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Standard Guide for Determination of Various Elements by Direct Current Plasma Atomic Emission Spectrometry[1]

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1. Scope

1.1 This guide covers procedures for using a Direct Current Plasma atomic emission spectrometer (DCP-AES) to determine the concentration of elements in solution. Recommendations are provided for preparing and calibrating the instrument, assessing instrument performance, diagnosing and correcting for interferences, measuring test solutions, and calculating results. A method to correct for instrument drift is included.

1.2 This guide does not specify all the operating conditions for a DCP-AES because of the differences between models of these instruments. Analysts should follow instructions provided by the manufacturer of the particular instrument.

1.3 This guide does not attempt to specify in detail all of the hardware components and computer software of the instrument. It is assumed that the instrument, whether commercially available, modified, or custom built, will be capable of performing the analyses for which it is intended, and that the analyst has verified this before performing the analysis.

1.4 *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.* Specific precautionary statements are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

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

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. Terminology

3.1 *Definitions:* For definitions of terms used in this guide, refer to Terminology E135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *background equivalent concentration (BEC), n—in DCP-AES*, the analyte concentration whose signal is equivalent to the signal generated by the plasma and matrix at the analyte line when the actual analyte concentration is zero.

3.2.2 *detection limit (DL), n*—in addition to the DL defined in Terminology E135, the following detection limits are described and used in this guide:

3.2.2.1 *instrumental detection limit (IDL), n—in DCP-AES*, the analyte concentration corresponding to three times the standard deviation of the background noise beneath the analyte line on a set of nine consecutive 10-s measurements of the background intensity of the blank.

3.2.2.2 *method detection limit (MDL), n— in DCP-AES*, the detection limit measured on the matrix blank.

3.2.3 *equivalent analyte concentration, n*—the apparent concentration of an interfering element on an anlalyte.

3.2.4 *linear dynamic range, n*—the concentration range from the limit of quantification to the highest concentration that remains within ±10 % of linearity based on lower concentrations.

3.2.5 *limit of quantification (LOQ), n*—the lowest concentration at which the instrument can measure reliably with a defined error and confidence level.

3.2.6 *sensitivity, n*—the slope of the analytical curve, which is the ratio of the change in emission intensity to the change in concentration.

4. Summary of Guide

4.1 Direct Current Plasma atomic emission spectrometers, either simultaneous or sequential, measure the concentration of

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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.

elements in solution. Samples, calibration and other solutions are nebulized and the aerosol is transported to the direct current plasma jet where excitation occurs and characteristic emission spectra are produced. The spectra are dispersed by an echelle grating and cross-dispersed by a prism or grating. The spectra then impinge on photomultiplier tubes, whose outputs are interpreted by a microprocessor/PC as emission intensities. Background correction can be used to compensate for some interferences. The microprocessor/PC generates calibration curves and calculates analyte concentration.

5. Significance and Use

5.1 Analyses using DCP-AES require proper preparation of test solutions, accurate calibration, and control of analytical procedures. ASTM test methods that refer to this guide shall provide specifics on test solutions, calibration, and procedures.

5.2 DCP-AES analysis is primarily concerned with testing materials for compliance with specifications, but may range from qualitative estimations to umpire analysis. These may involve measuring major and minor constituents or trace impurities, or both. This guide suggests some approaches to these different analytical needs.

5.3 This guide assists analysts in developing new methods.

5.4 It is assumed that the users of this guide will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that the work will be performed in a properly equipped laboratory.

5.5 This guide does not purport to define all of the quality assurance parameters necessary for DCP-AES analysis. Analysts should ensure that proper quality assurance procedures are followed, especially those defined by the test method. Refer to Guide E882.

6. Preparation of Solutions

6.1 Solutions are prepared for different purposes. Not all may be necessary for every test. Prepare only those directed by the method or required to meet specific experimental objectives.

6.2 *Rinse Solution*—Prepare a rinse solution to contain the acids or bases present in the test solution at the same concentration. Prepare a quantity sufficient to clean the end of the sample uptake tubing and to flush the sample introduction system between each determination of calibration solutions and test solutions. Occasionally, an analyte requires a conditioning time in the aspiration/nebulization system of the instrument. In this case, use the test solution as a rinse and allow a sufficient residence time before taking a reading.

