Designation: D7439 – 14

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 standard 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 standard test method assumes that samples will have been collected in accordance with Test Method D7035.

1.3 This standard 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 standard 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 the standard method for filters of 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 standard test method is not applicable to 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-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.

1.9 The values stated in SI units are to be regarded as standard.

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D4185 Practice 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 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

[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 A4.

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
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

2.2 *ISO and European Standards:*
ISO 1042 Laboratory Glassware—One-Mark Volumetric Flasks[3]
ISO 3585 Borosilicate Glass 3.3—Properties[3]
ISO 8655 Piston-Operated Volumetric Apparatus (6 parts)[3]
ISO 15202 Workplace Air—Determination of Metals and Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry (3 parts)[3]
ISO 17294 Water Quality—Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (2 parts)[3]
EN 1540 Workplace Atmospheres—Terminology[3]

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

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

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

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

3.2.3.1 *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.

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

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

3.2.5 *calibration curve*—a plot of instrument response versus concentration of standards **(1)**.[4]

3.2.6 *calibration solution*—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**

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

3.2.7 *chemical agent*—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. **EN 1540/ISO 15202**

3.2.8 *collision/reaction system*—any system, such as a transmission collision cell, to which an oscillating radio frequency potential is applied that is used for charge exchange neutralization of interfering ions in inductively coupled plasma mass spectrometry **(2)**.

3.2.8.1 *Discussion*—Some collision systems also have one or more reaction modes that can further reduce selected interferences.

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

3.2.9.1 *Discussion*—The CCB must be analyzed after the CCV (see 3.2.10). The measured concentration of the CCB

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

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

should not exceed 10 % of the applicable occupational exposure limit or minimum level of concern.

3.2.10 *continuing calibration verification (CCV)*—a solution (or set of solutions) of known analyte concentration used to verify freedom from excessive instrumental drift; the concentration is to be near the mid-range of a linear calibration curve. **E1613**

3.2.10.1 *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.

3.2.11 *field blank*—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. **ISO 15202/D7035**

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

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

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

3.2.14 *initial calibration blank (ICB)*—a standard containing no analyte that is used for the initial calibration. **E1613**

3.2.14.1 *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.

3.2.15 *initial calibration verification (ICV)*—a solution (or set of solutions) of known analyte concentration used to verify calibration standard levels; the concentration of analyte is to be near the mid-range of the calibration curve that is made from a stock solution having a different manufacturer or manufacturer lot identification than the calibration standards. **E1613**

3.2.15.1 *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.

3.2.16 *injector tube*—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**

3.2.17 *inner (nebulizer) argon flow*—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**

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

3.2.18.1 *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 3.2.28).

3.2.19 *instrumental QC standards*—these provide information on measurement performance during the instrumental analysis portion of the overall analyte measurement process. They include CCBs, CCVs, ICB, and ICVs. **E1613**

3.2.20 *intermediate (auxiliary) argon flow*—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**

3.2.21 *internal standard*—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**

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

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

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

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

3.2.24 *linear dynamic range*—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**

3.2.25 *load coil*—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**

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

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

3.2.27.1 *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.

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

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

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

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

3.2.30 *nebulizer*—a device used to create an aerosol from a liquid. **ISO 15202**

3.2.31 *outer (plasma) argon flow*—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**

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

3.2.33 *primary standard*—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. **D5011**

3.2.34 *reagent blank*—solution containing all reagents used in sample dissolution, in the same quantities used for preparation of blank and sample solutions. **ISO 15202**

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

3.2.35 *sample dissolution*—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**

3.2.36 *sample preparation*—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**

3.2.37 *sample solution*—solution prepared from a sample by the process of sample dissolution. **ISO 15202**

3.2.38 *secondary standard*—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. **D5011**

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

3.2.39.1 *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**).

3.2.40 *spiked reagent blank*—a reagent blank aliquot that is spiked with a known amount of analyte.

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

3.2.41 *spiked media blank*—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.

3.2.42 *spray chamber*—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**

3.2.43 *stock standard solution*—solution used for preparation of working standard solutions and/or calibration solutions, containing the analyte(s) of interest at a certified concentration(s) traceable to primary standards (National Institute of Standards and Technology or international measurement standards). **ISO 15202**

3.2.44 *test solution*—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**

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

3.2.45 *transport interference*—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**

3.2.46 *tune*—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**).

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

3.2.48 *working standard solution*—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**

3.2.49 *workplace*—the defined area or areas in which the work activities are carried out. **EN 1540**

4. Summary of Test Method

4.1 A known volume of air is drawn through a filter to collect airborne particulates suspected to contain metals or metalloids, or both, in accordance with Test Method D7035.

4.2 A known volume of air is drawn through a filter to collect airborne particulates suspected to contain metals or metalloids, or both, in accordance with Test Method D7035.

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 of the sample dissolution methods specified.

4.4 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 standard 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 A4. 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 ISO 1042, made of borosilicate glass and complying with the requirements of 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 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 A4. During sample preparation and analysis, use only reagents of analytical grade. The concentration of metals and metalloids of interest shall be less than 0.1 µg/L.

NOTE 3—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).

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 older 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 older 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 100 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 (typically between 1 µg/L and 100 µg/L).

NOTE 7—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, such as low-density polyethylene bottles, for a maximum period of one month.

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

NOTE 9—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.

NOTE 10—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 11—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).

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.

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 standard test method. It is also necessary when analyzing a new sample matrix that a scan for the presence of internal standards be performed.

9. Sampling Procedure

9.1 Samples to be prepared for analysis by this standard test method shall be collected in accordance with standard 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), and Annex A4 (hot block digestion).

NOTE 12—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.

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), and Annex A4 (hot block digestion). 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 13—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. (Appendix X4 provides 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), and Annex A4 (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-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 14—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 % (**5**). 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, and Annex A4, 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 15—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 16—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 17—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 18—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 19—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.

NOTE 20—High-efficiency nebulizers (for example, ultrasonic) give higher sensitivity than 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 (**6-9**). 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 21—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:*

TABLE 3 Recommended Analytical Isotopes and Examples of Instrumental Detection Limits (6-9)

Element	Recommended Analytical Isotopes[A]	Example Instrumental Detection Limits, mg/L[B]
Aluminum	27	0.0006-0.027
Antimony	121, 123	0.0002-0.0009
Arsenic	75	0.0006-0.02
Barium	135, 137, 138	0.00002-0.003
Beryllium	9	0.0001-0.003
Bismuth	209	0.00004-0.003
Boron	10, 11	0.001-0.003
Cadmium	106, 108, 111, 114	0.00009-0.0009
Calcium	43, 44	0.0002-1.5
Cesium	133	0.00001-0.0003
Chromium	52, 53	0.0002-0.013
Cobalt	59	0.00008-0.002
Copper	63, 65	0.0001-0.003
Gallium	69, 71	0.0002-0.0004
Germanium	72, 74	0.0003-0.002
Hafnium	178	0.0001-0.0008
Indium	115	0.00001-0.0007
Iron	56, 57	0.0003-0.46
Lead	206, 207, 208	0.00004-0.0006
Lithium	6, 7	0.00009-0.004
Magnesium	24, 25	0.00007-0.120
Manganese	55	0.00007-0.005
Mercury	199, 201, 202	0.0001-0.016
Molybdenum	95, 98	0.0001-0.002
Nickel	58, 60	0.0004-0.1
Niobium	93	0.00001-0.0006
Phosphorus	31	0.1-0.5
Platinum	195	0.00005-0.002
Potassium	39	0.0002-3.0
Rhodium	103	0.00001-0.0002
Selenium	77, 82	0.0007-0.4
Silver	107, 109	0.00005-0.002
Sodium	23	0.0003-2
Tellurium	125, 126	0.0001-0.0008
Thallium	203, 205	0.00004-0.0004
Tin	118, 120	0.0002-0.005
Tungsten	182, 184	0.0002-0.005
Uranium	238	0.00001-0.0001
Vanadium	51	0.0002-0.003
Yttrium	89	0.00002-0.0002
Zinc	64, 66, 68	0.0001-0.018
Zirconium	90	0.00003-0.0003

[A] Isotopes recommended for analytical determination are underlined. Alternate masses may be used but interferences must 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 (**6-9**) for additional details.

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 22—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 23—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 (**10**). Under normal circumstances, use the default sampling depth recommended by the instrument manufacturer. However, the sampling depth may be optimized for specific applications.

NOTE 24—In general, at constant power and nebulizer gas flow rate, an increase in sampling depth reduces the ion count (**6**).

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 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 25—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 26—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 27—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 28—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 29—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 30—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 31—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 (**11**).

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.

11.5.3 *Internal Standards*—The internal standard signal response in each sample test solution should be within 50 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 (**12**). 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 32—Although sampling is not expressly discussed in this standard 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 33—Applications of cause and effect analysis to analytical methods have been described in the published literature (**13**). 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. Calculate the mean concentration of each of the metals and metalloids of interest in the blank test solutions.

12.2 Calculate the mean concentration of each of the metals and metalloids of interest in the blank test solutions.

12.3 Calculate the mass concentration of each metal or metalloid of interest in the sample (at ambient conditions) using the equation:

$$\rho_M = \{[(\rho_{M,1} \times V_1 \times F) - (\rho_{M,0} \times V_0)]/1000\}/V \quad (1)$$

where:

ρ_M = calculated mass concentration of metal or metalloid in the air filter sample, in milligrams per cubic meter, at ambient conditions;
$\rho_{M,0}$ = the mean concentration of metal or metalloid in the blank solutions, in micrograms per liter;
$\rho_{M,1}$ = concentration of metal or metalloid in the sample test solution, in micrograms per liter;
V = volume, in liters, of the collected air sample;
V_0 = volume, in milliliters, of the blank solutions;
V_1 = volume, in milliliters, of the sample test solutions; and
F = dilution factor used (F = 1 in the absence of dilution).

