Designation: D7035 – 21

Standard Test Method for Determination of Metals and Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)[1]

This standard is issued under the fixed designation D7035; 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 collection, sample preparation, and analysis of airborne particulate matter for the content of metals and metalloids using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The method is generally applicable to occupational exposure monitoring.

1.2 This test method is applicable to personal sampling of the inhalable or respirable fraction of airborne particles and to area sampling.

1.3 This test method should be used by analysts experienced in the use of ICP-AES, the interpretation of spectral and matrix interferences, and procedures for their correction.

1.4 This test method specifies a number of alternative methods for preparing test solutions from samples of airborne particulate matter. One of the specified sample preparation methods is applicable to the measurement of soluble metal or metalloid compounds. Other specified methods are applicable to the measurement of total metals and metalloids.

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

1.6 The following is a non-exclusive list of metals and metalloids for which one or more of the sample dissolution methods specified in this document is applicable. However, there is insufficient information available on the effectiveness of dissolution methods for those elements in italics.

Aluminum	*Indium*	Sodium
Antimony	Iron	Strontium
Arsenic	Lead	*Tantalum*
Barium	Lithium	Tellurium
Beryllium	Magnesium	Thallium
Bismuth	Manganese	Tin
Boron	Molybdenum	Titanium
Cadmium	Nickel	Tungsten
Calcium	Phosphorus	*Uranium*
Cesium	Platinum	Vanadium
Chromium	Potassium	Yttrium
Cobalt	*Rhodium*	Zinc
Copper	Selenium	Zirconium
Hafnium	Silver	

1.7 This test method is not applicable to the sampling of elemental mercury, or to inorganic compounds of metals and metalloids that are present in the gaseous or vapor state.

1.8 No detailed operating instructions are provided because of differences among various makes and models of suitable ICP-AES 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.

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

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

1.11 *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.*

1.12 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.

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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.

D1356 Terminology Relating to Sampling and Analysis of Atmospheres
D4185 Test Method for Measurement of Metals in Workplace Atmospheres by Flame Atomic Absorption Spectrophotometry
D4840 Guide for Sample Chain-of-Custody Procedures
D5337 Practice for Flow Rate Adjustment of Personal Sampling Pumps
D6062 Guide for Personal Samplers of Health-Related Aerosol Fractions
D6785 Test Method for Determination of Lead in Workplace Air Using Flame or Graphite Furnace Atomic Absorption Spectrometry
D7202 Test Method for Determination of Beryllium in the Workplace by Extraction and Optical Fluorescence Detection
D7439 Test Method for Determination of Elements in Airborne Particulate Matter by Inductively Coupled Plasma–Mass Spectrometry
D7440 Practice for Characterizing Uncertainty in Air Quality Measurements
D8344 Practice for Ammonium Bifluoride and Nitric Acid Digestion of Airborne Dust and Dust-Wipe Samples for the Determination of Metals and Metalloids
D8358 Guide for Assessment and Inclusion of Wall Deposits in the Analysis of Single-Stage Samplers for Airborne Particulate Matter
E288 Specification for Laboratory Glass Volumetric Flasks
E438 Specification for Glasses in Laboratory Apparatus
E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
E1154 Specification for Piston or Plunger Operated Volumetric Apparatus
E1370 Guide for Air Sampling Strategies for Worker and Workplace Protection
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]
E1728 Practice for Collection of Settled Dust Samples Using Wipe Sampling Methods for Subsequent Lead Determination
E3203 Test Method for Determination of Lead in Dried Paint, Soil, and Wipe Samples by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

2.2 *ISO Standards:*[4]

ISO 4225 Air quality — General aspects
ISO 7708 Particle size definitions for health-related sampling
ISO 15202 Workplace air — Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry (3 parts)
ISO 18158 Workplace atmospheres — Terminology
ISO 20581 Workplace atmospheres — General requirements for the performance of procedures for the measurement of chemical agents

3. Terminology

3.1 *Definitions*—For definitions of pertinent terms not listed here, see Terminology D1356.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *atomic emission*—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 3.2.31).

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. **E3203**

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 a 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 *chemical agent, n*—any chemical element or compound, on its own or admixed as it occurs in the natural state or as produced, used or released, including release as waste, by any work activity, whether or not produced intentionally and whether or not placed on the market. **ISO 4225**

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

3.2.10.1 *Discussion*—The measured concentration of the CCB is to be (at most) less than five times the instrumental detection limit.

3.2.11 *excitation interferences, n*—non-spectral interferences that manifest as a change in sensitivity due to a change

[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.

in inductively coupled plasma conditions when the matrix of a calibration or test solution is introduced into the plasma. **ISO 15202**

3.2.12 *field blank, n*—sampling media (for example, an air filter) that is exposed to the same handling as field samples, except that no sample is collected (that is, no air is purposely drawn through the sampler). **D6785**

3.2.12.1 *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.