6.3 *Reagent Blank Solution*—This solution consists of all reagents and other additions at the same concentration used in preparing the test solution. Carry this solution through the entire sample preparation procedure.

6.4 *Matrix Blank Solution*—Prepare this solution to be as close in composition to the test solution as possible (including dissolution reagents and matrix elements), but omitting the elements to be determined. The matrix elements should be of high purity.

6.5 *Control*—Select a reference material or other material of known composition and prepare it as directed in the test method. Analyze the control regularly as a blind sample and use the results for quality control as directed in Guide E882.

6.6 *Calibration Solutions*—The number and type of these solutions will depend on the method, and on the type of DCP-AES instrument and its microprocessor/PC. Generally, prepare two instrument calibration solutions, one high concentration, and one low concentration or a blank, that bracket the expected concentration range of the sample test solutions. More may be prepared if the microprocessor/PC can utilize them, especially if the analyte composition of the test solutions is expected to cover a wide range or if the calibration curve is non-linear. Prepare the calibration solutions by adding aliquots from stock solutions to solutions that are similar to the matrix of the test sample.

6.6.1 Match the matrix of the calibration solutions as closely as possible to that of the test solution in acidity, total solids, reagents, and matrix elements, especially if easily ionized elements (EIE) are present. Some matrix elements may be eliminated if it can be shown by spike addition or standard additions that the effect on the test solution analytes is insignificant. Use stock solutions or pure elements prepared by a method similar to that used to prepare the test solutions. If the composition of the test solution is unknown to the extent that matrix-matched solutions cannot be prepared, or if a sufficiently pure matrix material is not available, refer to the method of standard additions described in 6.7 and 10.6.

NOTE 1—If the instrument is designed to use a blank as the low concentration calibration solution, prepare it the same way as the high concentration calibration solution is prepared, omitting the elements to be determined. Where matrix-matched calibration solutions are employed, this will be the matrix blank solution.

6.6.2 *Optimum Calibration Solution Concentration Range*—For calibration in the linear range, the highest concentration should be no more than 85 % of the upper limit of the calibration curve linearity. For an instrument that accepts a low concentration calibration solution, its concentration should be at least four times the method detection limit and above the limit of quantification (LOQ).

6.7 *Standard Additions Solutions*—Prepare as directed in either 6.7.1 or 6.7.2 as follows:

6.7.1 Prepare four separate test solutions of the sample. To all but one, add known amounts of the analyte equal to (0.5, 1.0, and 1.5) times or (1.0, 2.0, and 3.0) times the expected concentration of the analyte(s) in the test solution. The original analyte concentration must be at or above it's LOQ. The final analyte concentration in the highest spike must not be greater than the linear range of the emission line used. Dilute all solutions to the mark and mix. Prepare an equal volume of the reagent blank solution when using 10.6.2.

6.7.2 Transfer four equal volumes of a test solution to four volumetric flasks of the same size. To all but one, add known amounts of the analyte equal to 0.5, 1.0, and 1.5, or 1.0, 2.0, and 3.0 times the expected concentration of the analyte(s) in the test solution. The final analyte concentration in the test solution should be at or above the LOQ. The final analyte concentration in the highest spike should not exceed the linear

dynamic range of the emission line used. Dilute all solutions to the mark and mix. Prepare an equal volume of the reagent blank solution if using 10.6.2. Multiply the final value by a factor to compensate for dilution.

6.8 *Calibration Verification Solution*—To verify the calibration, prepare one or more solutions whose concentrations are between the highest concentration calibration solution and the LOQ.

6.9 *Spike Recovery Sample*—Prepare a test solution as directed in the method. Add a spike of the analyte(s) equal to at least 5 times each analyte's LOQ.

6.10 *Limit of Quantification (LOQ) Solution*—Prepare a solution containing amounts of analyte three to six times the method detection limit or 10 % to 20 % of the BEC and matched as closely to the matrix as possible.

