Designation: D7035 – 16

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

This standard is issued under the fixed designation D7035; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method specifies a procedure for collection, sample preparation, and analysis of airborne particulate matter for the content of metals and metalloids using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

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

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

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

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

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

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

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

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

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

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

1.11 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety 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
D6062 Guide for Personal Samplers of Health-Related Aerosol Fractions

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[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.

Current edition approved Oct. 1, 2016. Published October 2016. Originally approved in 2004. Last previous edition approved in 2010 as D7035 – 10. DOI: 10.1520/D7035-16.

[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.

D6785 Test Method for Determination of Lead in Workplace Air Using Flame or Graphite Furnace Atomic Absorption Spectrometry

D7202 Test Method for Determination of Beryllium in the Workplace by Extraction and Optical Fluorescence Detection

D7439 Test Method for Determination of Elements in Airborne Particulate Matter by Inductively Coupled Plasma–Mass Spectrometry

D7440 Practice for Characterizing Uncertainty in Air Quality Measurements

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1370 Guide for Air Sampling Strategies for Worker and Workplace Protection

E1613 Test Method for Determination of Lead by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Flame Atomic Absorption Spectrometry (FAAS), or Graphite Furnace Atomic Absorption Spectrometry (GFAAS) Techniques

E1728 Practice for Collection of Settled Dust Samples Using Wipe Sampling Methods for Subsequent Lead Determination

2.2 *ISO and European Standards:*

ISO 1042 Laboratory Glassware—One-mark Volumetric Flasks[3]

ISO 3585 Glass Plant, Pipelines and Fittings—Properties of Borosilicate Glass[3]

ISO 7708 Particle Size Definitions for Health-Related Sampling[3]

ISO 8655 Piston-Operated Volumetric Instruments (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 18158 Workplace Atmospheres—Terminology[3]

EN 482 Workplace Atmospheres—General Requirements for the Performance of Procedures for the Measurement of Chemical Agents[4]

3. Terminology

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

3.2 *Definitions:*

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

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

3.2.2 *axial plasma*—a horizontal inductively coupled plasma that is viewed end-on (versus radially; see 3.2.30).

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

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

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

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

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

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

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

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

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

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

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

3.2.11.1 *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 consisting of three concentric tubes, the outer two usually made from quartz, that is used to support and introduce sample into an ICP discharge. **ISO 15202**

3.2.14 *injector tube*—the innermost tube of an inductively coupled plasma torch, usually made of quartz or ceramic

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

[4] Available from CEN Central Secretariat: rue de Stassart 36, B-1050 Brussels, Belgium.

materials, through which the sample aerosol is introduced to the plasma. **ISO 15202**

3.2.15 *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**

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

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

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

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

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

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

3.2.21 *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**

3.2.22 *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**

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

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

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

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

3.2.25 *method quantitation limit (MQL)*—the minimum concentration of an analyte that can be measured with acceptable precision, ordinarily taken to be at least ten times the standard deviation of the mean blank signal (**1**).[5]

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

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

3.2.27 *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 to 15 L/min. **ISO 15202**

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

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

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

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

3.2.32 *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**

3.2.33 *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**

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

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

3.2.35 *sampling site*—a local geographic area that contains the sampling locations. **E1728**

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

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

3.2.37 *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**

3.2.38 *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).

3.2.39 *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

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

differences in dissolved solids content, type and concentration of acid, and so forth). **ISO 15202**

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

3.2.40 *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**

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

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

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

4. Summary of Test Method

4.1 A known volume of air is drawn through a filter (or filter capsule) to collect airborne particles suspected to contain metals or metalloids, or both. The sampling device (sampler) is ordinarily designed to collect the inhalable fraction of airborne particles; however, sampling of the respirable fraction (or other) is also possible (see Guide D6062; ISO 7708).

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

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

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

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

5. Significance and Use

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

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

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

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

6. Sampling Apparatus and Materials

6.1 *Sampling Equipment:*

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

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

NOTE 4—Some inhalable samplers are designed to collect the inhalable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler (separate from the filter) is not considered part of the sampled air. Other inhalable samplers are designed such that all airborne particles which pass through the entry orifice(s) are of interest, hence particulate matter deposited on the inner walls of the sampler does form part of the sample. In such cases it will be necessary to account for particulate material collected on the inner walls of the sampler (in addition to that collected on the filter). Refer to Appendix X5 for additional information.

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

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

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

NOTE 7—Some respirable samplers are designed to collect the respirable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler (separate from the filter) is not considered part of the sampled air. Other respirable samplers are designed such that all airborne particles which pass through the entry orifice(s) are of interest, hence particulate matter deposited on the inner walls of the sampler does form part of the sample. In such cases it will be necessary to account for particulate material collected on the inner walls of the sampler (in addition to that collected on the filter). Refer to Appendix X5 for additional information.

6.1.3 *Filters or Filter Capsules,* of a diameter suitable for use with the samplers, and a collection efficiency of not less than 99.5 % for particles with a 0.3 µm diffusion diameter (see ISO 7708). The filters (or filter capsules) shall have a very low background metal content (typically less than 0.1 µg of each metal or metalloid of interest per filter), and they should be compatible with the anticipated sample preparation method. See Appendix X1 for guidance on filter selection.

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

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

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

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

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

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

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

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

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

7. Sampling Procedure

7.1 *Sampling Period:*

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

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

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

7.2 *Preparation for Sampling:*

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

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

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

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

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

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

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

7.3 *Sampling Position:*

7.3.1 *Personal Sampling*—The sampler shall be positioned in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, for instance, fastened to the worker's lapel or shirt collar. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, for example, to a belt around the waist.

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

7.4 *Collection of Samples:*

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

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

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

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

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

7.5 *Transportation:*

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

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

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

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

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

8. Hazards

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

8.2 *Concentrated perchloric acid* is corrosive and oxidizing, and its vapor is an irritant. Perchloric acid forms explosive compounds with organics and many metal salts. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Use suitable personal protective equipment (including impermeable gloves, safety goggles, laboratory coat, and so forth) when working with perchloric acid. Carry out sample dissolution with perchloric acid in a fume hood with a scrubber unit that is specially designed for use with $HClO_4$. See Appendix X1 for further pertinent safety information.

8.3 *Concentrated hydrofluoric acid* is highly corrosive, and is very toxic by inhalation or contact with the skin. Avoid exposure by contact with the skin or eyes, or by inhalation of HF vapor. It is essential to use suitable personal protective equipment, including impermeable gloves and eye protection) when working with HF. Use a fume hood when working with concentrated HF and when carrying out open-vessel dissolution with HF. See Appendix X1 for further pertinent safety information.

