Designation: ~~E3203 – 19a~~ E3203 – 21

Standard Test Method for Determination of Lead in Dried Paint, Soil, and Wipe Samples by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)[1]

This standard is issued under the fixed designation E3203; 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 test method specifies a procedure for analysis of dried paint, soil, and dust wipe samples collected in and around buildings and related structures for lead content using inductively coupled plasma-optical emission spectroscopy (ICP-OES).

1.2 This test method should be used by analysts experienced in the use of ICP-OES, the interpretation of spectral and matrix interferences, and procedures for their correction. For determination of lead (Pb) and other metals in air by ICP-OES, see Test Method D7035.

1.3 This test method cites specific methods for preparing test solutions of dried paint, soil, and wipe samples for analysis.

1.4 It is the user's responsibility to ensure the validity of this test method for sampling materials of untested matrices.

1.5 No detailed operating instructions are provided because of differences among various makes and models of suitable ICP-OES instruments. Instead, the analyst shall follow the instructions provided by the manufacturer of the particular instrument. This test method does not address comparative accuracy of different devices or the precision between instruments of the same make and model.

1.6 This test method contains notes that are explanatory and are not part of the mandatory requirements of this test method.

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7.1 *Exception*—The inch-pound and SI units shown for wipe sampling data are to be individually regarded as standard for wipe sampling data.

1.8 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

---

[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.12 on Sampling and ~~Analysis,~~Analysis of ~~Lead,~~Lead for Exposure and Risk Assessment.

Current edition approved ~~Nov. 1, 2019~~Sept. 1, 2021. Published ~~November 2019~~September 2021. Originally approved in 2019. Last previous edition approved in 2019 as E3203 – ~~19.~~19a. DOI: ~~10.1520/E3203-19A.~~10.1520/E3203-21.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water
D1356 Terminology Relating to Sampling and Analysis of Atmospheres
D6785 Test Method for Determination of Lead in Workplace Air Using Flame or Graphite Furnace Atomic Absorption Spectrometry
D6966 Practice for Collection of Settled Dust Samples Using Wipe Sampling Methods for Subsequent Determination of Metals
D7035 Test Method for Determination of Metals and Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
D7440 Practice for Characterizing Uncertainty in Air Quality Measurements
E631 Terminology of Building Constructions
E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
E1583 Practice for Evaluating Laboratories Engaged in Determination of Lead in Paint, Dust, Airborne Particulates, and Soil Taken From and Around Buildings and Related Structures
E1605 Terminology Relating to Lead in Buildings
E1613 Test Method for Determination of Lead by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Flame Atomic Absorption Spectrometry (FAAS), or Graphite Furnace Atomic Absorption Spectrometry (GFAAS) Techniques (Withdrawn 2021)[3]
E1644 Practice for Hot Plate Digestion of Dust Wipe Samples for the Determination of Lead
E1645 Practice for Preparation of Dried Paint Samples by Hotplate or Microwave Digestion for Subsequent Lead Analysis
E1726 Practice for Preparation of Soil Samples by Hotplate Digestion for Subsequent Lead Analysis
E1727 Practice for Field Collection of Soil Samples for Subsequent Lead Determination
E1728 Practice for Collection of Settled Dust Samples Using Wipe Sampling Methods for Subsequent Lead Determination
E1729 Practice for Field Collection of Dried Paint Samples for Subsequent Lead Determination
E1792 Specification for Wipe Sampling Materials for Lead in Surface Dust
E1908 Practice for Sample Selection of Debris Waste from a Building Renovation or Lead Abatement Project for Toxicity Characteristic Leaching Procedure (TCLP) Testing for Leachable Lead (Pb)
E1979 Practice for Ultrasonic Extraction of Paint, Dust, Soil, and Air Samples for Subsequent Determination of Lead
E2115 Guide for Conducting Lead Hazard Assessments of Dwellings and of Other Child-Occupied Facilities
E2271/E2271M Practice for Clearance Examinations Following Lead Hazard Reduction Activities in Multifamily Dwellings
E2913/E2913M Practice for Hotplate Digestion of Lead from Composited Wipe Samples
E2914/E2914M Practice for Ultrasonic Extraction of Lead from Composited Wipe Samples
E3074/E3074M Practice for Clearance Examinations Following Lead Hazard Reduction Activities in Single Family Dwellings, in Individual Units of Multifamily Dwellings, and in Other Child-Occupied Facilities