7. Hazards

7.1 Protect eyes from the intense ultraviolet (UV) radiation of the plasma.

7.2 Follow the manufacturer's recommended operating practices for initiating the plasma and operating the instrument.

7.3 Ensure that HF-resistant materials are used when analyzing solutions containing hydrofluoric acid. Avoid strongly caustic solutions that may cause the ceramic sleeves of the electrodes to fuse.

7.4 For other safety precautions, refer to Practice E50.

8. Characterization of Analytical Lines

8.1 *Overview:*

8.1.1 When researching a new method, use the recommendations in this section to select a wavelength and evaluate the possible interferences. Measure the approximate linear range, background equivalent concentration, sensitivity, LOQ detection limit experimentally, and ascertain that they are adequate for the analysis. Once these have been established for a specific instrument, periodic confirmation is recommended and especially whenever a change is made in the hardware (for example, transport or detection devices) or optics. Confirm by analysis of controls, including limit of quantification measurements when required, that the daily performance of the instrument meets the criteria of the method.

8.1.2 When adapting a documented test method for the first time, confirm that freedom from interferences, linearity, detection limit, LOQ and sensitivity meet the criteria of the method.

8.1.3 For lists of wavelengths and information on their characteristics, refer to Harrison,[3] Meggers,[4] Phelps,[5] Reader,[6] or Winge.[7]

8.1.3.1 In the laddered array of spectra from the DCP's echelle grating, some wavelengths appear in two adjacent orders. These wavelengths usually have similar intensities. Occasionally, one may prove more useful for a specific application.

8.2 *Interferences*—Several types of interferences may affect measurements. This is especially true for test solutions containing high concentrations of solids or acids or containing elements having intense emission, a large number of atomic emission lines, or high concentrations of easily ionized elements (EIEs). The presence of interferences should be considered when selecting calibration solutions and the method of analysis. See 8.2.3 for suggestions on how to compensate for interferences.

8.2.1 *Types of Interference:*

8.2.1.1 *Chemical Interferences*—Effects from excitation, molecular compound formation, and solvent vaporization.

8.2.1.2 *Physical Interferences*—Factors that change the rate of sample delivery such as viscosity, surface tension, and reaction with parts of the sample delivery system.

8.2.1.3 *Spectral Interferences*—Spectral line or molecular band overlap from the matrix or solvents, background resulting from continuum radiation, or stray light.

8.2.2 *Diagnosis of Interferences*—Use the following procedures for each new sample matrix:

8.2.2.1 *Comparison with Alternative Method(s) of Analysis*—Use established methods to compare analytical results where possible.

8.2.2.2 *Wavelength Scanning*—If possible, scan the wavelength region near the analyte emission to detect spectral interferences and high background in calibration solutions, test solutions, and solutions containing suspected interfering elements.

8.2.2.3 *Spike Recovery*—Add a known quantity or spike of the analyte equal to at least five times the LOQ. It should be recovered to within $\pm$ 2 σ of 100 %, where σ is the standard deviation of at least three replicate measurements. If not, a matrix effect or other interference may be present.

8.2.2.4 *Serial Dilution*—If the analyte concentration is sufficiently high, analysis of a ten-fold dilution should agree with the expected concentration to within 5 %. If not, a chemical or physical interference may be present.

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[3] Harrison, G. R., *MIT Wavelength Tables Vol. 1, 2nd Edition*, MIT Press, August 1969.

[4] Meggars, W. F., Corliss, C. H., and Scribner, B. F., *Table of Spectral Intensities: Part I—Arranged by Elements: Part II—Arranged by Wavelengths*, NBS Monograph No. 145, Government Printing Office, Washington, D. C. (1975).

[5] Phelps, F. M., *MIT Wavelength Tables, Vol. II, Wavelenghts by Element*, MIT Press, November 1982.

[6] Reader, J. and Corliss, C. H., *NSRDS-NBS 68, Wavelengths and Transition Probabilities for Atoms and Atomic Ions*, Washington, D. C., 1980.

[7] Winge, R. K., Fassel, V. A., Peterson, V. J., and Floyd, M. A., *Inductively Coupled Plasma-Atomic Emission Spectroscopy: An Atlas of Spectral Information*, Elsevier Science Publishers, Amsterdam, 1985.