3.2.13 *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**

3.2.14 *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**

3.2.15 *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**

3.2.16 *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; typically 0.5 L/min – 2 L/min. **ISO 15202**

3.2.17 *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**

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

3.2.18 *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**

3.2.19 *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; typically 0.1 L/min – 2 L/min. **ISO 15202**

3.2.20 *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**

3.2.21 *limit value, n*—reference figure for concentration of a chemical agent in air. **ISO 15202**

3.2.22 *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**

3.2.23 *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**

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

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

3.2.24.1 *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**

3.2.25 *measuring procedure, n*—procedure for sampling and analyzing one or more chemical agents in the air, including storage and transportation of the sample(s). **ISO 15202**

3.2.26 *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**).[5]

3.2.26.1 *Discussion*—The MQL is also known as the limit of quantitation.

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

3.2.28 *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; typically 7 to 15 L/min. **ISO 15202**

3.2.29 *personal sampler, n*—a device attached to a person that samples air in the breathing zone. **ISO 18158**

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

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

3.2.32 *respirable fraction, n*—the mass of inhaled particles penetrating to the unciliated airways. **ISO 7708**

3.2.33 *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**

3.2.34 *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. **ISO 15202**

3.2.35 *sampling location, n*—a specific area within a sampling site that is subjected to sample collection. **E1728**

3.2.35.1 *Discussion*—Multiple sampling locations are commonly designated for a single sampling site.

3.2.36 *sampling site, n*—a local geographic area that contains the sampling locations. **E1728**

3.2.36.1 *Discussion*—A sampling site is generally limited to an area that is easily covered by walking.

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

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

3.2.38 *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**

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

3.2.40 *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**

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

3.2.41 *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**

3.2.42 *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**

3.2.43 *workplace, n*—the defined area or areas in which the work activities are carried out. **ISO 18158**

3.2.44 *x-y centering (for an axial plasma), n*—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 A known volume of air is drawn through a sampler containing a sampling substrate (such as a filter, foam, or filter capsule) to collect airborne particles suspected to contain metals or metalloids, or both. The sampling device (sampler) is ordinarily designed to collect the inhalable fraction of airborne particles; however, sampling of the respirable fraction (or other) is also possible (see Guide D6062; ISO 7708).

4.2 The filter (or filter capsule) and collected sample are subjected to a dissolution procedure in order to extract target elemental analytes of interest. The sample dissolution procedure may consist of one or two methodologies: one for soluble or one for total metals and metalloids, or both. Candidate procedures, based on hot plate, hot block, or microwave digestion, are used for dissolution of filter samples for subsequent determination of 'total' or 'soluble' inhalable (or respirable) metals and metalloids.

4.3 In general, particulate metals and metalloids (and their compounds) that are commonly of interest in samples of workplace air are converted to water- or acid-soluble ions in sample solutions by one or more of the sample dissolution methods specified.

4.4 Test solutions prepared from the sample solutions after sample dissolution are analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES) to determine the concentration of target elements in the sampled air.

NOTE 1—The sampling and sample preparation procedures described in this standard may be suitable for preparation of samples for subsequent analysis by other methods besides ICP-AES (for example: flame atomic absorption spectrometry (see Practice D4185), graphite furnace atomic absorption spectrometry, inductively coupled plasma – mass spectrometry (ICP-MS); see Test Method D7439), electroanalysis, and so forth).

5. Significance and Use

5.1 The health of workers in many industries is at risk through exposure by inhalation to toxic metals and metalloids. Industrial hygienists and other public health professionals need to determine the effectiveness of measures taken to control workers' exposures, and this is generally achieved by making workplace air measurements. This test method has been promulgated in order to make available a standard methodology for making valid exposure measurements for a wide range of metals and metalloids that are used in industry. It will be of benefit to agencies concerned with health and safety at work; industrial hygienists and other public health professionals; analytical laboratories; industrial users of metals and metalloids and their workers, and other groups.

5.2 This test method specifies a generic method for determination of the mass concentration of metals and metalloids in workplace air using ICP-AES.

5.3 The analysis results can be used for the assessment of workplace exposures to metals and metalloids in workplace air.

5.4 When sampling and analysis is carried out in accordance with this test method, the overall procedure normally satisfies the performance requirements of ISO 20581.

NOTE 2—Refer to Guide E1370 for guidance on the development of appropriate exposure assessment and measurement strategies.

