



Designation: E305 – 21

Standard Practice for Establishing and Controlling Spark Atomic Emission Spectrochemical Analytical Curves¹

This standard is issued under the fixed designation E305; 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.

1. Scope

1.1 This practice provides direction for establishing and controlling spark atomic emission spectrochemical analytical curves. The generation of analytical curves and their control are considered as separate though interrelated operations. This practice is applicable to spark atomic emission spectrometers.

NOTE 1—X-ray fluorescence spectrometric applications are no longer covered by this practice. See Guides E1361 and E1621 for discussion of this technique.

1.1.1 Since software programs are readily available to compute multiple linear regressions that can be used to generate analytical curves and since most instruments include this feature, this practice does not address this procedure. However, some recommendations are given to evaluate the equations that are generated.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.3 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E1329 Practice for Verification and Use of Control Charts in

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.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Spectrochemical Analysis (Withdrawn 2019)³

E1361 Guide for Correction of Inter-element Effects in X-Ray Spectrometric Analysis

E1621 Guide for Elemental Analysis by Wavelength Dispersive X-Ray Fluorescence Spectrometry

3. Terminology

3.1 For definitions of terms used in this practice, refer to Terminology E135.

NOTE 2—Spectrometer manufacturers tend to use the term “standardization” in their software. The correct technical term is “drift correction,” which is used in this practice.

4. Summary of Practice

4.1 Systematic and random errors that occur in obtaining data are reviewed. Background corrections are considered as well as interferences from other elements. Calibration, drift correction, and verification procedures are discussed, including the use of reference materials and the generation of data. A basis is given for evaluating first, second, third, and higher degree analytical curves.

5. Significance and Use

5.1 This practice is intended to provide fundamental direction for the calibration, drift correction, and periodic control of the analytical curves for spark atomic emission spectrometers.

5.2 It is assumed that this practice will be used by trained operators capable of performing the procedures described herein.

6. Precautions

6.1 *Potential Errors:*

6.1.1 *Bias Because of Incorrect Calibration*—In the procedure for quantitative spectrochemical analysis, the initial generation of the analytical curve relates element composition or relative composition to spectral intensity or intensity ratio. The accuracy of the calibration may be affected by a number of factors, such as incorrect values for element compositions, heterogeneity of the reference materials, spectral interferences,

³ The last approved version of this historical standard is referenced on www.astm.org.

and matrix effects. These factors may cause a shift in the analytical curve, thereby leading to bias in the analytical data generated. It is the user's responsibility to apply calibration models designed to evaluate the effect of, and mathematically correct for, spectral interferences and matrix effects.

6.1.1.1 Calibration bias because of incorrect element compositions is minimized by the use of certified reference materials (CRMs). These CRMs may be augmented with 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 Standard Institution). The inclusion of production materials analyzed by independent methods permits determining whether bias exists because of differences between the metallurgical conditions of the CRMs and typical samples. In the absence of CRMs, it is helpful to use several reference materials from a variety of sources to detect bias in these materials.

6.1.1.2 In general, the use of a large number of reference materials will aid in the detection and rejection of those that appear to be inaccurate. Exercise caution when rejecting data that appears to be inaccurate as it may be reflecting complicated matrix effects or the impact of unknown variables.

6.1.1.3 It is advisable that analyzed materials used as calibration reference materials (RMs) be tested initially for heterogeneity.

6.1.2 *Bias Because of Experimental Variations*—Bias may arise from experimental variations occurring within the operational procedure (for example, change in optics, source parameters, etc.). Such changes may result in bias because of changes in sensitivity or background resulting in displacement of the analytical curve. The analyst may attempt to reduce bias from experimental variations during the initial calibration procedure by replication and by measuring the reference materials in random order; but bias may be detected later during subsequent operations, as described in 8.3.1.

6.2 Random Errors:

6.2.1 *Measurement Error*—Measurement repeatability may be assessed using an estimate of standard deviation of repeated measurements. 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 ,

where:

$$s = \sqrt{\sum(x_i - \bar{x})^2 / (n - 1)}$$

and where:

x_i = are individual values

\bar{x} = average x_i , and

n = number of measurements.