8.2.2.5 *Equivalent Analyte Concentration*—To obtain a quantitative measurement of the amount of interference from individual elements, measure the equivalent analyte concentration by testing 1000-mg/L solutions of these elements without using background correction.

8.2.3 *Correction for Interference Effects*—If interference effects are indicated, use one or more of the following techniques:

8.2.3.1 *Alternative Wavelength*—Select an analyte emission line free from spectral interferences and having the required sensitivity, linear range and detection limits if one can be found.

8.2.3.2 *Background Correction*—If the instrument is equipped for background correction, scan the samples and calibration solutions. Select one or more background correction positions in a level area of the background, preferably at a low point. Refer to instrument operating manuals for specific background correction procedures. Confirm with spikes and controls that background correction is working properly.

8.2.3.3 *Standard Additions*—Prepare the standard addition test solutions by adding known increments of analyte(s) as directed in 6.7. Test as directed in 10.6. In most cases, this will compensate for chemical and physical interferences, but not for spectral interferences.

8.2.3.4 *Dilution*—If the analyte concentration is sufficiently high, the analyte can be determined on a dilution. A ten-fold dilution may reduce the effect of some interferences, especially matrix enhancement. Prepare different calibration solutions as required. Dilution will not reduce spectral interferences if the analyte and interfering wavelength are close or coincident.

8.2.3.5 *Matrix-Matching*—Match the matrix of the calibration solutions to that of the test solution as closely as possible. Ascertain that the matrix is free of the analyte. If the matrix has a well-defined, small amount of analyte, add this to the amount measured by the instrument when the results are calculated or add it to the nominal concentration of the calibration solutions.

8.2.3.6 *Calculated Compensation*—Use equivalent analyte concentrations to correct for known amounts of interfering elements.

8.2.3.7 *Buffers*—Additions of lithium, sodium, potassium, and lanthanum, alone or in combination, have been reported to significantly reduce chemical interferences. Buffer concentrations normally range from 0.1 % to 3 % w/v.

8.3 *Linear Dynamic Range*—Prepare a known solution of high concentration, a blank, and others at approximately (0.01, 0.1, 0.3, and 0.7) times the concentration of the high concentration solution. Selection of the high concentration is somewhat arbitrary: it may range from 1000 mg/L or more for a relatively weak emission line to 10 mg/L for an exceedingly strong line.

8.3.1 *Upper Limit*—Calibrate the instrument using the highest concentration calibration solution and the blank. Analyze the other solutions as test solutions, monitoring the calibration solutions for drift and correcting as necessary. If the linearity solutions show a deviation from the expected value of more than 10 %, repeat the process using one of the lower concentrations as the high calibration solution. The upper limit of the linear range is established when the less concentrated solutions deviate from the expected value by less than 10 %.

8.3.2 *Lower Limit*—The lower end of the linear range is the LOQ.

8.3.3 The linear range can vary with the matrix.

8.4 *Background Equivalent Concentration (BEC)*—Calibrate the DCP with a high concentration calibration solution that is approximately 20 times the expected BEC and a blank. Block the entrance slit and measure while in the sample analysis mode. Record the absolute value of the resulting negative concentration as the BEC. The BEC is approximately equal to the intercept of a linear calibration curve.

8.5 *Detection Limits (DL)*—Follow the directions in the test method for determining and interpreting detection limit(s). If no instructions are available, determine the detection limit(s) as follows:

8.5.1 *Instrument Detection Limit (IDL)*—The IDL is used for characterizing and comparing analytical lines. Calibrate the instrument with a high concentration single-element calibration solution and a blank. The calibration solution should be between three and ten times the BEC. Set the instrument to take nine 10-*s* integrations and display the standard deviation. Measure the blank solution as a test solution three times. Calculate the instrument detection limit as follows:

$$IDL = 3\sqrt{(\sigma_1^2+\sigma_2^2+\sigma_3^2)/3} \quad (1)$$

where σ_1, σ_2, and σ_3 are the standard deviations obtained on the three replicate readings of the blank.

