



Designation: ~~D7035-04~~ Designation: D7035 - 10

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

~~1.3 This 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.~~

~~1.4 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.~~

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

1.5 It is the user's responsibility to ensure the validity of the standard method for filters of untested matrices.

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

~~1.5 The 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.~~

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

~~1.7 The values stated in SI units are to be regarded as the standard.~~

~~1.8~~

1.7 The 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 This test method is under the jurisdiction of ASTM Committee [D22 on Sampling and Analysis of Atmospheres](#) and is the direct responsibility of Subcommittee [on Air Quality](#) and is the direct responsibility of Subcommittee [D22.04 on Workplace Atmospheres](#).

Current edition approved October 1, 2004. Published October 2004. DOI: 10.1520/D7035-04 on Workplace Air Quality.

Current edition approved April 1, 2010. Published June 2010. Originally approved in 2004. Last previous edition approved in 2004 as D7035 - 04. DOI: 10.1520/D7035-10.

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 the method.

1.10 The values stated in SI units are to be regarded as the 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](#)

D5011 [Practices for Calibration of Ozone Monitors Using Transfer Standards](#)

D6062 [Guide for Personal Samplers of Health-Related Aerosol Fractions](#)

D6785 [Test Method for Determination of Lead in Workplace Air Using Flame or Graphite Furnace Atomic Absorption Spectrometry](#)

D7202 [Test Method for Determination of Beryllium in the Workplace Using Field-Based Extraction and Fluorescence Detection](#)

D7439 [Test Method for Determination of Elements in Airborne Particulate Matter by Inductively Coupled PlasmaMass 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 6879 [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 12235 [15202 Chemistry—General Guidelines for Inductively Coupled Plasma-Atomic Emission Spectrometry \(2 parts\)](#)³

ISO 15202 [Workplace Air—Determination of Metals and Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry \(3 parts\)](#)³

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

EN 1540 [Workplace Atmospheres—Terminology](#)⁴

EN 1540 [Workplace Atmospheres—Terminology](#)⁴

3. Terminology

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

3.2 *Definitions:*

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

3.2.2 *area sampler*—a device, not attached to a person, that is used to sample air in a particular location.

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

3.2.3.1 *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.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ 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.

- 3.2.4 *axial plasma*—a horizontal inductively coupled plasma that is viewed end-on (versus radially; see 3.2.43).
- 3.2.5 *background correction*—the process of correcting the intensity at an analytical wavelength for the intensity due to the underlying spectral background of a blank. — ~~ISO15202~~ **ISO 15202**
- 3.2.6 *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**
- 3.2.7 *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**
- 3.2.8 *bias*—consistent deviation of the results of a measurement process from the true value of the air quality characteristic itself. **ISO 6879**
- 3.2.9 *blank solution*—solution prepared by taking a reagent blank or field blank through the same procedure used for sample dissolution.
- 3.2.10 *breathing zone*—the space around a worker’s face from where he or she takes his or her breath. For technical purposes a more precise definition is as follows: A hemisphere (generally accepted to be 0.3 m in radius) extending in front of the human face, centered on the midpoint of a line joining the ears; the base of the hemisphere is a plane through this line, the top of the head and the larynx. The definition is not applicable when respiratory protective equipment is used. — ~~EN1540~~ **EN 1540**
- 3.2.11 *calibration blank solution*—calibration solution prepared without the addition of any stock standard solution or working standard solution. **ISO 15202**
- 3.2.11.1 *Discussion*—The concentration of the analyte(s) of interest in the calibration blank solution is taken to be zero.
- 3.2.12 *calibration curve*—a plot of instrument response versus concentration of standards **(1)**⁵.
- 3.2.13 *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**
- 3.2.13.1 *Discussion*—The technique of matrix matching is normally used when preparing calibration solutions.
- 3.2.14 *chemical agent*—any chemical element or compound, on its own or admixed as it occurs in the natural state or as produced, used or released including release as waste, by any work activity, whether or not produced intentionally and whether or not placed on the market. — ~~EN1540~~ **EN 1540**
- 3.2.15 *continuing calibration blank (CCB)*—a solution containing no analyte added, that is used to verify blank response and freedom from carryover. **E1613**
- 3.2.15.1 *Discussion*—The measured concentration of the CCB is to be (at most) less than five times the instrumental detection limit.
- 3.2.16 *continuing calibration verification (CCV)*—a solution (or set of solutions) of known analyte concentration used to verify freedom from excessive instrumental drift; the concentration is to be near the mid-range of a linear calibration curve. **E1613**
- 3.2.16.1 *Discussion*—The CCV must be matrix matched to the acid content present in sample digestates or extracts. The CCV must be analyzed before and after all samples and at a frequency of not less than every ten samples. The measured value is to fall within $\pm 10\%$ of the known value.
- 3.2.17 *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. — ~~ISO15202~~ **ISO 15202**
- 3.2.18 *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**
- 3.2.18.1 *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.
- 3.2.19 *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. — ~~ISO15202~~ **ISO 15202**
- 3.2.20 *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. — ~~ISO15202~~ **ISO 15202**
- 3.2.21 *inhalable fraction*—the total airborne particle mass fraction inhaled through the nose and mouth, that is, which enters the respiratory system. **D6062**
- 3.2.22 *injector tube*—the innermost tube of an inductively coupled plasma torch, usually made of quartz or ceramic materials, through which the sample aerosol is introduced to the plasma. — ~~ISO15202~~ **ISO 15202**

