Designation: E 1097 – 97

Standard Guide for Direct Current Plasma Emission Spectrometry Analysis[1]

This standard is issued under the fixed designation E 1097; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide covers procedures for using a direct current argon plasma atomic emission spectrometer 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 direct current plasma 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 8.

2. Referenced Documents

2.1 *ASTM Standards:*

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[2]
E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals[3]
E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[3]
E 743 Guide for Spectrochemical Laboratory Quality Assurance[4]
E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data[4]
E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory[4]
E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method[4]
E 1832 Practice for Describing and Specifying a Direct-Current Plasma Optical Emission Spectrometer [4]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this guide, refer to Terminology E 135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *background equivalent concentration (BEC), n*—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*—the lowest detectable quantity equal to three times the standard deviation of a blank. Types of detection limits are as follows:

3.2.2.1 *approximate detection limit (ADL), n*—three percent of the background equivalent concentration for an analytical line not background corrected. The ADL is a useful check on daily performance.

3.2.2.1.1 *Discussion*—The IDL and MDL are useful in establishing the low end of the linear range and as a guide in the preparation of calibration and check solutions.

3.2.2.2 *instrumental detection limit (IDL), n*—For d-c plasma, 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. The IDL is useful in characterizing and comparing analytical lines.

3.2.2.3 *method detection limit (MDL), n*—the detection limit measured on the matrix blank. The MDL indicates the effect of the matrix.

3.2.3 *equivalent analyte concentration, n*—the apparent concentration of an interfering element on an analyte, determined by measuring a 1000-mg/L solution of the interfering element at the analyte wavelength.

3.2.4 *interference, n*—any chemical, physical, or spectral effect that changes the apparent net emission intensity from a spectral line other than a change in concentration of the element emitting that spectral line.

3.2.5 *linear dynamic range, n*—the concentration range from the quantifiable limit to the highest concentration that

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[1] This guide is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.20 on General Analytical Practices.

Current edition approved Oct. 10, 1997. Published June 1998. Originally published as E-3 Proposal P152. Last previous edition E 1097 – 93.

[2] *Annual Book of ASTM Standards*, Vol 14.02.

[3] *Annual Book of ASTM Standards*, Vol 03.05.

[4] *Annual Book of ASTM Standards*, Vol 03.06.

remains within ± 10 % of linearity based on lower concentrations.

3.2.6 *order, spectral, n*—the number of wavelength differences between reflections from successive grooves of a grating or echelle; typically one or two wavelengths for the first or second orders of a grating, 50 or 51 wavelengths for the fiftieth and fifty-first orders from an echelle.

3.2.6.1 *Discussion*—In the DCP echelle, a number of wavelengths appear in two adjacent orders, and these wavelengths usually have similar intensities.

3.2.7 *quantifiable limit (QL)*—the lowest concentration at which the instrument can measure reliably with a defined error and confidence level.

3.2.8 *sensitivity*—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 argon plasma atomic emission spectrometers, either simultaneous or sequential, measure elements in solution using atomic emission. Samples and calibration 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. They impinge on photomultiplier tubes, whose outputs are interpreted by a computer as emission intensities. Background correction can be used to compensate for some interferences. The computer generates calibration curves and calculates analyte concentration.

5. Significance and Use

5.1 Accurate application of direct current plasma spectrometry requires proper preparation of test solutions, accurate calibration, and control of analytical procedure, that are treated broadly in this guide, ASTM test methods that refer to this guide shall provide specifics on solutions, calibration, and procedures.

5.2 Application of direct current plasma 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 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 d-c plasma analysis. Analysts should ensure that proper quality assurance procedures are followed, especially those defined by the test method. Refer to Guides E 743 and E 882 or the USEPA Contract Laboratory Program.[5]

[5] *USEPA Contract Laboratory Program Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration, SOW 7/88*, Sample Management Office, P.O. Box 818, Alexandria, VA 22313, 1988.

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 standard reference material, certified reference material, or other material of known composition and prepare a solution of it according to the appropriate test method. This solution may be used to verify the initial calibration. Analyze the control regularly as a blind sample and use the results for quality control as directed in Guide E 882.

6.6 *Calibration Solutions*—The number and type of these solutions will depend on the method, and on the type of plasma instrument and its microprocessor. 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. Also prepare at least one other intermediate calibration solution. More may be prepared if the microprocessor can utilize them, especially if the test solutions are expected to have a large range of analyte composition of if the calibration curve is non-linear. Prepare them by adding aliquots from stock solutions to solutions that are similar in composition to 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 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 matched matrix 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 matched matrix 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, it's concentration should be at least four times the method detection limit and above the quantifiable limit.

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 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 quantifiable limit. 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 quantifiable limit. 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*—Prepare a solution whose concentration is in the midrange in the calibration curve. This may be one of the calibration solutions.

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 quantifiable limit.

6.10 *Quantifiable Limit 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 igniting 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 Practices E 50.

8. Characterization of Analytical Lines

8.1 *Overview*:

8.1.1 When setting up 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, and 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 means of controls or quantifiable limit measurements, or both, that the daily performance of the instrument meets the criteria of the method.

8.1.2 When using an established method for the first time, confirm that freedom from interferences, linearity, detection limit, and sensitivity meet the criteria of the method.

8.1.3 For information on wavelengths, refer to Bosshart,[6] Harrison,[7] or Winge[8].

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 emission lines, or high concentrations of easily ionized elements. 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 quantifiable limit. It should be recovered to within ± 2 s of 100 %, where *s* 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.

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.

[6] Bosshart, R. E., *Handbook of Spectral Line Characteristics for the DC Plasma Echelle Systems*, ARL Instruments, Sunland, CA 91040.

[7] Harrison, George, R., *MIT Wavelength Tables*, John Wiley and Sons Inc, New York, NY.

[8] 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.

8.2.3 *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.

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. Verify 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 background 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 effects 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 quantifiable limit.

NOTE 2—The linear range can vary with the matrix.

8.4 *Background Equivalent Concentration (BEC)*—Calibrate the dc plasma 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)*—Measure these as needed.

8.5.1 *Instrument Detection Limit (IDL)*—Calibrate the instrument with a high concentration 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:

$$IDL = 3\sqrt{(s_1^2 + s_2^2 + s_3^2)/3} \tag{1}$$

where s_1, s_2, and s_3 are the standard deviations obtained on the three different replications.

NOTE 3—The detection limits in Bosshart[6] were 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)*—Follow the instructions of 8.5.1, taking the measurements on the matrix blank. Calculate the MDL as follows:

$$MDL = 3\sqrt{(s_1^2 + s_2^2 + s_3^2)/3} \tag{2}$$

where s_1, s_2, and s_3 are the standard deviations.

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

NOTE 4—The detection limit for an analyte in a given matrix is often different from what is reported in the literature.

8.6 *Quantifiable Limit (QL)*—Measure the quantifiable limit as directed in the method of analysis.

8.6.1 If no directions are given, one approach is to use Eq 21 of Practice E 876:

$$QL = 2ts_c/\sqrt{np} \tag{3}$$

where:
t = multiplier from the student's t table,
s_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 quantifiable limit solution as a test solution four times, interspersing the measurements with test solutions, calibration verification solutions, and controls. Calculate the quantifiable limit as directed in Eq 21 of Practice E 876, 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:

$$QL = 10.6\, s_c \tag{4}$$

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