NOTE 2—The detection limit described by the instrument manufacturer was calculated as three times the average of the three standard deviations. Pooling the standard deviations yields slightly higher detection limits than those calculated by averaging.

8.5.2 *Method Detection Limit (MDL)*—The detection limit for an analyte in a given matrix is often different from what is reported in the literature. For an indication of the effect of the matrix, compare the MDL with the IDL. Follow the instructions of 8.5.1, taking the measurements on the matrix blank. Calculate the MDL as follows:

$$MDL = 3\sqrt{(\sigma_1^2+\sigma_2^2+\sigma_3^2)/3} \quad (2)$$

where σ_1, σ_2, and σ_3 are the standard deviations of the three replicate readings on the matrix blank.

8.5.2.1 An approximate MDL can be calculated as 3 % of the matrix-matched BEC or the matrix-matched calibration curve intercept when no background correction is used.

8.6 *Limit of Quantification (LOQ)*—Measure the LOQ as directed in the method of analysis.

8.6.1 If no directions are given, one approach is to calculate LOQ as directed in the following equation:

$$LOQ = 2t\sigma_c/\sqrt{np} \quad (3)$$

where:

t = multiplier from the student's t table,
σ_c = standard deviation in terms of concentration,
n = number of replicate readings, and

p = specified ratio of the range of the confidence interval to apparent concentration.

8.6.1.1 For example, measure the LOQ solution as a test solution four times, interspersing the measurements with test solutions, calibration verification solutions, and controls. Calculate the LOQ as directed in Eq 3, where p equals 0.3 at the 15 % confidence level and t for four samples at the 0.05 probability level equals 3.182. This simplifies to:

$$LOQ = 10.6\,\sigma_c \quad (4)$$

where σ_c (in concentration units) is the standard deviation of the four readings. In this example, LOQ is the level below which the error will be greater than 15 % at the 95 % confidence level.

8.6.2 LOQs should not change drastically (that is, by a factor greater than three) in properly controlled analyses. LOQs are affected by factors such as instrumental drift, plasma viewing region, background intensity, changes in sensitivity, and drift correction.

8.6.3 Using background correction often lowers the LOQ.

8.7 *Sensitivity*—For a linear calibration curve, calculate the slope in terms of change in intensity per unit of change in concentration as follows:

$$slope = (Y - Y')/(X - X') \quad (5)$$

where:

X = concentration of the high calibration solution,
X' = concentration of the low calibration solution,
Y = emission intensity of the high calibration solution, and
Y' = emission intensity of the low calibration solution.

9. Preparation of Apparatus

9.1 *Direct Current Plasma-Atomic Emission Spectrometer*—Select the operating parameters, including entrance and exit slit sizes, gas flow rates, photomultiplier tube voltages, integration time, number of integrations, and other necessary parameters according to the manufacturer's instructions or the particular method of analysis. Turn on the gases, initiate the plasma, and allow it to stabilize for 15 min to 30 min while aspirating water or rinse solution. Select the wavelength according to the method being used or determine it experimentally as directed in Section 8. While aspirating a solution of the analyte element, maximize the net emission intensity for the wavelength and plasma position. The net emission intensity is the emission intensity of the analyte minus the emission intensity of the blank solution.

9.1.1 The optimum plasma position is the position where the maximum net signal to background intensity is obtained. The plasma image appears as a "Y." In ascending order based on height above the junction of the three legs there are three regions: just below the excitation region but not in the plasma image (−1); the bottom of the excitation region (zero), and the top of the excitation region (+1). Once the wavelength is optimized, compare the difference between intensities of a calibration standard and blank at the three positions and select the region with the greatest difference. The lower position (−1) is particularly sensitive to changes in the plasma caused by fluctuations in gas pressure or erosion of the electrodes.

9.1.2 For test solutions containing high salt concentrations, optimize the plasma viewing region while aspirating the analyte having a matrix similar to the test solution.

9.1.3 In the multi-element mode some elements are measured at compromise conditions with regard to entrance slit sizes, viewing region, and other parameters.