12.4 Table 4 provides elemental equations that should be used when applicable to correct for specific interferences or isotopic variability.

NOTE 34—Use of the equations in Table 4 is typically applicable when a collision/reaction system is not being used.

13. Method Performance

13.1 *Method Detection Limits and Quantification Limits*—Method detection limits (MDLs) and method quantification limits (MQLs) depend on a number of factors, including the sample matrix (including sampling media), the sample preparation method, the mass selected, the analytical instrument used, the instrument operating parameters, and blank variability. MDLs and MQLs shown in Table 5 were estimated by preparing test solutions from mixed cellulose ester (MCE) filters, followed by analysis by ICP-MS (**14-16**). Results in the table are presented as examples of achievable MDLs and MQLs.

TABLE 4 Recommended Interference Correction Equations for Data Calculation

Element	Elemental Equation[A]	Note
Al	(1.000) (^{27}C)	...
Sb	(1.000) (^{121}C)	...
As	(1.000) (^{75}C) – (3.127) [(^{77}C) – (0.815) (^{82}C)]	B
Ba	(1.000) (^{137}C)	...
Be	(1.000) (^{9}C)	...
Cd	(1.000) (^{111}C) – (1.073) [(^{108}C) – (0.712) (^{106}C)]	C
Cr	(1.000) (^{52}C)	D
Co	(1.000) (^{59}C)	...
Cu	(1.000) (^{63}C)	...
Pb	(1.000) (^{206}C) + (1.000) (^{207}C) + (1.000) (^{208}C)	E
Mn	(1.000) (^{55}C)	...
Mo	(1.000) (^{98}C) - (0.146) (^{99}C)	F
Ni	(1.000) (^{60}C)	...
Se	(1.000) (^{82}C)	G
Ag	(1.000) (^{107}C)	...
Tl	(1.000) (^{205}C)	...
Th	(1.000) (^{232}C)	...
U	(1.000) (^{238}C)	...
V	(1.000) (^{51}C) – (3.127) [(^{53}C) – (0.113) (^{52}C)]	H
Zn	(1.000) (^{66}C)	...
Kr	(1.000) (^{83})	...
Pd	(1.000) (^{105})	...
Ru	(1.000) (^{99})	...
Sn	(1.000) (^{118})	...
Bi	(1.000) (^{209}C)	I
In	(1.000) (^{115}C) – (0.016) (^{118}C)	J
Sc	(1.0000) (^{45}C)	K
Tb	(1.000) (^{159}C)	...
Y	(1.000) (^{89}C)	I

[A] C = calibration blank subtracted counts at specified mass.
[B] Correction for chloride interference with adjustment for Se77. ArCl 75/77 ratio may be determined from the reagent blank.
[C] Correction for MoO interference. An additional isobaric elemental correction should be made if palladium is present.
[D] In 0.4 % v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank.
[E] Allowance for isotopic variability of lead isotopes.
[F] Isobaric elemental correction for ruthenium.
[G] Some argon supplies contain krypton as an impurity. Selenium is corrected for Kr82 by background subtraction.
[H] Correction for chloride interference with adjustment for Cr53. ClO 51/53 ratio may be determined from the reagent blank.
[I] May be present in environmental samples.
[J] Isobaric elemental correction for tin.
[K] Polyatomic ion interference.

TABLE 5 Estimated Method Detection Limits and Method Quantitation Limits[A]

Element	Isotope	MDL (MCE) (µg/L)	MQL (MCE) (µg/L)	Reference[B,C]
Al	27	0.23	0.77	(14)
As	75	0.069, 0.38, 0.0074	0.23, 1.27, 0.16	(14), (15), (16)
Be	9	0.0076, 0.05	0.025	(14), (15)
Cd	111,114	0.024, 0.00072	0.078, 0.0063	(14), (16)
Co	59	0.017, 0.00041	0.057, 0.0030	(14), (16)
Cr	52	0.17	0.55	(14)
Cu	63	0.24, 0.0044	0.79, 0.14	(14), (16)
Mg	24	0.28	0.93	(14)
Mn	55	0.023	0.076	(14)
Ni	60	0.0034	0.12	(16)
Pb	208	0.025, 0.0024	0.083, 0.014	(14), (16)
U	...	0.046	0.15	(15)
V	51	0.024	0.079	(14)
Zn	66	0.48	1.6	(14)

[A] Data are not available for the following elements: Ag, B, Ba, Bi, Ca, Cs, Fe, Ga, Ge, Hf, Hg, In, K, Li, Mo, Na, Nb, P, Pt, Rh, Sb, Se, Sn, Te, Tl, W, Y, and Zr.
[B] For reference (14), microwave digestion was used, and the sample matrix was 4% nitric acid. For reference (15), hot plate digestion with nitric and hydrochloric acids was used. For reference (16), open vessel microwave digestion was used, and the sample matrix was 4% nitric acid and 1% hydrochloric acid.
[C] For reference (16), the value listed under MDL is the detection limit of the analytical procedure (DLAP), defined as the response of the reagent blank plus three times the standard deviation, based on ten analyses of the reagent blank. The value listed under MQL is the reliable quantitation limit (RQL), defined as that amount of analyte spiked on a sampler which will give a detector response considered to be the lower limit for a precise quanjtitative measurement.

13.2 *Factors Affecting Precision and Bias*—The sample dissolution methods described in the Annexes are believed to be effective for most applications, that is, the analytical method is expected to exhibit negligible bias. However, the dissolution methods will not be effective in all instances (**17**). For certain target analytes and certain matrices, it may be necessary to investigate using an alternative sample dissolution method if it is found that recoveries are not quantitative. Factors such as matrix effects and the specific sample dissolution method employed will influence the analytical figures of merit obtained for the overall method.

13.3 *Statement of Precision and Bias*[5]—The precision of this test method is based on an interlaboratory study conducted in 2007. Twenty laboratories tested four different sample concentrations, for 21 metals. Every "test result" represents an individual determination. The laboratories reported three (and in some instances four) replicate results for each analysis in order to estimate the repeatability limits of the standard. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report No. D22-1035 and in Ref. (**18**). To address outliers that were observed, additional statistical analyses were conducted using robust multivariate methods (**19**). Table 6 contains the resulting values, for each of the 21 metals, including the concentration of each element in the sample, the number of reporting laboratories (n), bias, repeatability as represented by within-laboratory standard deviation (RSD_w), and reproducibility as represented by interlaboratory standard deviation (RSD_b).

TABLE 6 Precision and Bias Estimates[A]

Element	Loading (µg)	n	Bias	% RSD_w	% RSD_b
Al	0.250	14	0.20	1.28	0.60
	5.0	18	-0.14	0.74	0.60
	100	18	-0.14	0.14	0.13
Sb	0.025	11	-0.22	0.11	0.40
	0.50	14	-0.08	0.10	0.28
	10	15	-0.05	0.05	0.14
As	0.250	11	-0.13	0.03	0.08
	5.0	15	-0.02	0.04	0.08
	100	15	-0.06	0.04	0.06
Ba	0.250	16	-0.05	0.04	0.11
	5.0	17	-0.04	0.02	0.07
	100	17	-0.14	0.13	0.10
Be	0.025	11	-0.19	0.05	0.24
	0.50	15	-0.09	0.03	0.19
	10	16	-0.19	0.10	0.11
Cd	0.025	11	-0.13	0.12	0.30
	0.50	14	-0.03	0.03	0.08
	10	15	-0.17	0.09	0.10
Cr	0.250	17	-0.09	0.14	0.15
	5.0	20	-0.04	0.04	0.09
	100	20	-0.16	0.07	0.08
Co	0.025	11	-0.04	0.04	0.10
	0.50	15	-0.03	0.04	0.10
	10	16	-0.18	0.10	0.11
Cu	0.250	17	-0.04	0.08	0.14
	5.0	18	0.00	0.03	0.09
	100	18	-0.20	0.09	0.09
Fe	0.250	12	0.21	1.37	0.00
	5.0	14	0.00	0.18	0.16
	100	15	-0.10	0.07	0.12
Pb	0.025	12	0.01	0.07	0.18
	0.50	16	-0.04	0.05	0.18
	10	17	-0.15	0.08	0.11
Mg	0.250	14	0.04	0.59	0.42
	5.0	15	-0.04	0.09	0.27
	100	15	-0.18	0.09	0.14
Mn	0.025	11	0.12	0.16	0.21
	0.50	15	-0.03	0.04	0.11
	10	16	-0.22	0.09	0.13
Mo	0.025	13	-0.28	0.18	0.72
	0.50	15	-0.11	0.04	0.33
	10	17	-0.08	0.09	0.14
Ni	0.025	12	-0.20	0.34	0.80
	0.50	16	-0.12	0.08	0.18
	10	19	-0.25	0.09	0.13
Se	0.025	7	-0.08	0.50	0.68
	0.50	15	-0.19	0.30	0.16
	10	16	-0.17	0.07	0.08
Ag	0.025	6	0.18	0.93	0.00
	0.50	8	-0.09	0.34	0.33
	10	9	-0.26	0.21	0.46
Sn	0.025	10	-0.37	0.15	0.44
	0.50	13	-0.19	0.30	0.16
	10	14	-0.01	0.04	0.10
U	0.025	6	-0.22	0.04	0.24
	0.50	9	-0.06	0.02	0.05
	10	9	-0.08	0.08	0.11
V	0.025	6	-0.24	0.42	0.17
	0.50	9	-0.19	0.18	0.14
	10	14	-0.26	0.20	0.15
Zn	0.250	19	-0.34	0.51	1.02
	0.50	19	-0.08	0.06	0.18
	10	19	-0.20	0.09	0.11

[A] See ASTM Research Report No. D22-1035 and reference (**18**) for more information.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D22-1035. Contact ASTM Customer Service at service@astm.org.