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

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

9. Sample Preparation

9.1 *Reagents for Sample Preparation*—Details regarding reagents that are required for individual sample dissolution methods are given in Annex A1 through Annex A4. During sample preparation, use only reagents of analytical grade.

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

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

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

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

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

9.2 *Laboratory Apparatus for Sample Preparation*—Details regarding laboratory apparatus required for individual sample dissolution methods are given in Annex A1 through Annex A3. Ordinary laboratory apparatus are not listed, but are assumed to be present.

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

9.2.2 *Glassware,* beakers and volumetric flasks complying with the requirements of 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.

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

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

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

9.3 *Sample Preparation Procedures:*

NOTE 13—The sample dissolution methods described in Annex A1 through Annex A4 are generally suitable for use with analytical techniques other than ICP-AES, for example, atomic absorption spectrometry (AAS), and ICP-mass spectrometry (ICP-MS).

9.3.1 *Soluble Metal and Metalloid Compounds:*

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

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

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

9.3.2 *Total Metals and Metalloids and their Compounds:*

9.3.2.1 If results are required for total metals, or metalloids, or both, and their compounds, select a suitable sample preparation method from those specified in Annex A2 (hot plate digestion), Annex A3 (microwave digestion), or 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 15—In selection of a sample preparation method, consideration should be given to the metal or metalloid compounds that may be present in the test atmosphere. Some compounds, such as refractory metal oxides, may require a more robust sample preparation method than is required for other compounds, or for the metals or metalloids themselves.

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

9.3.3 *Deposits of Particles on Interior Sampler Surfaces*—Give consideration to metal and metalloid particles that may have deposited on interior sampler surfaces (for example, by becoming dislodged from the filter during transportation), and determine whether the sample of interest should include such particles. If the sample is determined to include such particles, determine a methodology for removing them from the interior sampler surfaces and including them in the analysis. (Appendix X5 provides additional information and suggested methodologies).

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

9.3.4 *Mixed Exposures:*

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

9.3.4.2 Select a suitable sample dissolution method for total metals and metalloids and their compounds (specified in Annex A2 for hot plate digestion, Annex A3 for microwave digestion, or Annex A4 for hot block digestion). Use this procedure to treat undissolved material left over after employing the preparation method for soluble metals and metalloids and their compounds (Annex A1), and prepare sample solutions, from which test solutions are prepared, for subsequent analysis by ICP-AES.

9.4 *Special Cases:*

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

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

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

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

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

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

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

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

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

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

10. Analysis

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

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

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

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

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

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

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

10.1.6 *Hydrochloric Acid Leach Solution,* 0.1 M.

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

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

10.1.9 *Stock Standard Solutions:*

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

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

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

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

10.1.10 *Calibration Solutions:*

10.1.10.1 From the stock standard solutions, prepare working standard solutions by serial dilutions; these shall include all the metals and metalloids of interest at suitable concentrations (typically between 1 mg/L and 100 mg/L, depending on the sensitivity of the emission lines to be measured).

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

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

10.1.10.3 From the working standard solutions, prepare a set of calibration solutions (at least two) by serial dilutions, covering the range of concentrations for each of the metals and metalloids of interest. Also prepare a calibration blank solution. During preparation of calibration solutions, add reagents (for example, acids), as required, to matrix-match the calibration solutions with the test solutions. Prepare calibration solutions fresh daily.

NOTE 23—The shelf life of stock standard and working standard solutions may be extended if they are demonstrated, by comparison with calibration verification solutions, to be acceptable.

NOTE 24—The type(s) and volume(s) of reagents required to matrix match the calibration and test solutions will depend on the sample dissolution method used.

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

NOTE 25—Internal standard solutions may be used to correct for instrument drift and physical interferences. Internal standard solutions are usually single-element standard stock solutions, which are commercially available or can be prepared from high-purity metals and metalloids or their salts.

NOTE 26—Internal standards, if utilized, should be added to blanks, samples and standards in a like manner. Internal standards may be added to each test solution during the sample preparation process or, alternatively, by use of an on-line internal standard addition system.

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

10.1.13 *Argon,* suitable for use in ICP-AES.

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

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

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

10.2.2 *Glassware,* beakers and volumetric flasks complying with the requirements of ISO 1042, made of borosilicate glass complying with the requirements of ISO 3585. Glassware shall be cleaned before use by soaking in diluted nitric acid for at least 24 hours and then rinsing thoroughly with water. Alternatively, before use, glassware shall be cleaned with a suitable laboratory detergent using a laboratory washing machine.

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

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

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

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

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

10.3 *Analysis Procedure:*

10.3.1 *Method Optimization:*

10.3.1.1 *General Guidance*—Optimize the test method and validate the performance of the method for analysis of test solutions, in accordance with the performance criteria provided in this test method, or specified customer requirements, or both, using sample solutions prepared as described in Section 9 of this test method, which is suitable for use with the available ICP-AES instrument(s). Use the default instrument conditions given by the manufacturer as a starting point in the method development process. Refer to guidance on ICP-AES method development available in textbooks, instrument manuals, and standards.

NOTE 28—ICP-AES analysis of test samples prepared from workplace air samples is applicable to a wide range of instruments, for example simultaneous or sequential instruments with photomultiplier or solid state detection systems. Each of these different types of instruments needs to be set up and operated in a different manner. There are some principles that apply to the development of method for all instruments, but there are also many parameters that are only applicable to particular instruments or types of instruments.

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

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

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

10.3.1.3 *Spectral Interferences*—Give consideration to the significance of any known spectral interferences in the context of the measurement task. For each potentially useful analytical wavelength, refer to published information, and consider the relationship between the magnitude of interferences and the relative exposure limits of the interferents and elements to be determined. For example, if the measurement task entails testing compliance with exposure limit values, an interferent present at 10× its limit value will cause a positive bias of >10 % if $[10 \times (LV_a / LV_i) \times (\rho_a / 1000)] > 0.1$, where LV_a is the limit value, in mg/m^3, of the analyte; LV_i is the limit value, in mg/m^3, of the interferent; and ρ_a is the apparent analyte concentration, in mg/L, caused by an interferent concentration of 1000 mg/L. If the sum of all potential interferences is greater than 0.1× the limit value of the analyte when each of the interferents is present at 10× its limit value, use an alternative analytical wavelength or apply interelement corrections.

NOTE 31—Interelement correction is not normally necessary for measurements made to test compliance with limit values. It is best avoided, if possible, by selecting an alternative analytical wavelength that is free from or less prone to interference. Also, for some measurement tasks, there might be a need to obtain quantitative measurements at concentrations below 0.1× the limit value.