9.2 *Calibration*—Calibrate as directed by the manufacturer's instructions and as directed by the specific test method if one is available. The instrument's microprocessor/PC generates the calibration coefficients using the emission intensity from the calibration solutions. A curve can also be generated manually as directed in 9.2.3. Either the instrument's coefficients or the manual curve may be used to determine the concentrations of test solutions, other calibration solutions, controls, and verifiers. The following types of calibration may be used:

9.2.1 *Linear Calibration:*

9.2.1.1 *For Test Solutions Less Than 100 Times the LOQ*—Calibrate with a high- and low-concentration calibration solution (the low-concentration calibration solution may be a blank.) Enter the calibration solution concentrations. Analyze the high-concentration calibration solution, the blank, and the verifier or control. Standardize or recalibrate for any of the following reasons: if the high-concentration calibration solution, verifier, or control differ from the expected value by more than 10 % (or other agreed upon value), or if the absolute reading of the blank is greater than the LOQ. Repeat the verification of the updated curve.

9.2.1.2 *For Test Solutions Greater Than 100 Times the LOQ*—Calibrate with a high- and low-concentration calibration solution (the low-concentration calibration solution may be a blank.) Enter the calibration solution concentrations. Analyze the high-concentration calibration solution, the blank, and the verifier or control. Standardize or recalibrate for any of the following reasons: if the high-concentration calibration solution, verifier, or control differ from the expected value by more than 5 % (or other agreed upon value), or if the absolute reading of the blank is greater than five times the LOQ. Repeat the verification of the updated curve.

9.2.2 *Non-Linear Calibration*—The concentrations of the calibration solutions should closely bracket those of the test solution. Values of 5 % higher and 5 % lower are recommended. Closely bracketing calibration solutions may also be used in the linear portion of a curve. Use of calibration standard solutions that are within 10 % of one another may result in a high background status message from the instrument panel in some models; this may be ignored. Verify the calibration as directed in 9.2.1.2.

9.2.3 *Multi-Point Calibration:*

9.2.3.1 For Instruments Using Two-point Calibration: Set the instrument with a high-calibration solution and a low-calibration solution or blank as directed by the manufacturer's instructions, recording the emission intensity. Record the emission intensities of at least three other calibration solutions covering the concentration range between the high- and low-calibration solutions, using more if the curve is non-linear.

Generate the curve with a pocket calculator or graph paper by plotting either raw or net emission intensities of the calibration solutions on the ordinate and the corresponding concentrations on the abscissa.

9.2.3.2 For Instruments Capable of Multi-point Calibration: Follow manufacturer's instructions for an instrument whose microprocessor/PC accepts multipoint calibration data and generate curves automatically. Verify the calibration as directed in 9.2.1.1 or 9.2.1.2.

10. Procedure

10.1 Prepare the test solution as directed by the method of analysis or the analytical plan. The concentration of the analyte should be at least at or above the LOQ. It should be within the linear range of the analytical curve at the wavelength selected, unless the calibration process is performed according to 9.2.2.

10.2 Set the operating parameters, calibrate the spectrometer, and verify the calibration. Flush the system with a rinse solution for 10 s (or an amount of time specified in the method of analysis) between each calibration solution and test solution.

10.3 Analyze one or more test solutions, rinsing between each. Record the concentration. Analyze a high-concentration verifier and LOQ solution after each ten (or fewer) test solutions.

10.3.1 If the verifier differs from the established value by more than 10 % (or some other established control limit), recalibrate or standardize the instrument. Verify the calibration and measure the test solutions again.

10.3.2 If the test solutions are between the LOQ and 30 times the LOQ, and if the LOQ solution deviates from the expected value by more than half the quantifiable limit, recalibrate, standardize, or drift correct.

10.3.3 If the test solutions are between 30 times and 100 times the LOQ, and if the LOQ solution deviates from the expected value by more than twice the LOQ, recalibrate, standardize, or drift correct.

10.3.4 If the test solutions are greater than 100 times the LOQ, and if the LOQ solution deviates from the expected value by more than three times the LOQ, recalibrate, standardize, or drift correct.

