



Standard Practice for Verification and Use of Control Charts in Spectrochemical Analysis¹

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1. Scope

1.1 This practice covers procedures for determining if a spectrochemical analysis is under statistical control.

1.2 Criteria are presented for determining when corrective action is required.

1.3 Control will be effected by using verifiers to test instrument response. It is recommended, although not required, that this be accompanied by the plotting of control charts.

1.4 The preparation of control charts is described.

1.5 *Limitations*—The procedures that are described do not apply to analyses that require a calibration each time a set of analyses is run. Reference is made specifically to atomic emission spectrometry, but the practice has a more general application.

1.6 This practice does not apply to validation procedures that monitor the correctness of calibration.

2. Referenced Documents

2.1 ASTM Standards:²

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

E158 Practice for Fundamental Calculations to Convert Intensities into Concentrations in Optical Emission Spectrochemical Analysis³

E305 Practice for Establishing and Controlling Atomic Emission Spectrochemical Analytical Curves

E456 Terminology Relating to Quality and Statistics

E876 Practice for Use of Statistics in the Evaluation of Spectrometric Data³

2.2 Other ASTM Documents:

MNL 7A Manual on Presentation of Data and Control Chart Analysis⁴

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminologies **E135** and **E456** and Practice **E876**. Refer also to the glossary of terms and symbols appearing in **MNL 7A**.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *control limits*—in control charts, the upper and lower limits of a statistic that are not expected to be exceeded, designated as UCL and LCL respectively in this practice. For the statistic that is the average of more than one reading or determination, the upper and lower limits will be equidistant from a central line (CL) representing the expected average. For the statistic of either standard deviation or range, the upper limit will be farther from the central line if the lower limit is zero.

3.2.2 *normalization*—a procedure for correcting readings to a common basis. A special case of normalization is standardization in which readings are made to conform to an existing calibration. Normalization permits gathering data in different periods of time and correcting for drift in a way that may be independent of standardization routines.

3.2.3 *variation*—difference in an observed value from an accepted value.

3.2.3.1 *assignable cause*—variation which can be identified and corrected. It may be the result of a condition of an instrument or a method of operation. For example, signal intensities may be affected because a spectrometer is not profiled properly.

3.2.3.2 *chance or common cause*—random variation which consistently affects a system, contributing to the imprecision in a predictable way. In the application of control charts, the assumption is made that chance causes of variation are normally distributed.

4. Significance and Use

4.1 Consistency in analysis depends on being aware of a significant change in instrumental response, such as that caused

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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.

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

⁴ *ASTM Manual Series*, ASTM, 7th edition, 2002.

by drift or changes in analytical precision, or both, and taking corrective action. The usual corrective action for drift is standardization. Standardization, however, when there is no real need, can only broaden the spread of subsequent analyses. One purpose of this practice is to set guidelines that will avoid “unnecessary standardization.”

4.2 To control manufacturing processes, there must be confidence that a consistent material is being produced and that the analysis of the material is reliable. For assurance that the material meets specification, a purchaser may require the supporting record of control charts to assess that proper analytical control has been maintained.

4.3 Ideally, variations in analytical results may be held to chance causes. The concept of a confidence interval or limits on a control chart is based on what can be expected when all normal precautions are exercised. When results appear to go out of control, the analyst should consider and correct what might be an assignable cause. As experience is accumulated, however, it may not seem unusual for readings to drift with time as optics degrade, detector response changes, or excitation conditions change, for example, when deposits build up on a counter electrode (a correctable assignable cause), or the longer range effects as an X-ray tube deteriorates.

5. Problems in Applying Control

5.1 A complication in effecting verification control or in using control charts with spectrochemical analyses is that the measurements being taken are not absolute. Determinations depend upon comparisons of one measurement to another: the relative intensity of an analytical line to the relative intensity of an internal standard line in atomic emission spectrometry; the interrelationship of counts in X-ray spectrometry under some specified condition of maintaining a fixed intensity from an irradiating source and holding to a consistent response from a detector with or without pulse height analyzers and with or without an external monitor; and the relative response in integrating for fixed times with ostensibly constant radiation sources. Added to these is the complication of background signal in all techniques.

5.2 It is important to recognize that there are several sources of random variation, including variations from the measuring method as well as inhomogeneity in the specimens. The device being used to test analytical response is the analytical system itself. This differs from normal statistical process control where an independent and usually more accurate measuring device is used to verify the process variability.

6. Verifiers

6.1 It is recommended that readings for all potential verifiers as well as standardants be established by measuring them along with the calibrants.

6.1.1 Ideally, the full set of potential standardants and verifiers should be run before and after a series of calibrants to permit normalizing all calibration data to a common basis. To achieve the best normalization of data, readings should be recorded for all elements of interest on every standardant and verifier, even if there is no knowledge of expected concentrations. Unless there is a marked change in the before and after

measurements, the averages of a set of before and after readings will be used for normalization.

NOTE 1—If there appears to be a drift between readings of standardants obtained before and after a set of calibrants has been run, an instrument problem may need to be investigated and corrected or the operational environment improved. Reliable calibration data can be obtained only if an instrument shows a stable operation. Practice E876 describes ways to test for drift.

6.1.1.1 Unless a curve fitting routine is being used that requires “standardizing” before running a set of reference materials it is recommended that no normalization be done until all calibration data has been recorded. Strictly speaking standardization, as defined in Terminology E135, only can be done after a calibration has been established. If a normalization to some prescribed set of readings is done as if it were a standardization before each time a set of reference materials is run, the resulting record of readings can be treated as if no standardization had been done.

6.1.2 Choose one set of averages of before and after readings of 6.1.1 as the norm. A grand overall average of the sets may be used if that seems like a reasonable median of all sets. Exclude any readings for an element in a reference material that does not show comparable repeatability to what was observed for that element in other materials. For higher-level readings, the comparison should be made to observed relative repeatabilities.

6.1.2.1 For an ideal normalization of readings, determine the regression fit of a set of observed readings, x , to expected readings, y . This linear regression, which is also supported by Practice E305, commonly is done on electronic calculators or computers by the following equations to determine a slope, m , and a constant, k , which can be used to correct observed readings to an established norm:

$$m = \frac{n\sum xy - \sum x(\sum y)}{n\sum(x^2) - (\sum x)^2} \quad (1)$$

and

$$k = (\sum y - m\sum x)/n \quad (2)$$

where the summations of functions of x and y are as follows:

x = the observed average readings of an element in a calibration set,

y = the expected normal readings for that element, and

n = the number of pairs of x and y readings.

