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Standard Practice for Measurement of Metals in Workplace Atmosphere by Flame Atomic Absorption Spectrophotometry¹

This standard is issued under the fixed designation D 4185; 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.

^{e1} NOTE—Keywords added to Section 14 editorially in October 2001.

1. Scope

1.1 This practice covers the collection, dissolution, and determination of trace metals in workplace atmospheres, by atomic absorption spectrophotometry.

1.2 The sensitivity, detection limit, and optimum working concentration for 23 metals are given in **Table 1**.

1.3 *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.* (Specific safety precautionary statements are given in Section 9.)

2. Referenced Documents

2.1 *ASTM Standards:*²

D 1193 Specification for Reagent Water

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere

D 3195 Practice for Rotameter Calibration

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this practice, refer to Terminology **D 1356**.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *blank signal*—that signal which results from all added reagents and a clean membrane filter ashed exactly as the samples.

3.2.2 *detection limit*—that concentration of a given element which produces a signal three times the standard deviation of the blank signal.

¹ This practice is under the jurisdiction of ASTM Committee D22 on Air Quality and are the direct responsibility of Subcommittee D22.04 on Workplace Atmospheres.

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

3.2.3 *working range for an analytical precision better than 3 %*—the range of sample concentrations that will absorb 10 to 70 % of the incident radiation (0.05 to 0.52 absorbance unit).

NOTE 1—Values for detection limit may vary from instrument to instrument.

4. Summary of Practice

4.1 The samples are collected on membrane filters and treated with nitric acid to destroy the organic matrix and to dissolve the metals present. The analysis is subsequently made by flame atomic absorption spectrophotometry (AAS).

4.2 Samples and standards are aspirated into an appropriate AAS flame. A hollow cathode or electrodeless discharge lamp for the metal being determined provides a source of characteristic radiation energy for that particular metal. The absorption of this characteristic energy by the atoms of interest in the flame is related to the concentration of the metal in the aspirated sample. The flame and operating conditions for each element are listed in **Table 2**.

5. Significance and Use

5.1 Exposure to some metal-containing particulates has been demonstrated to cause dermatitis, skin ulcers, eye problems, chemical pneumonitis, and other physical disorders (**1**).³

5.2 AAS is capable of quantitatively determining most metals in air samples at the levels required by federal, state, and local occupational health and air pollution regulations.

6. Interferences

6.1 In AAS the occurrence of interferences is less common than in many other analytical techniques. Interferences can occur, however, and when encountered are corrected for as indicated in the following sections. The known interferences and correction methods for each metal are indicated in **Table 2**. The methods of standard additions and background monitoring and correction (**2-5**) are used to identify the presence of an interference. Insofar as possible, the matrix of sample and standard are matched to minimize the possible interference.

³ Boldface numbers in parentheses refer to the list of references appended to these methods.

TABLE 1 Detection Limits and Optimum Working Concentration for 23 Metals

Element	Detection Limit, µg/mL (approximately three times standard deviation) ^A	Optimum Linear Range Upper Limit, µg/mL	TLV, mg/m ³ (elements, compound classes, and oxides) ^B
Ag	0.001	5	0.1 (metal) 0.01 (soluble compounds as Ag)
Al	0.04	50	2.0 (soluble salts and alkyls not otherwise classified) 10 (metal dust and oxide) 5 (pyro powder and welding fume)
Ba	0.01	10	0.5 (soluble compounds)
Bi	0.03	10	No Limit expressed for this element
Ca	0.002	1	2 (oxide as CaO)
Cd	0.0008	1	0.01 (elemental and compounds—total dust) 0.002 (elemental compounds—respirable fraction)
Co	0.009	5	0.02 (elemental and inorganic) 0.1 (carbonyl and hydrocarbonyl)
Cr	0.003	5	0.5 (metal and Cr III compounds) 0.05 (water soluble Cr VI compounds) 0.01 (insoluble Cr VI compounds)
Cu	0.002	5	0.2 (fume) 1 (dust and mists as Cu)
Fe	0.005	5	5 (iron oxide fume) 5 (soluble salts as Fe)
In	0.03	50	0.1 (metal and compounds)
K	0.003	1	No Limit expressed for this element
Li	0.0008	1	No Limit expressed for this element
Mg	0.0002	0.5	10 (as MgO fume)
Mn	0.002	5	0.2 (elemental and inorganic compounds)
Na	0.0003	0.5	No Limit expressed for this element
Ni	0.006	5	0.05 (elemental, soluble and insoluble compounds)
Pb	0.02	10	0.15 (inorganic compounds, fume, dust)
Rb	0.003	5	No Limit expressed for this element
Sr	0.003	5	No Limit expressed for this element
Tl	0.02	50	0.1 (soluble compounds)
V	0.06	100	0.05 (pentoxide, respirable dust or fume, as V ₂ O ₅)
Zn	0.002	1	10 (oxide dust as ZnO) 5 (oxide fume as ZnO)