10.4 *Drift Correction:*

10.4.1 *Overview*—A drift in the readings of the verifiers and calibration solutions (both high and low) suggests that the readings of the test solutions have drifted correspondingly. Correcting for this drift using calculations may be helpful for semiquantitative measurements during routine analysis using a well-understood method. Drift correction should not be used for an umpire analysis (see 5.2) or when the test solution is so close to a specification limit that the drift correction makes a difference either way. Instead, the instrument should be recalibrated or standardized and the analysis repeated.

10.4.1.1 *Technique*—Measure the solutions in the following sequence: low-concentration calibration solution (or blank), high-concentration calibration solution, test solution(s) interspersed with LOQ solutions, low-concentration calibration high-concentration calibration solution. Assign to each reading an integer corresponding to its position in the sequence. For each test solution, calculate a drift-corrected high- and low-calibration solution concentration according to the following:

$$H_C = [(H_F - H_I) \times (S_S - I_H)/(F_H - I_H)] + H_I \quad (6)$$

$$L_C = [(L_F - L_I) \times (S_S - I_L)/(F_L - I_L)] + L_I$$

where:

H_C = drift-corrected high-calibration solution concentration corresponding to a particular sample test solution at that point in the sequence,

H_F = final concentration reading of the high-concentration calibration solution,

H_I = initial concentration reading of the high-concentration calibration solution,

L_C = drift corrected low-calibration solution concentration corresponding to the same sample test solution at that point in the sequence,

L_F = final concentration reading of the low-concentration calibration solution,

L_I = initial concentration reading of the low-concentration calibration solution,

S_S = integer corresponding to the sample position,

I_H = integer corresponding to the position of the initial reading of the high-concentration calibration solution,

F_H = integer corresponding to the position of the final reading of the high-concentration calibration solution,

I_L = integer corresponding to the position of the initial reading of the low-concentration calibration solution, and

F_L = integer corresponding to the position of the final reading of the low-concentration calibration solution.

10.4.1.2 Calculate the corrected concentration, T_C, for each sample from the following equation:

$$T_C = (T_O - L_C) \times (H_N - L_N)/(H_C - L_C) + L_N \quad (7)$$

where:

L_C = drift corrected low-calibration solution concentration corresponding to the same sample test solution at that point in the sequence,

H_C = drift-corrected high-calibration solution concentration corresponding to a particular sample test solution at that point in the sequence,

H_N = nominal concentration of the high-calibration solution,

L_N = nominal concentration of the low-calibration solution, and

T_O = observed concentration reading of the sample.

10.4.1.3 This assumes linear drift over time. The times for solution introduction, solution analysis, and for rinsing should be constant. Use of an autosampler is recommended.

10.4.1.4 The number of test and LOQ solutions measured between the two sets of calibration solutions should not exceed ten, not including the calibration solutions.

10.4.1.5 Recalibrate or standardize if the measured concentrations of the calibration solutions exceed by more than 50 % the allowable calibration deviations in 9.2.1.

10.4.1.6 Computer software for some DCP-AES instruments contains a drift-correction protocol that may be used.

10.4.2 *Direct Ratio:*

10.4.2.1 *Overview*—The direct ratio method is suggested for semiquantitative estimation of analytes in concentrations greater than 50 times the LOQ. For precise analyses or for analyses at concentrations less than 50 times the LOQ, use the drift correction sequence (see 10.4.1.1), where the blank or a low-concentration solution is also monitored and used in the correction.

10.4.2.2 *Technique*—Prepare a number of solutions covering the expected range of the test solutions. Calibrate the instrument and verify the calibration as described in Section 9. Measure the concentration of a test solution, then measure the concentration of the solution closest to its concentration. Calculate the concentration of the test solution according to the following formula:

$$T_C = T_R\,(C_n/C_R) \tag{8}$$

where:

T_C = corrected concentration of the test solution,
T_R = instrument reading of the test solution concentration,
C_n = nominal concentration of the known solution, and
C_R = instrument reading of the known solution.