2.2 *ISO and European Standards:*[4]

ISO 1042 Laboratory ~~Glassware – One-Mark Volumetric Flasks~~glassware – One-mark volumetric flasks
ISO 3585 Borosilicate ~~Glass~~glass 3.3 – Properties
ISO 8655 ~~Piston-Operated Volumetric Apparatus~~Piston-operated volumetric apparatus (6 Parts)
ISO 15202 Workplace ~~Air~~air – Determination of ~~Metals~~metals and ~~Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry~~metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry (3 Parts)
ISO/IEC 17025 General ~~Requirements~~requirements for the ~~Competence~~competence of ~~Testing~~testing and ~~Calibration Laboratories~~calibration laboratories

2.3 *Other Standards:*

EPA SW-846 Test Method 311 Toxicity Characteristic Leaching Procedure[5]
JCGM 100 Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement[6]

3. Terminology

3.1 For definitions of pertinent terms not listed here, see Terminologies D1356, E631, and E1605.

---

[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] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[5] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

[6] Available from Bureau International des Poids et Mesures (BIPM), Pavillon de Breteuil F-92312, Sèvres Cedex, France, http://www.bipm.org.

3.2 *Definitions:*

3.2.1 *atomic emission, n*—characteristic radiation emitted by an electronically excited atomic species.

3.2.1.1 *Discussion*—

In atomic (or optical) emission spectrometry, a very high-temperature environment, such as a plasma, is used to create excited state atoms. For analytical purposes, characteristic emission signals from elements in their excited states are then measured at specific wavelengths.

3.2.2 *axial plasma, n*—a horizontal inductively coupled plasma that is viewed end-on (versus radially; see 3.2.27).

3.2.3 *background correction, n*—the process of correcting the intensity at an analytical wavelength for the intensity due to the underlying spectral background of a blank. **ISO 15202**

3.2.4 *background equivalent concentration, n*—the concentration of a solution that results in an emission signal of equivalent intensity to the background emission signal at the analytical wavelength. **ISO 15202**

3.2.5 *batch, n*—a group of field or quality control (QC) samples that are collected or processed together at the same time using the same reagents and equipment. **E1613**

3.2.6 *blank solution, n*—solution prepared by taking a reagent blank or field blank through the same procedure used for sample dissolution.

3.2.7 *calibration blank solution, n*—calibration solution prepared without the addition of any stock standard solution or working standard solution. **ISO 15202**

3.2.7.1 *Discussion*—

The concentration of the analyte(s) of interest in the calibration blank solution is taken to be zero.

3.2.8 *calibration solution, n*—solution prepared by dilution of the stock standard solution(s) or working standard solution(s), containing the analyte(s) of interest at the concentration(s) suitable for use in calibration of the analytical instrument. **ISO 15202**

3.2.8.1 *Discussion*—

The technique of matrix matching is normally used when preparing calibration solutions.

3.2.9 *continuing calibration blank (CCB), n*—a solution containing no analyte added, that is used to verify blank response and freedom from carryover. **E1613**

3.2.9.1 *Discussion*—

The absolute value of the measured concentration of the CCB is to be not more than 50 % of the lowest regulatory limit for the sample matrix analyzed or minimum level of concern.

3.2.10 *excitation interferences, n*—non-spectral interferences that manifest as a change in sensitivity due to a change in inductively coupled plasma conditions when the matrix of a calibration or test solution is introduced into the plasma. **ISO 15202**

3.2.11 *field blank, n*—sampling media (for example, a sampling wipe) that is exposed to the same handling as field samples, except that no sample is collected (that is, no surface is wipe sampled). **D6785**

3.2.11.1 *Discussion*—

Analysis results from field blanks provide information on the analyte background level in the sampling media, combined with the potential contamination experienced by samples collected within the batch resulting from handling.

3.2.12 *inductively coupled plasma (ICP), n*—a high-temperature discharge generated by a flowing conductive gas, normally argon, through a magnetic field induced by a load coil that surrounds the tubes carrying the gas. **ISO 15202**

3.2.13 *inductively coupled plasma (ICP) torch, n*—a device consisting of three concentric tubes, the outer two usually made from quartz, that is used to support and introduce sample into an ICP discharge. **ISO 15202**

3.2.14 *injector tube, n*—the innermost tube of an inductively coupled plasma torch, usually made of quartz or ceramic materials, through which the sample aerosol is introduced to the plasma. **ISO 15202**

3.2.15 *inner (nebulizer) argon flow, n*—the flow of argon gas that is directed through the nebulizer and carries the sample aerosol through the injector and into the plasma.