^A Detection limit data and precision information supplied by Perkin-Elmer Corp., Norwalk, CT.

Note—These detection limits represent ideal laboratory conditions; variability due to sampling, digestion, reagents, and sample handling has not been taken into account.

^B Threshold Limit Values of Airborne Contaminants and Physical Agents adopted by ACGIH for 1994–1995. Values are elemental concentration except as noted.

6.2 Background or nonspecific absorption can occur from particles produced in the flame which can scatter light and produce an apparent absorption signal. Light scattering may be encountered when solutions of high salt content are being analyzed. They are most severe when measurements are made at shorter wavelengths (for example, below about 250 nm). Background absorption may also occur as the result of the formation of various molecular species which can absorb light. The background absorption can be accounted for by the use of background correction techniques (2).

6.3 Spectral interferences are those interferences which result from an atom different from the one being measured that absorbs a portion of the radiation. Such interferences are extremely rare in AAS. In some cases multielement hollow cathode lamps may cause a spectral interference by having closely adjacent emission lines from two different elements. In general, the use of multielement hollow cathode lamps is discouraged.

6.4 Ionization interference occurs when easily ionized atoms are being measured. The degree to which such atoms are ionized is dependent upon the atomic concentration and the presence of other easily ionized atoms. This interference can be controlled by the addition of a high concentration of another easily ionized element which will buffer the electron concentration in the flame.

6.5 Chemical interferences occur in AAS when species present in the sample cause variations in the degree to which atoms are formed in the flame, or when different valence states of a single element have different absorption characteristics. Such interferences may be controlled by adjusting the sample matrix or by the method of standard additions (3). Also, the use

of lanthanum as a releasing element minimizes the interference from the formation of involatile compounds in the flame. Lanthanum forms involatile compounds preferentially with the interferent so that the analyte stays free.

6.6 Physical interferences may result if the physical properties of the samples vary significantly. Changes in viscosity and surface tension can affect the sample aspiration rate and thus cause erroneous results. Sample dilution or the method of standard additions, or both, are used to correct such interferences. High concentrations of silica in the sample can cause aspiration problems. No matter what elements are being determined, if large amounts of silica are extracted from the samples they shall be allowed to stand for several hours and centrifuged or filtered to remove the silica.

6.7 This procedure describes a generalized method for sample preparation which is applicable to the majority of samples. There are some relatively rare chemical forms of a few of the elements listed in Table 1 that will not be dissolved by this procedure. If such chemical forms are suspected, results obtained using this procedure shall be compared with those obtained using an appropriately altered dissolution procedure. Alternatively, the results may be compared with values obtained using a technique that does not require dissolving the sample (for example, X-ray fluorescence or activation analysis).

7. Apparatus

7.1 Sampling Apparatus:

7.1.1 Cellulose Ester or Cellulose Nitrate Membrane Filters, with a pore size of 0.8 µm mounted in a 37-mm diameter two- or three-piece filter cassette.