6. Sampling Apparatus and Materials

6.1 *Sampling Equipment:*

6.1.1 *Inhalable Samplers,* designed to collect the inhalable fraction of airborne particles (see Guide D6062), for use when the exposure limits for metals and metalloids of interest apply to the inhalable fraction.

NOTE 3—In general, personal samplers for collection of airborne particles do not exhibit the same size-selective characteristics if used for area sampling.

NOTE 4—Some inhalable samplers are designed to collect the inhalable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler (separate from the filter) is not considered part of the sampled air. Other inhalable samplers are designed such that all airborne particles which pass through the entry orifice(s) are of interest, hence particulate matter deposited on the inner walls of the sampler does form part of the sample. In such cases it will be necessary to account for particulate material collected on the inner walls of the sampler (in addition to that collected on the filter). Refer to Guide D8358 for additional information.

6.1.2 *Respirable Samplers,* designed to collect the respirable fraction of airborne particles (see Guide D6062), for use

when the exposure limits for the metals and metalloids of interest apply to the respirable fraction.

NOTE 5—Cyclone-type samplers are typically used for personal sampling, while cascade impactors are often used to characterize the particle size distribution in area sampling.

NOTE 6—In lieu of inhalable and respirable samplers, multi-fraction samplers, where applicable, may be used to collect airborne particles of alternative size distributions (see Guide D6062).

NOTE 7—Some respirable samplers are designed to collect the respirable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler (separate from the filter) is not considered part of the sampled air. Other respirable samplers are designed such that all airborne particles which pass through the entry orifice(s) are of interest, hence particulate matter deposited on the inner walls of the sampler does form part of the sample. In such cases it will be necessary to account for particulate material collected on the inner walls of the sampler (in addition to that collected on the filter). Refer to Guide D8358 for additional information.

6.1.3 *Filters or Filter Capsules,* of a diameter suitable for use with the samplers, and a collection efficiency of not less than 99 % for particles with a 0.3 µm diffusion diameter (see ISO 7708). The filters (or filter capsules) shall have a very low background metal content (typically less than 0.1 µg of each metal or metalloid of interest per filter), and they should be compatible with the anticipated sample preparation method. See Appendix X1 for guidance on filter selection.

NOTE 8—Filters of diameter 25 mm or 37 mm are commonly used for sampling airborne particles in workplaces.

6.1.4 *Sampling Pumps,* with an adjustable flow rate, portable. Pumps shall be capable of maintaining the selected flow rate between 1 L/min and 5 L/min for personal or area sampling, and to within ±5 % of the nominal value throughout the sampling period. For personal sampling, the pumps shall be battery-powered, and they shall be capable of being worn by the worker without impeding normal work activity.

6.1.5 *Flow Meter,* portable, with an accuracy that is sufficient to enable the volumetric flow rate to be measured to within ±2 %. The calibration of the flow meter shall be checked against a primary standard, that is, a flow meter whose accuracy is traceable to national standards.

6.1.6 *Flexible Tubing,* of a diameter suitable for making a leak-proof connection from the sampling pumps to the samplers.

6.1.7 *Belts or Harnesses,* to which sampling pumps can conveniently be fixed for personal sampling (except where the pumps are small enough to fit in workers' pockets).

6.1.8 *Clips,* for attaching samplers to the workers' clothing within the breathing zone.

6.1.9 *Flat-tipped Forceps,* for loading and unloading filters into samplers.

6.1.10 *Filter Transport Cassettes,* or similar (if required), in which to transport samples to the laboratory.

6.1.11 *Watch or Clock,* for use in recording of starting and ending times of sampling periods.

7. Sampling Procedure

7.1 *Sampling Period:*

7.1.1 Select a sampling period that is appropriate for the measurement task, but ensure that it is long enough to enable the metals and metalloids of interest to be determined with acceptable overall uncertainty at levels of industrial hygiene significance.

7.1.1.1 For metals and metalloids with short-term exposure limits, the sampling time shall be as close as possible to the reference period, which is typically 15 minutes (minimum 5 minutes, maximum 30 minutes).

7.1.1.2 For metals and metalloids with long-term exposure limits, samples shall be collected for the entire working period, if possible; otherwise, obtain consecutive samples during a number of representative work episodes. The sampling time shall be as close as possible to the reference period, which is typically 8 hours (minimum 7 hours, maximum 10 hours).

7.2 *Preparation for Sampling:*

7.2.1 *Handling of Filters*—To minimize the risk of damage or contamination, handle filters only with clean flat-tipped forceps, and in a clean, uncontaminated area free from high concentrations of air particles.

7.2.2 *Cleaning of Samplers*—Unless disposable filter cassettes are used, clean the samplers before use. Disassemble the samplers (if necessary), soak in detergent solution, rinse thoroughly with water, wipe with absorptive tissue, and allow to dry before (re)assembly.