3.2.15.1 *Discussion*—

Typically 0.5 to 2 L/min. **ISO 15202**

3.2.16 *instrumental detection limit (IDL), n*—the lowest concentration at which the instrumentation can distinguish analyte content from the background generated by a minimal matrix. **E1613**

3.2.16.1 *Discussion*—

The IDL pertains to the maximum capability of an instrument and should not be confused with the method detection limit (MDL).

3.2.17 *interelement correction, n*—a spectral interference correction technique in which emission contributions from interfering elements that emit radiation at the analyte wavelength are subtracted from the apparent analyte emission after measuring the interfering element concentrations at other wavelengths. **ISO 15202**

3.2.18 *intermediate (auxiliary) argon flow, n*—the flow of argon gas that is contained between the intermediate and center (injector) tubes of an inductively coupled plasma torch.

3.2.18.1 *Discussion*—

Typically 0.1 to 2 L/min. **ISO 15202**

3.2.19 *internal standard, n*—a non-analyte element, present in all calibration, blank, and sample solutions, the signal from which is used to correct for non-spectral interference or improve analytical precision. **ISO 15202**

3.2.20 *linear dynamic range, n*—the range of concentrations over which the calibration curve for an analyte is linear. It extends from the detection limit to the onset of calibration curvature. **ISO 15202**

3.2.21 *load coil, n*—a length of metal tubing (typically copper) which is wound around the end of an inductively coupled plasma torch and connected to the radio frequency generator. **ISO 15202**

3.2.21.1 *Discussion*—

The load coil is used to inductively couple energy from the radio frequency generator to the plasma discharge.

3.2.22 *matrix interference, n*—interference of a non-spectral nature which is caused by the sample matrix.

3.2.22.1 *Discussion*—

Matrix matching involves preparing calibration solutions in which the concentrations of acids and other major solvents and solutes are matched with those in the test solutions. **ISO 15202**

3.2.23 *method quantitation limit (MQL), n*—the minimum concentration of an analyte that can be measured with acceptable precision, ordinarily taken to be at least ten times the standard deviation of the mean blank signal (**1**).[7]

3.2.23.1 *Discussion*—

The MQL is also known as the limit of quantitation.

3.2.24 *nebulizer, n*—a device used to create an aerosol from a liquid. **ISO 15202**

3.2.25 *outer (plasma) argon flow, n*—the flow of argon gas that is contained between the outer and intermediate tubes of an inductively coupled plasma torch.

3.2.25.1 *Discussion*—

Typically 7 to 15 L/min. **ISO 15202**

3.2.26 *pneumatic nebulizer, n*—a nebulizer that uses high-speed gas flows to create an aerosol from a liquid. **ISO 15202**

[7] The boldface numbers in parentheses refer to a list of references at the end of this standard.

3.2.27 *radial plasma, n*—an inductively coupled plasma that is viewed from the side (versus axial).

3.2.28 *sample dissolution, n*—the process of obtaining a solution containing the analyte(s) of interest from a sample. This may or may not involve complete dissolution of the sample. **D6785**

3.2.29 *sample preparation, n*—all operations carried out on a sample, after transportation and storage, to prepare it for analysis, including transformation of the sample into a measurable state, where necessary.

3.2.30 *spectral interference, n*—an interference caused by the emission from a species other than the analyte of interest. **ISO 15202**

3.2.31 *spray chamber, n*—a device placed between a nebulizer and an inductively coupled plasma torch whose function is to separate out aerosol droplets in accordance with their size, so that only very fine droplets pass into the plasma, and large droplets are drained or pumped to waste. **ISO 15202**

3.2.32 *stock standard solution, n*—solution used for preparation of working standard solutions and/or calibration solutions, containing the analyte(s) of interest at a certified concentration(s) traceable to primary standards (National Institute of Standards and Technology (NIST) or international measurement standards).