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

NOTE 32—Axial viewing of the plasma might be necessary to obtain the necessary quantification limits, but it is more susceptible than radial viewing to spectral interferences.

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

NOTE 33—Ultrasonic nebulizers give higher sensitivity than conventional pneumatic nebulizers. However, they are less corrosion-resistant. For instance, if test solutions contain hydrofluoric acid, it will be necessary to use a corrosion-resistant sample introduction system.

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

NOTE 34—Scanning, sequential, monochromater-based instruments enable measurements over the entire ultraviolet/visible spectrum. Grating instruments and instruments with solid state detectors also allow for a wide spectral range. However, simultaneous, conventional polychromator-based instruments are more limited in that users can only select from the analytical lines that are available given a particular instrument configuration. If available, it is advisable to use more than one emission line for each analyte to check for any problems not identified during method development.

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

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

NOTE 36—Different instrument types use different means of making off-peak background correction measurements. In some instruments (such as those using monochromators or polychromators), the analyte intensity is measured first, and then separate measurements are made at the wavelengths used for background correction. However, grating instruments with solid-state detectors measure analyte and background signals simultaneously. Measurements employing simultaneous background correction reduce noise due to sample introduction, and they are fast since no additional analysis time is required to make off-peak measurements.

NOTE 37—Some ICP-AES software features the use of chemometrics to automatically select parameters such as background correction points. Also, software can be used to perform intelligent optimization studies with minimal user interaction.

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

NOTE 38—Interelement correction factors can be generated from the apparent analyte concentrations obtained by analyzing individual, spectrally pure test solutions containing high concentrations (for example, 1000 mg/L) of interfering elements. Alternatively, if calibration solutions contain varied concentrations of the analyte and interfering element(s), data handling software of some instruments may be used to calculate and apply interference corrections automatically.

10.3.1.9 *Plasma Conditions:*

(1) Gas Flows—Under normal conditions, use the default gas flows recommended by the instrument manufacturer for inner, intermediate, and outer argon flows. However, if desired, the nebulizer (inner) argon flow may be optimized for specific applications.

NOTE 39—The nebulizer argon flow can be critical because it largely determines the residence time of the analyte in the plasma. The longer the residence time, the greater the likelihood of the analyte to be atomized, excited, and ionized. For an element that emits strong ionic lines and has a high ionization potential, a long residence time is desired. Hence a lower nebulizer argon flow rate could be used to obtain higher sensitivity for such an element (provided that the nebulizer efficiency does not fall off significantly when the flow rate is reduced). On the other hand, for elements that emit strong atomic lines and are easily ionized, a faster flow rate could be used so that the atoms are not ionized before excitation takes place.

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

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

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

NOTE 41—The viewing height can be optimized for a selected analyte line or lines. This is because different regions of the plasma are characterized by different temperatures, and each analytical wavelength has an optimum temperature at which its emission line is most intense.

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

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

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

10.3.1.13 *Calibration Solutions:*

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

NOTE 42—Even if an internal standard is used, it is recommended that matrix matching is also carried out. In general, it is preferable to match the matrix of the calibration and test solutions, rather than rely on the use of internal standards to correct for transport and excitation interferences.

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

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

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

NOTE 44—A single internal standard may be used to correct for transport interferences that arise from a matrix mismatch between the calibration and test solutions, and for changes in nebulizer efficiency that can occur during analysis. Internal standards may also be used to correct for excitation interferences that arise from a matrix mismatch between the calibration and test solutions and for changes in plasma conditions that can occur during analysis as a result of fluctuations in power or gas flows, or both. Multiple internal standards need to be used, and the wavelengths at which they are measured need to be carefully selected, so that the characteristics of the analyte emission lines closely match those of the internal standard emission lines. Use of internal standards can also improve analytical precision for simultaneous instruments by reducing the effect of noise associated with sample introduction.

10.3.2 *Instrument Performance Checks:*

10.3.2.1 *Visual Inspection*—The user shall perform regular visual checks to ensure that the instrument and ancillaries are in good order before commencing work. Follow the instrument manufacturer's recommendations. Further guidance is given in Appendix X3.

10.3.2.2 *Performance Checks and Fault Diagnostics*—The user shall carry out performance checks daily to verify that the ICP-AES instrument is operating in accordance with specifications. More rigorous fault diagnostics shall be used if it is suspected that the instrument is not functioning properly. Follow the instrument manufacturer's recommendations. Further guidance is given in Appendix X4.

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

10.3.3 *Routine Analysis:*

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

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

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

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

10.3.3.4 *Analysis:*

(1) Aspirate the calibration solutions into the plasma in order of increasing concentration, and make emission measurements for each solution. Generate a calibration function for the metals and metalloids of interest, preferably using linear regression via the instrument's computer. It is recommended that the emission intensity of the calibration blank is subtracted for emission intensities of other calibration solutions, and that the calibration function is forced through the origin. Repeat the calibration if the correlation of determination (R^2) for any of the elements of interest is <0.999.

NOTE 47—If R^2 <0.999, it might 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.

(2) Aspirate the laboratory blank solutions and the test solutions into the plasma, and make emission measurements for each solution. Use the calibration function to determine the concentrations of metals and metalloids of interest.

(3) Analyze the calibration blank and mid-range calibration solutions after the initial calibration, and then after (at least) every twenty test solutions. If the measured concentration of an element of interest in the continuing calibration blank (CCB) is above its method detection limit, or if the measured concentration of an element of interest in the continuing calibration verification (CCV) sample has changed by more than ±5 %, take one of the following corrective measures. Either use the instrument software to correct for the observed sensitivity change (reslope facility), or 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.

(4) If interelement correction is used, analyze interference check solutions to verify that the interelement correction procedure is effective at each of the analytical wavelengths concerned.

(5) Analyze quality control solutions at a minimum frequency of 1 per 20 test samples, and use the results to monitor the performance of the analytical procedure.

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

NOTE 48—For most metals and metalloids, the relative standard deviation will be <1 % if the measured concentration is above the quantification limit.

(7) If the concentration of any of the metals and metalloids of interest in a sample 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). Alternatively, use a suitable alternative analytical wavelength.

10.4 *Estimation of Detection and Quantification Limits:*

10.4.1 *Estimation of the Instrumental Detection Limit:*

10.4.1.1 Estimate the instrumental detection limit (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 49—The IDL is of use in identifying changes in instrument performance, but it is not a method detection limit (MDL) (**6**). The IDL is likely 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.

10.4.1.2 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.

10.4.1.3 Make at least ten consecutive emission 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 50—An alternative procedure for estimating the IDL involves the analysis of blanks fortified with the metals and metalloids of interest at values spanning the predicted IDL (**6**).

