Designation: D7439 – 21

Standard Test Method for Determination of Elements in Airborne Particulate Matter by Inductively Coupled Plasma–Mass Spectrometry[1]

This standard is issued under the fixed designation D7439; 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 sample preparation and analysis of airborne particulate matter for the content of metals and metalloids in workplace air samples using inductively coupled plasma–mass spectrometry (ICP-MS). This test method can be used for other air samples provided the user ensures the validity of the test method (by ensuring that appropriate data quality objectives can be achieved).

1.2 This test method assumes that samples will have been collected in accordance with Test Method D7035 with consideration of guidance regarding wall deposits provided in Guide D8358.

1.3 This test method should be used by analysts experienced in the use of ICP-MS, 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 samples collected from untested matrices.

1.6 Table 1 provides a non-exclusive list of metals and metalloids for which one or more of the sample dissolution methods specified in this document is applicable.

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

1.8 Table 3 provides examples of instrumental detection limits (IDL) that can be achieved with this test method. Table 5 provides examples of method detection limits (MDL) that can be achieved.

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

1.10 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 test method contains notes that are explanatory and are not part of the mandatory requirements of the method.

1.12 *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.*

1.13 *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

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

D5011 Practices for Calibration of Ozone Monitors Using Transfer Standards

D6785 Test Method for Determination of Lead in Workplace

[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.

TABLE 1 Applicable Metals and Metalloids

Element	Symbol	CASRN[A]	Element	Symbol	CASRN[A]	Element	Symbol	CASRN[A]
Aluminum	Al	7429-90-5	Antimony	Sb	7440-36-0	Arsenic	As	7440-38-2
Barium	Ba	7440-39-3	Beryllium	Be	7440-41-7	Bismuth	Bi	7440-69-9
Boron	B	7440-42-8	Cadmium	Cd	7440-43-9	Calcium	Ca	7440-70-2
Cesium	Cs	7440-46-2	Chromium	Cr	7440-47-3	Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8	Gallium	Ga	7440-55-3	*Germanium*[B]	*Ge*	*7440-56-4*
Hafnium	Hf	7440-58-6	Indium	In	7440-74-6	Iron	Fe	7439-89-6
Lead	Pb	7439-92-1	Lithium	Li	7439-93-2	Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5	*Mercury*[B]	*Hg*	*7439-97-6*	Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0	*Niobium*[B]	*Nb*	*7440-03-1*	Phosphorus	P	7723-14-0
Platinum	Pt	7440-06-4	Potassium	K	7440-09-7	Rhodium	Rh	7440-16-6
Selenium	Se	7782-49-2	Silver	Ag	7440-22-4	Sodium	Na	7440-23-5
Tellurium	Te	13494-80-9	Thallium	Tl	7440-28-0	Tin	Sn	7440-31-5
Tungsten	W	7440-33-7	Uranium	U	7440-61-1	Vanadium	V	7440-62-2
Yttrium	Y	7440-65-5	Zinc	Zn	7440-66-6	Zirconium	Zr	7440-67-7

[A] CASRN = Chemical Abstracts Service Registry Number
[B] For the elements in italics, there is insufficient information available on the effectiveness of the sample dissolution procedures in Annex A1 through Annex A5.

Air Using Flame or Graphite Furnace Atomic Absorption Spectrometry
D7035 Test Method for Determination of Metals and Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
D7202 Test Method for Determination of Beryllium in the Workplace by Extraction and Optical Fluorescence Detection
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
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
E1154 Specification for Piston or Plunger Operated Volumetric Apparatus
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]
E3193 Test Method for Measurement of Lead (Pb) in Dust by Wipe, Paint, and Soil by Flame Atomic Absorption Spectrophotometry (FAAS)
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 1042 Laboratory glassware — One-mark volumetric flasks
ISO 3585 Borosilicate glass 3.3 — Properties
ISO 4225 Air quality — General aspects — Vocabulary
ISO 8655 Piston-operated volumetric apparatus (6 parts)
ISO 15202 Workplace air — Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry (3 parts)
ISO 17294 Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) (2 parts)
ISO 18158 Workplace air — Terminology

3. Terminology

3.1 *Definitions*—For definitions of other terms used in this test method, refer to Terminology D1356.

3.1.1 *analytical recovery, n*—ratio of the mass of analyte measured to the known mass of analyte in the sample, expressed as a percentage. **D6785**

3.1.2 *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**

3.1.3 *blank solution, n*—solution prepared by taking a reagent blank, laboratory blank or field blank through the same procedure used for sample dissolution. **ISO 15202**

3.1.3.1 *Discussion*—A blank solution may need to be subjected to further operations, such as addition of an internal standard, if the sample solutions are subjected to such operations in order to produce test solutions that are ready for analysis.

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

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

[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.

3.1.5 *calibration curve, n*—a plot of instrument response versus concentration of standards (**1**).[5]

3.1.6 *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**

3.1.6.1 *Discussion*—The technique of matrix matching is normally used when preparing calibration solutions.