14. Records

14.1 *Information Pertinent to Sample Preparation and Analysis*—The following information shall be supplied to the laboratory analyzing the sample(s):

14.1.1 The unique sample identification code(s);

14.1.2 Sample collection time and volume;

14.1.3 The type and dimensions of filter(s) used;

14.1.4 A list or lists of the metals and metalloids to be determined;

14.1.5 Details regarding the person to whom the analysis results shall be returned; and

14.1.6 Any special requirements (such as sample preparation method requested).

14.2 *Laboratory Records*—The following information shall be recorded by the person(s) carrying out the laboratory analysis. This information shall be passed to the person(s) responsible for completing the laboratory test report:

14.2.1 A statement to indicate the confidentiality of the information supplied, if appropriate;

14.2.2 Details of all reagent sources, including lot numbers, used for sample preparation and analysis;

14.2.3 Details of laboratory apparatus used for sample preparation and analysis, where this is relevant (for instance, record the serial number of equipment when there is more than one item of equipment of the same type in the laboratory);

14.2.4 Any deviations (and rationale for deviations) from the specified methods; and

14.2.5 Any unusual events or observations during sample preparation and analysis.

15. Report

15.1 Data to report shall include, at a minimum, the following:

15.1.1 All sample receipt and chain-of-custody information (see Guide D4840 for additional details);

15.1.2 Sample analysis results (for example, value, corresponding sample identifier and units of measure);

15.1.3 Applicable quality assurance and/or quality control data;

15.1.4 Identity of laboratory and analyst(s);

15.1.5 Information on sample preparation procedure(s) used;

15.1.6 Information on instrumentation and equipment used; and

15.1.7 Any other information deemed appropriate.

16. Keywords

16.1 analysis; elements; mass spectrometry; metals; metalloids; sample preparation; workplace air

ANNEXES

(Mandatory Information)

A1. SAMPLE DISSOLUTION OF SOLUBLE METAL AND METALLOID COMPOUNDS

A1.1 *Overview*:

A1.1.1 This Annex specifies a method for the dissolution of soluble metal and metalloid compounds using a suitable leach solution. Leach solutions specified include deionized water, or 1.0 M hydrochloric acid.

NOTE A1.1—The use of a collision/reaction system is recommended when selecting a dissolution method that uses hydrochloric acid. Chloride ions can produce polyatomic interferences. See Appendix X3 for additional information.

A1.1.2 The method is applicable when it is desired to obtain analytical results for soluble metals and metalloids.

A1.1.3 The sample dissolution method is applicable to the following metals and metalloids for which ACGIH TLVs have been set (**20**). The sample dissolution method may also be applicable to other elements for which exposure limits have not been established.

Aluminum	Rhodium
Barium	Silver
Molybdenum	Thallium
Nickel	Tungsten
Platinum	Uranium

A1.1.4 The sample dissolution method specified here can also be used for the dissolution of soluble zinc compounds, for example, for the determination of zinc chloride in the presence of zinc oxide in galvanizing fume.

A1.2 *Effectiveness of the Sample Dissolution Method*:

A1.2.1 Soluble compounds of metals and metalloids are essentially defined by the specific leach solutions and leach conditions used in the measurement methods prescribed for their determination (**21**). This is because, except for compounds that are very soluble or very insoluble in water, solubility can be dependent upon the nature of the leach solution and particle size, solute/solvent ratio, temperature, etc. Consequently the sample dissolution method, by definition, gives the desired result.

A1.2.2 Although the sample dissolution method for soluble metals and metalloid compounds described in this standard is design-based, there are circumstances in which it can give incorrect results. In particular, erroneous results can occur if a soluble compound reacts with the filter material or a contaminant on the filter to produce a less soluble or insoluble compound or compounds. For example, low recoveries will be obtained for soluble silver compounds if the filter used is contaminated with chloride. It is therefore important that

proper consideration is given to chemical compatibility when selecting a filter for collecting samples of soluble metal compounds (see Test Method D7035). If it is believed that there could be a chemical compatibility problem, tests should be performed to confirm that analytical recovery is satisfactory before samples are collected.

A1.3 *Summary of Dissolution Method*—The filter and collected sample are treated with a suitable leach solution and agitating in a water bath at 37 ± 2°C for 1 hour. The resultant sample solution is filtered through a membrane filter to remove undissolved particulate material, and a test solution is prepared for subsequent measurement of dissolved soluble metals and metalloids by ICP-MS.

A1.4 *Reagents*—The concentration of metals and metalloids of interest shall be less than 0.1 mg/L.

NOTE A1.2—It may be necessary to use reagent solutions of higher purity in order to obtain adequate detection limits for some metals and metalloids.

A1.4.1 *Water,* deionized, ASTM Type I (see Specification D1193).

A1.4.2 *Hydrochloric Acid Leach Solution,* 0.1 M.

A1.4.3 *Diluted Nitric Acid,* 10 % v/v (1+9 HNO_3 : H_2O).

A1.5 *Laboratory Apparatus*—Ordinary laboratory apparatus, plus equipment specified in Section 6, and:

A1.5.1 *Beakers,* 50 mL capacity, with watch glasses to fit, suitable for preparation of test solutions.

NOTE A1.3—50-mL beakers are not required if the leach step is carried out within the sampler.

A1.5.2 *Volumetric Flasks,* 10-mL capacity, for preparation of test solutions.

A1.5.3 *Plastic Labware:*

A1.5.3.1 *Disposable Test Tubes,* polypropylene, 10-mL minimum capacity, graduated, suitable for placement of test solutions;

A1.5.3.2 *Disposable Syringes,* polypropylene, 5-mL capacity, suitable for use with disposable syringe filters; and

A1.5.3.3 *Disposable Syringe Filters,* polypropylene, incorporating a suitable membrane filter (for example, polytetrafluoroethylene), with a pore size of 0.8 µm or less, for use with disposable syringes.

A1.5.4 *Suction Filtration Equipment:*

NOTE A1.4—Suction filtration is not required if disposable syringe filters are used to remove undissolved particulate matter from the sample solutions.

A1.5.4.1 *Suction Filtration Apparatus,* typically a water-operated or electrically-driven vacuum pump, connected to a conical flask fitted with a filter funnel/support assembly.

NOTE A1.5—Alternative suction filtration apparatus is commercially available that permits simultaneous vacuum filtration of multiple sample solutions.

A1.5.4.2 *Membrane Filters,* of a diameter suitable for use with the suction filtration apparatus, and inert to reaction with the extracted soluble metal and metalloid analyte(s).

NOTE A1.6—Membrane filters used should be selected carefully, taking into account their solubility in any subsequent sample preparation method for determination of total metals and metalloids (see Test Method D7035).

A1.5.5 *Water Bath,* with temperature control; and

A1.5.6 *Shaker or Stirrer,* comprised of chemically inert material, for agitation of leach solutions within the water bath.

A1.6 *Procedure*—For personal protection and for prevention of sample contamination, wear disposable gloves while carrying out sample preparation steps.

A1.6.1 *Leach Solution*—Select a suitable leach solution according to the nature of the solubility of the metal and/or metalloid compounds of interest, and taking account of the definition of 'soluble' as it applies in the case of pertinent occupational exposure limits.

NOTE A1.7—National occupational exposure limits for soluble and/or metalloid compounds typically apply to water-soluble compounds. However, various nations have established exposure limits that relate to the use of a specific leach solution and/or leach conditions in the sample dissolution method.

A1.6.1.1 For soluble metal and metalloid compounds that have been assigned exposure limits, choose from the following options for leaching the sample filter:

(1) Deionized water for Al, Ag, Ba, Cr, Fe, Mo, Ni, Pt, Rh, Tl, W, U (**21**).

(2) 0.1 M Hydrochloric acid for Al, Ba, Cr, Fe, Mo, Pt, Rh, W, U (**22**).

NOTE A1.8—This leachate is not applicable to the dissolution of soluble silver or thallium compounds, owing to the formation of insoluble chlorides (**19**).

(3) 10 % Nitric acid for Ag, Tl (**22**).

A1.6.1.2 Follow the instructions given in national standards or regulations if these prescribe that a specific leach solution and/or leach condition is to be used when measuring the soluble compounds of (a) particular metal(s) or metalloid(s).

A1.6.2 *Preparation of Sample Solutions*—Wear disposable gloves during sample preparation in order to avoid the possibility of contamination from the hands.

A1.6.2.1 Open the filter transport cassettes, sampler filter cassettes or samplers containing the filters, and transfer each filter into an individual, labeled 50-mL beaker using clean flat-tipped forceps. Follow the sample procedure for the blank filters.