10.4.2 *Estimation of the Method Detection Limit and the Method Quantitation Limit:*

10.4.2.1 Estimate the method detection limit (MDL) and method quantitation limit (MQL) for each of the metals and metalloids of interest under the working analytical conditions, and repeat this exercise whenever experimental conditions are changed.

10.4.2.2 Prepare at least ten blank test solutions from unused filters of the same type used for sample collection. Follow the appropriate sample dissolution procedure used to prepare sample test solutions.

10.4.2.3 Make emission 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.

10.5 *Quality Control:*

10.5.1 *Laboratory Blanks*—Carry reagent blanks (water and reagents) and media blanks (unspiked filters) throughout the entire sample preparation and analytical process to determine whether the samples are being contaminated from laboratory activities. Process reagent blanks at a frequency of at least 1 per 20 samples, minimum of one per batch.

10.5.2 *Quality Control Samples:*

10.5.2.1 Carry spiked filters and spiked duplicate filters 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 spiked value. Spiked samples and spiked duplicate samples consist of filters to which known amounts of the metals and metalloids of interest have been added. Process these quality control samples in accordance with a frequency of at least 1 per 20 samples, minimum of one per batch.

10.5.2.2 Monitor the performance of the method by plotting control charts of the relative percent recoveries and of the relative percent differences between the spiked samples and spiked duplicate samples. 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.

10.5.3 *Certified Reference Materials (CRMs)*—If available, certified reference materials (CRMs) for the metals and metalloids of interest shall be analyzed prior to or during routine use of the sample preparation and analytical method to establish whether the percent recovery relative to the certified value is satisfactory.

NOTE 51—Typically, recoveries of 100 ± 10 % are desired. However, for certain sample matrices, wider performance limits may be deemed acceptable.

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

10.6 *Measurement Uncertainty*—It is recommended that the laboratory estimate and report the uncertainty of their measurements in accordance with ISO guidelines (**7**). 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 52—Applications of cause and effect analysis to analytical methods have been described in the published literature (**8**). 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 $\sqrt{3}$. Systematic errors include, for example, those associated with analytical recovery, sampling recovery, preparation of working standard solutions, dilution of test solutions, and so forth.

11. Expression of Results

11.1 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.

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

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

$$\rho_M = \{[(\rho_{M,l} \times V_l \times F) - (\rho_{M,0} \times V_0)] \times 1{,}000\}/V \qquad (1)$$

where:

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

11.4 If it is necessary to recalculate concentrations to reference conditions (for example, if sampling at high elevations), apply a correction in accordance with:

$$\rho_{M,\ corr} = \rho_M \times [(101.3 \times T)/(P \times 293)] \qquad (2)$$

where:

$\rho_{M,\ corr}$ = corrected concentration of metal or metalloid in the collected air filter sample, in milligrams per cubic metre, at reference conditions;
ρ_M = calculated mass concentration of metal or metalloid in the air filter sample, in milligrams per cubic metre, at ambient conditions;
T = mean temperature, in kelvins, during the sampling period;
P = mean atmospheric pressure, in kilopascals, during the sampling period;
293 = reference temperature, in kelvins; and
101.3 = reference atmospheric pressure, in kilopascals.

12. Method Performance

12.1 *Method Detection Limits and Quantitation Limits*—Method detection limits (MDLs) and method quantitation limits (MQLs) depend on a number of factors, including the sample matrix (including sampling media), the sample preparation method, the analytical wavelength selected, the analytical instrument used, the instrument operating parameters, and blank variability. MDLs and MQLs shown in the table below were estimated by preparing test solutions from mixed cellulose ester (MCE) and polyvinyl chloride (PVC) filters, using microwave digestion in nitric acid and subsequent analysis by ICP-AES (**9**). Results in the table are presented as examples of achievable MDLs and MQLs.

Element	λ(nm)	MDL (MCE) (µg/sample)	MDL (PVC) (µg/sample)	MQL (MCE) (µg/sample)	MQL (PVC) (µg/sample)
Ag	328.3	0.1	0.1	0.3	0.3
Al	308.2	1	2	3	7
As	193.8	1	2	3	7
B	249.7	0.5	0.4	1.6	1.3
Ba	493.4	0.06	0.2	0.2	0.7
Be	313.0	0.009	0.008	0.03	0.03
Ca	315.9	2	2	7	7
Cd	228.8	0.1	0.2	0.3	0.7
Co	228.6	0.3	0.7	1	2.3
Cr	267.7	0.4	0.7	1.3	2.3
Cu	324.8	0.07	0.08	0.2	0.3
Fe	259.9	2	4.7	7	16
K	766.5	2	3	7	10
Li	670.8	0.03	0.06	0.1	0.2
Mg	279.1	0.5	0.9	1.7	3
Mn	257.6	0.02	0.09	0.07	0.3
Mo	202.0	0.2	0.4	0.7	1.3
Na	589.0	4	5	13	17
Ni	231.6	0.2	0.3	0.7	1
P	214.9	2	2	7	7
Pb	220.4	0.6	1	2	3
Pt	265.9	8	9	26	30
Sb	206.8	0.4	0.7	1.3	2.3
Se	196.1	3	5	10	17
Sn	189.9	0.8	0.7	3	2
Sr	421.6	0.02	0.04	0.07	0.13
Te	214.3	2	4	7	13
Ti	337.3	0.2	0.2	0.7	0.7
Tl	190.0	0.9	2	3	7
V	292.4	0.1	0.1	0.3	0.3
Y	371.0	0.02	0.07	0.07	0.23
Zn	213.9	0.1	0.2	0.3	0.7
Zr	339.2	0.06	0.2	0.2	0.7

12.2 *Precision and Bias:*

12.2.1 *General Considerations*—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 (**10**). 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.

12.2.2 *Filters*—Figures of merit for microwave digestion in nitric acid and ICP-AES analysis of MCE and PVC filter samples (n = 6) spiked with known amounts of metals and metalloids (**9**) are shown in the table below. However, it is emphasized that the percent recoveries and relative standard deviations presented in the table are from filters spiked with the analytes of interest in originally liquid form. Realistic samples will most likely exhibit poorer precision and greater bias, and these factors must be taken into account during method validation.