3.1.7 *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**

3.1.8 *collision cell, n*—chamber in the ion path between m/z separation elements, or between ion source acceleration region and the first analyzer, in tandem mass spectrometry in space configurations (**2**).

3.1.9 *collision reaction cell, n*—collision cell for removal of interfering ions by ion/neutral reactions in ICP-MS (**2**).

3.1.10 *continuing calibration blank (CCB), n*—a solution containing no analyte added, that is used to verify blank response and freedom from carryover. **E1613/E3203**

3.1.10.1 *Discussion*—The CCB must be analyzed after the CCV (see 3.1.11). The measured concentration of the CCB should not exceed 10 % of the applicable occupational exposure limit or minimum level of concern.

3.1.11 *continuing calibration verification (CCV), n*—a solution (or set of solutions) of known analyte concentration used to verify freedom from excessive instrumental drift. **E1613/E3203**

3.1.11.1 *Discussion*—The concentration of the CCV is to be near the mid-range of a linear calibration curve.

3.1.11.2 *Discussion*—The CCV must be matrix matched to the acid content present in sample digestates or extracts. The CCV must be analyzed before and after all samples and at a frequency of not less than every ten samples. The measured value is to fall within ±10 % of the known value.

3.1.12 *field blank, n*—sampling media (for example, an air filter) that is taken through the same handling procedure as a sample, except that no sample is collected (that is, no air is purposely drawn through the sampler), and is then returned to the laboratory for analysis. **D7035**

3.1.12.1 *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.

3.1.13 *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**

3.1.14 *inductively coupled plasma (ICP) torch, n*—a device used to support and introduce sample into an ICP discharge. **ISO 15202**

3.1.15 *initial calibration blank (ICB), n*—a standard containing no analyte that is used for the initial calibration and zeroing of the instrument response. **E1613/E3193**

3.1.15.1 *Discussion*—The ICB must be matrix matched to the acid content of sample extracts and digestates. The ICB must be measured during and after calibration. The measured concentration of the ICB should not exceed 10 % of the applicable occupational exposure limit or minimum level of concern.

3.1.16 *initial calibration verification (ICV), n*—a solution (or set of solutions) of known analyte concentration used to verify calibration standard levels. **E1613/E3193**

3.1.16.1 *Discussion*—The concentration of analyte is to be near the mid-range of the calibration curve. It is made from a stock solution having a different manufacturer or manufacturer lot identification than the calibration standards. **E1613/E3193**

3.1.16.2 *Discussion*—The ICV must be matrix matched to the acid content of sample extracts or digestates. The ICV must be measured after calibration and before measuring any sample digestates or extracts. The measured value is to fall within ±10 % of the known value.

3.1.17 *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**

3.1.18 *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**

3.1.19 *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/E3203**

3.1.19.1 *Discussion*—The IDL can be determined from blank, acidified, deionized, or ultrapure water as the matrix and from the same calculation methods used to determine a method detection limit (see 3.1.28).

3.1.20 *instrumental QC standards, n*—these provide information on measurement performance during the instrumental analysis portion of the overall analyte measurement process. **E1613/E3193**

3.1.20.1 *Discussion*—These standards include CCBs, CCVs, ICBs, and ICVs.

3.1.21 *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**

3.1.22 *internal standard, n*—non-analyte element, present in all solutions analyzed, the signal from which is used to correct for matrix interferences or improve analytical precision. **ISO 15202**

3.1.22.1 *Discussion*—The internal standard is added in known and constant amount(s) to all analyzed solutions. This is

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

used to correct for instrument drift and some matrix effects by measuring the relative instrument response of the internal standard(s) to the other analytes that are components of the same solution. The element(s) selected for use as an internal standard must be initially absent from the sample solution.

3.1.23 *laboratory blank, n*—unused sample media (for example, an air filter), taken from the same batch used for sampling, that does not leave the laboratory. **ISO 15202**

3.1.24 *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**

3.1.25 *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**

3.1.26 *matrix interference, n*—interference of a non-spectral nature which is caused by the sample matrix. **ISO 15202**

3.1.27 *matrix matching, n*—a technique used to minimize the effect of the test solution matrix on the analytical results. **ISO 15202**

3.1.27.1 *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.

3.1.28 *method detection limit (MDL), n*—the minimum concentration of an analyte that can be reported with a 99 % confidence that the value is above zero. **D1356**

3.1.28.1 *Discussion*—The MDL is also known as the limit of detection (LOD) (**3**).

3.1.29 *method quantitation limit (MQL), n*—the minimum concentration of an analyte that can be measured with acceptable precision. **D7035**

3.1.29.1 *Discussion*—The MQL is also known as the limit of quantitation (**3**).

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

3.1.31 *occupational exposure limit value (OELV), n*—limit of the time-weighted average of the concentration of a chemical agent in the air within the breathing zone of a worker in relation to a specified reference period **ISO 18158**

3.1.31.1 *Discussion*—The term "limit value" is often used as a synonym for OELV, but the latter is preferred because there is more than one limit value (for example, biological limit value and OELV).