6.2.1.1 Errors in determining the average signal intensity or intensity ratio from reference materials occur because of statistical variation, less than optimum excitation parameters, and elevated specimen heterogeneity. Increasing the number of replicate measurements and using the average of the values will reduce the effect of statistical variation and minor elevated specimen heterogeneity. The use of optimum excitation conditions, including sufficient preburn and integration times, will also reduce statistical variations and increase accuracy.

7. Calibration

7.1 *Spectral Background*—Background intensities vary throughout the spectral regions. Correcting for the background in measurements of weak spectral line intensities (those slightly more intense than background) can improve the measurements. However, the effectiveness of the correction must be evaluated. The need for background correction varies with the type of material being analyzed. Ensure that background correction is necessary and can be accomplished consistently before proceeding.

7.1.1 *Background Correction*—Methods of background correction may use either a dynamic correction or a shifting of spectra through exit slits to read background near a line.

7.1.1.1 In a dynamic background correction, a selected portion of the background of a spectrum is integrated simultaneously with analytical signals. When this integrated measurement is strong and broad enough to give a consistent sampling, it can be used to subtract out background. A background area signal may be strengthened by using a wide exit slit or by using an extra-sensitive detector, or by a combination of these. Because the dynamic approach is difficult to control and may depend on maintaining consistent response from two detectors, it is rarely used in photomultiplier systems. It can be used more effectively with solid-state detector systems.

NOTE 3—Measurement of spectral intensity may not be truly simultaneous even with solid-state detectors. Some spectrometer designs read multiple regions of a detector in rapid succession, not in true simultaneity. Such a design can be subject to instrument drift.

7.1.1.2 Shifting to read background has validity only if the generation of background intensity shows little variation from measurement to measurement.

7.2 Generation of the Analytical Curve:

7.2.1 *Calibration Reference Materials (RMs)*, preferably CRMs as described in 6.1.1.1, should span the composition ranges and types of materials expected. Extrapolation should be avoided. It is recommended that the number of calibration RMs used for each curve be twice the number of coefficients to be determined by regression. This includes the curve parameters and any correction coefficients.

7.2.1.1 Minimally, there should be at least one more data point than the number of coefficients or constants in the equation. If this minimum is not met, the calculation of a supposed regression fit will merely make the resulting curve go through each data point as if each was absolutely correct, negating the purpose of making a least square fit of data. In fact, reputable curve fitting software will reject such an attempt to calculate the parameters, citing that there is insufficient data.

7.2.1.2 If the composition range exceeds one order of magnitude or if several calibration RMs are close to each other in composition, the use of more calibration RMs is recommended, preferably at least three per order of magnitude, spaced as equally apart as possible.

7.2.2 *Drift Correction Samples and Verifiers*—All materials that may be useful in monitoring and normalizing calibrations should be measured in a random order along with calibration RMs. Control and drift correction samples shall have reasonably low heterogeneity that provide repeatable measurements

over time. The repeatability standard deviation for suitable material shall be less than or equal to the interlaboratory repeatability goal for the test method. In general, calibration RMs should not be used as drift correction samples or verifiers.

7.2.3 Number of Replications—The number of replications for each calibration RM, drift correction sample, and verifier shall be at least as great as the number replications to be made for each specimen in a determination.

7.3 Generating Multiple Linear Regression—As stated in **1.1.1**, software can provide the needed multiple linear regression for developing equations of first, second, third, and higher order polynomials and incorporate corrections for interferences from other elements. When using higher order polynomials, the useable portion of a curve must not be near to a maximum or a minimum nor include a point of inflection. See **7.3.2.2**.

7.3.1 Typically, the data used for calibration are relative intensities, the ratio of intensity of a spectral line to an internal standard line. When the scope of an analysis involves significant change in the composition of the internal standard element, the relative intensity of the spectral line is plotted against a relative mass fraction, that is, the known mass fraction of the calibration RM divided by the mass fraction of the matrix element, and usually multiplied by 100. The software must be able to convert relative mass fractions to actual mass fractions.