NOTE 9—A laboratory washing machine may be used for cleaning of samplers.

7.2.3 *Loading Filters (or Filter Capsules) into Samplers*—Load clean samplers with unused, clean filters (or filter capsules), seal each sampler with its protective cover or plug (to prevent contamination), and label each sampler so that it can be uniquely identified.

7.2.4 *Setting the Flow Rate*—In a clean area, where the concentration of air particles is low, connect each loaded sampler to a sampling pump, ensuring no leakage. Remove the protective cover or plug from each sampler, and switch on the sampling pump. If necessary, allow the sampling pump operating conditions to stabilize. Attach the flow meter to the sampler so that it measures the flow through the inlet orifice of the sampler, and set the required volumetric flow rate between 1 and 5 L/min. Ensure that the flow rate is adjusted in accordance with Practice D5337. Switch off the sampling pump and seal the sampler with its protective cover or plug (to prevent contamination during transport to the sampling location).

NOTE 10—Higher-flow samplers (to >10 L/min) are available for use in special cases.

7.2.5 *Field Blanks*—Retain as blanks, at least one unused loaded sampler from each batch of twenty prepared (that is, a minimum frequency of 5 %). The minimum number of field blanks to collect for each batch of samples used is three. Treat these in the same manner as those used for sampling (with respect to storage and transport to and from the sampling location), but draw no air through the filters (or filter capsules). Label these samples in the same fashion as the collected samples.

7.3 *Sampling Position:*

7.3.1 *Personal Sampling*—The sampler shall be positioned in the worker's breathing zone, as close to the mouth and nose

as is reasonably practicable, for instance, fastened to the worker's lapel or shirt collar. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, for example, to a belt around the waist.

7.3.2 *Area Sampling*—The sampler shall be positioned either: *(1)* in a position that is sufficiently remote from the work processes, in order to characterize the background level(s) of metals and metalloids in the workplace; or *(2)* in a position that is near a suspected source of workplace air contamination, in order to assess whether high levels of metals and metalloids are generated by the work activity.

7.4 *Collection of Samples:*

7.4.1 When ready to begin sampling, remove the protective cover or plug from the sampler, and switch on the sampling pump. Record the time and flow rate at the start of the sampling period.

7.4.2 For long-term sampling, periodically (ordinarily a minimum of every 2 hours) check the flow rate of the sampling pump (using the flow meter), and also check the sampler for overloading. If the flow rate has changed significantly (±5 %), consider the sample to be invalid. If the sampler shows evidence of overloading (for example, as evidenced by excess dust loading within the sampler), replace it with a new sampler (that is, take consecutive samples (see Guide E1370)).

NOTE 11—Owing to greater sampling capacity, filter capsules are useful for sampling in high-dust environments.

7.4.3 At the end of the sampling period, record the time and determine the duration of the sampling period. Measure the flow rate at the end of the sampling period using the flow meter, and record the measured value. Consider the sample to be invalid if there is evidence that the sampling pump was not operating properly throughout the sampling period.

7.4.4 Record the sample identity and all relevant sampling data (such as work activity, sampling period, sampling location(s), mean flow rate, volume of air sampled). Calculate the mean flow rate by averaging the flow rates at the start and at the end of the sampling period. Calculate the volume of air sampled, in litres, by multiplying the mean flow rate (in litres per minute) by the duration of the sampling period (in minutes).

7.5 *Transportation:*

7.5.1 For reusable samplers that collect airborne particles on the filter (or filter capsules), remove the filter (or filter capsule) from each sampler (with clean flat-tipped forceps), place in a labeled filter transport cassette, and enclose. Take particular care to prevent the collected sample from becoming dislodged from heavily loaded filters (unless filter capsules are used). Alternatively, transport samples to the laboratory within the samplers in which they were collected.

7.5.2 For samplers that have an internal filter cassette, remove the cassette from each sampler and fasten with its lid or transport clip, and transport the sample cassettes to the laboratory.

7.5.3 For samplers of the disposable cassette type, transport samples to the laboratory within the samplers in which they were collected.

7.5.4 Transport the samples to the laboratory in a container that has been designed to prevent damage to the samples in transit, and which has been labeled to ensure proper handling.

7.5.5 *Chain of Custody*—Follow sampling chain of custody procedures to ensure sample traceability. Ensure that the documentation which accompanies the samples is suitable for a chain of custody to be established in accordance with Guide D4840.

8. Hazards

8.1 *Concentrated nitric acid* is corrosive and oxidizing, and nitric acid vapor is an irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Use suitable personal protective equipment (including impermeable gloves, safety goggles, laboratory coat, and so forth) when working with concentrated nitric acid, and carry out open-vessel sample dissolution with nitric acid in a fume hood.