3.1.31.2 *Discussion*—An example of an OELV would be a Permissible Exposure Limit (PEL) such as those established by the U.S. Occupational Safety and Health Administration.

3.1.32 *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 L/min – 15 L/min. **ISO 15202**

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

3.1.34 *primary standard, n*—an acceptable reference sample or device used for establishing measurement of a physical quantity, directly defined and established by some authority, against which all secondary standards are compared. **adapted from D5011**

3.1.35 *reagent blank, n*—all reagents used in sample preparation, in the same quantities used to prepare blank and sample solutions. **ISO 18158**

3.1.35.1 *Discussion*—The reagent blank is used to assess contamination from the laboratory environment and to characterize background from the reagents used in sample preparation. **ISO 18158**

3.1.36 *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/ISO 15202**

3.1.37 *sample preparation, n*—all operations carried out on a sample, usually after transportation and storage, to prepare it for analysis, including transformation of the sample into a measurable state, where necessary. **ISO 18158**

3.1.38 *sample solution, n*—solution prepared from a sample by the process of sample dissolution. **ISO 15202**

3.1.39 *secondary standard, n*—an acceptable reference sample or device used for establishing measurement of a physical quantity, used as a means of comparison, but checked against a primary standard. **adapted from D5011**

3.1.40 *spectral interference, n*—an isobaric interference caused by a species other than the analyte of interest.

3.1.40.1 *Discussion*—Spectral interferences may involve an atomic, polyatomic, or doubly-charged ion species. An example of an atomic interference is $^{40}Ar^{+}$ on $^{40}Ca^{+}$. An example of a polyatomic interference is $^{40}Ar^{16}O^{+}$ on $^{56}Fe^{+}$. An example of a doubly-charged ion interference is $^{48}Ti^{2+}$ on $^{24}Mg^{+}$ (**4**).

3.1.41 *spiked reagent blank, n*—a reagent blank aliquot that is spiked with a known amount of analyte.

3.1.41.1 *Discussion*—Analysis results for spiked reagent blanks are used to provide information on the precision and bias of the overall analysis process.

3.1.42 *spiked media blank, n*—a reagent blank aliquot that includes the sampling media (that is, filter), but includes no actual sample, that is spiked with a known amount of analyte.

3.1.43 *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**

3.1.44 *stock standard solution, n*—solution used for preparation of working standard solutions 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). **ISO 15202**

3.1.45 *test solution, n*—blank solution or sample solution that has been subjected to all operations required to bring it into a state in which it is ready for analysis. **ISO 15202**

3.1.45.1 *Discussion*—"Ready for analysis" includes any required dilution(s) or addition of an internal standard, or both. When blank solutions and sample solutions are not subjected to any further operations before analysis, they then are in fact test solutions.

3.1.46 *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**

3.1.47 *tune, n*—analyze a solution containing a range of isotopic masses to establish ICP-MS mass-scale accuracy, mass resolution, signal intensity, and precision prior to calibration **(1)**.

3.1.48 *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**

3.1.49 *working standard solution, n*—solution, prepared by dilution of the stock standard solution(s), that contains the analyte(s) of interest at a concentration(s) better suited for preparation of calibration solutions than the concentration(s) of the analyte(s) in the stock standard solution(s). **ISO 15202**

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *collision/reaction system, n*—any system (for example, a collision cell or a collision reaction cell) that is used for charge exchange neutralization of interfering ions in ICP-MS.

3.2.1.1 *Discussion*—Collision/reaction systems utilize one or more techniques to reduce or eliminate spectral interferences. These may include (but are not necessarily limited to) oscillating radio frequency, ion-neutral reactions, and kinetic energy discrimination. References **(5)** and **(6)** provide additional information.

4. Summary of Test Method

4.1 A known volume of air is drawn through appropriate sampling media to collect airborne particulates suspected to contain metals or metalloids, or both, in accordance with Test Method D7035, taking into account additional information and methodologies in Guide D8358.

4.2 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 of the sample dissolution methods specified.

4.3 Test solutions, prepared from the sample solutions after sample dissolution, are analyzed using inductively coupled plasma – mass spectrometry (ICP-MS) to determine the concentration of target elements in the sampled air.

NOTE 1—The sample dissolution procedures described in this standard may be suitable for preparation of samples for subsequent analysis by other methods besides ICP-MS (for example: inductively coupled plasma–emission spectrometry as described in Test Method D7035, flame atomic absorption spectrophotometry as described in Practice D4185, graphite furnace atomic absorption spectrometry, 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 workplace exposure. This is generally achieved by making workplace air measurements. This test method has been developed to make available a standard methodology for 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; analytical laboratories; industrial hygienists and other public health professionals; 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 concentration of metals and metalloids in workplace air samples using ICP-MS. For many metals and metalloids, analysis by ICP-MS may be advantageous, when compared to methods such as ICP atomic emission spectrometry, due to its sensitivity and the presence of fewer spectral interferences.

