



Designation: E 305 – 89 (Reapproved 1994)^{e1}

Standard Practice for Establishing and Controlling Spectrochemical Analytical Curves¹

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 (ϵ) indicates an editorial change since the last revision or reapproval.

^{e1} 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 Analysis²
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²
- E 178 Practice for Dealing with Outlying Observations³
- E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data⁴

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

¹ 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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² *Annual Book of ASTM Standards*, Vol 03.05.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ *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, σ . 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 σ , 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 $16n$.

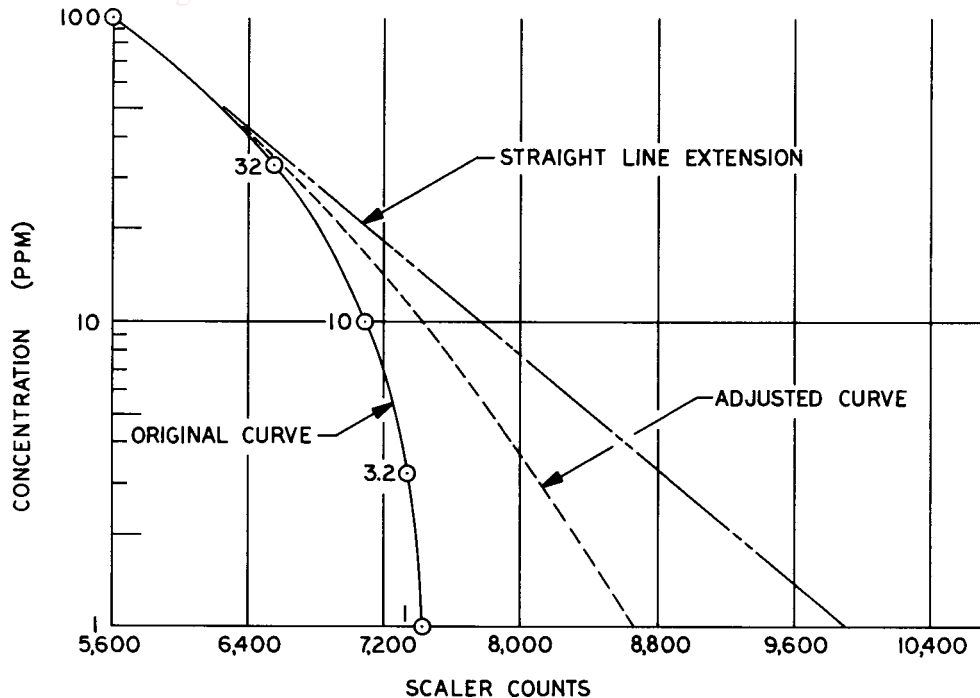


FIG. 1 Background Correction with Logarithmic Readout System

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:

σ = 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.

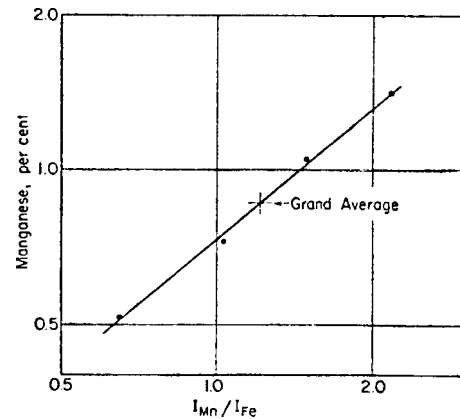


FIG. 2 Curve Drawn from Data in Table 1 with the Technique Described in 7.2.3.3

TABLE 1 Data and Computations for a Straight Line Analytical Curve

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

^A Average intensity ratio for each reference material.

^B Grand average of log percent Mn converted into percent Mn.

^C Grand average of log percent Mn.

^D Grand average of log I_{Mn}/I_{Fe} converted into I_{Mn}/I_{Fe}.

^E Grand average of log I_{Mn}/I_{Fe}.

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

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

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

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

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