TABLE 2 The AAS Flame and Operating Conditions for Each Element

Element	Type of Flame	Analytical Wavelength, nm	Interferences ^A	Remedy ^A	Reference
Ag	Air-C ₂ H ₂ (oxidizing)	328.1	IO ₃ ⁻ , WO ₄ ⁻² , MnO ₄ ⁻² , Cl ⁻ , F ⁻	<i>B</i>	(5,10)
Al ^C	N ₂ O-C ₂ H ₂ (reducing)	309.3	ionization, SO ₄ ⁻² , V	<i>B,D,E</i>	(4)
Ba	N ₂ O-C ₂ H ₂ (reducing)	553.6	ionization, large concentration Ca	<i>D,F</i>	(1,4)
Bi	Air-C ₂ H ₂ (oxidizing)	223.1	none known		
Ca	Air-C ₂ H ₂ (oxidizing)	422.7	ionization (slight) and chemical ionization	<i>D,E</i>	(1,4)
	N ₂ O-C ₂ H ₂ (reducing)				
Cd	Air-C ₂ H ₂ (oxidizing)	228.8	none known		
Co ^C	Air-C ₂ H ₂ (oxidizing)	240.7	none known		
Cr ^C	Air-C ₂ H ₂ (reducing)	357.9	Fe, Ni, oxidation state of Cr	<i>B</i>	(4)
Cu	Air-C ₂ H ₂ (oxidizing)	324.8	none known		
Fe	Air-C ₂ H ₂ (oxidizing)	248.3	high Ni concentration, Si	<i>B</i>	(1,4)
In	Air-C ₂ H ₂ (oxidizing)	303.9	Al, Mg, Cu, Zn, H _x PO ₄ ^{x-3}	<i>B</i>	(11)
K	Air-C ₂ H ₂ (oxidizing)	766.5	ionization	<i>D</i>	(1,4)
Li	Air-C ₂ H ₂ (oxidizing)	670.8	ionization	<i>D</i>	(12)
Mg	Air-C ₂ H ₂ (oxidizing)	285.2	chemical ionization	<i>D,E</i>	(1,4)
	N ₂ O-C ₂ H ₂ (reducing)				
Mn	Air-C ₂ H ₂ (oxidizing)	279.5	Si		
Na	Air-C ₂ H ₂ (oxidizing)	589.6	ionization	<i>E</i>	(1,4)
Ni	Air-C ₂ H ₂ (oxidizing)	232.0	none known		
Pb	Air-C ₂ H ₂ (oxidizing)	217.0	Ca, high concentration SO ₄ ⁻²	<i>B</i>	(9)
		283.3			
Rb	Air-C ₂ H ₂ (oxidizing)	780.0	ionization	<i>D</i>	(1,10)
Sr	Air-C ₂ H ₂ (oxidizing)	460.7	ionization and chemical ionization	<i>D,E</i>	(1,10)
	N ₂ O-C ₂ H ₂ (reducing)				
Tl	Air-C ₂ H ₂ (oxidizing)	276.8	none known		
Va	N ₂ O-C ₂ H ₂ (reducing)	318.4	ionization		
Zn	Air-C ₂ H ₂ (oxidizing)	213.9	none known		

^A High concentrations of silicon in the sample can cause an interference for many of the elements in this table and may cause aspiration problems. No matter what elements are being measured, if large amounts of silica are extracted from the samples the samples should be allowed to stand for several hours and centrifuged or filtered to remove the silica.

^B Samples are periodically analyzed by the method of additions to check for chemical interferences. If interferences are encountered, determinations must be made by the standard additions method or, if the interferent is identified, it may be added to the standards.

^C Some compounds of these elements will not be dissolved by the procedure described here. When determining these elements one should verify that the types of compounds suspected in the sample will dissolve using this procedure (see 12.2).

^D Ionization interferences are controlled by bringing all solutions to 1000 ppm cesium (samples and standards).

^E 1000-ppm solution of lanthanum as a releasing agent is added to all samples and standards.

^F In the presence of very large calcium concentrations (greater than 0.1 % a molecular absorption from CaOH may be observed. This interference may be overcome by using background corrections when analyzing for barium.