NOTE A1.9—Alternatively, sample dissolution can be carried out directly within the samplers (**23, 24**), in which case there is no need to open the samplers and remove the filters.

A1.6.2.2 Accurately pipet 5 mL of leach solution into each beaker. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler form part of the sample, used the leach solution to carefully wash any particulate material adhering to the internal surfaces of the sampler into the beaker.

NOTE A1.10—Alternatively, the leach may be carried out in the sampler, if it is water-tight when the outlet is sealed and if it is of sufficient capacity. In this case, the leach solution should be added to each sampler via the air inlet orifice, and the samplers should be positioned above the water bath in a suitable manner so that spillage and contamination of the sample solutions is avoided.

A1.6.2.3 Cover each beaker with a watch glass, place in a water bath at 37 ± 2°C, and agitate mechanically for 60 min, ensuring that the sample filters are fully immersed throughout the leach period. Do not use ultrasonic agitation to promote sample dissolution.

A1.6.3 *Filtration of Sample Solutions*—Remove undissolved material from the sample solution using a syringe filter or suction filtration apparatus, as described below.

NOTE A1.11—If a test solution is also to be prepared for the determination of insoluble compounds of metals and metalloids, it may be necessary to use suction filtration equipment to retain the undissolved material for subsequent sample treatment.

A1.6.3.1 *Removal of Undissolved Material Using a Syringe Filter:*

(1) Pipet an additional 4 mL of leach solution into each beaker, and swirl to mix.

(2) Pipet 0.5 mL of concentrated nitric acid into a labeled disposable, graduated 10-mL test tube (for stabilization of the metals and metalloids of interest in the test solution to be analyzed).

(3) Draw up approximately 5 mL of each sample solution into a disposable syringe.

(4) Fit each syringe with a syringe filter, and dispense the sample solution through the filter into the disposable test tube (containing 0.5 mL of nitric acid) until the liquid level reaches the 5 mL graduation line of the test tube. Close the tube and mix thoroughly to produce the test solution.

NOTE A1.12—The sample solution may be made up to a larger volume if more than 5 mL of test solution is required for analysis.

(5) Dispose of the syringes and syringe filters after filtering one sample solution. Do not re-use syringes and syringe filters.

A1.6.3.2 *Removal of Undissolved Material Using Suction Filtration:*

(1) Filter each sample solution through a membrane filter using suction filtration apparatus, so as to collect the filtrate in a labeled disposable, graduated 10-mL test tube.

NOTE A1.13—If the leach was carried out within the sampler, the sample filter itself can be used to filter the sample solution (**20**). This can be done by connecting the outlet orifice of the sampler directly to a suction filtration apparatus, and capturing the filtrate into the test tube.

(2) Rinse the sample filter and beaker with three 1-mL aliquots of leach solution, allowing the liquid to completely drain from the filter funnel of the suction filtration apparatus between washings.

(3) Remove the test tube from the suction filtration apparatus, and pipet concentrated nitric acid, until the liquid level reaches the 10 mL graduation line of the test tube, to stabilize the solution of the metals and metalloids of interest. Close the tube and mix thoroughly to produce the test solution.

NOTE A1.14—The sample solution may be made up to a larger volume if more than 10 mL of test solution is required for analysis.

(4) Keep the test solutions for analysis by ICP-MS.

(5) If the filtered, undissolved material is to be further prepared for determination of insoluble metal and metalloid compounds, retain the membrane filters used in suction filtration for subsequent sample processing by placing them into clean 50-mL beakers and covering them with watch glasses.

A2. HOT PLATE DISSOLUTION OF METAL AND METALLOID COMPOUNDS

A2.1 *Overview*:

A2.1.1 This Annex specifies a method for dissolution of metals and metalloids and their compounds on a hot plate. Options are given for use of various acid mixtures to be employed for sample dissolution.

NOTE A2.1—The use of a collision/reaction system is recommended when selecting a dissolution method that uses hydrochloric acid or sulfuric acid. Chloride and sulfate ions can produce polyatomic interferences. See Appendix X3 for additional information.

A2.1.2 The metals and metalloids for which one or more of the sample dissolution methods specified in this Annex is (are) applicable are listed below:

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

A2.2 *Summary of Hot Plate Dissolution*:

A2.2.1 The filter and collected sample are transferred to a beaker and heated on a hot plate in a strong acid mixture (which may also contain hydrogen peroxide). The beaker contents are brought to a boil until nearly all of the acid mixture has been driven off. This procedure serves to dissolve target metals and metalloids which may be present in the sample.

A2.2.2 For some target elements, additional acid is added prior to a second hot plate reheating.

A2.2.3 The sample solution is allowed to cool, and is then diluted with water to produce a test solution for subsequent analysis.

A2.3 *Effectiveness of Hot Plate Dissolution Methods*:

A2.3.1 *Mixtures of Hydrochloric and Nitric Acids*—Hot plate extraction in mixtures of hydrochloric and nitric acids has been shown to be effective for the dissolution of numerous metals and metalloids (Al, As, Ag, Ba, Be, Bi, Ca, Cd, Co, Cs, Cu, In, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Sn, Sr, Te, Ti, Tl, Y, Zn, Zr) present in air filter samples (**25-29**). This acid mixture may be effective for the dissolution of other elements (for example U, V) from airborne particulate matter. Hydrochloric

acid is an effective solvent for many metal oxides, phosphates, sulfides, and basic silicates, while nitric acid is an oxidizing agent that effectively dissolves many metals and metalloids and their compounds (**30**). This acid mixture is not effective for the dissolution of acidic silicates and some metal oxides that are resistant to acid attack.

A2.3.2 *Mixtures of Sulfuric Acid and Hydrogen Peroxide*—Hot plate extraction in mixtures of sulfuric acid and hydrogen peroxide has been shown to be effective for the dissolution of numerous elements (Al, Ag, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Se, Te, Sn, V, Zn) present in air filter samples (**25, 26**). This acid mixture may be effective for the dissolution of other metals and metalloids (for example B, Bi, Cs, In, K, Li, Na, Sr, Ti, Tl, U, Y) from airborne particulate matter. Sulfuric acid is effective for dissolution purposes owing in part to its high boiling point (340°C), which facilitates decomposition of substances which may not break down at lower temperatures. Some elements (for example Ba, Ca, Pb) form insoluble sulfates, which may be alleviated by the addition of hydrochloric acid. Sulfuric acid and hydrogen peroxide is not effective for the dissolution of silicate materials and some metal oxides that are resistant to acid attack.

A2.3.3 *Mixtures of Nitric Acid and Perchloric Acid*—Hot plate extraction in mixtures of nitric acid and perchloric acid has been shown to be effective for the dissolution of numerous elements (Al, Ag, As, Be, Cd, Ca, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pt, Se, Te, Ti, Tl, V, Y, Zn, Zr) from airborne particulate matter (**26, 27**). This acid mixture may be effective for the dissolution of other metals and metalloids (for example Bi, Cs, K, Sb, Sr, U) from airborne particulate matter. Perchloric acid is a strong oxidizing agent and solvent, and is especially useful for dissolving ferroalloys. Neither nitric acid or perchloric acids, nor their mixtures, are effective for the dissolution of silicate materials. Addition of hydrochloric acid can aid in the dissolution of certain elements (such as Te) from especially difficult sample matrices.

A2.3.4 *Alternative Acid Mixtures*—All candidate sample preparation methods should be verified with respect to their suitability for dissolving elements of interest from the particular materials which could be present in the test atmosphere. An alternative, more vigorous sample dissolution method is required for sample matrices that are especially difficult to solubilize, and for elements for which a candidate dissolution procedure is not applicable. For example, the use of hydrofluoric acid (HF) is ordinarily necessary for the dissolution of metals and metalloids that are bound to silicate materials (**23, 27**), and may be required for refractory metal oxides. (**Warning—**Extreme care must be taken when using hydrofluoric acid in sample preparations (see Appendix X1 for pertinent safety information).)

NOTE A2.2—If hydrofluoric acid is employed in sample preparation, it will be necessary to use corrosion-resistant laboratory ware made from materials that are not attacked by HF (for example, polytetrafluorethylene [PTFE]), as well as platinum cones in the ICP-MS.

A2.4 *Reagents*—The concentration of metals and metalloids of interest shall be less than 0.1 mg/L.

NOTE A2.3—It may be necessary to use reagents of higher purity in order to obtain adequate detection limits for some metals and metalloids.

A2.4.1 *Water,* deionized, ASTM Type I (see Specification D1193).

A2.4.2 *Hydrochloric Acid (HCl),* concentrated, ρ ~1.18 g/mL, ~36 % (m/m).

A2.4.3 *Nitric Acid (HNO_3),* concentrated, ρ ~1.42 g/mL, ~70 % (m/m).

A2.4.4 *Nitric Acid,* diluted 1+1: Carefully and slowly begin adding 250 mL of concentrated nitric acid to 250 mL of water in a 1-L polypropylene bottle by adding the acid in small aliquots. Between additions, swirl to mix, and run cold water over the side of the bottle to cool the contents. When addition of concentrated HNO_3 is complete, swirl to mix the contents, allow to cool to room temperature, close the bottle with its screw cap, and mix thoroughly.

A2.4.5 *Perchloric Acid ($HClO_4$),* concentrated, ρ ~1.67 g/mL, ~70 % (m/m).

A2.4.6 *Sulfuric Acid (H_2SO_4),* concentrated, ρ ~1.84 g/mL, ~98 % (m/m).