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

6. Apparatus

6.1 *Apparatus for Sample Preparation and Analysis*—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.

6.1.1 *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.

6.1.2 *Glassware,* beakers and volumetric flasks complying with the requirements of Specification E288 or ISO 1042, made of borosilicate glass and complying with the requirements of Specification E438 or ISO 3585. Glassware shall be cleaned before use by soaking in 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.

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

6.1.4 *Piston-operated Volumetric Pipettors and Dispensers,* complying with the requirements of Specification E1154 or ISO 8655, for pipetting and dispensing of leach solutions, acids, and so forth.

6.1.5 *Polyethylene Bottles,* low density, with leak-proof screw cap.

6.1.6 *Inductively Coupled Plasma–Mass Spectrometer,* computer-controlled, equipped with an auto-sampler.

NOTE 2—An auto-sampler having a flowing rinse is strongly recommended.

7. Reagents

7.1 *Reagents for Sample Preparation and Analysis*—Details regarding reagents that are required for individual sample dissolution methods are given in Annex A1 through Annex A5. During sample preparation and analysis, use only reagents of spectroscopic grade or greater purity. The concentration of metals and metalloids of interest shall be less than 0.1 µg/L. The use of ultrapure acids is recommended.

NOTE 3—Reagents of higher purity are needed in order to obtain adequate detection limits for some metals and metalloids (for example, for beryllium measurements, a Be concentration of less than 0.01 µg/L is recommended).

7.1.1 *Water,* complying with the requirements for ASTM Type I water (see Specification D1193).

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

7.1.3 *Laboratory Detergent,* suitable for cleaning of laboratory ware. The use of detergents containing phosphorus or other potential analytes should be avoided.

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

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

NOTE 4—Use of HCl is typically not recommended in ICP-MS systems that do not include a collision/reaction system, or when such a system is not used.

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

NOTE 5—Use of H_2SO_4 is typically not recommended in ICP-MS systems that do not include a collision/reaction system, or when such a system is not used.

7.1.7 *Stock Standard Solutions:*

7.1.7.1 For 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 6—Commercially available stock standard solutions for metals and metalloids have nominal concentrations of 10 to 10 000 mg/L for single element standards, and 10 to 1000 mg/L for multielement standards.

7.1.7.2 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.

7.1.7.3 Store stock standard solutions in suitable containers, such as low-density polyethylene bottles.

7.1.8 *Working Standard Solutions and Calibration Solutions:*

7.1.8.1 From the stock standard solutions, prepare working standard solutions by serial dilutions; these shall include all the metals and metalloids of interest at suitable concentration.

NOTE 7—Suitable concentrations will typically fall between 1 µg/L and 100 µg/L; however, newer ICP-MS systems can detect some metals and metalloids reliably at levels below 1 µg/L.

NOTE 8—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.

7.1.8.2 Store working standard solutions in suitable containers for a maximum period of one month.

NOTE 9—Containers such as bottles made of perfluoroalkoxy (PFA) polymer, polytetrafluoroethylene (PTFE), or low-density polyethylene are normally suitable.

7.1.8.3 From the working standard solutions, prepare a set of calibration solutions by serial dilutions, covering the range of concentrations for each of the metals and metalloids of interest. It is recommended that a minimum of three calibration solutions be prepared. 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. Calibration solutions should be prepared fresh daily.

NOTE 10—The shelf life of calibration solutions may be extended if they are demonstrated, by comparison with calibration verification solutions, to be acceptable.

NOTE 11—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.

7.1.9 *Internal Standard Stock Solutions:*

7.1.9.1 Select elements to be used as internal standards. Table 2 provides a list of elements frequently used. For full mass range scans use a minimum of three internal standards with the use of five suggested. Internal standards in low, middle, and high mass ranges are recommended.

NOTE 12—Internal standards are recommended in all analyses to correct for instrument drift and physical interferences. Internal standards should be added to blanks, samples and standards in a like manner. Internal standards are typically selected to match the mass range of the analytes of interest; however, for analytes with high ionization potential (such as arsenic and selenium), consideration should be given to matching ionization potential.

NOTE 13—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.

7.1.9.2 Use stock standard solutions to prepare test solutions that contain the internal standard elements. Observe the manufacturer's expiration date or recommended shelf life.

7.1.10 *Argon,* high purity grade (99.99 % or better).

TABLE 2 Internal Standards and Limitations of Use

Internal Standard	Mass	Possible Limitation
Lithium	6	May be present in samples
Scandium[A]	45	Polyatomic ion interference; may be present in samples
Yttrium[A]	89	May be present in samples
Rhodium	103	...
Indium[A]	115	Isobaric interference by Sn
Terbium[A]	159	...
Holmium	165	...
Lutetium	175	...
Platinum	195	...
Bismuth[A]	209	May be present in samples

[A] Internal standards recommended for use with this test method. It is also necessary when analyzing a new sample matrix that a scan for the presence of internal standards be performed.