7.1.2 *Portable, Battery-Operated Personal Sampling Pumps*, equipped with a flow-monitoring device (rotameter, critical orifice) or a constant-flow device and capable of drawing 2 L/min of air through the 0.8- μ m filter membranes for a period of 8 h.

7.2 Analytical Apparatus:

7.2.1 *Atomic Absorption Spectrophotometer*, equipped with air/acetylene and nitrous oxide/acetylene burner heads.

7.2.2 *Hollow Cathode or Electrodeless Discharge Lamp*, for each element to be determined.

7.2.3 *Deuterium Continuum Lamp*.

7.2.4 *Compressed Air*—Appropriate pressure reducing regulator with base connections (see instrument manufacturer's instructions).

7.2.5 *Acetylene Gas and Regulator*—A cylinder of acetylene equipped with a two-gage, two-stage pressure-reducing regulator with hose connections. (See instrument manufacturer instructions.)

7.2.6 *Nitrous Oxide Gas and Regulator*—A cylinder of nitrous oxide equipped with a two-gage, two-stage pressure-reducing regulator and hose connections. Heat tape with the temperature controlled by a rheostat may be wound around the second stage regulator and hose connection to prevent freeze-up of the line. (See instrument manufacturer instructions.)

7.2.7 *Beakers*, Phillips or Griffin, 125-mL, borosilicate glass.

7.2.8 *Centrifuge Tubes*, 15-mL, graduated, borosilicate glass.

7.2.9 *Miscellaneous Borosilicate Glassware (Pipets and Volumetric Flasks)*—All pipets and volumetric flasks shall be calibrated Class A volumetric glassware.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁴ Other grades may be used provided it can be demonstrated that they are of sufficiently high purity to permit their use without decreasing the accuracy of the determinations.

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean Type II reagent water conforming to Specification **D 1193**.

8.3 *Hydrochloric Acid (HCl)*—Concentrated hydrochloric acid, 12 *N*, specific gravity 1.19.

8.4 *Nitric Acid (HNO₃)*—Redistilled, concentrated nitric acid, 16 *N*, specific gravity 1.42.

8.5 *Standard Stock Solutions* (1000 µg/mL) for each of the metals listed in **Table 1**. These solutions are stable for one year when stored in polyethylene bottles and can be obtained from commercial sources or prepared in the laboratory in the following manner:

8.5.1 *Stock Aluminum Solution*—Dissolve 1.000 g of aluminum wire in a minimum volume of 1 + 1 HCl. Dilute to volume in a 1-L flask with purified water.

8.5.2 *Stock Barium Solution*—Dissolve 1.779 g of barium chloride (BaCl₂·2H₂O) in water. Dilute to volume in a 1-L flask with purified water.

8.5.3 *Stock Bismuth Solution*—Dissolve 1.000 g of bismuth metal in a minimum volume of 6 *N* HNO₃. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.4 *Stock Cadmium Solution*—Dissolve 1.000 g of cadmium metal in a minimum volume of 6 *N* HCl. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.5 *Stock Calcium Solution*—To 2.497 g of primary standard calcium carbonate (CaCO₃) add 50 mL of distilled water. Add dropwise a minimum volume of HCl (approximately 10 mL) to dissolve the CaCO₃. Dilute to volume in a 1-L flask with purified water.

8.5.6 *Stock Chromium Solution*—Dissolve 3.735 g of potassium chromate (K₂CrO₄) in distilled water. Dilute to volume in a 1-L flask with purified water.

8.5.7 *Stock Cobalt Solution*—Dissolve 1.000 g of cobalt metal in a minimum volume of 1 + 1 HCl. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.8 *Stock Copper Solution*—Dissolve 1.000 g of copper metal in a minimum volume of 6 *N* HNO₃. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.9 *Stock Indium Solution*—Dissolve 1.000 g of indium metal in a minimum volume of 1 + 1 HCl. Addition of a few drops of HNO₃ and mild heating will aid in dissolving the metal. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.10 *Stock Iron Solution*—Dissolve 1.000 g of iron wire in 50 mL of 6 *N* HNO₃. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.11 *Stock Lead Solution*—Dissolve 1.598 g of lead nitrate (Pb(NO₃)₂) in 2 % (v/v) HNO₃. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.12 *Stock Lithium Solution*—Dissolve 5.324 g of lithium carbonate (Li₂CO₃) in a minimum volume of 6 *N* HCl. Dilute to volume in a 1-L flask with purified water.