Element	MCE: % Recovery & RSD @ 3 × MQL	MCE: % Recovery & RSD @ 300 × MQL	PVC: % Recovery & RSD @ 3 × MQL	PVC: % Recovery & RSD @ 300 × MQL
Ag	95.5; 1.0	99.0; 0.5	63.0; 7.4	3.9; 9
Al	92.7; 1.0	98.7; 0.5	115; 2.0	105; 0.6
As	101; 2.2	107; 0.3	93.3; 1.0	116; 1.7
B	112; 3.0	99.5; 0.5	86.4; 2.8	101; 0.8
Ba	104; 3.1	101; 0.4	107; 3.0	102; 1.0
Be	95.8; 2.4	103; 0.7	102; 8.6	108; 0.9
Ca	107; 2.9	104; 0.6	105; 0.9	98.1; 0.6
Cd	98.8; 3.5	104; 0.7	110; 3.2	112; 1.5
Co	99.7; 1.7	103; 0.6	89.9; 3.4	114; 1.4
Cr	103; 7.9	94.2; 3.4	103; 0.5	93.0; 0.7
Cu	98.8; 3.5	101; 0.4	107; 3.6	100; 0.6
Fe	112; 2.4	103; 0.3	113; 4.9	97.2; 0.8
K	98.3; 5.7	98.8; 0.5	107; 16.5	90.0; 2.1

Element	MCE: % Recovery & RSD @ 3 × MQL	MCE: % Recovery & RSD @ 300 × MQL	PVC: % Recovery & RSD @ 3 × MQL	PVC: % Recovery & RSD @ 300 × MQL
Li	92.4; 3.0	95.1; 0.7	97.5; 2.5	82.0; 3.8
Mg	89.3; 3.5	98.2; 0.3	105; 0.9	97.5; 0.8
Mn	86.2; 2.4	103; 0.4	110; 1.5	116; 1.3
Mo	96.8; 5.4	110; 0.4	89.8; 2.2	100; 1.5
Na	100; 0.8	97.7; 0.5	125; 8.6	83.0; 2.5
Ni	98.3; 5.2	104; 0.6	106; 4.8	111; 0.8
P	100; 5.7	104; 0.3	86.4; 0.8	103; 1.7
Pb	98.9; 3.9	95.7; 0.6	95.9; 3.1	101; 1.5
Pt	98.3; 0.3	95.7; 1.5	91.3; 3.6	105; 0.9
Sb	94.4; 3.2	103; 0.3	25.3; 59	112; 0.9
Se	104; 3.2	106; 0.3	99.9; 0.5	99.7; 0.8
Sn	105; 5.0	90.3; 3.2	37.9; 8.2	92.3; 1.3
Sr	92.6; 2.4	97.5; 0.6	100; 0.5	99.5; 0.5
Te	90.1; 2.2	103; 0.6	95.8; 6.2	111; 0.9
Ti	101; 1.7	98.8; 0.6	81.7; 3.9	103; 1.0
Tl	103; 4.1	99.3; 0.4	80.4; 4.9	97.2; 1.5
V	93.3; 4.7	103; 0.3	101; 1.5	99.4; 2.3
Y	107; 4.4	102; 3.3	106; 2.5	105; 0.7
Zn	106; 1.3	97.4; 3.4	93.5; 3.5	94.0; 0.6
Zr	93.1; 5.4	95.4; 1.0	103; 2.4	102; 1.4

12.2.3 *Filter Capsules*—An interlaboratory study (ILS) was carried out to evaluate the use of acid-soluble cellulosic air sampling capsules for their suitability in the measurement of trace elements in workplace atmospheric samples (**11**). The performance evaluation materials used consisted of cellulose acetate capsules melded to mixed-cellulose ester filters that were dosed with multiple elements from commercial standard aqueous solutions. The capsules were spiked with the following 33 elements of interest in workplace air monitoring. The elemental loading levels were certified by an accredited provider of certified reference materials. Triplicates of media blanks and multi-element-spiked capsules at three different elemental loadings were sent to each participating laboratory; the elemental loading levels were not revealed to the laboratories. The volunteer laboratories were asked to prepare the samples by acid dissolution and to analyze aliquots of extracted samples by inductively coupled plasma atomic emission spectrometry in accordance with methods described in Annex A2 – Annex A4. It was requested that the study participants report their analytical results in units of µg of each target element per internal capsule sample. Analytical figures of merit (bias, precision and accuracy) for cellulosic filter capsules obtained from the ILS (**11**) are shown in the following table. For the majority of the elements investigated (30 out of 33), the study accuracy estimates obtained satisfied the NIOSH accuracy criterion (A < 25 %) (**1**). This investigation demonstrated the utility of acid-soluble internal sampling capsules for multi-element analysis by atomic spectrometry.

Element	Bias	n^A	$\check{S}^B$	$_{\mathrm{rT}}{}^C$	Accuracy	$A_{U95}{}^D$
Ag	–0.184	21	0.041	0.065	0.290	0.314
Al	–0.0414	21	0.006	0.050	0.124	0.143
As	0.0141	23	0.016	0.052	0.107	0.124
Ba	–0.0206	23	0.036	0.062	0.128	0.149
Be	0.00536	27	0.025	0.056	0.110	0.127
Ca	–0.0367	24	0.001	0.050	0.119	0.136
Cd	0.0133	26	0.022	0.055	0.111	0.127
Co	0.0238	27	0.036	0.062	0.129	0.149
Cr	–0.0281	26	0.046	0.068	0.144	0.166
Cu	0.00347	26	0.017	0.053	0.104	0.119
Fe	0.0476	27	0.011	0.051	0.132	0.148
In	–0.103	15	0.056	0.075	0.226	0.260
K	–0.0239	17	0.029	0.058	0.123	0.147
La	0.0119	12	0.025	0.056	0.112	0.140
Li	–0.0447	21	0.039	0.064	0.149	0.173
Mg	–0.0219	21	0.012	0.051	0.109	0.128
Mn	0.00127	27	0.039	0.063	0.124	0.143
Mo	0.0169	27	0.032	0.060	0.121	0.140
Ni	0.0498	27	0.055	0.074	0.172	0.196
P	0.0310	16	0.010	0.051	0.115	0.137
Pb	0.00439	27	0.006	0.050	0.099	0.114
Sb	–0.00631	25	0.013	0.052	0.102	0.118
Se	0.0864	22	0.055	0.075	0.209	0.236
Sn	–0.00541	15	0.117	0.128	0.250	0.304
Sr	0.00930	20	0.011	0.051	0.102	0.120
Te	0.0256	15	0.063	0.081	0.166	0.201
Ti	0.0305	20	0.032	0.059	0.131	0.154
Tl	0.00128	20	0.030	0.058	0.114	0.135
V	0.0143	27	0.020	0.054	0.109	0.126
W	–0.0240	15	0.010	0.051	0.110	0.134
Y	0.00971	15	0.020	0.054	0.107	0.130
Zn	0.00873	27	0.013	0.052	0.103	0.118
Zr	–0.0206	17	0.033	0.060	0.124	0.149

[A] Number of reported results minus outliers (Grubbs' test, 1% confidence level).
[B] Precision $\check{S}$ = total relative standard deviation (TRSD) (**1**).
[C] Overall precision $\check{S}_{rT}=\sqrt{\check{S}^2+(0.05)^2}$
[D] Upper 95 % confidence limit of accuracy estimate.