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 X1 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 X1 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. Sampling Procedure

9.1 Samples to be prepared for analysis by this test method shall be collected in accordance with test method D7035.

10. Sample Preparation

10.1 *Soluble Metals and Metalloids and their Compounds:*

10.1.1 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-MS.

10.1.2 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-MS 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 (microwave digestion), Annex A4 (hot block digestion), and Annex A5 (microwave digestion).

NOTE 14—The methods prescribed in Annex A2 through Annex A5 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.

10.2 *Total Metals and Metalloids and their Compounds:*

10.2.1 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 (microwave digestion), Annex A4 (hot block digestion), and Annex A5 (microwave 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.

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

10.3 *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. See Guide D8358 for additional information and suggested methodologies.

10.4 *Mixed Exposures:*

10.4.1 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-MS.

10.4.2 Select a suitable sample preparation method from those specified in Annex A2 (hot plate digestion), Annex A3 (microwave digestion), Annex A4 (hot block digestion), and Annex A5 (microwave 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-MS.

10.5 *Special Cases:*

10.5.1 *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.

10.5.1.1 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. An example evaluation material would be a representative certified reference material (CRM).

NOTE 16—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 quantities of material are often much more easily dissolved than greater quantities.

10.5.1.2 For soluble metals and metalloids, analytical recovery is best determined by analyzing spiked media blanks (that is, filters spiked with solutions containing known masses of the soluble compound(s) of interest).

10.5.1.3 Recovery should be at least 90 % of the known value for all elements included in the spiked media blanks, with a relative standard deviation of less than 5 % (**7**). If the analytical recovery is outside the required range of acceptable values, investigate the use of an alternative sample dissolution method.

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

10.5.2 *Treatment of Undissolved Material Following Sample Dissolution*—If undissolved residue remains after carrying out sample dissolution using hot plate, microwave, or hot block techniques (Annex A2, Annex A3, Annex A4, and Annex A5 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.

11. Analysis

11.1 *Method Optimization:*

11.1.1 *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 9of this test method, which is suitable for use with the available ICP-MS 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-MS method development available in textbooks, instrument manuals, and standards (for example, ISO 17294).

NOTE 17—ICP-MS analysis of test solutions prepared from workplace air samples is applicable to a wide range of instruments. For example, ICP-MS systems may be equipped with a collision/reaction system, of which there are several types. 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 methods for all ICP-MS instruments, but there are also many parameters that are only applicable to particular instruments.

11.1.2 *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 a limit value, use the following equation to calculate the least amount of 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 = the required lower limit of the analytical range, in µg, of the metal or metalloid;
LV = the limit value, in mg/m^3, for the metal or metalloid;
q_v = the design flow rate of the sampler to be used, in L/min (in accordance with Test Method D7035); and
t_{min} = the minimum sampling time that will be used, in min.

Then calculate the required quantitation 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 18—In some instances, it may not be possible to achieve a quantitation limit that is 0.1 × the limit 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 19—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 m_L would be used.

11.1.3 *Interferences*—Give consideration to the significance of any known interferences in the context of the measurement task (see Appendix X3 for information). For each potentially useful mass-to-charge ratio, refer to published information, and consider the relationship between the magnitude of interferences and the relative limit values of the elements to be determined. If the sum of all potential interferences is greater than 0.1 × the limit value of the analyte, consider alternatives, such as an alternative mass-to-charge ratio or use of a collision/reaction system (if available). See Appendix X3 for additional information.

NOTE 20—The use of interference correction equations for isobaric overlaps is especially suitable when the source of the interference is known and constant (for example, acid matching with known quantities of HCl).

NOTE 21—The use of a collision/reaction system may eliminate many isobaric elemental or polyatomic interferences, and (if available) is typically preferable over use of alternative mass-to-charge ratios that may not be as sensitive as the primary mass-to-charge ratio for the analyte of interest.

11.1.4 *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.

11.1.4.1 High-efficiency nebulizers (for example, ultrasonic) can improve method sensitivity as compared to conventional pneumatic nebulizers. However, they can be less corrosion-resistant. For instance, if test solutions contain hydrofluoric acid, it will be necessary to use a corrosion-resistant sample introduction system and platinum cones.

11.1.5 *Analytical Mass*—Select one or more analytical mass(es) on which to make measurements for each metal and metalloid of interest. Table 3 provides information on recommended masses and instrumental detection limits that may be achieved under optimal conditions (**8-11**). Take into consideration the relative abundance of the metal or metalloid at the selected mass(es), the required quantitation limits, and interferences that could be significant at each candidate mass. Ordinarily the most sensitive mass will be the most favorable, but it is necessary to avoid the use of masses on which there is spectral overlap or significant background.

NOTE 22—The use of multiple masses, with appropriate use of spectral fitting software available on most ICP-MS systems, may be used to overcome many spectral overlaps or other interferences. Additionally, the use of a collision/reaction system may affect recommended isotopes.