A2.4.7 *Sulfuric Acid,* diluted 1+1: Carefully and slowly begin adding 250 mL of concentrated sulfuric acid to 250 mL of water in a 1-L polypropylene bottle by adding the acid in small aliquots. Between additions, swirl to mix, and run cold water over the side of the bottle to cool the contents. When addition of concentrated H_2SO_4 is complete, swirl to mix the contents, allow to cool to room temperature, close the bottle with its screw cap, and mix thoroughly.

A2.4.8 *Hydrogen Peroxide (H_2O_2),* ~30 % (m/m). (**Warning—**Hydrogen peroxide is corrosive and oxidizing. Use suitable personal protective equipment (such as gloves, face shield, etc.) when working with H_2O_2.)

A2.5 *Laboratory Apparatus*—Ordinary laboratory apparatus, plus equipment specified in Section 6, and:

A2.5.1 *Beakers,* 50-mL capacity, with watch glasses to fit the beakers.

A2.5.2 *Volumetric Flasks,* 25-mL.

A2.5.3 *Hot Plate,* thermostatically controlled, capable of maintaining a surface temperature of up to at least 200°C.

NOTE A2.4—The efficiency of thermostatted hot plates is sometimes deficient, and the surface temperature can vary considerably with position on hot plates with large surface areas. It is therefore recommended to characterize the performance of the hot plate before use.

A2.6 *Procedure*—For personal protection and for prevention of sample contamination, wear disposable gloves while carrying out sample preparation steps.

A2.6.1 Open the filter transport cassettes, sample filter cassettes, or samplers. Transfer each filter into an individual, labeled 50-mL beaker using clean, flat-tipped forceps. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler forms part of the sample, use a small volume of diluted (1+9) nitric acid to carefully wash any particulate material adhering to the internal surfaces into the beaker. Follow the same procedure for blank filters. In consideration of target

elemental analytes, choose one of the procedures below (A2.6.2, A2.6.3, or A2.6.4) for sample dissolution.

A2.6.2 *Dissolution with Hydrochloric and Nitric Acids:*

A2.6.2.1 Add 3 mL of concentrated hydrochloric acid to each beaker, and allow to stand for several minutes. Then add 2 mL of 1+1 nitric acid, and cover with a watch glass.

A2.6.2.2 Place the beakers on the hot plate, and heat them at a surface temperature of ~140°C in a fume hood for approximately 10 minutes. Then slide back the watch glasses so that the beakers are only partially covered, and continue to heat the beakers until about 1 mL of acid solution remains in each beaker. (**Warning—**Spattering can occur if heating is too vigorous.)

A2.6.2.3 Remove each beaker from the hot plate and allow to cool. Then slowly and carefully add 5 mL of HCl to each beaker, and wash down the inside of each beaker with a small volume of water or 1+9 HNO_3.

A2.6.2.4 Return the beakers to the hot plate, and heat the sample solutions until they are near boiling. Then remove the beakers from the hot plate and allow to cool.

A2.6.2.5 Carefully wash down the watch glass and the inside of each beaker with water or 1+9 HNO_3. Quantitatively transfer the beaker contents to an individual, labeled 25-mL volumetric flask. Dilute to the mark with water, stopper, and mix thoroughly.

A2.6.2.6 Keep the test solutions for subsequent analysis by ICP-MS.

A2.6.3 *Dissolution with Sulfuric Acid and Hydrogen Peroxide:*

A2.6.3.1 Add 4 mL of 1+1 sulfuric acid and 1 mL of hydrogen peroxide to each beaker, and cover with a watch glass.

A2.6.3.2 Place the beakers on the hot plate, and heat them at a surface temperature of ~140°C in a fume hood for approximately 10 minutes.

A2.6.3.3 Increase the hot plate temperature to ~200°C, and then slide back the watch glasses so that the beakers are only partially covered. Continue to heat the beakers until dense white sulfur trioxide fumes are evolved, and about 1 mL of acid solution remains in each beaker. If the solution darkens, carefully add hydrogen peroxide drop-wise until it becomes colorless or slightly yellow in appearance. Avoid taking the solution to dryness, and discard any solutions inadvertently taken to dryness. (**Warning—**Spattering can occur if heating is too vigorous and if hydrogen peroxide is added too rapidly.)

A2.6.3.4 Remove each beaker from the hot plate and allow to cool. Then slowly and carefully add 5 mL of HCl to each beaker, and wash down the inside of each beaker with a small volume of water or 1+9 HNO_3. (**Warning—**Spattering can occur if sulfuric acid is still hot and HCl is added too rapidly.)

A2.6.3.5 Lower the hot plate surface temperature to ~140°C, return the beakers to the hot plate, and heat the sample solutions until they are near boiling. Then remove the beakers from the hot plate and allow to cool.

A2.6.3.6 Carefully wash down the watch glass and the inside of each beaker with water or 1+9 HNO_3. Quantitatively transfer the beaker contents to an individual, labeled 25-mL volumetric flask. Dilute to the mark with water, stopper, and mix thoroughly.

A2.6.3.7 Keep the test solutions for subsequent analysis by ICP-MS.

A2.6.4 *Dissolution with Nitric Acid and Perchloric Acid:*

A2.6.4.1 Add 5 mL of concentrated nitric acid to each beaker, and cover with a watch glass.

A2.6.4.2 Place the beakers on the hot plate, and heat them at a surface temperature of ~140°C in a fume hood for approximately 10 minutes. Then slide back the watch glasses so that the beakers are only partially covered, and carefully add 1 mL of perchloric acid to each beaker.

A2.6.4.3 Increase the hot plate temperature to ~175°C, and apply heat to the beakers until dense white perchloric acid fumes are evolved, and about 1 mL of acid solution remains in each beaker. If the solution darkens, carefully add nitric acid drop-wise until it becomes colorless or slightly yellow in appearance. (**Warning—**spattering can occur if heating is too vigorous and if nitric acid is added too rapidly.)

A2.6.4.4 Cover each beaker completely with a watch glass, and continue to heat for one minute. Remove each beaker from the hot plate and allow to cool.

A2.6.4.5 If chromium is to be measured, add 1 mL of H_2O_2 to each beaker, and let sit for several minutes. Lower the hot plate surface temperature to ~140°C, return the beakers to the hot plate, and boil gently for a few minutes to remove the hydrogen peroxide. Finally, remove the beakers from the hot plate and allow the sample solutions to cool once more.

A2.6.4.6 Slowly and carefully add 5 mL of HCl to each beaker, and wash down the inside of each beaker with a small volume of water or 1+9 HNO_3.

A2.6.4.7 Lower the hot plate surface temperature to ~140°C, return the beakers to the hot plate, and heat the sample solutions until they are near boiling. Then remove the beakers from the hot plate and allow to cool again.

A2.6.4.8 Carefully wash down the watch glass and the inside of each beaker with water or 1+9 HNO_3. Quantitatively transfer the beaker contents to an individual, labeled 25-mL volumetric flask. Dilute to the mark with water, stopper, and mix thoroughly.

NOTE A2.5—If 1+9 HNO_3 is used for washing in steps A2.6.3.6 and A2.6.4.8, the resulting acid concentration will be high (20 % HNO_3), and it will be necessary to ensure the use of corrosion resistance in the ICP-MS (such as the use of platinum cones).

A2.6.4.9 Keep these test solutions for subsequent analysis by ICP-MS.

A3. MICROWAVE DISSOLUTION OF METAL AND METALLOID COMPOUNDS

A3.1 *Overview*:

A3.1.1 This annex specifies a method for dissolution of metals and metalloids and their compounds using a closed-vessel microwave digestion system. Options are given for use of various acid mixtures to be employed for sample dissolution.

NOTE A3.1—Although not covered here, an alternative microwave digestion technique entails the use of open vessels, rather than closed. If it is desired to use open-vessel microwave digestion, the data quality objectives of the method for target analytes should be equivalent to those for closed-vessel digestion.

A3.1.2 The metals and metalloids for which one or more of the sample dissolution methods specified in this Annex is (are) applicable are listed below:

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

A3.2 *Summary of Microwave Dissolution Procedure*:

A3.2.1 The filter and collected sample are placed in a microwave transparent digestion vessel.

A3.2.2 Nitric acid solution, or nitric acid plus perchloric acid (4:1), is introduced into the vessel, which is then sealed and heated under pressure in a laboratory microwave digestion system. A second microwave heating is then carried out using hydrochloric acid.

A3.2.3 The sample solution is allowed to cool, and is then diluted with water to produce a test solution for subsequent analysis by ICP-MS.

A3.3 *Effectiveness of Microwave Dissolution*—The use of microwave assisted methods can be advantageous since sample dissolution times can be shortened considerably in comparison to more conventional techniques such as hot plate digestion (**27**). In particular, the boiling points of acids are raised when they are heated under pressure, as they are in closed vessel microwave digestion systems. For example, the boiling point of nitric acid is elevated to 180–190°C at ~700 kPa, compared to its boiling point of 120°C at atmospheric pressure. At these higher temperatures, samples are attacked more rapidly, and often more effectively.

A3.3.1 *HNO_3/HCl*—Using the specified method employing nitric and hydrochloric acids, dissolution of airborne particulate matter collected on membrane filters is believed to be effective for numerous metals and metalloids (Ag, Al, As, B, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Tl, U, V, W, Y, Zn). This acid mixture may be effective for the dissolution of other elements (for example Bi, Cs, Hf, In, Li, P, Pt, Rh, Sn, Ta, Te, Ti, Zr) from airborne particulate matter.