6.1.2.2 Apply the appropriate m and k corrections to the averages of the verifiers and standardants, as well as to the calibrants in each calibration set, as follows:

$$R_N = mR_O + k \quad (3)$$

where:

R_N = normalized reading, and

R_O = observed average reading.

The grand averages of the normalized readings of the standardants and verifiers will become the values used for standardizing.

6.1.3 If the analytical system only can support the “two-point” standardization, and if the only permissible normalization is a quasi-standardization, before collecting calibration

data it is still advisable to record all readings for all elements in all reference materials to establish a full record of what can be expected for all the reference materials (see 8.6). The initial set of “normal” readings are reasonable starting points. Neither the preferred method of using a regression fit nor the recommendation of waiting until all data have been logged before assigning normal values are infallible. Modification of these values always should be an option as more experience is gained. It is expected, however, that the preferred methods will arrive at the ideal normal values earlier.

6.1.3.1 If the operating system is based on two-point standardization, Eq 3 still would be used to normalize or standardize readings. The generation of slope and constant corrections, however, would be as follows:

$$m = (H_R - L_R)/(H_O - L_O) \quad (4)$$

and

$$k = H_R - m(H_O) \quad (5)$$

where:

H_R = reference or normal reading of the high standardant,

L_R = reference or normal reading of the low standardant,

H_O = observed reading of the high standardant, and

L_O = observed reading of the low standardant.

6.1.4 If data are later transformed by a slope and intercept to give a different scaling for the calibration, the same transformation must be applied to the readings of standardants and verifiers.

6.2 If a verifier (or a new standardant) is established after a calibration has been defined, the expected reading can be established as follows:

6.2.1 Shortly after a standardization, run the verifier in replicate and keep a record of its average reading. Average a minimum of ten such observations made after new standardizations to obtain a good representation of the expected reading.

6.2.1.1 Normalization coefficients are determined by making a linear regression fit of normal readings as a function of observed readings, such as is done in Practice E305 in establishing a straight line relationship by the method of least squares. The “normal” set of readings can be either overall averages or a set that appears to be a median of all sets. The “slope” of this regression becomes the proportional factor, m , and the “intercept” the constant, k .

6.2.2 If a verifier must be established in a shorter time than the requirements of 6.2.1, a set of standardants and selected calibrants can be run with the verifier. The data may then be analyzed as described in 6.2.1.1, with the expected readings of standardants and calibrants used as the normal readings. This should be repeated at least two more times. Average the corrected verifier readings to obtain a good estimate of the expected reading.

6.2.2.1 The estimate of standard deviation for the verifier can be improved by pooling with readings that are similar or it can be defined by an overall pattern of deviation with intensity.

6.3 *Final statements of performance of a verifier* should be in terms of concentration. Standard deviations in terms of intensity / intensity ratio reading can be converted to an equivalent standard deviation in terms of concentration by

multiplying by the slope of the of the calibration equation at the point of the verifier reading. Details are given in Annex A1.

6.3.1 If a deliberate change is made in the slope of a calibration curve after the collection of data, such as might be done in the transformation in 6.1.4, the effective standard deviation of the reading will be the previous observed standard deviation divided by the factor used to change the slope of the curve. Thus, if a standard deviation has been calculated as being 0.6 when a curve slope (change of concentration divided by change in reading) at some point was 0.4, it would become 0.3 if the curve was made twice as steep, that is, when the slope at the same point was changed to 0.8.

7. Use of Confidence Interval to Control Spectrochemical Analysis

7.1 Practice E876 uses Student’s t -table to establish the range of reading or concentration around an average that will include the true reading or concentration at some confidence level. The calculation includes the standard deviation of the measurement. To be effective, the standard deviation should be estimated with at least 16 df. The interval straddling the average will be $\pm ts / \sqrt{n}$, where t is a factor from the t -table for some probability level, s is the estimate of standard deviation, and n is the number of readings taken for one observation. If control of a method depends upon observing an intensity reading, the confidence interval may be in terms of an intensity reading. If a method uses a computer to display concentration, the confidence interval should be in terms of concentration.

7.1.1 If the confidence interval is used to judge when drift has occurred, it will be appropriate to use a confidence level of 95 % to anticipate when control may be in jeopardy.

7.1.2 It will be satisfactory to use 2.0 as an approximation of a t -factor for the 95 % confidence. When it is observed that a verifier has exceeded this range, often referred to as a “2-sigma” limit, a standardization should be done. This can be a half correction if the verifier reads less than three times the standard deviation, the “3-sigma” limit. Practice E305 describes procedures for half corrections. See also 8.5.3.

7.1.3 Any verifier which exceeds the “3-sigma” limit will require a full standardization correction unless there is an assignable cause for the divergence. For an assignable cause, a second verification can be made after correcting the problem to see if standardization is necessary.

8. Use of Control Charts to Control Spectrochemical Analysis

8.1 Like confidence interval, control charts include upper and lower limits based on repeatability. Since observations are made on more than isolated tests of a verifier, correction is not required when a “2-sigma” limit has been reached, as called for in 7.1.2. Other indicators, however, may call for correction before a verifier has reached the “3-sigma” limit. Other observations include monitoring precision and the pattern of the measurements.

8.2 To control a spectrochemical analysis, use one chart to plot the data of the average readings or determinations made on a verifier and another chart to monitor the precision of the

measurement. The latter can either be an estimate of standard deviation or a calculation of range of any one set of observations.

NOTE 2—Process control is often able to operate satisfactorily with single samples and measurements, and to monitor range by comparing a current observation with a previous one. For spectrochemical analysis, however, it is generally preferable to make at least duplicate determinations. Whatever replication is selected, it should be used consistently for all observations in order to avoid warping the monitoring of precision. (MNL 7A, however, does explain how to handle cases in which uneven sampling is used.)

8.2.1 The appropriate control is one in which the results expected for a verifier are known. This fits the category of *Control With Respect to a Given Standard* that is covered in Sections 18 through 21 in MNL 7A.

8.3 Two types of control can be maintained:

8.3.1 *Record of Verifier Response During Routine Operation that Establishes that a Method Is Being Maintained in Statistical Control*—This permits maintaining the instrument in an efficient manner and holding analyses to as small a variation as possible.

8.3.2 *Record of Verifier Response that Establishes that Drift Is Being Properly Controlled by Standardization*—If there is a need for frequent, routine standardization, control charts may be used to monitor the effectiveness of the standardization by recording verifier response after a standardization. When verifier readings go out of limits under these conditions, correction may require redetermining the relative signals of standardants, verifiers, and calibrants.