8.2 *Concentrated perchloric acid* is corrosive and oxidizing, and its vapor is an irritant. Perchloric acid forms explosive compounds with organics and many metal salts. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Use suitable personal protective equipment (including impermeable gloves, safety goggles, laboratory coat, and so forth) when working with perchloric acid. Carry out sample dissolution with perchloric acid in a fume hood with a scrubber unit that is specially designed for use with $HClO_4$. See Appendix X2 for further pertinent safety information.

8.3 *Concentrated hydrofluoric acid* is highly corrosive, and is very toxic by inhalation or contact with the skin. Avoid exposure by contact with the skin or eyes, or by inhalation of HF vapor. It is essential to use suitable personal protective equipment, including impermeable gloves and eye protection) when working with HF. Use a fume hood when working with concentrated HF and when carrying out open-vessel dissolution with HF. See Appendix X2 for further pertinent safety information.

8.4 *Concentrated hydrochloric acid* is corrosive, and HCl vapor is an irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of the vapor. Use suitable personal protective equipment (such as gloves, face shield, and so forth) when working with HCl. Handle open vessels containing concentrated HCl in a fume hood. The vapor pressure of HCl is high, so beware of pressure buildup in stoppered flasks when preparing mixtures containing HCl.

8.5 *Concentrated sulfuric acid* is corrosive and causes burns. Vapor produced when concentrated H_2SO_4 is heated is an irritant. Avoid exposure by contact with the skin or eyes. Use suitable personal protective equipment (such as gloves, face shield, and so forth) when working with H_2SO_4. Carry out sample dissolution with H_2SO_4 in a fume hood. Exercise caution when diluting H_2SO_4 with water, as this process is very exothermic. Do not add water to H_2SO_4, since it reacts violently when mixed in this manner; rather, prepare H_2SO_4/H_2O mixtures by adding H_2SO_4 to water.

9. Sample Preparation

9.1 *Reagents for Sample Preparation*—Details regarding reagents that are required for individual sample dissolution

methods are given in Annex A1 through Annex A5. During sample preparation, use only reagents of spectroscopic grade or better.

9.1.1 *Water,* complying with the requirements for ASTM Type II water (see Specification D1193). It is recommended that the water used be obtained from a water purification system that delivers ultra-pure water having a resistivity greater than 18 MΩ-cm at 25°C.

9.1.2 *Nitric Acid* (HNO_3), concentrated, ρ ~1.42 g/mL (~70 % m/m). The concentration of metals and metalloids of interest shall be less than 0.1 µg/mL.

NOTE 12—It will be necessary to use reagents of higher purity in order to obtain adequate detection limits for some metals and metalloids, (for example, beryllium).

9.1.3 *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.

9.1.4 *Laboratory Detergent,* suitable for cleaning of samplers and laboratory ware.

9.2 *Laboratory Apparatus for Sample Preparation*—Details regarding laboratory apparatus required for individual sample dissolution methods are given in Annex A1 through Annex A5. Ordinary laboratory apparatus are not listed, but are assumed to be present.

9.2.1 *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.

9.2.2 *Glassware,* beakers and volumetric flasks complying with the requirements of Specification E288, made of borosilicate glass and complying with the requirements of Specification E438. Glassware shall be cleaned before use by soaking in 1+1 nitric acid: water for at least 4 hours and then rinsing thoroughly (at least 3 times) with ASTM Type 1 water, and allowed to dry. Alternatively, before use, glassware shall be cleaned by using commercial, automatic laboratory washing equipment that performs a similar process.

9.2.3 *Flat-Tipped Forceps,* polytetrafluoroethylene (PTFE)-tipped, for unloading filters from samplers or from filter transport cassettes.

9.2.4 *Piston-Operated Volumetric Pipettors and Dispensers,* complying with the requirements of Specification E1154, for pipetting and dispensing of leach solutions, acids, and so forth.

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

9.3 *Sample Preparation Procedures:*

NOTE 13—The sample dissolution methods described in Annex A1 through Annex A5 are generally suitable for use with analytical techniques other than ICP-AES, for example, atomic absorption spectrometry (AAS), and ICP-mass spectrometry (ICP-MS).

9.3.1 *Soluble Metal and Metalloid Compounds:*

9.3.1.1 If results are required for soluble metal, or metalloid compounds, or both, use the sample dissolution method specified in Annex A1 to prepare sample solutions from which test solutions are prepared for analysis by ICP-AES.