11.1.6 *Plasma Conditions:*

11.1.6.1 *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 inner (nebulizer) argon flow may be optimized for specific applications.

NOTE 23—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. In ICP-MS, ionization rather than excitation is desired. The appropriate residence time for each analyte will depend on its ionization potential. Determination of the appropriate flow rate must also consider the efficiency of the nebulizer, as low flow rates may cause nebulizer efficiency to drop off significantly.

11.1.6.2 *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 24—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 ionization, a higher power may provide greater sensitivity. For analytes with low ionization potential, a lower power may provide greater sensitivity.

11.1.6.3 *Sampling Depth*—This refers to the distance of the sampling cone from the top turn of the load coil, in millimetres (**12**). Under normal circumstances, use the default sampling depth recommended by the instrument manufacturer. However, the sampling depth may be optimized for specific applications.

NOTE 25—In general, at constant power and nebulizer gas flow rate, an increase in sampling depth reduces the ion count (**8**).

11.1.7 *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).

11.1.8 *Sample Introduction Rate*—Under normal circumstances, use the sample uptake rate recommended by the

TABLE 3 Recommended Analytical Isotopes and Examples of Instrumental Detection Limits (8-11)

Element Name	Element Symbol	Recommended Analytical Isotopes[A]	Example Instrumental Detection Limits, µg/L[B]
Aluminum	Al	27	0.00001–0.111
Antimony	Sb	121, 123	0.00003–0.0037
Arsenic	As	75	0.0003–0.227
Barium	Ba	135, 137, 138	0.00002–0.0004
Beryllium	Be	9	<0.00001–0.168
Bismuth	Bi	209	<0.00001–0.0004
Boron	B	10, 11	0.0002–0.253
Cadmium	Cd	106, 108, 111, 114	0.00005–0.0004
Calcium	Ca	43, 44	0.00005–0.093
Cerium	Ce	140	0.00001–0.00005
Cesium	Cs	133	0.00002–0.003
Chromium	Cr	52, 53	0.00005–0.032
Cobalt	Co	59	<0.00001–0.0061
Copper	Cu	63, 65	0.00003–0.0046
Gallium	Ga	69, 71	0.00004–0.0045
Germanium	Ge	72, 74	0.0004–0.0037
Gold	Au	197	0.00005–0.0009
Hafnium	Hf	178	0.00001–0.0003
Indium	In	115	0.00001–0.0004
Iridium	Ir	193	0.00004–0.0004
Iron	Fe	56, 57	0.0001–0.018
Lead	Pb	206, 207, 208	0.00001–0.0004
Lithium	Li	6, 7	<0.00001–0.183
Lutetium	Lu	175	<0.00001–0.00004
Magnesium	Mg	24, 25	0.00001–0.022
Manganese	Mn	55	0.00005–0.018
Mercury	Hg	199, 201, 202	0.00018–0.0092
Molybdenum	Mo	95, 98	0.00003–0.0027
Neodynium	Nd	146	<0.00001–0.0003
Nickel	Ni	58, 60	0.00006–0.0047
Niobium	Nb	93	<0.00001–0.0003
Osmium	Os	189	0.00006–0.00029
Palladium	Pd	105	0.00008–0.0029
Phosphorus	P	31	0.0166–0.6
Platinum	Pt	195	0.00003–0.0003
Potassium	K	39	0.00004–1.81
Rhenium	Re	185	0.00004–0.0003
Rhodium	Rh	103	0.00001–0.0004
Rubidium	Rb	85	0.0001–0.0015
Ruthenium	Ru	101	0.00002–0.0003
Samarium	Sm	147	0.00002–0.0002
Scandium	Sc	45	0.00067–0.013
Selenium	Se	77, 78, 82	0.0003–0.25
Silicon	Si	28	0.084–0.1
Silver	Ag	107, 109	0.00003–0.0009
Sodium	Na	23	0.00001–1.289
Strontium	Sr	88	0.00002–0.0009
Tantalum	Ta	125	<0.00001–0.0007
Tellurium	Te	125	<0.00001–0.0049
Terbium	Tb	159	<0.00001–0.00003
Thallium	Tl	203, 205	<0.00001–0.0005
Thorium	Th	232	<0.00001–0.00005
Thulium	Tm	169	<0.00001–0.00003
Tin	Sn	118, 120	0.00003–0.016
Titanium	Ti	47	0.00003–0.0066
Tungsten	W	182, 184	0.00002–0.0014
Uranium	U	238	<0.00001–0.00007
Vanadium	V	51	0.00001–0.726
Ytterbium	Yb	172	<0.00001–0.0001
Yttrium	Y	89	<0.00001–0.00007
Zinc	Zn	64, 66, 68	0.0001–0.016
Zirconium	Zr	90	0.00002–0.0004

[A] Isotopes recommended for analytical determination are underlined. Alternate masses may be more appropriate in some applications. Appropriate method validation (for example, method parameters, interferences) should be documented.