8.4 *Preparation of Control Charts*—See Fig. 1 for a typical display of a control chart in which range, R , is used to monitor repeatability. Prepare a similar graph with appropriate scales for $\bar{X}$ values and for R or s values.

8.4.1 *Average Measurements*:

8.4.1.1 Draw a horizontal line for the expected average measurement of the verifier, X_0 , and mark as being CL, central line.

8.4.1.2 Calculate the upper and lower control limits, “3-sigma” limits, using the following two equations:

$$UCL_X = X_0 + As_0 \quad (6)$$

$$LCL_X = X_0 - As_0 \quad (7)$$

where:

$A = 3/\sqrt{n}$, the factor appearing in Table 1 for n observations, and

s_0 = established standard deviation of a measurement. See 9.1.1.

Draw horizontal lines for these and mark as being UCL and LCL.

8.4.2 *Precision*—Precision (or imprecision) can be monitored by determining either the standard deviation of a measurement or the range, the difference between the largest and smallest observed value. For the normal replication of spectroscopic measurements, the use of range is generally preferred.

8.4.2.1 *Using Range (R)*—Calculate the central line using the following equation:

$$CL_R = d_2s_0 \quad (8)$$

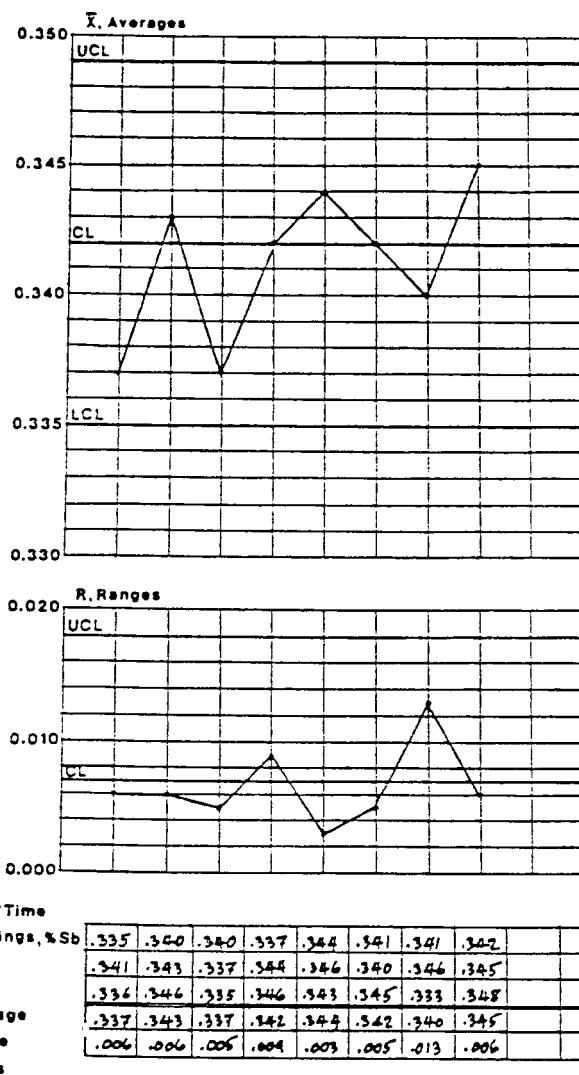


FIG. 1 Control Chart for Antimony in Solder

Also calculate the upper and lower control limits using the following two equations:

$$UCL_R = D_2s_0 \quad (9)$$

$$LCL_R = D_1s_0 \quad (10)$$

where d_2 , D_2 , and D_1 are factors from Table 1 for the appropriate number of observations. (For less than seven measurements, the lower control limit is zero). Draw horizontal lines for these and mark appropriately.

8.4.2.2 *Using Standard Deviation (s)*—Calculate the central line using the following equation:

$$CL_S = c_4s_0 \quad (11)$$

Also calculate the upper and lower control limits using the following two equations:

$$UCL_S = B_6s_0 \quad (12)$$

$$LCL_S = B_5s_0 \quad (13)$$

where c_4 , B_6 , and B_5 are factors from Table 1 for the appropriate number of observations. (For less than six measurements, the lower control limit is zero.) Draw horizontal lines for these and mark appropriately.

TABLE 1 Factors for Computing Control Chart Lines, Standard Given^A

Number of Observations, n	Averages		Standard Deviations			Ranges		
	Control Limits	Central Line	Control Limits		Central Line	Control Limits		
	A^B	C_4	B_5	B_6	d_2	D_1	D_2	
2	2.121	0.7979	0	2.606	1.128	0	3.686	
3	1.732	0.8862	0	2.276	1.693	0	4.358	
4	1.500	0.9213	0	2.088	2.059	0	4.698	
5	1.342	0.9400	0	1.964	2.326	0	4.918	
6	1.225	0.9515	0.029	1.874	2.534	0	5.078	
7	1.134	0.9594	0.113	1.806	2.704	0.204	5.204	
8	1.061	0.9650	0.179	1.751	2.847	0.388	5.306	
9	1.000	0.9693	0.232	1.707	2.970	0.547	5.393	
10	0.949	0.9727	0.276	1.669	3.078	0.687	5.469	

^A Abbreviated table from ASTM STP 15D, p. 93, Table 3.

^B The factor $A = 3/\sqrt{n}$.

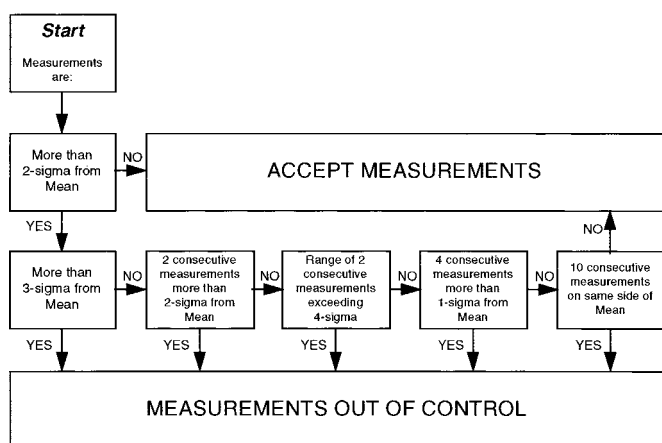


FIG. 2 Westgard Rules

8.4.3 *Plotting*—As data is obtained for a verifier, show a record of standardized readings with calculations of average and range or standard deviation. Follow the form shown in Fig. 1. Include date and time as well as notations on what corrective action was taken or what extraordinary conditions prevailed at specified times.