9.3.1.2 Alternatively, if it is known that no insoluble compounds of the metals, or metalloids, or both, of interest are used in the workplace, and that none are produced in the processes carried out, prepare test solutions for ICP-AES analysis using one of the sample dissolution methods for total metals and metalloids and their compounds, as prescribed in Annex A2 (hot plate digestion), Annex A3 or Annex A5 (microwave digestion), and Annex A4 (hot block digestion).

NOTE 14—The methods prescribed in Annex A2 through Annex A4 are not specific for soluble metal, or metalloid compounds, or both. However, in these circumstances, they may be used as an alternative to the method described in Annex A1, if this is more convenient.

9.3.2 *Total Metals and Metalloids and their Compounds:*

9.3.2.1 If results are required for total metals, or metalloids, or both, and their compounds, select a suitable sample preparation method from those specified in Annex A2 (hot plate digestion), Annex A3 or Annex A5 (microwave digestion), or Annex A4 (hot block digestion). Practice D8344 may also be suitable. Take into consideration the applicability of each method for dissolution of target metals and metalloids of interest from materials that could be present in the test atmosphere (refer to the clause on the effectiveness of the sample dissolution method in the annex in which the method is specified), and the availability of the required laboratory apparatus.

NOTE 15—In selection of a sample preparation method, consideration should be given to the metal or metalloid compounds that may be present in the test atmosphere. Some compounds, such as refractory metal oxides, may require a more robust sample preparation method than is required for other compounds, or for the metals or metalloids themselves.

9.3.2.2 Use the selected sample dissolution method to prepare, from which test solutions are prepared, sample solutions for analysis of total metals and metalloids and their compounds by ICP-AES.

9.3.3 *Deposits of Particles on Interior Sampler Surfaces*—Give consideration to metal and metalloid particles that may have deposited on interior sampler surfaces (for example, by becoming dislodged from the filter during transportation), and determine whether the sample of interest should include such particles. If the sample is determined to include such particles, determine a methodology for removing them from the interior sampler surfaces and including them in the analysis. Guide D8358 provides additional information and suggested methodologies.

NOTE 16—The use of filter capsules (in lieu of filters) alleviates this potential problem (**2**).

9.3.4 *Mixed Exposures:*

9.3.4.1 If analytical results are required for both soluble and insoluble metals, or metalloids, or both, and their compounds, first use the sample preparation procedure specified in Annex A1 to prepare sample solutions, from which test solutions are prepared, for determination of soluble metal and metalloid compounds for subsequent analysis by ICP-AES.

9.3.4.2 Select a suitable sample dissolution method for total metals and metalloids and their compounds (specified in Annex A2 for hot plate digestion, Annex A3 or Annex A5 for microwave digestion, or Annex A4 for hot block digestion). Use this procedure to treat undissolved material left over after employing the preparation method for soluble metals and metalloids and their compounds (Annex A1), and prepare

sample solutions, from which test solutions are prepared, for subsequent analysis by ICP-AES.

9.4 *Special Cases:*

9.4.1 *Effectiveness of Sample Dissolution Procedure*—If there is any doubt about whether the selected sample preparation method will exhibit the required analytical recovery when used for dissolution of the metals and metalloids of interest from materials that could be present in the test atmosphere, determine its effectiveness for the particular application.

9.4.1.1 For total metals and metalloids, analytical recovery may be estimated by analyzing a performance evaluation material of known composition that is similar in nature to the materials being produced in the workplace, for example, a representative certified reference material (CRM).

NOTE 17—It should be recognized that, for a bulk sample, certain physical characteristics, such as particle size and agglomeration, could have a significant influence on the efficacy of its dissolution. Also, smaller amounts of material are often much more easily dissolved than greater quantities.

9.4.1.2 For soluble metals and metalloids, analytical recovery is best determined by analyzing filters or filter capsules spiked with solutions containing known masses of the soluble compound(s) of interest.

9.4.1.3 Recovery should be at least 90 % of the known value for all elements included in the spiked filters or filter capsules, with a relative standard deviation of less than 5 % (**3**). If the analytical recovery is outside the required range of acceptable values, investigate the use of an alternative sample dissolution method.

9.4.1.4 Do not use a correction factor to compensate for an apparently ineffective sample dissolution method, since this might equally lead to erroneous results.

9.4.2 *Dislodgement of Particles During Sample Transport*—When the filter transport cassettes or samplers are opened, look for evidence that particles have become dislodged from the filter during transportation. If this appears to have occurred, consider whether to discard the sample as invalid, or whether to wash the internal surfaces of the filter transport cassette or sampler into the sample dissolution vessel (with dilute nitric acid) in order to recover the dislodged material. See Guide D8358 for guidance on inclusion of all material collected within air samplers.

NOTE 18—Another technique that can be used to account for dislodged particles involves carrying out sample dissolution within the sampling cassette itself (**4**).