3.2.33 *transport interference, n*—non-spectral interference caused by a difference in viscosity, surface tension, or density between the calibration and test solutions (for example, due to differences in dissolved solids content, type and concentration of acid, and so forth). **ISO 15202**

3.2.33.1 *Discussion*—
Such differences produce a change in nebulizer efficiency and hence in the amount of analyte reaching the plasma.

3.2.34 *ultrasonic nebulizer, n*—a nebulizer in which the aerosol is created by flowing a liquid across a surface that is oscillating at an ultrasonic frequency. **ISO 15202**

3.2.35 *viewing height (for a radial plasma), n*—the position in a radial plasma from where the emission measured originates; generally given as the distance, in millimetres, above the load coil. **ISO 15202**

3.2.36 *x-y centering (for an axial plasma), v*—horizontal and vertical adjustment of an axial plasma to establish optimal viewing conditions, such that only emission from the central channel of the plasma is measured. **ISO 15202**

4. Summary of Test Method

4.1 Test solutions prepared from the sample solutions after sample dissolution using Practices E1644, E1645, E1726, E1979, E2913/E2913M, or E2914/E2914M are analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) to determine the concentration of lead.

5. Significance and Use

5.1 This test method is intended for use with other standards that address the collection and preparation of samples (dusts by wipe, dried paint chips, and soils) that are obtained during the assessment or mitigation of lead hazards from buildings and related structures.

5.2 Laboratories analyzing samples obtained during the assessment or mitigation of lead hazards from buildings and related structures shall conform to Practice E1583, or shall be recognized for lead analysis as promulgated by authorities having jurisdiction, or both.

NOTE 1—In the United States of America, laboratories performing analysis of samples collected during lead-based paint activities are required to be accredited to ISO/IEC 17025 and to other requirements promulgated by the Environmental Protection Agency (EPA).

5.3 This test method may also be used to analyze similar samples from other environments such as toxic characteristic extracts of waste sampled using Guide E1908 as prepared for analysis using EPA SW-846 Test Method 1311.

6. Interferences

6.1 For measurements made using the analytical wavelengths selected, no spectral interferences were observed, and thus interference correction was not found to be necessary. However, it is important to determine whether interference correction is necessary under the test conditions used.

7. Apparatus and Materials

7.1 *Argon,* suitable for use in ICP-OES.

7.1.1 *Laboratory Detergent,* suitable for cleaning of laboratory ware.

7.2 *Laboratory Apparatus for Analysis*—Original laboratory apparatus are not listed, but are assumed to be present.

7.2.1 *Disposable Gloves,* impermeable and powder-free, to avoid the possibility of contamination and to protect them from contact with toxic and corrosive substances. PVC gloves are suitable.

7.2.2 *Glassware,* beakers and volumetric flasks complying with the requirements of ISO 1042, made of borosilicate glass complying with the requirements of ISO 3585. ~~Glassware shall be cleaned before use by soaking in diluted nitric acid and then rinsing thoroughly with water. Alternatively, before use, glassware shall be cleaned with a suitable laboratory detergent.~~

7.2.3 *Flat-Tipped Forceps,* for unloading filters from samplers or from filter transport cassettes.

7.2.4 *Piston-Operated Volumetric Pipettors and Dispensers,* complying with the requirements of ISO 8655, for pipetting and dispensing of leach solutions, acids, standard solutions, and so forth.

7.2.5 *Plastic Bottles,* 1-L capacity, with leak-proof screw cap.

7.2.6 *Inductively Coupled Plasma-Optical Emission Spectrometer,* computer-controlled, equipped with an auto-sampler.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[8] Other grades may be used, provided that it can be demonstrated that they are of sufficiently high purity to permit their use without decreasing the accuracy of the determinations.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean Type II reagent water conforming to Specification D1193.

8.3 *Nitric Acid* (HNO_3),concentrated, ρ ~1.42 g⁄mL (~70 % m/m).

8.4 *Nitric Acid* (HNO_3),diluted 1 + 9 (10 % v⁄v). Carefully and slowly begin adding 50 mL of concentrated nitric acid to 450 mL of water.

8.5 *Hydrochloric Acid* (HCl),concentrated, ρ ~1.18 g⁄mL (~36 % m/m).

[8] ~~*Reagent Chemicals, American Chemical Society Specifications,*~~*ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.6 *Hydrochloric Acid Leach Solution,* 0.1 M.

