when working at the 95 % confidence level.

### 8.2.2 Standardization Procedure:

8.2.2.1 Excite the reference material or reference materials a minimum of two times. Outliers should be eliminated using the procedure described in Practice E 178 and the reference materials rerun. If no suspect readings can justifiably be eliminated, additional excitations will minimize the error from any doubtful readings.

8.2.2.2 Standardization can be performed using one or more reference materials. If the average reading of the reference material is within  $\pm 2s/\sqrt{n_s}$ , the system may be assumed to be standardized. If the deviation is greater than  $2s/\sqrt{n_s}$  but less than  $4s/\sqrt{n_s}$ , a full or half correction may be made so that each reference material is at or equally near the assigned value. If the deviation is greater than  $4s/\sqrt{n_s}$ , a full correction should be applied or election may be made to recalibrate the system. Corrections may be made manually or by computer. In all cases where corrections are made, the reference material should be rerun to verify that the system is standardized.

8.2.2.3 On instruments with a logarithmic readout, excite the reference materials used for standardization and record the element readings. For a full correction, add or subtract the difference between these readings and the assigned value for each element. Halfway corrections are accomplished by adding or subtracting half the difference to bring readings halfway toward the assigned values. These adjustments can be made manually or by computer.

8.2.2.4 On instruments with linear readout, standardization can be done with one reference material if the bias applied to readings remains fixed. Corrections are then made as in 8.2.2.3. If a pair of reference materials is used for standardization, the two readings can be made equal to their assigned values by adjusting a gain until the desired spread between the two readings is obtained followed by an adjustment in bias to bring them to assigned values. (See Note 11 for precautions on shifting bias settings.) Alternatively, bias may be held fixed and gain adjusted so that one reference material is made to read as much higher than its assigned value as the other reference material is lower. The bias should be adjusted only if gain alone cannot bring both readings within  $\pm 2s/\sqrt{n_s}$  of assigned values. Halfway corrections are particularly appropriate in cases where the bias is adjusted to avoid causing an excessive shift. For halfway corrections, adjust gain so that the spread between the readings of the two reference materials is the average of the previous spread and the assigned spread. Then shift the bias to make each pair of readings equally close to assigned values. These adjustments can be made manually or by computer.

NOTE 11—When the readout system has a bias control, attention should be given to how much bias is being applied. If a large bias is used either to reduce background or to shift low concentration readings, so as to magnify the spread between high concentration readings, it is important to monitor the bias and to establish what is normal. If, on restandardizing, the resulting bias appears to be abnormal, the standardization should be repeated. The bias can be determined on some instruments by switching to “zero” and reading the amount of the displacement directly, or by



switching off the bias and observing the change in a reading.

8.2.3 *Frequency of Verification*—Establish the frequency of verification based on the criterion that the reading of a single excitation of reference material can be held within  $\pm 2s$  of the assigned value. If the frequency is such that results of a single excitation are consistently more than  $\pm 2s$  and none of the physical variables (optics, excitation, etc.) has changed, then the frequency of verification should be increased.

### 8.3 *Detecting and Correcting Curve Shift and Rotation:*

8.3.1 A frequent routine monitoring of a verification can be made with a single verifier which closely represents the material being analyzed. Excite the control reference material as many times as is normally done for running specimens, but at least in duplicate. As long as the average reading of the reference material falls within  $\pm 2s/\sqrt{n_s}$  of its assigned value, the standardization may be assumed to be in control. If the deviation is greater than  $\pm 2s/\sqrt{n_s}$  restandardize as in 8.2.2.1. In this case, if the reference material reads within  $\pm 4s/\sqrt{n_s}$  an election may be made to make halfway corrections as described in 8.2.2.3 or 8.2.2.4 before restandardizing. If halfway corrections have not been made and 8.2.2.2 indicates that the element is standardized, proceed with the additional checks of 8.3.2.

8.3.2 Excite a high and low concentration reference material other than those used for standardization or routine checking, if available. These reference materials should be excited as many times as is normally done for running specimens, but at least in

duplicate. If these average readings both fall within  $\pm 2s/\sqrt{n_s}$  of assigned values, the element may be considered to be in control and additional excitations should be made of the reference material to establish a new assigned value for its reading. It would also be appropriate at this time to review all recent data or to take additional readings to re-establish the estimate of the standard deviations of the measurements (See Note 12). If the average reading of either or both of the high and low concentration reference materials falls outside  $\pm 2s/\sqrt{n_s}$  of assigned or expected values, adjust readings or make corrections and recheck standardization as in 8.2.2.1. If these readings are within  $\pm 4s/\sqrt{n_s}$  of the expected values, an election may be made to make halfway corrections; otherwise, a new analytical curve should be constructed as described in 7.2 and revised assigned readings established for the standardization and control reference materials. It would also be appropriate to re-establish the estimate of the standard deviations of the measurements.

NOTE 12—The value of  $s$  should not change appreciably, but it should be revised periodically as additional data is collected after the initial standardization. The method for calculating a pooled standard deviation is described in Practice E 876. It is also helpful to plot the readings as a function of time to detect systematic shifts.

## 9. Keywords

9.1 analytical curve; calibration; drift; optical emission; standardization; x-ray fluorescence

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