NOTE 19—The use of filter capsules (in lieu of filters) ameliorates potential problems due to filter overloading (**2**).

9.4.3 *Treatment of Undissolved Material Following Sample Digestion*—If undissolved residue remains after carrying out sample digestion using hot plate, microwave, or hot block techniques (Annex A2 and Annex A3, respectively), further sample treatment may be required in order to dissolve target analyte elements. This would normally entail filtration to capture the undissolved material, with subsequent digestion of the residue using an alternative sample preparation method.

10. Analysis

10.1 *Reagents for Analysis*—During the analysis, use only reagents of spectroscopic grade or better. The concentration of metals and metalloids of interest shall be less than 0.1 µg/mL.

NOTE 20—It will be necessary to use reagents of higher purity in order to obtain adequate detection limits for some metals and metalloids (for example, beryllium).

10.1.1 *Water,* complying with the requirements for ASTM Type II water (see Specification D1193). It is recommended that the water used be obtained from a water purification system that delivers ultra-pure water having a resistivity greater than 18 MΩ-cm at 25°C.

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

10.1.3 *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.

10.1.4 *Ammonium Citrate Leach Solution,* 17 g/L $(NH_4)_2HC_6H_5O_7$ and 5 g/L $C_6H_8O_7{\cdot}H_2O$. Weigh 17 g di-ammonium hydrogen citrate, $(NH_4)_2\ HC_6H_5O_7$, and 5 g citric ammonium monohydrate, $C_6H_8O_7{\cdot}H_2O$, into a 500 mL beaker. Add 250 mL of water and swirl to dissolve. Quantitatively transfer the solution into a 1-L volumetric flask, dilute to the mark with water, stopper and mix thoroughly. Check the solution pH, and if necessary adjust the pH to 4.4 with ammonia or citric acid.

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

10.1.6 *Hydrochloric Acid Leach Solution,* 0.1 M.

10.1.7 *Perchloric Acid* ($HClO_4$), concentrated, ρ ~1.67 g/mL, ~70 % (m/m).

10.1.8 *Sulfuric Acid* (H_2SO_4), concentrated, ρ ~1.84 g/mL, ~98 % (m/m).

10.1.9 *Stock Standard Solutions:*

10.1.9.1 To prepare stock standard solutions, use commercial single-element or multi-element standard solutions with certified concentrations traceable to primary standards (National Institute of Standards and Technology or international measurement standards). Observe the manufacturer's expiration date or recommended shelf life.

NOTE 21—Commercially available stock solutions for metals and metalloids typically have concentrations of 1000 or 10 000 mg/L for single element standards, and 10 to 1000 mg/L for multielement standards.

10.1.9.2 Alternatively, prepare stock standard solutions from high-purity metals and metalloids or their 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.

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

10.1.10 *Calibration Solutions:*

10.1.10.1 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 1 mg/L and 100 mg/L, depending on the sensitivity of the emission lines to be measured).

NOTE 22—Analytes that are grouped together in working standard solutions should be chosen carefully to ensure chemical compatibility and to avoid spectral interferences. Also, the type and volume of each acid added should be selected carefully to ensure the stability of elements of interest.

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

10.1.10.3 From the working standard solutions, prepare a set of calibration solutions (at least two) by serial dilutions, covering the range of concentrations for each of the metals and metalloids of interest. 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. Prepare calibration solutions fresh daily.

NOTE 23—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 24—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.

10.1.11 *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 25—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 26—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.

10.1.12 *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 mg/L 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.

10.1.13 *Argon,* high-purity (99.99% or better), suitable for use in ICP-AES.

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

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

10.2.1 *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.

10.2.2 *Glassware,* beakers and volumetric flasks complying with the requirements of Specification E288, made of borosilicate glass complying with the requirements of Specification E438. Glassware shall be cleaned before use by soaking in diluted nitric acid for at least 24 hours and then rinsing thoroughly with water. Alternatively, before use, glassware shall be cleaned with a suitable laboratory detergent using a laboratory washing machine.

10.2.3 *Flat-tipped Forceps,* for unloading filters from samplers or from filter transport cassettes.

10.2.4 *Piston-Operated Volumetric Pipettors and Dispensers,* complying with the requirements of Specification E1154, for pipetting and dispensing of leach solutions, acids, standard solutions, and so forth.

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

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

NOTE 27—An auto-sampler having a flowing rinse is recommended.

10.3 *Analysis Procedure:*

10.3.1 *Method Optimization:*

10.3.1.1 *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 9 of this test method, which is suitable for use with the available ICP-AES 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-AES method development available in textbooks, instrument manuals, and standards.