9. Equipment Preparation

9.1 Wash glassware and plastic equipment with laboratory detergent, rinse with tap water, soak for at least 4 hours in volume fraction 35 % nitric acid and water, rinse three times with ASTM Type I Water, and allow to dry preferably in a fume hood. Commercial, automatic systems are available that perform a similar process.

9.2 Alternatively, soak glassware and plastic equipment in volume/volume 1+1 nitric acid and water in a plastic tub preferably in a working hood with the hood sash down, rinse three times with ASTM Type I Water, and allowed to dry preferably in a fume hood.

10. Safety Procedures

10.1 Hazards to personnel exist in the operation of the ICP-OES. Do not operate any ICP-OES unit until the manufacturer's instruction manual has been read and completely understood. Follow all safety instructions in the manual and the safety requirements pertaining to the handling, storage, and use of compressed gases.

10.2 Hazards to personnel exist in all operations in which hot, concentrated mineral acids are used. The appropriate laboratory procedures for working with reagents of this nature shall be observed.

10.3 Lead and lead compounds are hazardous to health and shall be handled in a manner consistent with the danger they present.

10.4 The instrument exhaust gases are toxic, corrosive vapors. The instrument exhaust gases shall be mechanically exhausted from the laboratory (see instrument manufacturer's instructions).

11. Sampling Collection and Preparation

11.1 *Sample Collection*—Collect samples, as appropriate to the matrix of interest, using Practices D6966, E1727, E1728, E1729, E2271/E2271M, or E3074/E3074M, or combinations thereof.

11.2 *Sample Preparation*—Prepare samples for analysis, as appropriate to the matrix of interest, using Practices E1644, E1645, E1726, E1979, E2913/E2913M, or E2914/E2914M.

12. Calibration and Standardization

12.1 To prepare stock standard solutions, use commercial single-element or multi-element standard solutions with certified concentrations traceable to primary standards (NIST or international measurement standards). Observe the manufacturer's expiration date or recommended shelf life.

12.1.1 Alternatively, prepare stock standard solutions from lead or lead salts. The procedure used to prepare the solutions shall be fit for purpose, and the calibration of any apparatus used shall be traceable to primary standards. The maximum recommended shelf life is one year from date of initial preparation.

12.1.2 Store stock standard solutions in suitable containers, such as 1-L polypropylene bottles.

12.1.3 *Calibration Solutions:*

12.1.3.1 From the stock standard solutions, prepare working standard solutions by serial dilutions; these shall include all the metals and metalloids of interest at suitable concentrations (typically between 0.05 and 100 mg/L, depending on the sensitivity of the emission lines to be measured). Also prepare a calibration blank solution. During preparation of calibration solutions, add reagents (for example, acids), as required, to matrix-match the calibration solutions with the test solutions.

12.1.3.2 Store working standard solutions in suitable containers, such as 1-L polypropylene bottles, for a maximum period of one month.

NOTE 2—The shelf life of stock standard and working standard solutions may be extended if they are demonstrated, by comparison with calibration verification solutions, to be acceptable.

NOTE 3—The type(s) and volume(s) of reagents required to matrix match the calibration and test solutions will depend on the sample dissolution method used.

12.2 *Internal Standard Stock Solutions*—If required, use standard stock solutions to prepare test solutions that contain the internal standard element(s). The internal standard element(s) shall be compatible with the test solution matrix, and the matrix of the internal standard stock solution shall be compatible with the analyte metals and metalloids of interest. Observe the manufacturer's expiration date or recommended shelf life.

NOTE 4—Internal standard solutions may be used to correct for instrument drift and physical interferences. Internal standard solutions are usually single-element standard stock solutions, which are commercially available or can be prepared from high-purity metals and metalloids or their salts.

NOTE 5—Internal standards, if utilized, should be added to blanks, samples, and standards in a like manner. Internal standards may be added to each test solution during the sample preparation process or, alternatively, by use of an on-line internal standard addition system.

12.2.1 *Interference Check Solutions*—If interelement correction is to be carried out, use a stock standard solution to prepare an interference check solution by serial dilution for each interferent to attain a suitable concentration (for example, between 50 and 200 mg/L). If appropriate, matrix match the interference check solutions and test solutions. Store interference check solutions in suitable containers, such as 1-L polypropylene bottles, for a maximum period of one month.