8.4.3.1 Join successive data points by straight lines. Normal, proper control will appear with points randomly scattering above and below central lines with no points exceeding limits.

8.5 Corrective Action:

8.5.1 Use the Westgard Rules Flowchart⁵ (see Fig. 2) to determine when measurements for a given channel are out of control and require standardization.

NOTE 3—No action is required if measurements are within “2-sigma” of the CL line.

8.5.2 Options before undertaking a standardization:

8.5.2.1 Check for proper gap between sample and electrode, cleanliness of excitation area, argon pressure and flow correctness, argon leaks, and that the spectrometer is correctly profiled and repeat the verification.

8.5.2.2 Even if the profile did not require correction, reanalyze the verifier and average readings with the earlier test.

Multiply the overall average by 1.4 and plot this as a data point. Standardize only if the new data point still plots beyond the UCL or LCL line.

8.5.3 Make half standardization, if possible, when four out of five successive data points fall more than “1-sigma” from the CL line.

NOTE 4—Half corrections are discussed in Practice E305. This refinement is practical only for relatively stable analytical systems.

8.5.4 *Overall Observations*—For a normal distribution approximately two thirds of the X values should appear in the middle third of the plotting area between the upper and lower control limits.

8.5.4.1 If many more than one third of the points on the precision chart are above the middle third of the plotting area, there likely will be a similar disproportion in analysis and this indicates a problem in the development or detection of a signal. The cause of the malfunction should be investigated.

8.5.4.2 If precision remains normal, but the analysis shows less than two thirds of its points in the middle of the plotting area, this may be an indication that a spectrometer or excitation source has become less stable or that control has been lost in the preparation of a specimen.

8.5.4.3 When analysis shows more than two thirds of its points within the middle third of the plotting area and the precision chart shows either this or its points crowded toward the lower limit (which is usually zero), an investigation should be made to determine what improved the analysis with the intention of redefining what should be controlled. If the latter improvement can be maintained, the estimate of precision should be redefined and the limits recalculated. See Section 9.

8.6 *Advantage of Having Multi-Point References*—If a situation develops in which a verifier no longer has most of its readings in the central portion of a control chart and nothing seems to be wrong with the instrument, it is likely that there has been a change in the chemistry of at least one of the reference materials. The problem may not be with the verifier since a particular standardant might be warping the standardization. This could be particularly true with two-point standardization. Armed with expected readings for all the standardants and verifiers, the multi-point standardization of 6.1.2.1 can be done, off line, independently of the operating program. Correct all readings with Eq 3 and note the differences between corrected readings and expected readings. An abnormally large

⁵ Harmonized Guidelines for Internal Quality Control in Analytical Chemistry Laboratories, ISO/REMCO N271, Revision, November 1994.

difference would indicate a change in chemistry that might be addressed by reassigning the expected reading of the aberrant material.

8.6.1 If multi-point standardization is being done routinely, it would be advisable to keep a record of all corrected readings. These could be inspected periodically to detect if a reference material is changing.

8.7 *Optional Control*—Intermediate limit lines may be shown at 0.7 (or $1/\sqrt{2}$) of the distance from the central line to the “3-sigma” limits. They represent the limits that would apply if the replication of measurements was doubled. This is close to the “2-sigma” limit often shown on control charts. The “2-sigma” lines would be at 0.67 ($2/3$) of the distance from the central line. If the average of two successive verifier checks falls beyond one of these intermediate limits, standardize unless there is an assignable cause for the divergence.

9. Determination of Standard Deviation

9.1 All of the formulae for calculating central lines and control lines, as well as for confidence intervals, require an estimate of the standard deviation of a measurement.

9.1.1 *Standard Deviations for Control Charts*—In general, the standard deviation, s_o , needed for control charts should be the standard deviation that could be expected for a set of values that is typical for the multiplets in a single standardization. No standardization is perfect. Each time it is run it can be expected that a verifier would truly read somewhat higher or lower than expected. Even small drifts can occur at different times of running a verifier. Looking at the total number of corrected readings that a verifier shows over a period of time would tend to give an inflated estimate of standard deviation. Pooling standard deviations of multiplets observed at any one time (see Practice E876) gives the ideal s_o for use in the various equations for determining control lines. That is true for plotting range or standard deviation plots. It is also true if standardization is done by a multi-point standardization in which the verifier showed only its own deviations.

9.1.1.1 A problem occurs when a unit is under two-point standardization control. By its nature, two-point standardization makes the high and low standardants read exactly what they are expected to read. Actual deviations in these standardant readings, therefore, are added to the deviations incurred by the verifier. A study of this has demonstrated that a plotting of verifier readings shows poor control chart plotting if the ideal s_o of 9.1.1 is used. In cases in which two-point standardization is used, wider settings of limits are needed. The larger s values obtained in a large sampling of individual verifier readings generated by different standardizations provides realistic control chart plotting for verifiers. See Appendix X1.

9.1.1.2 If a multi-point standardization only has a high standardant, a low standardant, and a verifier, the regression favors a closer fit to the high standardant. This regression can be modified by weighting measurements by the reciprocal of the reading. In this case, the equation for the slope becomes:

$$m = \frac{\sum(1/x)\sum y - n\sum(y/x)}{\sum(1/x)\sum x - n^2} \quad (14)$$

The equation for determining the constant remains as Eq 2.

9.2 *Standard Deviation of Reading (s_R)*—As mentioned in 6.3, a usable estimate of the standard deviation of a reading (or of intensity ratio), s_R , may be made from data collected in a calibration, particularly if some pooling can be done with individual estimates of standard deviation or from being able to establish an overall pattern of how standard deviation varies with the level of reading. See Note 5. When a confidence interval or a control chart is stated in terms of s_R , the precision determined during calibration can be used directly to determine limits, if the degree of freedom in calculating s_R is at least 16. Additional measurements of a verifier may be needed to define the s_R that can be used.

NOTE 5—The materials used for calibrants, standardants, or verifiers may not all be consistent in precision measurements, particularly if some have inhomogeneities. Any materials that consistently show greater deviations should not be included in a pooling of standard deviations or relative standard deviations. Materials that show poorer precision generally should not be used as verifiers or standardants.