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

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. **ISO15202**

3.2.18 **ISO 15202**

3.2.23 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. **ISO15202**

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. **ISO15202**

3.2.20 intermediate (auxiliary) argon flow—the flow of argon gas that is contained between the intermediate and center (injector) tubes of an inductively coupled plasma torch; typically 0.1 L/min – 2 L/min. **ISO15202**

3.2.21 **ISO 15202**

3.2.24 instrumental detection limit (IDL)—an instrumental measurement value that is used to provide a lower concentration limit for reporting optimum quantitative analysis data for a given instrument. —the lowest concentration at which the instrumentation can distinguish analyte content from the background generated by a minimal matrix. **E1613**

3.2.21.1 E1613

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

3.2.22—The IDL pertains to the maximum capability of an instrument and should not be confused with the method detection limit (MDL; see 3.2.35).

3.2.25 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**

3.2.26 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**

3.2.27 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**

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

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

3.2.30 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. **ISO15202**

3.2.23 **ISO 15202**

3.2.31 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. **ISO15202**

3.2.23.1 **ISO 15202**

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

3.2.24

3.2.32 matrix interference—interference of a non-spectral nature which is caused by the sample matrix. **ISO15202**

3.2.25 **ISO 15202**

3.2.33 matrix matching—a technique used to minimize the effect of the test solution matrix on the analytical results.

ISO15202

3.2.25.1 **ISO 15202**

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

3.2.26

3.2.34 measuring procedure—procedure for sampling and analyzing one or more chemical agents in the air, including storage and transportation of the sample(s). **ISO15202**

3.2.27 **ISO 15202**

3.2.35 method detection limit (MDL)—the minimum concentration of an analyte measured in the sample matrix which gives a mean signal of at least three times the standard deviation of the mean blank signal—**the minimum concentration of an analyte that can be reported with a 99 % confidence that the value is above zero.** **D1356**

3.2.35.1 Discussion—The MDL is also known as the limit of detection (LOD) (**†2**).

3.2.28

3.2.36 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 (**†2**).