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

13. Records

13.1 *Log Forms and Notebooks*—Field data related to sample collection shall be documented in a sample log form or field notebook. If field notebooks are used, then they shall be bound with pre-numbered pages. All entries on sample data forms and field notebooks shall be made using ink with the signature and date of entry. Any entry errors shall be corrected by using only a single line through the incorrect entry (no scratch outs) accompanied by the initials of the person making the correction, and the date of the correction.

NOTE 53—Field notebooks are useful for recording field data even when preprinted sample data forms are used.

13.2 *Sampling Information*—The following information shall be recorded by the person(s) carrying out the sampling. This information shall be passed to the person(s) responsible for completing the test report:

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

13.2.2 A complete identification of the sample, including the date and place of sampling, the type of sample (personal or area), personal identifier for the individual whose breathing zone was sampled (for each personal sample) or the location at which the occupational environment was sampled (for each area sample), a brief description of the work activities that were carried out during the sampling period, and a unique sample identification code;

13.2.3 The make, type and diameter of filter or filter capsule used;

13.2.4 The make and type of sampler used;

13.2.5 The make and type of sampling pump used, and its identification;

13.2.6 The make and type of flow meter used, the primary standard against which the calibration of the flow meter was checked, and the range of flow rates over which the calibration was checked;

13.2.7 The time at the start and end of the sampling period, and the duration of the sampling period (in minutes);

13.2.8 The mean flow rate during the sampling period (in L/min);

13.2.9 The volume of air sampled (in litres); and

13.2.10 The name of the person who collected the sample.

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

13.3.1 The unique sample identification code(s);

13.3.2 The type of filter(s) or filter capsule used;

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

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

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

13.4 *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:

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

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

13.4.3 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);

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

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

14. Report

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

14.1.1 All sample receipt and chain-of-custody information;

14.1.2 Sample analysis results;

14.1.3 Applicable quality assurance / quality control data;

14.1.4 Identity of laboratory and analyst(s);

14.1.5 Information on sample preparation procedure(s) used;

14.1.6 Information on instrumentation and equipment used; and

14.1.7 Any other information deemed appropriate.

15. Keywords

15.1 analysis; atomic spectrometry; elements; 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, 1.0 M hydrochloric acid, or ammonium citrate buffer made up from 17 g/L di-ammonium hydrogen citrate and 5 g citric ammonium monohydrate.

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

A1.1.3 Metals and metalloids for which ACGIH TLVs have been set (**12**) are listed below. The sample dissolution method specified is applicable to those elements, but may also be applicable to other elements for which exposure limits have not been established.

Aluminum
Barium
Chromium
Iron
Molybdenum
Nickel
Platinum
Rhodium
Silver
Thallium
Tungsten
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 (**13**). 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, and so forth. 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 Appendix X1). 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.

NOTE A1.1—The above considerations also apply to filter capsules, where used in lieu of filters.

A1.3 *Summary of Dissolution Method*—The filter (or filter capsule) 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-AES.

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

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 II (see Specification D1193).

A1.4.2 *Ammonium Citrate Leach Solution,* 17 g/L $(NH_4)_2HC_6H_5O_7$ and 5 g/L $C_6H_8O_7 \cdot H_2O$. Weigh 17 g di-ammonium hydrogen citrate, $(NH_4)_2\ HC_6H_5O_7$, and 5 g citric ammonium monohydrate, $C_6H_8O_7 \cdot H_2O$, into a 500 mL beaker. Add 250 mL of water and swirl to dissolve. Quantitatively transfer the solution into a 1-L volumetric flask, dilute to the mark with water, stopper and mix thoroughly. Check the solution pH, and if necessary adjust the pH to 4.4 with ammonia or citric acid.

A1.4.3 *Hydrochloric Acid Leach Solution,* 0.1 M.

A1.4.4 *Diluted Nitric Acid,* 10 % v/v (1 + 9 $HNO_3 : H_2O$).

A1.5 *Laboratory Apparatus*—Ordinary laboratory apparatus, plus equipment specified in 9.2, and

A1.5.1 *Beakers,* 50 mL capacity, with watch glasses to fit, suitable for preparation of test solutions; and 500 mL capacity, for preparation of ammonium citrate leach solution.

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; and 1-L capacity, for preparation of ammonium citrate leach solution.

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.

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 or Filter Capsules,* 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 filter materials used should be selected carefully, taking into account their solubility in any subsequent sample preparation method for determination of total metals and metalloids (see Appendix X1).

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

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 in accordance with the nature of the solubility of the metal, or metalloid compounds, or both, 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 metal, or metalloid compounds, or both, typically apply to water-soluble compounds. However, various nations have established exposure limits that relate to the use of a specific leach solution, or leach conditions, or both, 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, Pt, Rh, Tl, W, U. (**13**)

(2) 0.1 M Hydrochloric acid for Al, Ba, Cr, Fe, Mo, Pt, Rh, W, U. (**14**)

NOTE A1.8—This leachate is not applicable to the dissolution of soluble silver or thallium compounds, owing to the formation of insoluble chlorides (**14**).

(3) 10 % Nitric acid for Ag, Tl. (**14**)

(4) Ammonium citrate solution for Ni. (**15**)

NOTE A1.9—Ammonium citrate solution is preferred for leaching soluble nickel compounds because of its buffering and chelating properties (**15**). It minimizes pH changes during leaching, and also reduces the likelihood of hydrolysis of higher valence state ions. Since citrate complexes of nickel are relatively weak, the solubility of "insoluble" nickel compounds is unaffected.

A1.6.1.2 Follow the instructions given in national standards or regulations if these prescribe that a specific leach solution, or leach condition, or both, 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 or filter capsules.

NOTE A1.10—Alternatively, sample dissolution can be carried out directly within the samplers (**4, 15**), 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, use the leach solution to carefully wash any particulate material adhering to the internal surfaces of the sampler into the beaker.

NOTE A1.11—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 A1.12—If a test solution is also to be prepared for the determination of insoluble compounds of metals and metalloids, it is 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 A1.13—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 A1.14—If the leach was carried out within the sampler, the sample filter itself can be used to filter the sample solution (**4**). 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 (or filter capsule) 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 A1.15—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-AES.

(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.