9.3 *Standard Deviation of Concentration (s_C)*—If a confidence interval or a control chart is stated in terms of concentration, the s_R of a verifier may be converted into the equivalent standard deviation in terms of concentration, s_C . Alternatively, normalized readings obtained during calibration may be applied individually to calibration equations to observe deviations in calculated concentration. A verifier may also be burned repeatedly as an unknown sample after a calibration has been established to determine s_C . To do so, enough significant digits must appear in the concentration calculations to show statistical variation. Generally, the number of decimal points displayed in final concentrations from computer software is insufficient to obtain valid estimates of standard deviation. It may be possible, however, to modify the computer software setting to show a valid standard deviation based on the many decimal points it carries in concentration calculations.

9.3.1 The conversion factor for converting s_R to s_C is the slope of the calibration curve at the point of the reading. The slope is the first deviation of the calibration equation. Details on these conversions appear in the annex.

10. Keywords

10.1 confidence interval; control charts; normalization; standardization; verification

(Mandatory Information)
A1. CONVERSION OF INTENSITY / INTENSITY RATIO READING STANDARD DEVIATION TO CONCENTRATION STANDARD DEVIATION

A1.1 As stated in 9.3.1, the conversion factor for converting s_R to s_C depends upon the slope of the calibration curve and can be calculated from the first derivative of the calibration equation.

A1.1.1 The simplest conversion is with a linear relationship with no interelement corrections. In this, concentration, C , is:

$$C = a_0 + a_1 x \quad (\text{A1.1})$$

where x is the reading.

The slope or the first derivative of Eq A1.1 is:

$$dC/dx = a_1 \quad (\text{A1.2})$$

Then:

$$s_C = a_1 s_R \quad (\text{A1.3})$$

A1.1.2 For a high-order polynomial with no matrix correction, the slope is dependent upon the reading. From:

$$C = a_0 + a_1 x + a_2 x^2 + a_3 x^3, \quad (\text{A1.4})$$

$$dC/dx = a_1 + 2a_2 x + 3a_3 x^2 \quad (\text{A1.5})$$

Then:

$$s_C = (a_1 + 2a_2 x + 3a_3 x^2) s_R \quad (\text{A1.6})$$

A1.2 When a calibration involves an interelement correction, the primary effect from the curve slope and the secondary effect from an interelement correction can be determined separately by using partial derivatives. An overall effect may then be determined by finding the root mean square of the individual effects.

A1.2.1 For an additive correction such as

$$C = a_0 + a_1(x + kZ) + a_2(x + kZ)^2 + a_3(x + kZ)^3 \quad (\text{A1.7})$$

where:

k = reading correction factor of an interfering element,
and

Z = concentration of the interfering element,

the main calibration slope is:

$$\partial C/\partial x = a_1 + 2a_2(x + kZ) + 3a_3(x + kZ)^2. \quad (\text{A1.8})$$

The contribution to deviation from the imprecision of the interfering element is:

$$\partial C/\partial Z = k[a_1 + 2a_2(x + kZ) + 3a_3(x + kZ)^2] \quad (\text{A1.9})$$

In terms of effects on concentration, these translate to:

$$s_{C1} = [a_1 + 2a_2(x + kZ) + 3a_3(x + kZ)^2] s_R \quad (\text{A1.10})$$

and

$$s_{C2} = k[a_1 + 2a_2(x + kZ) + 3a_3(x + kZ)^2] s_Z \quad (\text{A1.11})$$

where s_Z is the standard deviation of the interfering element in terms of concentration. (If the method of internal standard

dilution is used, “concentration” will actually be relative concentration. See A1.4.)

The overall effect on s_C then becomes:

$$s_C = \sqrt{s_{C1}^2 + s_{C2}^2} \quad (\text{A1.12})$$

A1.2.2 For a multiplicative effect expressed as

$$C = (a_0 + a_1 x)/(1 + kZ), \quad (\text{A1.13})$$

$$\partial C/\partial x = a_1/(1 + kZ) \quad (\text{A1.14})$$

and

$$\partial C/\partial Z = -k(a_0 + a_1 x)/(1 + kZ)^2 = -kC/(1 + kZ) \quad (\text{A1.15})$$

Then, as was done for Eq A1.10 and Eq A1.11:

$$s_{C1} = [a_1/(1 + kZ)] s_R \quad (\text{A1.16})$$

and

$$s_{C2} = [-kC/(1 + kZ)] s_Z \quad (\text{A1.17})$$

The overall effect is calculated using Eq A1.12.

A1.3 Corrections can take other mathematical forms. They may be treated similarly by using partial derivatives. If more than one interelement correction is needed, each has its own effect that can be handled with an additional partial derivative. The number of squared items appearing under the square root sign in a final equation, such as Eq A1.12, will then be more than two.

A1.4 *Internal Standard Dilution*—Practice E158 explains how to use concentration ratio plots to extend analyses to systems where the concentration of the internal standard varies. This permits calculating the concentration of the matrix element in a way that is more precise than simply getting that concentration by difference. After determining standard deviations in terms of relative concentrations for all elements being measured, a two-fold accounting of deviations is needed to determine standard deviation in terms of actual concentrations. Letting c represent final percent concentrations:

$$c = 100C/(1 + S) \quad (\text{A1.18})$$

where:

C = relative concentration for some element, and

S = sum of all relative concentrations except the matrix element.

Eq A1.18 can be restated as:

$$c = 100C/(1 + D + C) \quad (\text{A1.19})$$

where $D = S - C$.

Now:

$$\begin{aligned} \partial c/\partial C &= [100/(1 + D + C) - 100C]/(1 + D + C)^2 \quad (\text{A1.20}) \\ &= 100(1 + D)/(1 + D + C)^2 \\ &= 100(1 + S - C)/(1 + S)^2 \end{aligned}$$

Letting dev_C represent the deviation contributed by s_C , the deviation in the relative concentration becomes:

$$\text{dev}_C = [100(1 + S - C)/(1 + S)^2]s_C \quad (\text{A1.21})$$

But there is also a contribution to imprecision from the deviation in the D term:

$$\partial c/\partial D = -100C/(1 + D + C)^2 = -100C/(1 + S)^2 \quad (\text{A1.22})$$

Letting dev_D represent the deviation contributed by D :

$$\text{dev}_D = [-100C/(1 + S)^2](s_D) \quad (\text{A1.23})$$

where:

$$s_D = \sqrt{s_S^2 - s_C^2}, \text{ and}$$

s_S^2 = total variance of all relative concentrations except the matrix element.

