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

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

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