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

A2.2 Summary of Hot Plate Dissolution

A2.2.1 The filter (or filter capsule) 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 (**15**, **16**, **17**, **18**, **19**). 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 (**20**). 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 (**21**, **22**). 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 nitric and hydrochloric acids. 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 (**22**, **23**). 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 (**4, 20**), and may be required for refractory metal oxides.

NOTE A2.1—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)).

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

NOTE A2.2—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 II (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, and so forth) when working with H_2O_2.)

A2.5 *Laboratory Apparatus*—Ordinary laboratory apparatus, plus equipment specified in 9.2, and:

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

A2.5.2 *Volumetric Flasks,* 10-mL or 25-mL.

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

NOTE A2.3—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 (or filter capsule) 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 or filter capsules. In consideration of target elemental analytes, choose one of the procedures below (see 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 10-mL or 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-AES.

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. (**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 10-mL or 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-AES.

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 hydrogen peroxide 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 10-mL or 25-mL volumetric flask. Dilute to the mark with water, stopper, and mix thoroughly.

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

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

A3.2 Summary of Microwave Dissolution Procedure

A3.2.1 The filter (or filter capsule) 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-AES.

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 (**24**). 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 (**4, 20**), and may be required for refractory metal oxides. (**Warning—**Extreme care must be taken when using hydrofluoric acid in sample preparations (see Appendix X2 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)).

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

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 II (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 9.2, and:

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

A3.5.2 *Volumetric Flasks,* 10-mL or 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 s. 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.

A3.5.4.1 **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 (or filter capsule) 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 or filter capsules.

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 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 volumetric flask. Dilute to the mark with water, stopper, and mix thoroughly to produce the test solution.

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

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).

A4. HOT BLOCK DISSOLUTION OF METAL AND METALLOID COMPOUNDS

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

[A] Valid up to 25,000 µg/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 (or filter capsule) 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 (**25**) 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 (**4, 20**), 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 (**26**), 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 7, 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 or filter capsules.

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 five 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 five 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. GUIDANCE ON SELECTION OF FILTER MEDIA

INTRODUCTION

The following guidance is intended to help the user choose the most suitable filter for a particular application. It is not an exhaustive treatise on the subject, but covers only the basics of those matters that merit consideration.

X1.1 Collection Efficiency

X1.1.1 Most filters that are used for sampling airborne particulate matter have the required collection efficiency for sampling the inhalable fraction of airborne particles. Such filters include depth filters, such as glass and quartz fiber filters, and membrane filters, such as mixed cellulose ester (MCE) filters, and membrane filters made from polymers such as polyvinyl chloride (PVC) or polytetrafluorethylene (PTFE).

X1.1.2 Cellulose (paper) filters can have a collection efficiency significantly below 99 %, and are generally unsuitable for sampling airborne particles. However, they are sometimes treated with a reagent, for example sodium carbonate, and are used as a secondary medium to collect inorganic gases or vapors, such as arsenic trioxide.

X1.1.3 Certain processes carried out at elevated temperatures can produce ultra-fine airborne particles condensed from the vapor phase, known as fume. Filters used to sample airborne particulate matter can have reduced collection efficiency for these very small particles, which are significantly smaller than 1 µm in aerodynamic diameter. However, ultrafine particles often agglomerate soon after formation to produce larger particles which are efficiently collected. In general, filters that have a collection efficiency of 99.5 % or better for particles with aerodynamic diameter of 0.3 µm or greater are therefore suitable for sampling fume.

X1.2 Dust-Loading Capacity

X1.2.1 Membrane filters are manufactured from a variety of polymeric materials by a number of different processes. In each case the result is a thin, flexible disc of micro-porous material, with well-defined pore size, pore structure, and pore density. Retention of particles takes place on the surface of membrane filters, which results in their having a relatively low dust-loading capacity in comparison with depth filters. If an excessive amount of dust is collected on a membrane filter, this can result in blockage of the pores, and consequent failure of the sampling pump. Sampling times should therefore be kept reasonably short when sampling with membrane filters in a dusty environment; alternatively, depth filters could be used. Increased dust-loading capacity is afforded by using filter capsules (**2**, **11**).

X1.2.2 Depth filters consist of fibers which have been pressed together to form an irregular three-dimensional mesh. Particles are not only retained at the surface, but are also captured within the structure of the filter, that is, in its depths. This gives depth filters a significantly higher dust-loading capacity than membrane filters. In this respect, depth filters are ordinarily a better choice than membrane filters when sampling for long periods in dusty environments. However, depth filters tend to have a higher background metal content than membrane filters, particularly for certain metals, and this needs to be considered when selecting the filter material to be used for sampling.

X1.3 Metal Content

X1.3.1 The metal content of filters (or filter capsules) should be as low as possible, since it can make a significant contribution to the blank, the variability of which determines in part the lower limit of the working range of the analytical method. Exactly how low the metal content of the filters should be depends upon the applicable exposure limit. For each metal or metalloid of interest, the lower limit of the working range of the analytical method should be less than the amount of metal that would be collected when sampling air at 0.1 times the limit value over the selected sampling period at the selected flow rate. If this condition is not met, and it is suspected that the metal content of the filters might be significantly high, consideration should be given to using an alternative filter medium.

X1.3.2 Membrane filters (and filter capsules) generally have a very low background metal content, and in this respect are suitable for nearly all applications.

X1.3.3 Glass fiber filters are unsuitable for use when sampling for certain metals, for example Al, Ca, and Zn, for which they have a relatively high blank value. This is also true of quartz fiber filters, but to a lesser extent.

X1.4 Weight Stability

X1.4.1 If the filters (or filter capsules) are to be weighed in order to determine the amount of dust collected, it is important that they are resistant to moisture retention, so that blank weight changes that can occur as a result of changes in atmospheric conditions (temperature and humidity) are as low and as repeatable as possible. For example, MCE filters are generally unsuitable for gravimetric analysis since they absorb significant moisture. Cellulosic filter capsules are unsuitable for gravimetric analysis owing to weight instability. PVC filters are widely used when gravimetric analysis is required; however, wall deposits (see Appendix X5) would not be included. PVC filter capsules are useful for gravimetric analysis but are unsuitable for multielement analysis because of ICP-AES matrix effects. PVC filter capsules may be suitable for soluble metals analysis.

X1.4.2 If glass or quartz fiber filters are used, it is important that they are not excessively friable, since this can introduce weighing errors due to loss of filter material. Quartz fiber filters are often more friable than glass fiber filters; however, this disadvantage is counter-balanced by their lower background metal content.

X1.5 Solubility

X1.5.1 For ICP-AES analysis, the filters (or filter capsules) should be either wholly soluble or wholly insoluble when using the selected sample preparation method. This is because partially dissolved filters can make subsequent handling of sample solutions difficult, or they can cause analytical errors due to matrix mismatches between sample solutions and calibration solutions, or both.