3.2.29

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

3.2.37 <i>nebulizer</i> —a device used to create an aerosol from a liquid.	ISO15202
3.2.30	ISO 15202
3.2.38 <i>outer (plasma) argon flow</i> —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.	ISO15202
3.2.31	ISO 15202
3.2.39 <i>overall uncertainty (of a measuring procedure or of an instrument)</i> —quantity used to characterize as a whole the uncertainty of a result given by an apparatus or measuring procedure. It is expressed as a percentage by a combination of bias and precision, usually in accordance with the formula: $[(1\mu - x_{ref}) + 2s] / x_{ref} \times 100$ where μ is the mean value of results of a number of repeated measurements; x_{ref} is the true or accepted reference value of concentration, and s is the standard deviation of repeated measurements.	EN482
3.2.32	EN 482
3.2.40 <i>personal sampler</i> —a device attached to a person that samples air in the breathing zone.	EN1540
3.2.33	EN 1540
3.2.41 <i>pneumatic nebulizer</i> —a nebulizer that uses high-speed gas flows to create an aerosol from a liquid.	ISO15202
3.2.34	ISO 15202
3.2.42 <i>primary standard</i> —an acceptable reference sample or device used for establishing measurement of a physical quantity, directly defined and established by some authority, against which all secondary standards are compared.	D5011
3.2.35	
3.2.43 <i>radial plasma</i> — an inductively coupled plasma that is viewed from the side (versus end-on).	
3.2.36	
3.2.44 <i>reagent blank</i> —solution containing all reagents used in sample dissolution, in the same quantities used for preparation of blank and sample solutions.	ISO 15202
3.2.45 <i>reference period</i> —the specified period of time stated for the exposure limit of a specific chemical agent.	D6785
3.2.36.1	
3.2.45.1 <i>Discussion</i> —Examples of exposure limits having different reference values include short-term and long-term exposure limits, such as those established by the ACGIH (23).	
3.2.37	
3.2.46 <i>respirable fraction</i> —the mass of inhaled particles penetrating to the unciliated airways.	ISO7708
3.2.38	ISO 7708
3.2.47 <i>sample dissolution</i> —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
3.2.39	
3.2.48 <i>sample preparation</i> —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.	D6785
3.2.40	ISO 15202
3.2.49 <i>sample solution</i> —solution prepared from a sample by the process of sample dissolution.	ISO 15202
3.2.50 <i>sampling device; sampler</i> —for purposes of this standard, a device for collecting airborne particles.	
3.2.40.1	
3.2.50.1 <i>Discussion</i> —Devices used to collect airborne particles are often referred to by a number of other terms, such as sampling heads, filter holders, filter cassettes, and so forth.	
3.2.41	
3.2.51 <i>sampling location</i> —a specific area within a sampling site that is subjected to sample collection.	E1728
3.2.41.1	
3.2.51.1 <i>Discussion</i> —Multiple sampling locations are commonly designated for a single sampling site.	
3.2.42	
3.2.52 <i>sampling site</i> —a local geographic area that contains the sampling locations.	E1728
3.2.42.1	
3.2.52.1 <i>Discussion</i> —A sampling site is generally limited to an area that is easily covered by walking.	
3.2.43	
3.2.53 <i>secondary standard</i> —an acceptable reference sample or device used for establishing measurement of a physical quantity, used as a means of comparison, but checked against a primary standard.	D5011
3.2.44	
3.2.54 <i>spectral interference</i> —an interference caused by the emission from a species other than the analyte of interest.	ISO15202
3.2.45	ISO 15202
3.2.55 <i>spray chamber</i> —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. **ISO15202**
- 3.2.46 **ISO 15202**
- 3.2.56 *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).
- 3.2.57 *test solution*—solution prepared by the process of sample dissolution and subjected to any further operations necessary to bring it into a state ready for analysis. **D6785**
- 3.2.47—*blank solution or sample solution that has been subjected to all operations required to bring it into a state in which it is ready for analysis.* **ISO 15202**
- 3.2.58 *time-weighted average (TWA) concentration*—the concentration of a chemical agent in the atmosphere, averaged over the reference period. **D6785**
- 3.2.47.1 **D6785**
- 3.2.58.1 *Discussion*—A more detailed discussion of TWA concentrations and their use can be found in the ACGIH “TLV Handbook” (23).
- 3.2.48
- 3.2.59 *transport interference*—non-spectral interference caused by a difference in viscosity, surface tension, or density between the calibration and test solutions (for example, due to differences in dissolved solids content, type and concentration of acid, and so forth). **ISO15202**
- 3.2.48.1 **ISO 15202**
- 3.2.59.1 *Discussion*—Such differences produce a change in nebulizer efficiency and hence in the amount of analyte reaching the plasma.
- 3.2.49
- 3.2.60 *ultrasonic nebulizer*—a nebulizer in which the aerosol is created by flowing a liquid across a surface that is oscillating at an ultrasonic frequency. **ISO15202**
- 3.2.50 **ISO 15202**
- 3.2.61 *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. **ISO15202**
- 3.2.51 **ISO 15202**
- 3.2.62 *workplace*—the defined area or areas in which the work activities are carried out. **EN1540**
- 3.2.52 **EN 1540**
- 3.2.63 *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 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 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 either hot plate, hot plateblock, 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 dissolution/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); inductively coupled plasma – mass spectrometry (ICP-MS), electroanalysis, and so forth); 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 standard 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 so forth; 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 inductively coupled plasma atomic emission spectrometry.

~~NOTE 2—For some elements the sampling and sample preparation steps described herein may be used for subsequent analysis by other means, for example, atomic absorption spectrometry or electroanalysis. ICP-AES.~~

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

~~NOTE 3—Refer to Guide 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 4—In 3—In general, personal samplers for collection of airborne particles do not exhibit the same size-selective characteristics if used for area sampling.~~

~~NOTE 5—Some 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 65—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 7—In 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 8—Some 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*, 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 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 98—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 10—A 9—A laboratory washing machine may be used for cleaning of samplers.

7.2.3 *Loading Filters into Samplers*—Load clean samplers with unused, clean filters, 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).

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. 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 ($\pm 5\%$), 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)).

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, remove the filter 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. 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. Sample Preparation 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 HClO₄. 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 H₂SO₄ 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 H₂SO₄. Carry out sample dissolution with H₂SO₄ in a fume hood. Exercise caution when diluting H₂SO₄ with water, as this process is very exothermic. Do not add water to H₂SO₄, since it reacts violently when mixed in this manner; rather, prepare H₂SO₄/H₂O mixtures by adding H₂SO₄ 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 A3 through Annex A4. During sample preparation, use only reagents of analytical grade.