12.3 The run order of standards and client samples per matrix of interest is shown as Table 1. Frequency and acceptance limits for standards are also shown.

13. Procedure

13.1 *Method Optimization:*

13.1.1 *General Guidance*—Optimize the test method and validate the performance of the method for analysis of test solutions in accordance with the performance criteria provided in this test method, or specified customer requirements, or both, using sample solutions prepared as described in Section ~~10~~11 of this test method, which is suitable for use with the available ICP-OES

TABLE 1 ICP-OES Run Order with Frequency and Acceptance Limits for Standards

Name	Use	Specification
Calibration Standards	Instrument calibration	Must be matrix matched to digestates/extracts. Must be measured prior to measuring any sample digestates or extracts. Correlation coefficient of ≥0.995, as measured using linear regression on instrument response versus concentration. Must include a blank solution.
Independent Calibration Verification (ICV)	Once per day after calibration	Mid-range calibration standard must be measured after calibration; measured value within ±10 % of known value.
Initial Calibration Blank (ICB)	Once per run at the beginning of the run	Absolute value not more than 50 % of the lowest regulatory limit for the sample matrix analyzed or minimum level of concern.
Interference Check Sample (ICS)	At the beginning and end of each run or twice every 12 h	Within 20 % of known value.
Sample Analysis	N/A	Samples exceeding the calibration range should be diluted and rerun.
Continuing Calibration Verification (CCV)	At the end of a sample run, as well as every 12 h, or according to instrument manufacturer's recommendations, or according to instrument Performance Characteristic Sheet (PCS), or at a predetermined Standard Operating Procedure (SOP) frequency, whichever is most frequent.	Within ±20 % of known value.
Continuing Calibration Blank (CCB)	After each ICS and CCV	Absolute value not more than 50 % of the lowest regulatory limit for the sample matrix analyzed or minimum level of concern.

instrument(s). Use the default instrument conditions given by the manufacturer as a starting point in the method development process. Refer to guidance on ICP-OES method development available in textbooks, instrument manuals, and standards.

NOTE 6—ICP-OES analysis applies to a wide range of instruments, for example, simultaneous or sequential instruments with photomultiplier or solid state detection systems. Each of these different types of instruments needs to be set up and operated in a different manner. There are some principles that apply to the development of method for all instruments, but there are also many parameters that are only applicable to particular instruments or types of instruments.

13.1.2 *Quantitation Limit*—An instrumental measurement value that is used to provide a lower concentration limit for reporting quantitative analysis data for a given analytical method.

NOTE 7—Any sample that generates a lead measurement below the quantitation limit is reported as a less-than value using the quantitation limit value multiplied by the appropriate dilution factors resulting from preparation of the sample for instrumental analysis.

13.1.3 *Spectral Interferences*—Give consideration to the significance of any known spectral interferences in the context of the measurement task. For each potentially useful analytical wavelength, refer to published information, and consider the relationship between the magnitude of interferences and the relative exposure limits of the interferents and elements to be determined. For example, if the measurement task entails testing compliance with exposure limit values, an interferent present at 10× its limit value will cause a positive bias of >10 % if:

$$[10 \times (LV_a / LV_i) \times (\rho_a / 1000)] > 0.1 \quad (1)$$

where:

LV_a = limit value, in mg/m^3, of the analyte,
LV_i = limit value, in mg/m^3, of the interferent, and
ρ_a = apparent analyte concentration, in mg/L, caused by an interferent concentration of 1000 mg/L.

If the sum of all potential interferences is greater than 0.1× the limit value of the analyte when each of the interferents is present at 10× its limit value, use an alternative analytical wavelength or apply interelement corrections.

NOTE 8—Interelement correction is not normally necessary for measurements made to test compliance with limit values. It is best avoided, if possible, by selecting an alternative analytical wavelength that is free from or less prone to interference. Also, for some measurement tasks, there might be a need to obtain quantitative measurements at concentrations below 0.1× the limit value.

13.1.4 *Axial or Radial Viewing of the Plasma*—If an instrument with an axial ICP torch and an instrument with a radial ICP torch are both available (or if a dual-view instrument is available), decide which orientation is best suited to the measurement task. It might be that it is best to use an axial plasma to make measurements at some analytical wavelengths, while a radial plasma may be better suited for measurements at other wavelengths.