X1.5.2 If the sample preparation method selected involves quantitative transfer of the sample solution to volumetric glassware prior to analysis, the filters used for sampling should preferably be completely soluble when using the chosen sample preparation method. MCE filters (and cellulosic filter capsules (**2**, **11**)) are soluble in nitric acid, so these are suitable for use when this acid is used in the selected sample preparation method. Quartz fiber filters are soluble in hydrofluoric acid, and so are suitable for use when this acid is used. Other filter media might be equally suitable.

X1.5.3 If sample solutions are to be made to volume in the sample dissolution vessel (for example, a graduated centrifuge tube), it is unimportant whether or not the filters are soluble when using the selected sample preparation procedure.

X1.6 *Chemical Compatibility*—If chemical analysis of the sample is also to be carried out by a method not described in this standard, the filters cannot be of a type which can react with the chemical agent to be determined. For example, PTFE membrane filters are suitable for sampling alkaline dusts, for which determination of hydroxide and the associated alkali metal (Li, Na, K, Cs) could be required.

X2. SPECIAL SAFETY PRECAUTIONS WHEN USING HYDROFLUORIC OR PERCHLORIC ACIDS

X2.1 Special Precautions for Use of Hydrofluoric Acid

X2.1.1 **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.

X2.1.2 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 X2.1—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.

X2.1.3 When using hydrofluoric acid, it is recommended that disposable gloves are worn underneath suitable rubber gloves, in order to provide added protection for the hands.

X2.1.4 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 advice immediately in case of an accident. Calcium gluconate has a limited lifetime and should be replaced prior to its expiration date.

X2.2 Special Precautions for Use of Perchloric Acid

X2.2.1 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.

X2.2.2 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.

X2.2.3 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.

X3. GUIDANCE ON MAINTENANCE OF ICP-AES INSTRUMENTATION

X3.1 *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:

X3.1.1 Maintenance and calibration of certain instrument components could be beyond the capability of the laboratory;

X3.1.2 Instrument upgrades, both software and hardware, are often included in maintenance packages;

X3.1.3 It might not be possible to obtain spare parts and other consumables from sources other than the manufacturer; and

X3.1.4 Some accreditation programs require users to have a maintenance contract.

X3.2 In-House Maintenance

X3.2.1 *Instrument Log Book*—It is advisable to maintain an instrument log book to record, at a minimum, the following:

X3.2.1.1 Details regarding service contracts and contacts;

X3.2.1.2 Service reports;

X3.2.1.3 Instrument usage (that is, who used the instrument, for what analyses, and for how long); and

X3.2.1.4 Details of faults and replacement of user-serviceable parts.

X3.2.2 *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:

X3.2.2.1 *Air Filters*—Check for overloading, and clean or replace if clogged.

X3.2.2.2 *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).

X3.2.2.3 *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).

X3.2.2.4 *Exhaust System*—Check for loose connections, leaks, and leakages; verify performance of the ventilation system (refer to the manual for specific details).

X3.2.3 *Instrument Maintenance*—The following instrument checks should be carried out on a routine basis:

X3.2.3.1 *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.

X3.2.3.2 *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.

X3.2.3.3 *Nebulizer*—Periodically check for clogging, and check o-rings and couplings between the nebulizer and spray chamber.

X3.2.3.4 *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.

X3.2.3.5 *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.

X3.2.3.6 *Waste Container*—Periodically check the waste container, and empty it if there is a risk of overfilling.

X3.2.3.7 *Autosampler and Related Sample Introduction Accessories*—Periodically check the components and interfaces with the instrument; follow manufacturer's guidelines.

X3.2.3.8 *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.

X3.2.3.9 *Torch Box*—Periodically check for signs of corrosion or leakage.

X3.2.3.10 *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.

X3.2.3.11 *Spectrometer*—Periodically check and clean or replace purge windows. For some instruments it may be necessary to periodically check wavelength calibration routines. A service engineer might be required for specialized inspections.

X3.2.3.12 *Computer*—Periodically back up data files, delete unwanted files, and check network connections.

X4. EXAMPLES OF PERFORMANCE CHECKS AND FAULT DIAGNOSTICS FOR ICP-AES

X4.1 *Visual Bullet Test*—This is a simple visual test for a radial plasma that can be performed daily. The user introduces a solution containing 1,000 mg/L or more of an element whose atomic emission produces a well-defined "bullet" in the center of the ICP discharge. The presence of the bullet indicates that the sample is reaching the plasma, while the vertical position of the bullet within the discharge is an indicator of the gas flow and RF power settings being used for the radial plasma. Sodium and yttrium are good elements of choice for conducting this test.

X4.2 *Signal Intensity*—The number of emission counts for a given concentration of an element can be used as a quick instrument diagnostic. Since emission counts vary from day to day, this is usually more useful for trend analysis than as an absolute indicator of performance.

X4.3 *Background Equivalent Concentration*—The background equivalent concentration gives an indication of the relative sensitivity of an emission line in comparison to the emission background at the same wavelength. If higher than normal, this can indicate that there are problems with the efficiency of the sample introduction system (although there are a number of other possible causes).

X4.4 *Precision*—The short-term precision obtained for repeat measurements of a strong emission line can be used as an indicator of the noise associated with sample introduction. The precision for an argon emission line can be used as a diagnostic for the RF generator.

X4.5 *Ion/Atom Ratio*—The ratio of the emission intensity of an ion line to that of an atomic line may be used as a diagnostic indicator of the relative excitation conditions within the plasma. The Mg(II) 280 nm / Mg(I) 285 nm line intensity ratio has been recommended for this test (27). Because ion/atom ratios are sensitive to RF power, nebulizer flow and viewing height, they can be used to check that relative excitation conditions remain unchanged. Running an analysis under a specific set of conditions is vital if interference correction factors or stored calibration curves are used in analysis.

X4.6 *Wavelength/Peak Alignment*—All dispersive instruments are subject to drift, and it is therefore important to ensure that the spectrometer wavelength is calibrated properly prior to analysis. For some instruments, this is done automatically by the instrument software.

X5. SAMPLER WALL DEPOSITS (28, 29, 30)

X5.1 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.

X5.2 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. Table X5.1 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.

X5.3 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. For other samplers, it is recommended that the wall deposits should be evaluated.

X5.4 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.

X5.5 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.

X5.6 Alternatively, sampler inserts, consisting of capsules

TABLE X5.1 CFC Maximum and Median Wall Deposits (28)

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

attached to filters (**2, 11**), can be used in lieu of rinsing and wiping techniques that are otherwise necessary to account for internal sampler wall deposits.

X5.7 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.

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