7.3.1.1 Additive Effect—The addition of a signal from another element. The regression must include an additional term that will define the factor needed to subtract this interference as a function of mass fraction of the interfering element. In practice, this may sometimes be an addition rather than a subtraction.

7.3.1.2 Multiplicative Effect—An effect on the calibration RM signal that depends on both the analyte signal and the mass fraction of the interfering element. The regression must include an additional term that will define a factor such as k in $(1 \pm kc)x$, where c is the mass fraction of the interfering element, and x is either the intensity for the analyte or a preliminary estimate of its mass fraction.

7.3.1.3 Introducing corrections for elemental interferences may pose a problem. Even if the interference seems well supported by calibration RM, the increased variability from additional factors may be greater than the level of correction being made, in which case it would be better to opt for defining a family of calibrations instead of defining a general system. The limitation of utilizing a family of calibrations is that many more calibration RMs might be required.

7.3.2 Precautions in Generating Non-Linear Curves—Non-linear analytical curves should be plotted to observe the graphical relationship. Mathematical checks can also be used to calculate where any maxima, minima, or points of inflection occur.

7.3.2.1 By their nature, quadratic equations (second degree) always have a maximum or a minimum. These extremes pose no problem if not near the useful analytical range. If the mass fraction, y , is expressed as a quadratic equation:

$$y = a_0 + a_1x + a_2x^2 \quad (1)$$

where:

a_0, a_1, \dots, a_n = the coefficients of the calibration equation, and
 x = the reading obtained in a determination.

Eq 1 will reach a maximum or a minimum when the first order derivative of the equation is equal to zero, or:

$$dy/dx = a_1 + 2a_2x = 0$$

from which:

$$x = -a_1/2a_2 \quad (2)$$

7.3.2.2 A third degree equation is commonly used. Since its first order derivative has two roots it may have both a maximum and a minimum, unless the roots are imaginary. However, it will always have a point of inflection that should be considered. The third degree equation can be expressed as:

$$y = a_0 + a_1x + a_2x^2 + a_3x^3 \quad (3)$$

for which:

$$dy/dx = a_1 + 2a_2x + 3a_3x^2 = 0 \quad (4)$$

the roots of this equation are:

$$x = \left(-a_2 \pm \sqrt{a_2^2 - 3a_1a_3} \right) / 3a_3 \quad (5)$$

When the expression under the square root sign is negative, the roots are imaginary and there is neither a maximum nor a minimum. However, there is always a point of inflection that might be missed in evaluating a calibration. It is defined when the second derivative of **Eq 3** is made equal to zero:

$$d^2y/dx^2 = 2a_2 + 6a_3x = 0$$

for which:

$$x = -a_2/3a_3 \quad (6)$$

The third degree equation is capable of defining a calibration that appears to be linear at low mass fractions and with increased curvature at higher mass fractions. When it does so, there likely will be a point of inflection in the apparent linear section. It must be ascertained that, when there is a reversal of bending in that section, it does not detract from the virtual linearity.

7.3.2.3 The use of an equation of higher than third degree is discouraged. Lower residuals obtained through the use of such equations is deceptive and the use of these equations does not represent reality in instrumental analysis. Rather than using a fourth degree, or higher, equation, it might be better to restrict the definition to no more than a third degree by defining two curves to separately cover a lower and a higher mass fraction range. Typically, this might be a third degree equation for the higher mass fraction portion of the curve and a second, or even first degree equation for the lower mass fractions. If so, it would be desirable to have one curve (the higher mass fraction) become the controlling relationship at a specified mass fraction. The slopes of both curves should virtually be the same at the point where the transition is made.

NOTE 4—If a forced calculation is made in determining a curve fit in which the number of data points is equal to the number of constants of the polynomial, such as entering a data point twice, the fallacy could be observed when the resulting curve is plotted and it showed obvious unrealistic curvature and an unrealistic appearance of maxima and minima