NOTE 9—Axial viewing of the plasma might be necessary to obtain the necessary quantification limits, but it is more susceptible than radial viewing to spectral interferences.

13.1.5 *Sample Introduction System*—Decide on the type of sample introduction system to use. Take into consideration the required sensitivity and the nature of the test solution matrix. In most cases, the system supplied by the instrument manufacturer will be adequate.

NOTE 10—Ultrasonic nebulizers give higher sensitivity than conventional pneumatic nebulizers. However, they are less corrosion-resistant. For instance, if test solutions contain hydrofluoric acid, it will be necessary to use a corrosion-resistant sample introduction system.

13.1.6 *Analytical Wavelengths*—Select one or more emission lines on which to make measurements for lead, utilizing wavelength tables available in the literature (**2**). Take into consideration the wavelengths that are accessible on the instrument and recommended by the instrument manufacturer. Also take into consideration the background equivalent concentrations, the required quantitation limits, and spectral interferences that could be significant at each wavelength. Ordinarily the more sensitive emission lines will be most favorable, but it is necessary to avoid the use of wavelengths where there is spectral overlap or significant background interference.

NOTE 11—Scanning, sequential, monochromator-based instruments enable measurements over the entire ultraviolet/visible spectrum. Grating instruments and instruments with solid state detectors also allow for a wide spectral range. However, simultaneous, conventional polychromator-based instruments

are more limited in that users can only select from the analytical lines that are available given a particular instrument configuration. If available, it is advisable to use more than one emission line for lead to check for any problems not identified during method development.

13.1.7 *Background Correction*—Generate a spectral scan for each of the candidate analytical wavelengths while analyzing (*1*) a blank solution, (*2*) a calibration solution, and (*3*) a typical test solution into the plasma. Examine the line profiles and select points at which to make background correction measurements. Where applicable, make measurements at a single point to correct for a simple background shift, that is, a shift in background intensity that is essentially constant over a given range (for example, 0.5 nm) on either side of the analyte emission line. Alternatively, for a sloping background, make measurements at two points to correct for the non-constant background shift. Many software packages for ICP-OES instruments have automatic background correction with varying algorithms.

NOTE 12—Different instrument types use different means of making off-peak background correction measurements. In some instruments (such as those using monochromators or polychromators), the analyte intensity is measured first, and then separate measurements are made at the wavelengths used for background correction. However, grating instruments with solid-state detectors measure analyte and background signals simultaneously. Measurements employing simultaneous background correction reduce noise due to sample introduction, and they are fast since no additional analysis time is required to make off-peak measurements.

NOTE 13—Some ICP-OES software features the use of chemometrics to automatically select parameters such as background correction points. Also, software can be used to perform intelligent optimization studies with minimal user interaction.

13.1.8 *Interelement Correction*—If the only analytical wavelength(s) chosen suffer(s) from spectral overlap or complex background shift, consider the need to apply interelement correction. If this is necessary, generate and apply interelement correction factors. Alternatively, if the necessary software is available, use a chemometric technique (such as multicomponent spectral fitting) to perform interelement correction.

NOTE 14—Interelement correction factors can be generated from the apparent analyte concentrations obtained by analyzing individual, spectrally pure test solutions containing high concentrations (for example, 1000 mg/L) of interfering elements. Alternatively, if calibration solutions contain varied concentrations of the analyte and interfering element(s), data handling software of some instruments may be used to calculate and apply interference corrections automatically.

13.1.9 *Plasma Conditions:*

13.1.9.1 *Gas Flows*—Under normal conditions, use the default gas flows recommended by the instrument manufacturer for inner, intermediate, and outer argon flows. However, if desired, the nebulizer (inner) argon flow may be optimized for specific applications. The nebulizer argon flow can be critical because it largely determines the residence time of the analyte in the plasma. The longer the residence time, the greater the likelihood of the analyte to be atomized, excited, and ionized.

NOTE 15—For an element that emits strong ionic lines and has a high ionization potential, a long residence time is desired. Hence a lower nebulizer argon flow rate could be used to obtain higher sensitivity for such an element (provided that the nebulizer efficiency does not fall off significantly when the flow rate is reduced). On the other hand, for elements that emit strong atomic lines and are easily ionized, a faster flow rate could be used so that the atoms are not ionized before excitation takes place.