A3.3.2 *HNO_3/$HClO_4$/HCl*—The use of perchloric acid in concert with nitric and hydrochloric acids can give more complete sample dissolution in some instances, such as when the samples contain elemental carbon. The increased oxidation potential that results from the use of perchloric acid can also improve the analytical recovery for various metals and metalloids from certain types of material, for example, for chromium from welding fumes. For safety reasons, special care should be taken to use perchloric acid in limited quantities.

A3.3.3 *Alternative Acid Mixtures*—All candidate sample preparation methods should be verified with respect to their suitability for dissolving elements of interest from the particular materials which could be present in the test atmosphere. An alternative acid solution is required for sample matrices that are especially difficult to solubilize, and for elements for which a candidate dissolution procedure is not applicable. For example, the use of hydrofluoric acid (HF) is ordinarily necessary for the dissolution of metals and metalloids that are bound to silicate materials (**23, 29**), and may be required for refractory metal oxides. (**Warning—**Extreme care must be taken when using hydrofluoric acid in sample preparations (see Appendix X1 for pertinent safety information).)

NOTE A3.2—If hydrofluoric acid is employed in sample preparation, it will be necessary to use corrosion-resistant laboratory ware made from materials that are not attacked by HF (for example, polytetrafluorethylene [PTFE]), as well as platinum cones in the ICP-MS.

A3.4 *Reagents*—The concentration of metals and metalloids of interest shall be less than 0.1 mg/L.

NOTE A3.3—It may be necessary to use reagents of higher purity in order to obtain adequate detection limits for some metals and metalloids.

A3.4.1 *Water,* deionized, ASTM Type I (see Specification D1193).

A3.4.2 *Nitric Acid (HNO_3),* concentrated, ρ ~1.42 g/mL, ~70 % (m/m).

A3.4.3 *Hydrochloric Acid (HCl),* concentrated, ρ ~1.18 g/mL, ~36 % (m/m).

A3.4.4 *Perchloric Acid ($HClO_4$),* concentrated, ρ ~1.67 g/mL, ~70 % (m/m).

A3.5 *Laboratory Apparatus*—Ordinary laboratory apparatus, plus equipment specified in Section 6, and:

A3.5.1 *Beakers,* 50-mL capacity, with watch glasses to fit the beakers.

A3.5.2 *Volumetric Flasks,* 25-mL.

A3.5.3 *Microwave Digestion System,* designed for closed-vessel digestion in the laboratory. The microwave shall be equipped with power output regulation, and it should enable pressure control of microwave vessels. The microwave shall be fitted with a temperature control system capable of sensing the

temperature to ±2°C, and it shall provide automatic adjustment of microwave power within 2 seconds. The microwave cavity shall be corrosion resistant and well ventilated, with all electronics protected against corrosion to ensure safe operation. (**Warning—**Ensure that the manufacturer's safety recommendations are followed.)

A3.5.4 *Lined Microwave Sample Vessels,* 50-mL minimum volume, designed for carrying out microwave digestions at pressures of up to 3000 kPa or greater. The vessels shall be designed to allow for controlled pressure relief, and they shall be capable of withstanding an operating temperature of at least 180°C. Clean the sample vessels before use by soaking for a minimum of 12 h in (at least) 1+9 nitric acid and then rinsing thoroughly with water.

NOTE A3.4—Such vessels consist of an inner liner and cover made of microwave transparent and chemically resistant material (usually a fluorocarbon polymer such as tetrafluoro-methoxyl (TFM) polymer), which contains and isolates the sample solution from a high strength, outer vessel structure that is pressure-resistant. (**Warning—**The material from which the outer vessels are made is usually not as chemically resistant as the liner material. Since the outer vessels provide the physical strength required to withstand the high pressures generated within the inner liners, they shall be inspected regularly to check for any chemical or physical degradation.)

A3.6 *Procedure*—For personal protection and for prevention of sample contamination, wear disposable gloves while carrying out sample preparation steps.

A3.6.1 Open the filter transport cassettes, sample filter cassettes, or samplers. Transfer each filter into the liner of an individual, labeled microwave digestion vessel using clean, flat-tipped forceps. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler forms part of the sample, use a small volume of diluted (1+9) nitric acid to carefully wash any particulate material adhering to the internal surfaces into the beaker. Follow the same procedure for blank filters.

A3.6.2 Within a fume hood, carefully add *(a)* 5 mL of concentrated nitric acid or *(b)* 4 mL of concentrated nitric acid and 1 mL of concentrated perchloric acid to each liner. Cover each vessel liner with its lid.

A3.6.3 Seal the sample vessels and place them, evenly distributed, in the turntable of the microwave digestion system, following the manufacturer's instructions.

NOTE A3.5—Even, symmetrical spacing of vessels is usually needed to ensure uniform microwave heating of all vessel solutions.

A3.6.4 Program the microwave digestion system to operate the following temperature profile: *(1)* to reach an operating temperature of at least 180°C in less than 10 min; and *(2)* to hold the operating temperature of at least 180°C for at least an additional 15 min.

A3.6.5 When the program has run, allow the vessels to cool and permit the pressure to return to <70 kPa.

A3.6.6 Remove the turntable from the microwave digestion system and place in a fume hood. Carefully open each sample vessel.

A3.6.7 Carefully add 5 mL of concentrated hydrochloric acid to each vessel. Close the liners, seal the vessels, and repeat the microwave digestion program specified above.

A3.6.8 Allow the vessels to cool, and permit the pressure to return to atmospheric pressure.

A3.6.9 Carefully wash the lid and sides of each vessel liner with a small volume of water or 1+9 nitric acid, and quantitatively transfer the solution to an individual, labeled 25 mL volumetric flask. Dilute to the mark with water, stopper, and mix thoroughly to produce the test solution.

NOTE A3.6—If 1+9 HNO_3 is used for washing in step A3.6.9, the resulting acid concentration will be high (20 % HNO_3 and 20 % HCl). If the resulting solution is too viscous, it should be diluted with water (with caution to avoid spattering). It will be necessary to ensure the use of corrosion resistance in the ICP-MS (such as the use of platinum cones).

A3.6.10 Keep these test solutions for subsequent analysis by ICP-MS.

A4. HOT BLOCK DISSOLUTION OF METAL AND METALLOID COMPOUNDS (31)

A4.1 *Overview*:

A4.1.1 This annex specifies a method for dissolution of metals and metalloids and their compounds using a 95°C hot block digestion system.

A4.1.2 The metals and metalloids for which the sample dissolution method specified in this Annex is applicable are listed below (subject to the limitations described in A4.3.1 and A4.3.2):

Aluminum	Copper	Platinum
Antimony[A]	Gallium	Potassium
Arsenic	Indium	Selenium
Barium	Iron	Sodium
Beryllium	Lead[B]	Tellurium
Bismuth[C]	Magnesium	Thallium
Boron	Manganese	Tin[D]
Cadmium	Molybdenum	Vanadium
Calcium	Nickel	Yttrium
Chromium	Phosphorus	Zinc
Cobalt		

[A] Valid up to 25 000 mg/sample and within seven days of sample dissolution.
[B] Valid up to 50 000 mg/sample and at least 24 hours after sample dissolution; valid up to 15 000 mg/sample within 24 hours of sample dissolution.
[C] Valid up to 10 000 mg/sample and within seven days of sample dissolution.
[D] Valid up to 30 000 mg/sample and within seven days of sample dissolution.

A4.2 *Summary of Hot Block Dissolution Procedure*:

A4.2.1 The filter and collected sample are placed in a 50 mL transparent digestion vessel.

A4.2.2 Concentrated hydrochloric acid is introduced into the vessel, which is then capped and heated for 15 minutes in a laboratory hot block digestion system. A second heating is then carried out using nitric acid.

A4.2.3 The sample solution is allowed to cool, and is then diluted with water to produce a test solution for subsequent analysis by ICP-MS.

A4.3 *Effectiveness of Hot Block Dissolution*:

A4.3.1 *HCl/HNO$_3$*—Using the specified method employing hydrochloric and nitric acids, dissolution of airborne particulate matter collected on membrane filters has been shown **(31)** to be effective for numerous metals and metalloids (Al, As, B, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Ga, In, K, Mg, Mn, Mo, Na, Ni, Se, Te, Tl, V, Y, Zn). This acid mixture may be effective for the dissolution of other elements (for example Bi, Pb, Sb, Sn) from airborne particulate matter, with some restrictions as noted in the element table in A4.1.2. This method has not been demonstrated to be effective for welding fumes.

A4.3.2 *Alternative Acid Mixtures*—All candidate sample preparation methods should be verified with respect to their suitability for dissolving elements of interest from the particular materials which could be present in the test atmosphere. An alternative acid solution is required for sample matrices that are especially difficult to solubilize, and for elements for which a candidate dissolution procedure is not applicable. For example, the use of hydrofluoric acid (HF) is ordinarily necessary for the dissolution of metals and metalloids that are bound to silicate materials **(23, 29)**, and may be required for refractory metal oxides. (**Warning—**Extreme care must be taken when using hydrofluoric acid in sample preparations (see Appendix X1 for pertinent safety information).)

NOTE A4.1—If hydrofluoric acid is employed in sample preparation, it will be necessary to use corrosion-resistant laboratory ware made from materials that are not attacked by HF (for example, polytetrafluorethylene [PTFE]).