8.5.13 *Stock Magnesium Solution*—Dissolve 1.000 g of magnesium ribbon in a minimum volume of 6 *N* HCl. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.14 *Stock Manganese Solution*—Dissolve 1.000 g of manganese metal in a minimum volume of 6 *N* HNO₃. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.15 *Stock Nickel Solution*—Dissolve 1.000 g of nickel metal in a minimum volume of 6 *N* HNO₃. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.16 *Stock Potassium Solution*—Dissolve 1.907 g of potassium chloride (KCl) in purified water. Dilute to volume in a 1-L flask with purified water.

8.5.17 *Stock Rubidium Solution*—Dissolve 1.415 g of rubidium chloride (RbCl) in distilled water. Dilute to volume in a 1-L flask with purified water.

8.5.18 *Stock Silver Solution*—Dissolve 1.575 g of silver nitrate (AgNO₃) in 100 mL of purified water. Dilute to volume in a 1-L volumetric flask with 2 % (v/v) HNO₃. The silver nitrate solution will deteriorate in light and must be stored in an amber bottle away from direct light. New stock silver solution shall be prepared every few months.

8.5.19 *Stock Sodium Solution*—Dissolve 2.542 g of sodium chloride (NaCl) in purified water. Dilute to volume in a 1-L flask with purified water.

8.5.20 *Stock Strontium Solution*—Dissolve 2.415 g of strontium nitrate (Sr(NO₃)₂) in purified water. Dilute to volume in a 1-L flask with purified water.

8.5.21 *Stock Thallium Solution*—Dissolve 1.303 g of thallium nitrate (TlNO₃) in 10 % (v/v) HNO₃. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.22 *Stock Vanadium Solution*—Dissolve 1.000 g of vanadium metal in a minimum volume of 6 *N* HNO₃. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.5.23 *Stock Zinc Solution*—Dissolve 1.000 g of zinc metal in a minimum volume of 6 *N* HNO₃. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃.

8.6 *Working Standards*—Working standards are prepared by appropriate single or multiple dilutions of the standard solutions listed in 8.5. Mixed standards may be prepared keeping in mind any chemical incompatibilities. For those metals which in **Table 2** indicate chemical or ionization interferences, the final dilution shall contain 2 % (v/v) of the 50-mg/mL cesium and lanthanum solutions. In order to match the standard and sample matrices, the final dilution should be made so that it contains 10 % (v/v) HNO₃ or whatever acid mixture is used to prepare the sample. When using those atomic absorption spectrophotometers equipped with concentration read-out, follow the manufacturer's suggestions as to the spacing of the standard concentrations over the range of interest.

8.7 *Ionization and Chemical Interference Suppressants*:

8.7.1 *Cesium Solution (50 mg/mL)*—Dissolve 73.40 g of cesium nitrate (CsNO₃) in distilled water. Dilute to volume in a 1-L flask with purified water. When stored in a polyethylene bottle this solution is stable for at least one year.

8.7.2 *Lanthanum Solution (50 mg/mL)*—Dissolve 156.32 g of lanthanum nitrate (La(NO₃)₃·6H₂O) in 2 % (v/v) HNO₃. Dilute to volume in a 1-L flask with 2 % (v/v) HNO₃. When stored in a polyethylene bottle this solution is stable for at least one year.

9. Safety Precautions

9.1 Hazards to personnel exist in the operation of the atomic absorption spectrophotometer. AAS units are potentially dangerous when using a nitrous oxide/acetylene flame. Do not operate any AAS unit until the manufacturer's instruction