Designation: E305 – 13

Standard Practice for
Establishing and Controlling Atomic Emission Spectrochemical Analytical Curves[1]

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 covers guidance for establishing and controlling atomic emission spectrochemical analytical curves. The generation of analytical curves and their routine control are considered as separate although interrelated operations. This practice is applicable to atomic emission spectrometers.

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

1.1.1 Since computer programs are readily available to run multiple linear regressions that can be used to generate analytical curves and since most instruments include this feature, this practice does not go into detail on the procedure. However, some recommendations are given on evaluating 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 and health practices and determine the applicability of regulatory limitations prior to use.*

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 Spectrochemical Analysis
E1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis
E1621 Guide for X-Ray Emission Spectrometric Analysis

3. Terminology

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

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, standardization, and verification procedures are discussed, including the use of reference materials and the generation of data. A basis is given for evaluating second, third, and higher degree analytical curves.

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 for 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, 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 concentrations are minimized by the use of certified reference materials. These calibrants 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 Standards Institute). The inclusion of production materials analyzed by independent

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[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.

methods permits determining whether bias exists because of differences between the metallurgical conditions of the certified reference materials and typical samples. In the absence of certified reference materials, 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. Caution should be exercised in 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 calibrants be tested initially for homogeneity.

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, and so forth). 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 specimen inhomogeneity. Increasing the number of replicate measurements and using the average of the values will reduce the effect of statistical variation and minor specimen inhomogeneity. 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.

NOTE 2—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 may be made to have a strong signal 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 burn to burn.

7.2 *Generation of the Analytical Curve:*

7.2.1 *Calibrants,* preferably certified reference materials 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 calibrants to be used for each curve be twice the number of coefficients to be determined by regression. This includes the curve parameters and any correction coefficients. If the composition range exceeds one order of magnitude or if several calibrants are close to each other in composition, the use of more calibrants is recommended, preferable 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 burned in a random order along with calibrants. Control and drift correction samples shall be homogeneous such that they give 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, calibrants should not be used as drift correction samples or verifiers.

7.2.3 *Number of Replications for Each Reference Material*—The number of replications for each calibrant, 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, computer programs can provide the needed multiple linear regression for developing equations of 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 calibrant divided by the mass fraction of the matrix element, and usually multiplied by 100. The computer program 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 calibrant 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 calibrants, 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 downside of utilizing a family of calibrations is that such a restriction might require many more calibrants.

7.3.2 *Precautions in Generating Non-Linear Curves*—Non-linear analytical curves should be plotted to see that they present a reasonable looking 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 they are not near the useful analytical range. If the mass fraction, y, is expressed as a quadratic equation:

$$y = a_0 + a_1 x + a_2 x^2 \tag{1}$$

where:

$a_0, a_1, ...a_n$ = the coefficients of the polynomial, 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:

$$dy/dx = a_1 + 2a_2 x = 0$$

from which:

$$x = -a_1/2a_2 \tag{2}$$

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. It will always have a point of inflection, however, that should be considered. The third degree equation can be expressed as:

$$y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 \tag{3}$$

for which:

$$dy/dx = a_1 + 2a_2 x + 3a_3 x^2 = 0 \tag{4}$$

the roots of this equation are:

$$x = \left(-a_2 \pm \sqrt{a_2{}^2 - 3a_1 a_3}\right)/3a_3 \tag{5}$$

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 always is 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:

$$d^2y/dx^2 = 2a_2 + 6a_3 x = 0$$

for which:

$$x = -a_2/3a_3 \tag{6}$$

The third degree equation is capable of defining a calibration that appears to be linear at low mass fractions and picking up 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.

7.3.2.4 *Number of Data Points Required*—Although it might appear, mathematically, that it is only necessary to have as many data points as the number of constants in the polynomial being fitted, this is insufficient for defining a curve. There should be at least one more data point than the number of coefficients or constants of the polynomial. 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 programs will reject such an attempt to calculate the parameters, citing that there is insufficient data.

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 by 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 close together. This would not be as obvious as an error in defining a straight line from two points. The distortion is that although this is truly a fit, it is not a regression. What has not been readily recognized is that the common use of just a high and a low reference material to standardize an instrument, the so-called "two-point" standardization, merely arrives at a slope and intercept correction from a simple straight line without allowing for variations in the readings. A marked improvement in "reading" the drift correction samples occurs when at least one more drift correction sample is used, giving the system at least one degree of freedom. Practice E1329 presents data that shows how the "two point" standardization fails to function properly when tied in with control charts.

8. Controlling Curve Shift

8.1 *General Considerations*—Analytical curve shift can be caused by a change in such experimental variables as optics, excitation source, spectrometer electronics, or even ambient room conditions. Monitoring excitation conditions can provide some control. Controlling shifts by using control charts, as described in Practice E1329, is recommended.

8.1.1 *Verification*—Verifiers indicate when a new standardization is needed. A control chart for each verifier establishes its upper and lower control limits and provides a record of its repeatability. If control charts are not used, the need for standardization is indicated when the average reading of a verifier does not fit within the range of $\pm 2s/\sqrt{n_s}$ of the expected reading, where n_s is the replication of the verifier and s is the establish standard deviation of that verifier reading. There are additional rules for using control charts that can be applied at the users discretion.

Note 5—Verification also looks for a significant shift in readings. It should not be confused with drift, which may be observed as being a constant change that can be quantified and provide small corrections based on time. Drift control is important when testing for homogenity.

8.1.1.1 *Frequency of Verification*—Establish based on how frequently there is a need to perform a standardization. Verification should be performed more than twice as often as standardization.

8.2 *Standardization,* generally performed only when it is known that the analytical system has changed because of maintenance, (that is, cleaning the optics, installing new components, and so forth) or when a verifier indicates it is necessary.

8.3 *Drift Correction Samples and Verifiers* are tools that are used to control standardization. They are consumed and they may change composition as they are used. There must be an awareness of when they change, and replacements must be provided.

8.3.1 If standardization is controlled by *multi-point references*, as described in Practice E1329, a running record may be kept of the corrected readings of both the drift correction samples and the verifiers. In fact, verifiers are also considered to be drift correction samples and the standardization procedure provides an unbiased comparison of the corrected readings. The records will show when any of these references have shifted. When a significant shift is noted, a correction can be made in the listing of what is expected for that drift correction sample, if it still has acceptable repeatability, or the material should be replaced.

8.3.1.1 If standardization is controlled by *two-point references*, the drift correction samples are always "corrected" to their expected readings and all the variations will be reflected in the readings of the verifiers. Records might indicate a shift in verifier readings, but it would not be known if the shift came from the verifier or from one of the drift correction samples.

8.4 *Replacement of Drift Correction Samples and Verifiers* is aided if the need is anticipated and new materials are studied to see how they responded during standardization.

9. Keywords

9.1 analytical curves; atomic emissions; calibrations; interferences; standardization, including multi-point; verifications