13.1.9.2 *Radiofrequency (RF) Power*—Under normal circumstances, use the default RF power recommended by the instrument manufacturer. However, the RF power may be optimized for specific applications.

NOTE 16—The RF power applied to the plasma can be optimized in accordance with need. The more RF power that is applied to the plasma, the hotter it gets.

13.1.9.3 *Viewing Height (Radial Plasma)*—Under normal circumstances, use the default viewing height setting recommended by the instrument manufacturer. However, the viewing height may be optimized for specific applications.

NOTE 17—The viewing height can be optimized for a selected analyte line or lines. This is because different regions of the plasma are characterized by different temperatures, and each analytical wavelength has an optimum temperature at which its emission line is most intense.

13.1.10 *Instrument Operating Parameters*—Refer to the instrument manufacturer's instructions and determine the optimum settings for other relevant instrument operating parameters (for example, detector power, integration time, number of integrations, and so forth).

13.1.11 *Sample Introduction Rate*—Under normal circumstances, use the sample uptake rate recommended by the nebulizer manufacturer. However, the uptake rate may be optimized to achieve a suitable compromise between signal intensity and uptake rate

13.1.12 *Sample Wash-Out Parameters*—Use a suitable wash-out solution, wash-out time, wash-out rate, and read delay. Conduct tests to ensure that there is no significant carryover of analyte between measurements.

13.1.13 *Calibration Solutions:*

13.1.13.1 *Matrix Matching*—Unless an internal standard is used, match the matrix of the calibration solutions with that of the test solutions.

NOTE 18—Even if an internal standard is used, it is recommended that matrix matching is also carried out. In general, it is preferable to match the matrix of the calibration and test solutions, rather than rely on the use of internal standards to correct for transport and excitation interferences.

13.1.13.2 *Calibration Range*—Carry out experiments to determine the linear dynamic range for each of the selected analytical wavelengths under the intended operating conditions. Then select a range of analyte concentrations over which to prepare the calibration solutions.

NOTE 19—If more than one analytical wavelength is to be used, this will need to be taken into consideration when selecting the range of concentrations to be covered.

13.1.14 *Internal Standards*—Decide whether to use (an) internal standard(s) to correct for non-spectral interferences or to improve precision. Carefully select internal standard emission lines to ensure that they are suitable for the intended purpose, and exhibit adequate sensitivity. Ensure that internal standard elements are not present in the test solutions, and also ensure that the standard solutions for addition of internal standards are chemically compatible with the test solution matrix (that is, they must not cause precipitation).

NOTE 20—A single internal standard may be used to correct for transport interferences that arise from a matrix mismatch between the calibration and test solutions, and for changes in nebulizer efficiency that can occur during analysis. Internal standards may also be used to correct for excitation interferences that arise from a matrix mismatch between the calibration and test solutions and for changes in plasma conditions that can occur during analysis as a result of fluctuations in power or gas flows, or both. Multiple internal standards need to be used, and the wavelengths at which they are measured need to be carefully selected, so that the characteristics of the analyte emission lines closely match those of the internal standard emission lines. Use of internal standards can also improve analytical precision for simultaneous instruments by reducing the effect of noise associated with sample introduction.

13.2 *Instrument Performance Checks:*

13.2.1 *Visual Inspection*—The user shall perform regular visual checks to ensure that the instrument and ancillaries are in good order before commencing work. Follow the instrument manufacturer's recommendations. Further guidance is given in Appendix X1.

13.2.2 *Performance Checks and Fault Diagnostics*—The user shall carry out performance checks daily to verify that the ICP-OES instrument is operating in accordance with specifications. More rigorous fault diagnostics shall be used if it is suspected that the instrument is not functioning properly. Follow the instrument manufacturer's recommendations. Further guidance is given in Appendix X2.

NOTE 21—A comprehensive series of performance checks has been described in the literature (**3**), and this can be used to supplement performance checks and fault diagnostics recommended by the instrument manufacturer.

13.3 *Routine Analysis:*

13.3.1 *Dilution of Sample Solutions*—Perform any required dilution of sample solutions prior to addition of internal standards.

13.3.2 *Addition of Internal Standards*—If using (an) internal standard(s), add the same concentration to all solutions to be measured (that is, calibration solutions, blank solutions, test solutions, interference check solutions, and quality control sample solutions).