NOTE 28—ICP-AES analysis of test samples prepared from workplace air samples is applicable 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.

10.3.1.2 *Quantitation Limit*—For each metal and metalloid of interest, determine a value for the lower limit of the analytical range that will be satisfactory for the intended measurement task. For example, if the measurement task entails testing compliance with exposure limits, use the following equation to calculate the least amount of the metal or metalloid of interest that will need to be quantified when it is determined at the concentration of 0.1× its limit value: $m_L = 0.1 \times LV \times q_v \times t_{min}$, where m_L is the required lower limit of the analytical range, in µg, of the metal or metalloid; LV is the exposure limit value, in mg/m^3, for the metal or metalloid; q_v is the design flow rate of the sampler to be used, in L/min; and t_{min} is the minimum sampling time that will be used, in min. Then calculate the required quantification limit, in mg/L by dividing the lower limit of the analytical range, in µg, by the volume of the test solution, in mL.

NOTE 29—In some instances, it may not be possible to achieve a quantitation limit that is 0.1× the limit value of interest. In those instances, MDL data and other factors should be considered to achieve the lowest

quantitation limit that meets specified method requirements.

NOTE 30—For other measurement tasks it might be necessary to obtain quantitative measurements below 0.1 times the limit value, in which case an appropriate lower value for mL would be used.

10.3.1.3 *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 $[10 \times (LV_a / LV_i) \times (\rho_a / 1000)] > 0.1$, where LV_a is the limit value, in mg/m^3, of the analyte; LV_i is the limit value, in mg/m^3, of the interferent; and ρ_a is the 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 31—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.

10.3.1.4 *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 32—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.

10.3.1.5 *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 33—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.

10.3.1.6 *Analytical Wavelengths*—Select one or more emission lines on which to make measurements for each metal and metalloid of interest, utilizing wavelength tables available in the literature (**5**). Take into consideration the wavelengths that are accessible on the instrument to be used. Also take into consideration the background equivalent concentrations, the required quantitation limits, and spectral interferences that could be significant at each candidate wavelength. Ordinarily the more sensitive emission lines will be most favorable, but it is necessary to avoid the use of wavelengths on which there is spectral overlap or where there is significant background.

NOTE 34—Scanning, sequential, monochromater-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 each analyte to check for any problems not identified during method development.

NOTE 35—If there is direct spectral overlap and an alternate emission line is not available for analysis of the element of interest, it still might be possible to use interelement correction to correct for the interference.

10.3.1.7 *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.

NOTE 36—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 37—Some ICP-AES 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.

10.3.1.8 *Interelement Correction*—If the only analytical wavelength(s) available or a particular element of interest 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 38—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.

10.3.1.9 *Plasma Conditions:*

(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.

NOTE 39—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. 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.

(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 40—The RF power applied to the plasma can be optimized in accordance with the nature of the analyte. The more RF power that is applied to the plasma, the hotter it gets. For analytes that require more energy for excitation and ionization, a higher power provides greater sensitivity. For elements with low ionization potentials, a lower power provides increased sensitivity.

(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 41—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.

10.3.1.10 *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).

10.3.1.11 *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.

10.3.1.12 *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.

10.3.1.13 *Calibration Solutions:*

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

NOTE 42—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.

(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 43—If more than one analytical wavelength is to be used for a particular analyte, this will need to be taken into consideration when selecting the range of concentrations to be covered.

10.3.1.14 *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 44—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.

10.3.2 *Instrument Performance Checks:*

10.3.2.1 *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 X3.

10.3.2.2 *Performance Checks and Fault Diagnostics*—The user shall carry out performance checks daily to verify that the ICP-AES 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 X4.

NOTE 45—A comprehensive series of performance checks has been described in the literature (**6**), and this can be used to supplement performance checks and fault diagnostics recommended by the instrument manufacturer.

10.3.3 *Routine Analysis:*

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

10.3.3.2 *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).

NOTE 46—Internal standards may be added by pipetting a known volume of single-element stock standard solution into a known volume of each solution to be measured. Alternatively, the solution to be measured and a solution containing internal standard(s) may be mixed during sample introduction using a two-channel peristaltic pump, T-piece and mixing coil.

10.3.3.3 *Instrument Set-Up*—Set up the ICP-AES instrument in accordance with the method developed as described previously; follow manufacturer's instructions. Allow for the instrument to warm up; typical warm-up times are usually 30 to 60 minutes. It is advisable to aspirate reagent blank solution into the plasma during the warm-up period since plasma conditions could be different during analysis.

10.3.3.4 *Analysis:*

(1) Aspirate the calibration solutions into the plasma in order of increasing concentration, and make emission measurements for each solution. Generate a calibration function for the metals and metalloids of interest, preferably using linear