A4.3.3 *Ammonium Bifluoride*—A solution of 1 % ammonium bifluoride has been shown effective for dissolution of trace level beryllium, as described in Test Method D7202.

A4.4 *Reagents*—The concentration of metals and metalloids of interest shall be less than 0.1 mg/L.

NOTE A4.2—It may be necessary to use reagents of higher purity in order to obtain adequate detection limits for some metals and metalloids.

A4.4.1 *Water,* deionized, ASTM Type I (see Specification D1193).

A4.4.2 *Hydrochloric Acid (HCl),* concentrated, ρ ~1.18 g/mL, ~36 % (m/m).

A4.4.3 *Nitric Acid (HNO$_3$),* concentrated, ρ ~1.42 g/mL, ~70 % (m/m).

A4.4.4 *Ammonium Bifluoride Dissolution Solution*—1 % ammonium bifluoride (NH_4HF_2) solution (aqueous) for dissolution of beryllium in particulate matter. (**Warning—** Ammonium bifluoride is dissociated into HF and NH_4F in aqueous solution, and thus will etch glass. It is essential that corrosion-resistant laboratory ware be used.)

A4.5 *Laboratory Apparatus*—Ordinary laboratory apparatus, plus equipment specified in Section 6, and:

A4.5.1 *Hot Block Digestion Apparatus,* thermostatically controlled, capable of maintaining an internal temperature of 95°C for samples being digested, with wells appropriate for 50 mL digestion vessels.

NOTE A4.3—The actual internal temperature of samples being digested may vary from the digital readout. It is therefore recommended to characterize the performance of the hot block before use.

A4.5.2 *Digestion Vessels,* 50 mL, plastic, appropriate for the hot block apparatus being used, with caps.

A4.6 *Procedure*—For personal protection and prevention of sample contamination, wear disposable gloves while carrying out sample preparation steps.

A4.6.1 Open the filter transport cassettes, sample filter cassettes, or samplers. Transfer each filter into an individual, labeled 50 mL digestion vessel using clean, flat-tipped forceps. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or the sampler forms part of the sample, use a small volume of diluted (1+9) nitric acid to carefully wash any particulate matter adhering to the internal surfaces into the digestion vessel. Follow the same procedure for blank filters.

A4.6.2 *Dissolution with Hydrochloric and Nitric Acids:*

A4.6.2.1 Add 1.25 mL of concentrated hydrochloric acid to each digestion vessel, and cover with a plastic watch glass.

A4.6.2.2 Place the digestion vessels in the hot block apparatus and heat at an internal temperature of 95°C for 15 minutes.

A4.6.2.3 Remove the digestion vessels from the hot block apparatus and allow them to cool for at least 5 minutes.

A4.6.2.4 Carefully remove the watch glass from each digestion vessel, and add 1.25 mL of concentrated nitric acid. Replace the watch glass(es) and return the digestion vessel(s) to the hot block apparatus. Heat at an internal temperature of 95°C for 15 minutes.

A4.6.2.5 Remove the digestion vessels from the hot block apparatus and allow them to cool for at least 5 minutes.

A4.6.2.6 Carefully remove the watch glass from each digestion vessel and wash it down into the digestion vessel with Type I water.

A4.6.2.7 Dilute each sample to a final volume of 25 mL with Type I water. (**Warning—**Spattering can occur if acid is still hot and water is added too rapidly.) Cap and mix each sample.

A4.6.2.8 Keep these test solutions for subsequent analysis by ICP-MS.

A4.6.3 *Dissolution with 1 % Ammonium Bifluoride (Beryllium Only):*

A4.6.3.1 Follow the instructions for extraction of air filter samples given in Test Method D7202.

APPENDIXES

(Nonmandatory Information)

X1. SPECIAL SAFETY PRECAUTIONS WHEN USING PERCHLORIC OR HYDROFLUORIC ACIDS

X1.1 *Special Precautions for use of Hydrofluoric Acid*:

NOTE X1.1—**Warning:** Concentrated hydrofluoric acid 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 that suitable personal protective equipment (including suitable gloves and eye protection) is used when working with hydrofluoric acid. Handle vessels containing concentrated HF in a fume hood.

X1.1.1 Take extreme care when using hydrofluoric acid. Ensure that the nature and seriousness of hydrofluoric acid burns are understood before commencing work with this substance.

NOTE X1.2—The burning sensation associated with many concentrated acid burns (for example, nitric and hydrochloric acids) is not immediately apparent on exposure to hydrofluoric acid, and might not be felt for several hours. Relatively dilute solutions of hydrofluoric acid can also be absorbed through the skin, with serious effects similar to those resulting from exposure to the concentrated acid.

X1.1.2 When using hydrofluoric acid, it is recommended that disposable gloves are worn underneath suitable primary gloves, in order to provide added protection for the hands.

X1.1.3 Carry hydrofluoric acid burn cream (containing calcium gluconate) at all times while working with hydrofluoric acid, and for 24 hours afterwards. Apply the cream to any contaminated skin, after washing the affected area with copious amounts of water. Obtain medical attention immediately in case of an accident. Calcium gluconate has a limited lifetime and should be replaced prior to its expiration date.

X1.2 *Special Precautions for Use of Perchloric Acid*:

X1.2.1 Perchloric acid forms explosive compounds with organics and many metal salts. When performing sample dissolution using this acid, ensure that any organic material present is destroyed, for example by heating with nitric acid, before addition of perchloric acid.

X1.2.2 Do not allow perchloric acid solutions containing high concentrations of metal salts to boil to dryness. Solid perchloric acid is shock-sensitive and may explode.

X1.2.3 Perform sample digestions using a special fume hood designed for the use of perchloric acid, and incorporating a scrubbing system to remove acid vapors from exhaust gases so as to prevent the possibility of potentially explosive material accumulating in ducts.

X2. GUIDANCE ON MAINTENANCE OF ICP-MS INSTRUMENTATION

X2.1 *Maintenance Contract*—When entering into a maintenance contract, it is advisable to check the level of service offered, the response time for service, the level of experience and knowledge of service engineers, and the length of time the manufacturer will support the instrument and provide a source of spare parts and consumable items. A maintenance contract is advisable for the following reasons:

X2.1.1 Maintenance and calibration of certain instrument components could be beyond the capability of the laboratory;

X2.1.2 Instrument upgrades, both software and hardware, are often included in maintenance packages;

X2.1.3 It might not be possible to obtain spare parts and other consumables from sources other than the manufacturer; and

X2.1.4 Some accreditation systems require users to have a maintenance contract.

X2.2 *In-house Maintenance*:

X2.2.1 *Instrument Log Book*—It is advisable to maintain an instrument log book to record, at a minimum, the following:

X2.2.1.1 Details regarding service contracts and contacts;

X2.2.1.2 Service reports;

X2.2.1.3 Instrument usage (that is, who used the instrument, for what analyses, and for how long); and

X2.2.1.4 Details of faults and replacement of user-serviceable parts.

X2.2.2 *General Maintenance*—It is advisable to follow manufacturer's guidelines regarding maintenance. Failure to comply with such guidelines might invalidate maintenance contracts. At a minimum, the following checks should be carried out periodically:

X2.2.2.1 *Air Filters*—Check for overloading, and clean or replace if clogged.

X2.2.2.2 *Cooling System*—Check for loose connections and for signs of corrosion around metal couplings; check the filter; check water, antifreeze and fungicide levels (refer to the manual for specific details).

X2.2.2.3 *Gas Lines*—Check for loose connections, leaks, and kinks; verify performance of inline filters and oil traps, and check inlet pressures (refer to the manual for specific details).

X2.2.2.4 *Exhaust System*—Check for loose connections, leaks, and leakages; verify performance of the ventilation system (refer to the manual for specific details).

X2.2.3 *Instrument Maintenance*—The following instrument checks should be carried out on a routine basis:

X2.2.3.1 *Peristaltic Pump Tubing*—Check for depressions and flat spots in tubing prior to use. New tubing requires a break-in period. Ensure that suitable chemically-resistant tubing is used. Performance checks can be carried out volumetrically using a graduated cylinder and stopwatch.

X2.2.3.2 *Other Tubing*—Periodically, check connectors for blockages and deposits, and check for kinking or snagging if tubing is connected to an autosampler and an associated robotic arm.

X2.2.3.3 *Nebulizer*—Periodically check for clogging, and check o-rings and couplings between the nebulizer and spray chamber.

X2.2.3.4 *Spray Chamber*—Periodically check the spray chamber to ensure that it is clean and that waste is draining efficiently. Check seals and couplings between the spray chamber and torch.

X2.2.3.5 *Drain System*—Periodically check the liquid level within the waste container, and ensure that the waste flows smoothly to drain from the spray chamber. Check for kinks and clogs in waste tubing.

X2.2.3.6 *Waste Container*—Periodically check the waste container, and empty it if there is a risk of overfilling.

X2.2.3.7 *Autosampler and Related Sample Introduction Accessories*—Periodically check the components and interfaces with the instrument; follow manufacturer's guidelines.

X2.2.3.8 *ICP Torch*—Periodically check the ICP torch and its alignment. Check the position of the injector tube, and check it for accumulation of deposits/precipitates. Check the torch body for signs of corrosion and for buildup of residues. Check o-rings and seals for leakages. Follow manufacturer's guidelines if cleaning or replacement is required.

X2.2.3.9 *Torch Box*—Periodically check for signs of corrosion or leakage.