The standard deviation of an element in terms of final concentration is the root mean square of dev_C and dev_D :

$$s_C = \sqrt{\text{dev}_C^2 + \text{dev}_D^2} \quad (\text{A1.24})$$

A1.4.1 The standard deviation of the matrix element is determined from the root mean square of all the component elements measured. In a practical system, in which only one other element is high in concentration, the standard deviation of the matrix element will be very close to the standard deviation of that other high concentration element. Letting s_m represent the standard deviation of the matrix element:

$$s_m = \sqrt{s_1^2 + s_2^2 + \dots + s_n^2} \quad (\text{A1.25})$$

where the subscripts refer to the individual elements, totaling n in number.

APPENDIX

(Nonmandatory Information)

X1. EFFECT OF STANDARDIZATION

X1.1 Random numbers were compiled to represent the standardants and verifier used in a spectrometric determination of carbon in steel. Two hundred seventy random numbers were generated to represent three sets that would permit making thirty determinations of triplicates for each set. Specifically, the high set was devised to approach an average reading of 1.91642 and a σ of 0.016; the low set, 0.1859 with a σ of 0.002; and for the verifier, 0.5923 with a σ of 0.0037 (Readings were assumed to be equal to concentration).

X1.1.1 Trials were made to see how the commonly accepted two-point standardization (see 6.1.3.1) would affect the control chart plotting of a verifier if the “ideal” s_o of 9.1.1 was used to establish chart limits. Results are shown in Table X1.1, which shows the observed reading of triplicates and their averages, the slope, and constant corrections evolved from two-point standardization, and the resulting standardization of these readings and their averages. Also shown are the standard deviations of the triplicates, which were pooled to calculate the ideal s_o of 0.00392. The “error” column shows the deviation of the average standardized reading from the expected 0.5923. These were divided by one-third of the total spread from the CL_x to the UCL_x , the latter determined in Eq 6, to designate when an error exceeded a ± 1 sigma, a ± 2 sigma, or the ± 3 sigma, the upper or lower control chart limit. Similarly, the “range” column showed the observed range between the triplicate standardized readings and a similar assessment how

they would plot in a control chart. The “ $>1s$ ” columns were summed to show the balance between higher positive and negative deviations and counted to determine how many deviations exceeded $\pm 1s$. The verifier checked well on its precision of measurement with more than two-thirds of the range deviations falling within $\pm 1s$. The errors of the standardized $\bar{X}$ values showed only half falling within $\pm 1s$ and with two points falling outside the control chart limits.

X1.1.2 The same data was treated to a three-point standardization (see 6.1.2.1). Results appear in Table X1.2. In this case the verifier charted very well with more than two-thirds of the errors falling within $\pm 1s$ and with only one point exceeding $2s$. The range pattern was equally as good.

X1.1.3 A similar assessment can be made by observing Fig. X1.1, which graphically shows the comparisons. In both cases, there is no change in the chart limits. Only one plot is shown for range since these were basically the same for either standardization.

X1.2 Table X1.1 shows additional information. A second determination of the UCL_x and LCL_x limits were made using the higher standard deviation of 0.00468 calculated from all ninety of the standardized readings. When viewed under these limits the verifier looked acceptable even though one point, run 12, exceeded the upper limit, but barely, with an average of 0.6005 for a limit of 0.6004.

TABLE X1.1 Charting from Two-Point Standardization

Run	Observed Readings					Verifier for Carbon, Run in Triplicate					Standard Deviation	Error		Range	
	A	B	C	Average	Slope	Constant	A	B	C	Average		Observed	> 1s	Observed	> 1s
1	0.5837	0.5908	0.5885	0.5877	0.99827	0.0007	0.5834	0.5905	0.5883	0.5874	0.0036	-0.0049	-2	0.0071	
2	0.5945	0.5849	0.5950	0.5915	0.99593	0.0002	0.5923	0.5828	0.5928	0.5893	0.0056	-0.0030	-1	0.0100	
3	0.5998	0.5923	0.5952	0.5958	0.99126	0.0033	0.5979	0.5904	0.5933	0.5939	0.0037	0.0016		0.0074	
4	0.5949	0.5989	0.5910	0.5949	0.99782	-0.0008	0.5928	0.5968	0.5889	0.5928	0.0039	0.0005		0.0079	
5	0.5898	0.5972	0.5867	0.5912	0.99899	0.0002	0.5894	0.5968	0.5863	0.5908	0.0054	-0.0015		0.0105	1
6	0.5917	0.5938	0.5913	0.5923	0.99639	0.0001	0.5897	0.5917	0.5893	0.5902	0.0013	-0.0021		0.0024	-1
7	0.5860	0.5897	0.5931	0.5896	0.99468	-0.0004	0.5825	0.5862	0.5896	0.5861	0.0036	-0.0062	-2	0.0071	
8	0.5932	0.5891	0.5963	0.5929	1.01083	-0.0022	0.5975	0.5933	0.6006	0.5971	0.0037	0.0048	2	0.0073	
9	0.5888	0.5886	0.5919	0.5898	0.99247	-0.0002	0.5842	0.5840	0.5873	0.5852	0.0018	-0.0071	-3	0.0033	
10	0.5925	0.5914	0.5904	0.5915	1.01484	-0.0033	0.5980	0.5969	0.5959	0.5969	0.0010	0.0046	2	0.0021	-1
11	0.5951	0.5860	0.5858	0.5890	0.99614	0.0012	0.5940	0.5850	0.5847	0.5879	0.0053	-0.0044	-1	0.0093	
12	0.5965	0.5915	0.5976	0.5952	1.01048	-0.0009	0.6018	0.5968	0.6029	0.6005	0.0032	0.0082	3	0.0061	
13	0.5928	0.5903	0.5895	0.5909	0.99691	0.0003	0.5913	0.5888	0.5880	0.5894	0.0017	-0.0029	-1	0.0032	
14	0.5951	0.5964	0.5893	0.5936	1.00361	0.0002	0.5975	0.5988	0.5917	0.5960	0.0038	0.0037	1	0.0071	
15	0.5912	0.5948	0.5910	0.5923	1.00323	-0.0025	0.5907	0.5942	0.5904	0.5918	0.0021	-0.0005		0.0038	
16	0.5938	0.5923	0.5873	0.5911	0.99908	0.0005	0.5938	0.5922	0.5872	0.5911	0.0034	-0.0012		0.0066	
17	0.5879	0.5928	0.5985	0.5931	0.99725	-0.0002	0.5862	0.5910	0.5967	0.5913	0.0053	-0.0010		0.0105	1
18	0.5867	0.5937	0.5947	0.5917	0.99723	0.0031	0.5883	0.5952	0.5962	0.5932	0.0043	0.0009		0.0079	
19	0.5919	0.5939	0.5946	0.5935	0.99279	0.0011	0.5888	0.5908	0.5914	0.5903	0.0014	-0.0020		0.0026	-1
20	0.5941	0.5822	0.5962	0.5908	1.00669	-0.0001	0.5979	0.5860	0.6001	0.5947	0.0076	0.0024	1	0.0141	2
21	0.5935	0.5974	0.5883	0.5930	0.99552	0.0005	0.5913	0.5952	0.5862	0.5909	0.0045	-0.0014		0.0090	
22	0.5928	0.5922	0.5871	0.5907	1.00458	0.0013	0.5968	0.5962	0.5911	0.5947	0.0031	0.0024	1	0.0057	
23	0.5942	0.5895	0.5916	0.5918	1.00622	-0.0007	0.5972	0.5925	0.5946	0.5948	0.0024	0.0025	1	0.0047	
24	0.5925	0.5958	0.5948	0.5944	1.00763	-0.0039	0.5931	0.5964	0.5954	0.5950	0.0017	0.0027	1	0.0033	
25	0.5904	0.5888	0.5942	0.5911	1.00724	-0.0030	0.5917	0.5900	0.5956	0.5924	0.0028	0.0001		0.0055	
26	0.5932	0.5970	0.5899	0.5934	1.00468	-0.0020	0.5939	0.5978	0.5906	0.5941	0.0036	0.0018		0.0072	
27	0.5985	0.5949	0.5899	0.5944	1.00338	-0.0017	0.5988	0.5952	0.5903	0.5948	0.0043	0.0025	1	0.0086	
28	0.5938	0.5919	0.5918	0.5925	0.99813	0.0004	0.5931	0.5911	0.5911	0.5918	0.0011	-0.0005		0.0020	-1
29	0.5945	0.5874	0.5988	0.5936	0.98991	0.0041	0.5925	0.5856	0.5968	0.5916	0.0057	-0.0007		0.0113	1
30	0.5864	0.5973	0.5876	0.5904	0.99647	0.0004	0.5847	0.5956	0.5860	0.5888	0.0059	-0.0035	-1	0.0108	1
Using pooled std dev of triplicates:												sum	2	0.00747	2
												count	16	0.00682	9
CL for $X = 0.5923$												Pooled std dev from triplicates: 0.00392			
UCL for $X = 0.5923 + 1.732(0.00392) = 0.5991$												Std dev from all standardized readings: 0.00468			
LCL for $X = 0.5923 - 1.732(0.00392) = 0.5855$												Using std dev from all standardized readings:			
CL for $R = 1.693(0.00392) = 0.0066$												UCL for $X = 0.5923 + 1.732(0.00468) = 0.6004$			
UCL for $R = 4.358(0.00392) = 0.0171$												LCL for $X = 0.5923 - 1.732(0.00468) = 0.5842$			
LCL for $R = 0.0$															