10.5 *Method of Additions*—Use the method of additions when matrix effects are suspected and matrix-matched calibration solutions are unavailable. The concentration of the analyte should be between the LOQ and 50 times the LOQ. (Above that level the test solution can be diluted enough to minimize many of the matrix effects.) Prepare the test solutions as directed in 6.7. Use one of the following methods of analysis:

10.5.1 *Option 1*—Calibrate the instrument with a high-concentration calibration solution and a blank. Measure the concentrations of the analyte in the four solutions. Plot the data on graph paper, the added concentration on the abscissa and the corresponding concentration reading on the ordinate. Extrapolate the resulting straight line. The absolute value of the intercept on the *x*-axis (abscissa) is the concentration of the analyte in the test solution. Alternatively, use a linear regression program where intensity (y) is dependent on concentration (x). Solve for $y = 0$, that will be the concentration of the analyte. If both matched and non-matrix matched calibrations are used to prepare two curves, the difference in the two slopes is a measure of the matrix effect (enhancement or suppression.)

10.5.2 *Option 2*—Calibrate the instrument (within the linear range) using the highest spiked solution as the high-concentration calibration solution and assign it the value of the spike. Use the reagent blank as the low-concentration calibration solution. Aspirate and analyze each of the other three solutions, recording either the concentration reading or three emission intensity readings for each test solution, as well as for the high-concentration calibration solution and the reagent blank. Prepare a curve by plotting the added concentration on the abscissa and the concentration reading or the average relative emission intensity of the standard additions test solutions minus the average emission intensity of the reagent blank on the ordinate. Extrapolate the resulting straight line to the abscissa. The absolute value of the intercept is the concentration of the analyte in the test solution.

10.5.3 The method of standard additions is useful for estimating analytes in difficult matrices but is not recommended for umpire analysis. A limitation of the method of standard additions is that the reagent blank may not correct for sample matrix background levels. Use background correction whenever possible.

10.6 *Internal Standard:*

10.6.1 For simultaneous instruments, an internal standard can compensate for drift and physical interferences. Select an element that is unlikely to be present in calibration or test solutions, that has a sensitive line not subject to interferences by the matrix, and that does not interfere with the analyte. One of the most important criteria for selecting an internal standard line is that both the analyte line and the internal standard line should be either neutral atom transitions or ion transitions – mixed atom/ion lines seldom perform well. Ascertain that the internal standard intensity correlates positively with that of the analyte over the expected range of analyte concentrations. Calibrate it at the same time the other analytes are calibrated. Add the same defined amount (at least 100 times its LOQ) of the internal standard to each test solution. Do not add the internal standard to the calibration blank. Measure the internal standard with each test solution. When measuring trace impurities in a single element matrix, one of the matrix wavelengths may be used as an internal standard. More than one internal standard may be used in a test solution to correct different analytes.

10.6.2 For each analyte value, correct for the internal standard reading as follows:

$$C_C = C_R \times I_N/I_R \tag{9}$$

where:

C_C = corrected concentration of the analyte,
C_R = reading of the analyte,
I_N = nominal value of the internal standard, and
I_R = reading of the internal standard.

11. Calculation

11.1 Calculate the results, taking into account the mass of the test sample, the volume of the test solution, dilutions, interelement corrections, drift corrections, internal standards, and any other factors. Subtract the readings of the reagent blank from the instrument readings before calculating.

11.2 Carry more significant digits through the calculations than are required for the final result, then round as directed in Practice E29.

11.3 Report results lower than the LOQ or the scope as "less than" the LOQ determined for that group of test samples or less than the scope of the test method. For information on interpreting data and results, refer to Practice E1601.

12. Quality Control/Quality Assurance

12.1 Perform quality control/quality assurance procedures as directed in the test method or in Guide E882. Regularly

analyze the control as a blind sample to provide a record of control as directed in Guide E882.

12.2 Maintain required documentation for daily analyses as directed in the method or in Guide E882, including but not limited to instrument calibration and continuing verification, LOQ, test solutions, duplicates, controls, and spikes.

12.3 Maintain the appropriate or required documentation as directed in the method or in Guide E882 for initial methods development and periodic checks, including but not limited to: linear range, detection limits, interferences, BEC, and interelement corrections.

13. Keywords

13.1 DCP-AES; dc plasma guide; Direct Current Plasma atomic emission spectrometry; plasma; plasma operations