X2.2.3.10 *RF Generator*—Periodically check for signs of corrosion in RF generator and in components of the plasma initiation system. A service engineer might be required for specialized inspections.

X2.2.3.11 *Computer*—Periodically back up data files, delete unwanted files, and check network connections.

X2.2.3.12 *Vacuum Pumps*—Follow manufacturer's recommendations for oil changes (except for pumps that do not use oil) and applicable filter changes.

X2.2.3.13 *Sampler and Skimmer Cones*—Periodically inspect the cones and clean or replace them when the orifice shows evidence of deposits, discoloration, or distortion. Follow manufacturer's recommendations if cleaning or replacement is required.

X3. ICP-MS PRINCIPLE AND INTERFERENCES

X3.1 *Description of ICP-MS Principle*—This standard test method describes the multi-element determination of trace elements in air by inductively coupled plasma—mass spectrometry (ICP-MS). Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are typically detected by a continuous dynode electron multiplier assembly and the ion information processed by a data handling system. Interferences relating to the technique must be recognized and corrected for. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents, or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standardization.

X3.2 *Collision/Reaction Systems*—The majority of ICP-MS units currently being manufactured contain collision/reaction systems. These typically include transmission devices that cause collisional dissociation of polyatomic ion species so that they are eliminated as an interference.

X3.3 When collision/reaction system technology is not available, several types of interference effects may contribute to inaccuracies in the determination of trace elements. These interferences can be summarized as follows:

X3.3.1 *Isobaric Elemental Interferences*—Isobaric elemental interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. All elements determined by this standard test method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this standard test method (see Table 3), only selenium-82 (krypton) has isobaric elemental interferences. If alternative analytical isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. Mathematical correction factors should be tested, preferably by analysis of a suitable interference check standard. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios and instrument bias factors should be established prior to the application of any corrections.

X3.3.2 *Abundance Sensitivity*—Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak

is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

X3.3.3 *Isobaric Polyatomic Ion Interferences*—Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom that have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified, and these are listed in Table X3.1 together with the method element masses affected. Such interferences must be recognized, and when they cannot be avoided by the selection of an alternative analytical isotope, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

X3.3.4 *Physical Interferences*—Physical interferences are associated with the physical processes that govern the transport of the sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma—mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (for example, viscosity effects), at the point of aerosol formation and transport to the plasma (for example, surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the extraction, or skimmer cones, or both, reducing the effective diameter of the orifices and, therefore, ion transmission. Dissolved solids levels not exceeding 0.2 % (w/v) have been recommended to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards should have similar analytical behavior to the elements being determined. Selection of internal standards should consider, as appropriate, the mass ranges and/or the ionization potential of the analytes of interest.

X3.3.5 *Memory Interferences*—Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank consisting of HNO_3 (1+49) in water between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. Many ICP-MS systems are supplied with on-line memory evaluation checks, intelligent rinse modes, and autodilution options; use of these options should be considered where available. Alternatively, the rinse times necessary for a particular element may be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to ten times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of ten of the method detection limit should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of

TABLE X3.1 Common Molecular Ion Interferences

Molecular Ion	Mass	Element Interference[A]
Background Molecular Ions		
NH^+	15	...
OH^+	17	...
OH_2^+	18	...
C_2^+	24	...
CN^+	26	...
CO^+	28	...
N_2^+	28	...
N_2H^+	29	...
NO^+	30	...
NOH^+	31	...
O_2^+	32	...
O_2H^+	33	...
$^{36}ArH^+$	37	...
$^{36}ArH^+$	39	...
$^{40}ArH^+$	41	...
CO_2^+	44	...
CO_2H^+	45	Sc
ArC^+, ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	...
$ArOH^+$	57	...
$^{40}Ar\ ^{36}Ar^+$	76	Se
$^{40}Ar\ ^{38}Ar^+$	78	Se
$^{40}Ar_2^+$	80	Se
Matrix Molecular Ions		
Chloride		
$^{35}ClO^+$	51	V
$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar\ ^{35}Cl^+$	75	As
$Ar\ ^{37}Cl^+$	77	Se
Sulphate		
$^{32}SO^+$	48	...
$^{32}SOH^+$	49	...
$^{34}SO^+$	50	V, Cr
$^{34}SOH^+$	51	V
SO_2^+, S_2^+	64	Zn
$Ar\ ^{32}S^+$	72	...
$Ar\ ^{34}S^+$	74	...
Phosphate		
PO^+	47	...
POH^+	48	...
PO_2^+	63	Cu
ArP^+	71	...
Group I, II Metals		
$ArNa^+$	63	Cu
ArK^+	79	...
$ArCa^+$	80	...
Matrix Oxides[B]		
TiO	62 to 66	Ni, Cu, Zn
ZrO	106 to 112	Ag, Cd
MoO	108 to 116	Cd

[A] Method elements or internal standards affected by molecular ions.
[B] Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes be monitored if samples are likely to contain high levels of these elements. Mo is monitored as a method analyte.

a memory effect, and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected, the sample should be re-analyzed after a long rinse period.

X4. SAMPLER WALL DEPOSITS (32-34)

X4.1 Samplers for aerosols typically consist of a filter supported in a holder, though other collection substrates are also used, for example, impaction plates, foams. The entire device is considered to be an *aerosol sampler*. The sampling efficiency of the aerosol sampler is considered to be the air concentration calculated from the particulates collected by the sampler compared to the undisturbed concentration in air. All aerosol samplers exhibit a decrease in sampling efficiency with increasing particulate aerodynamic diameter. Some *size-selective samplers* are designed for a specific sampling efficiency over a range of aerodynamic diameters, in which case the actual sampling efficiency of the sampler is considered in reference to the stated efficiency. In some sampler designs (for example, cyclones) there is an internal separator to achieve the required size separation.

X4.2 The collection efficiency of an aerosol sampler has three components: aspiration (or entry efficiency), passage within the sampler (either from entry plane to collection substrate or, if an internal separator is present, both from entry plane to internal separator and from internal separator to collection substrate) and penetration (through the internal separator, if present). For any given design of sampler, the three components are functions of particle aerodynamic size and air flow-rate through the sampler. The aspiration efficiency also depends on wind speed and direction, while the sampler's angle to the vertical influences both aspiration and transport efficiency. Part of the sample will deposit on internal surfaces of the sampler as a result of losses during passage within the sampler. In addition, if the sampler is transported after sampling, particles already deposited on the substrate may become dislodged and add to deposits already on the internal surfaces (although this is likely of lesser importance). If the design specification for the sampler is to include all aspirated particles, these losses should be taken into account unless it can be shown that they can be disregarded. The table below provides median and maximum values of deposits on the walls for two commercially available samplers in common use. No pattern can be discerned from these data that would allow the use of correction factors without introducing a very large uncertainty.

X4.3 For some samplers, such as the GSP and CIP, the sample deposited on the collection substrate is considered to be the entire sample; that is, there are no wall deposits. Internal capsules that are digestible automatically include aerosol deposits not collected on the filter. For other samplers, it is recommended that the wall deposits should be evaluated.

X4.4 There exist several procedures that could be used to account for wall deposits. One method is digestion within the body of the sampler, which is the practice in some French standard methods. This procedure needs to be carefully designed with respect to the composition of the acid media, the composition of the substrate and the stability and integrity of the sampler. Another procedure, often followed, is to rinse the internal deposit into the digestion vessel containing the collection substrate. This may be quantitative if the deposit is very soluble or easily displaced, but that may not be the case, even when acid is used for the rinse. Brushing the deposit into the digestion vessel may not be quantitative, and may be a source of contamination. A procedure that has been tested in a limited evaluation and shown to be quantitative is wet-wiping of the internal surfaces.

X4.5 Wiping the internal surfaces of a sampler with a wetted wipe allows a combination of mechanical removal with wetting or solubilization. The choice of wipe is important. It must be free of significant contamination, and it must be compatible with the digestion and analytical procedure. The area of the wipe should be as small as possible in order not to unduly compromise the detection limits of the analysis, and quality control samples should be matched to the same matrix. Typically, the same material should be used as would be selected to perform a surface wipe sample for the element(s) of interest. If the most appropriate wipe material cannot be digested and analyzed in the same way as the collection substrate, it can be analyzed as a separate sample and the results combined. Where the procedure has not been validated to provide quantitative results for a first wipe, the analysis of a second wipe can be used as a guide to recovery.

X4.6 Where the validation of an air sampling and analytical method has not included a specific procedure for recovering and analyzing wall deposits, any procedure selected for this purpose will add an unknown amount to the uncertainty budget of the method. It is therefore recommended that any procedure be validated to determine the contribution to uncertainty.

TABLE X4.1 CFC Maximum and Median Wall Deposits (32)

Environment	n	Agent	Maximum Wall Deposit (%)	Median Wall Deposit (%)
Copper smelter	17	Pb	55	21
Lead ore mill	28	Pb	35	19
Solder manufacture	30	Pb	74	29
Battery production	16	Pb	66	28
Welding	10	Cr (VI)	55	5
Plating	12	Cr (VI)	17	12
Paint spray	29	Cr (VI)	12	7
Foundry	9	Zn	62	53
Zinc plating	18	Zn	91	27
Cast iron foundry	18	Fe	46	22
Grey iron foundry	18	Fe	77	24
Bronze foundry	6	Cu, Pb, Sn, Zn	45, 17, 0, 21	19, 13, 0, 15
Cuproberyllium	4	Cu, Be	40, 39	31, 12

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