TABLE X1.2 Charting from Three-Point Standardization

Run	Observed Readings					Verifier for Carbon, Run in Triplicate					Standard Deviation	Error		Range	
	A	B	C	Average	Slope	Constant	A	B	C	Average		Observed	> 1s	Observed	> 1s
1	0.5837	0.5908	0.5885	0.5877	0.99735	0.0032	0.5853	0.5924	0.5902	0.5893	0.0036	-0.0030	-1	0.0070	
2	0.5945	0.5849	0.5950	0.5915	0.99536	0.0017	0.5934	0.5840	0.5939	0.5904	0.0056	-0.0019		0.0100	
3	0.5998	0.5923	0.5952	0.5958	0.99155	0.0025	0.5972	0.5898	0.5927	0.5932	0.0037	0.0009		0.0074	
4	0.5949	0.5989	0.5910	0.5949	0.99792	-0.0011	0.5926	0.5965	0.5887	0.5926	0.0039	0.0003		0.0079	
5	0.5898	0.5972	0.5867	0.5912	0.99872	0.0009	0.5900	0.5973	0.5868	0.5914	0.0054	-0.0009		0.0105	1
6	0.5917	0.5938	0.5913	0.5923	0.99601	0.0011	0.5905	0.5925	0.5901	0.5910	0.0013	-0.0013		0.0024	-1
7	0.5860	0.5897	0.5931	0.5896	0.99352	0.0027	0.5849	0.5886	0.5920	0.5885	0.0036	-0.0038	-1	0.0071	
8	0.5932	0.5891	0.5963	0.5929	1.01174	-0.0046	0.5956	0.5914	0.5987	0.5952	0.0037	0.0029	1	0.0074	
9	0.5888	0.5886	0.5919	0.5898	0.99114	0.0034	0.5870	0.5868	0.5901	0.5879	0.0018	-0.0044	-1	0.0033	
10	0.5925	0.5914	0.5904	0.5915	1.01571	-0.0056	0.5962	0.5951	0.5941	0.5951	0.0010	0.0028	1	0.0021	-1
11	0.5951	0.5860	0.5858	0.5890	0.99532	0.0034	0.5957	0.5867	0.5864	0.5896	0.0053	-0.0027	-1	0.0093	
12	0.5965	0.5915	0.5976	0.5952	1.01201	-0.0050	0.5986	0.5936	0.5997	0.5973	0.0032	0.0050	2	0.0061	
13	0.5928	0.5903	0.5895	0.5909	0.99637	0.0018	0.5924	0.5899	0.5892	0.5905	0.0017	-0.0018		0.0032	
14	0.5951	0.5964	0.5893	0.5936	1.00430	-0.0016	0.5960	0.5974	0.5902	0.5945	0.0038	0.0022		0.0072	
15	0.5912	0.5948	0.5910	0.5923	1.00314	-0.0022	0.5909	0.5944	0.5906	0.5920	0.0021	-0.0003		0.0038	
16	0.5938	0.5923	0.5873	0.5911	0.99886	0.0011	0.5943	0.5927	0.5877	0.5915	0.0034	-0.0008		0.0066	
17	0.5879	0.5928	0.5985	0.5931	0.99707	0.0003	0.5865	0.5914	0.5971	0.5917	0.0053	-0.0006		0.0105	1
18	0.5867	0.5937	0.5947	0.5917	0.99741	0.0027	0.5879	0.5949	0.5958	0.5928	0.0043	0.0005		0.0079	
19	0.5919	0.5939	0.5946	0.5935	0.99243	0.0021	0.5895	0.5915	0.5921	0.5911	0.0014	-0.0012		0.0026	-1
20	0.5941	0.5822	0.5962	0.5908	1.00714	-0.0013	0.5970	0.5850	0.5991	0.5937	0.0076	0.0014		0.0141	2
21	0.5935	0.5974	0.5883	0.5930	0.99526	0.0012	0.5918	0.5957	0.5867	0.5914	0.0045	-0.0009		0.0090	
22	0.5928	0.5922	0.5871	0.5907	1.00502	0.0001	0.5958	0.5952	0.5901	0.5937	0.0031	0.0014		0.0057	
23	0.5942	0.5895	0.5916	0.5918	1.00668	-0.0019	0.5963	0.5915	0.5936	0.5938	0.0024	0.0015		0.0047	
24	0.5925	0.5958	0.5948	0.5944	1.00814	-0.0053	0.5921	0.5954	0.5944	0.5939	0.0017	0.0016		0.0033	
25	0.5904	0.5888	0.5942	0.5911	1.00727	-0.0031	0.5916	0.5900	0.5955	0.5924	0.0028	0.0001		0.0055	
26	0.5932	0.5970	0.5899	0.5934	1.00503	-0.0030	0.5932	0.5971	0.5899	0.5934	0.0036	0.0011		0.0072	
27	0.5985	0.5949	0.5899	0.5944	1.00385	-0.0029	0.5979	0.5942	0.5893	0.5938	0.0043	0.0015		0.0086	
28	0.5938	0.5919	0.5918	0.5925	0.99803	0.0006	0.5933	0.5913	0.5913	0.5920	0.0011	-0.0003		0.0020	-1
29	0.5945	0.5874	0.5988	0.5936	0.98979	0.0044	0.5928	0.5858	0.5971	0.5919	0.0057	-0.0004		0.0113	1
30	0.5864	0.5973	0.5876	0.5904	0.99581	0.0022	0.5861	0.5969	0.5873	0.5901	0.0059	-0.0022		0.0108	1
Using pooled std dev of triplicates:												sum	0	0.00747	2
Std dev from all standardized readings: 0.00392												count	7	0.00682	9
CL for $X = 0.5923$															
UCL for $X = 0.5923 + 1.732(0.00392) = 0.5991$															
LCL for $X = 0.5923 - 1.732(0.00392) = 0.5855$															
CL for $R = 1.693(0.00392) = 0.0066$															
UCL for $R = 4.358(0.00392) = 0.0171$															
LCL for $R = 0.0$															