[B] Instrument detection limits were based on three-standard-deviation data. Parameters such as the use of a clean room, the presence of a collision/reaction system and the mode in which that system was used (for example, no gas, collision gas, reaction gas, or both), the type of cone used (Ni or Pt), vary widely. See individual references (**8-11**) for additional details.

nebulizer manufacturer. However, the uptake rate may be optimized to achieve a suitable compromise between signal intensity and uptake rate.

11.1.9 *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.

11.1.10 *Calibration Solutions:*

11.1.10.1 *Matrix Matching*—Match the matrix of the calibration solutions with that of the test solutions.

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

NOTE 26—If more than one mass-to-charge ratio 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.

11.1.11 *Internal Standards*—Select an appropriate number and combination of internal standards to correct for instrument drift and physical interferences. For full mass range scans use a minimum of three internal standards with the use of five suggested. Ensure that the selected internal standard elements are suitable for the intended purpose, exhibit adequate sensitivity, are not present in the test solutions, and are chemically compatible with the test solution matrix (that is, they must not cause precipitation). Refer to Table 2 for a list of appropriate internal standards and limitations on the use of each.

NOTE 27—Internal standards may be used to correct for changes in nebulizer efficiency that can occur during analysis. While internal standards may also be used to correct for transport interferences that arise from a matrix mismatch between the calibration and test solutions, matching the matrix of the calibration and test solutions is generally preferable for that purpose.

11.2 *Instrument Performance Checks:*

11.2.1 *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 X2.

11.2.2 *Performance Checks and Fault Diagnostics*—The user shall carry out performance checks daily to verify that the 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 X3.

11.3 *Routine Analysis:*

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

11.3.2 *Addition of Internal Standards*—Add the same concentration of internal standards to all solutions to be measured (that is, calibration solutions, blank solutions, sample solutions, and quality control sample solutions).

NOTE 28—Internal standards may be added by pipetting a known volume of stock standard solution into a known volume of each solution to be measured. Alternatively, the solution to be measured and a solution containing internal standards may be mixed during sample introduction using a two-channel peristaltic pump, T-piece and mixing coil.

11.3.3 *Analysis of Mercury Particulate*—If mercury particles are (one of) the analyte(s) of interest, add a solution of gold in 2 % hydrochloric acid to all solutions to be measured, such that the final gold concentration in the solutions is 100 µg/L. Allow solutions to sit for at least one hour prior to analysis.

NOTE 29—Gold solution in HCl is used to minimize memory effects when mercury is an analyte of interest. Care is needed to ensure that the final HCl content in the solutions does not cause precipitation of elements incompatible with HCl, such as silver.

11.3.4 *Instrument Set-Up*—Set up the ICP-MS 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.

11.3.5 *Analysis:*

11.3.5.1 Aspirate the calibration solutions into the plasma, beginning with the initial calibration blank (ICB), in order of increasing concentration, and make measurements for each solution. Generate a calibration function for the metals and metalloids of interest, preferably using linear regression via the instrument's computer. Repeat the calibration if the coefficient of determination (R^2) for any of the elements of interest is <0.995.

NOTE 30—If $R^2 < 0.995$, it may be possible to remove an erroneous calibration point (for example, by using an outlier test), and then reprocess the data to obtain acceptable calibration. However, the minimum number of calibration solutions prescribed should be maintained. The recommended minimum number of calibration solutions is three.

11.3.5.2 Aspirate a second ICB solution, followed by an initial calibration verification solution (ICV), the laboratory blank solution(s), and the test solutions, into the plasma, and make measurements for each solution. Use the calibration function to determine the concentrations of metals and metalloids of interest.

11.3.5.3 Analyze a continuing calibration blank (CCB) solution and a continuing calibration verification (CCV) solution after (at least) every ten test solutions. If the measured concentration of an element of interest in the CCB solution is greater than five times the instrumental detection limit, or if the measured concentration of an element of interest in the CCV solution has changed by more than ±10 %, take one of the following corrective measures: *(1)* Use the instrument software to correct for the observed sensitivity change, or *(2)* suspend analysis and recalibrate the spectrometer. In either case, reanalyze the test solutions that were analyzed during the period in which the sensitivity change occurred, or reprocess the data to account for the observed sensitivity change.

11.3.5.4 Analyze quality control samples, as described in 11.5, at a minimum frequency of one pair per 20 test samples, and use the results to monitor the performance of the analytical procedure.

11.3.5.5 Analyze a CCB solution and a CCV solution at the end of each analytical batch.

11.3.5.6 Examine the precision (relative standard deviation) of all results, and repeat any analyses if the relative standard deviation is unacceptably high.

11.3.5.7 If the concentration of any of the metals and metalloids of interest in a test solution is found to be above the upper limit of the calibration range, dilute the sample by an appropriate factor, matrix-match as necessary, and repeat the analysis (and account for the dilution factor).