8.1.1

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.

8.1.29.1.2 *Nitric Acid (HNO₃)*, 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 1—It may be necessary to use nitric acid of higher purity in order to obtain adequate detection limits for some metals and metalloids. (**Warning**—Concentrated nitric acid is corrosive and oxidizing, and nitric acid fumes are 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.)

8.1.3 *10*—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 (HNO₃)*, diluted 1+9 (10 % v/v). Carefully and slowly begin adding 50 mL of concentrated nitric acid to 450 mL of water.

8.1.4

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

8.2

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.

8.2.1

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.

8.2.29.2.2 *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.

8.2.3

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

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

8.2.5

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

8-3

9.3 Sample Preparation Procedures:

~~NOTE 12—The~~ NOTE 11—The sample dissolution methods described in Annex A1 ~~through Annex A3 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).

8.3.1

9.3.1 Soluble Metal and Metalloid Compounds:

89.3.1.1 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.

89.3.1.2 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~~) and (~~hot plate digestion~~), Annex A3 (~~microwave digestion~~), (~~microwave digestion~~), and Annex A4 (hot block digestion).

~~NOTE 13—The methods prescribed in Annex A2 and Annex A3~~ NOTE 12—The methods prescribed in Annex A2 through Annex A4 are not specific for soluble metal, or metalloid compounds, or both. However, in these circumstances, they may be used as an alternative to the method described in Annex A1, if this is more convenient.

8.3.2

9.3.2 Total Metals and Metalloids and their Compounds:

89.3.2.1 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~~) and (~~hot plate digestion~~), Annex A3 (~~microwave 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.

8.3.2.2 Use the selected sample dissolution method to prepare test solutions for analysis of total metals and metalloids and their compounds by ICP-AES:

8.3.3 (~~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 13—In selection of a sample preparation method, consideration should be given to the metal or metalloid compounds that may be present in the test atmosphere. Some compounds, such as refractory metal oxides, may require a more robust sample preparation method than is required for other compounds, or for the metals or metalloids themselves.

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).

9.3.4 Mixed Exposures:

8.3.3.1 ~~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.

8.3.3.2 ~~Select~~ 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~~ or 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 test solutions for subsequent analysis by ICP-AES.

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

9.4 Special Cases:

8.4.1

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.

89.4.1.1 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 14—It should be recognized that the particle size of a bulk sample 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.

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

8.4.1.3 If the analytical recovery is outside the required range of acceptable values, investigate the use of an alternative sample dissolution method.

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

8.4.2 14—It should be recognized that, for a bulk sample, certain physical characteristics, such as particle size and agglomeration, could have a significant influence on the efficacy of its dissolution. Also, smaller 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 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, with a relative standard deviation of less than 5 % (4). 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 15—Another technique that can be used to account for dislodged particles involves carrying out sample dissolution within the sampling cassette itself (35).

8.4.3

9.4.3 *Treatment of Undissolved Material Following Sample Digestion*—If undissolved residue remains after carrying out sample digestion using hot plate, microwave, or microwave 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 acid solution(s), sample preparation method.

9.10. Analysis

9.1

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

9.1.1 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.

9.1.2

10.1.2 *Nitric Acid (HNO₃)*, concentrated, ρ ~1.42 g/mL (~70% m/m). (**Warning**—Concentrated nitric acid is corrosive and oxidizing, and nitric acid fumes are 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.)

9.1.3, concentrated, ρ ~1.42 g/mL (~70 % m/m).

10.1.3 *Nitric Acid (HNO₃)*, 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

10.1.4 *Ammonium Citrate Leach Solution*, 17 g/L (NH₄)₂HC₆H₅O₇ and 5 g/L C₆H₈O₇·H₂O. Weigh 17 g di-ammonium hydrogen citrate, (NH₄)₂ HC₆H₅O₇, and 5 g citric ammonium monohydrate, C₆H₈O₇·H₂O, 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.

9.1.5

10.1.5 *Hydrochloric Acid (HCl)*, concentrated, ρ ~1.18 g/mL, ~36% (m/m). (**Warning**—Concentrated hydrochloric acid is corrosive, and HCl vapor is 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 hydrochloric acid is high, so beware of pressure buildup in stoppered flasks when preparing mixtures containing HCl.)

9.1.6, concentrated, ρ ~1.18 g/mL, ~36 % (m/m).

10.1.6 *Hydrochloric Acid Leach Solution*, 0.1 M.