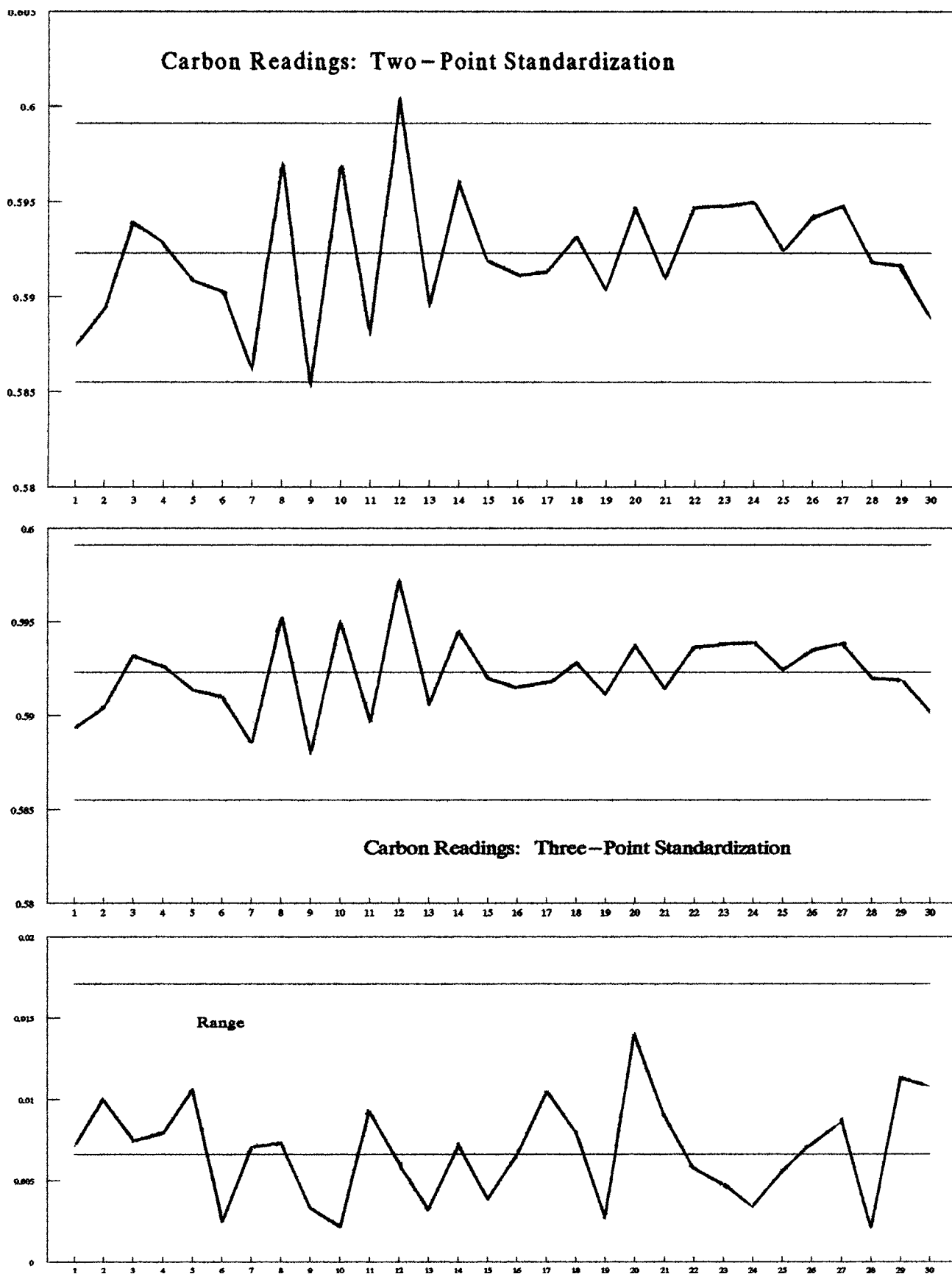


FIG. X1.1 Comparison of Two-Point and Three-Point Standardization

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