11.4 *Estimation of Detection and Quantitation Limits:*

11.4.1 *Estimation of the Instrumental Detection Limit (IDL):*

11.4.1.1 Estimate the IDL for each of the metals and metalloids of interest under the working analytical conditions, and repeat this exercise whenever the experimental conditions are changed.

NOTE 31—The IDL is of use in identifying changes in instrument performance, but it is not a method detection limit (MDL). The IDL is expected to be lower than the MDL because it only takes into account the variability between individual instrumental readings; determinations made on one solution do not take into consideration contributions to variability from the matrix or sample.

11.4.1.2 Prepare a test solution with concentrations of the metals and metalloids of interest near their anticipated IDLs by diluting working standard solutions or stock standard solutions by an appropriate factor. Follow the same procedure used for preparation of the calibration solutions.

11.4.1.3 Make at least ten consecutive measurements on the test solution, and calculate the IDL for each of the metals and metalloids of interest as three times the sample standard deviation of the mean concentration value.

NOTE 32—An alternative procedure for estimating the IDL involves the analysis of blank solutions fortified with the metals and metalloids of interest at values spanning the predicted IDL (**13**).

11.4.2 *Estimation of the Method Detection Limit (MDL) and the Method Quantitation Limit (MQL):*

11.4.2.1 Estimate the MDL and MQL for each of the metals and metalloids of interest under the working analytical conditions, and repeat this exercise whenever experimental conditions are changed.

11.4.2.2 Prepare at least ten blank test solutions from unused sample media (such as air filters) of the same type used for sample collection. Follow the appropriate sample preparation procedure used to prepare sample test solutions.

11.4.2.3 Make measurements on the test solutions, and calculate the MDL and MQL for each of the metals and metalloids of interest as three times and ten times the sample standard deviation of the mean concentration values, respectively.

11.5 *Quality Control:*

11.5.1 *Blank Solutions*—Carry reagent blanks, laboratory blanks, and (if used) field blanks throughout the entire sample preparation and analytical process to determine whether the samples are being contaminated from laboratory or field activities. Process reagent blanks at a frequency of at least one per 20 samples, minimum of one per batch.

11.5.2 *Quality Control Samples:*

11.5.2.1 Carry quality control samples throughout the entire sample preparation and analytical process to estimate the method accuracy on the sample batch, expressed as a percent recovery relative to the true value.

11.5.2.2 Process spiked reagent blanks and spiked media blanks at a frequency of at least one pair per 20 samples, minimum of one pair per batch.

11.5.2.3 Monitor the performance of the method by plotting control charts of the relative percent recoveries of the spiked reagent blanks and the spiked media blanks. Also, to evaluate method precision, plot control charts of the relative percent differences between duplicate spiked media blanks.

11.5.2.4 If quality control results indicate that the method is out of control, investigate the reasons for this, take corrective action, and repeat the analyses. See Guide E882 for general guidance on the use of control charts.

NOTE 33—When feasible, replicate analysis of one sample per batch, or per ten samples, should be considered as a good laboratory practice.

11.5.3 *Internal Standards*—The internal standard signal response in each sample test solution should be within 75 % to 125 % of the response in the calibration blank solution. For responses outside of this range, investigate the reasons, take corrective action, and repeat the analyses.

11.5.4 *External Quality Assessment*—If the laboratory carries out analysis of metals and metalloids in workplace air samples on a regular basis, it is recommended that the lab participate in relevant external quality assessment and proficiency testing schemes.

11.6 *Measurement Uncertainty*—It is recommended that the laboratory estimate and report the uncertainty of their measurements in accordance with ISO guidelines (**14**). This entails first constructing a cause and effect diagram to identify the individual sources of random and systematic error in the overall sampling and analytical method. These are then estimated, or determined, or both, experimentally and combined in what is referred to as an uncertainty budget. The combined uncertainty is ultimately multiplied by an appropriate coverage factor to produce an expanded uncertainty. A coverage factor of 2 is ordinarily recommended, as this gives a confidence level of approximately 95 % in the calculated value. See Practice D7440 for additional information.

NOTE 34—Although sampling is not expressly discussed in this test method, the sampling procedures in Test Method D7035 are incorporated by reference (see 9.1) and should be included in developing the overall uncertainty budget. In many cases, the sampling uncertainty exceeds the analytical uncertainty.

NOTE 35—Applications of cause and effect analysis to analytical methods have been described in the published literature (**15**). Terms that contribute to the random variability of an analytical method are generally accounted for in the measurement precision, which can be estimated from quality control data. Errors associated with instrumental drift can be estimated, assuming a rectangular probability distribution, by dividing the allowable drift before recalibration by the square root of 3. Systematic errors include, for example, those associated with analytical recovery, sampling recovery, preparation of working standard solutions, dilution of test solutions, and so forth.

12. Expression of Results

12.1 From measurements of the test samples, derive a single result for each of the metals and metalloids of interest.