 Designation: D 4185 – 96

An American National Standard

Standard Practice for
Measurement of Metals in Workplace Atmosphere by Flame Atomic Absorption Spectrophotometry[1]

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 sen

sitivity, 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:*

D 1193 Specification for Reagent Water[2]

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[3]

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere[3]

D 3195 Practice for Rotameter Calibration[3]

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.

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**).[4]

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.

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).

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_2O_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.

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.

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-µm 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.

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_2H_2 (oxidizing)	328.1	IO_3^-, WO_4^{-2}, MnO_4^{-2}, Cl^-, F^-	[B]	(5,10)
Al[C]	N_2O-C_2H_2 (reducing)	309.3	ionization, SO_4^{-2}, V	[B,D,E]	(4)
Ba	N_2O-C_2H_2 (reducing)	553.6	ionization, large concentration Ca	[D,F]	(1,4)
Bi	Air-C_2H_2 (oxidizing)	223.1	none known		
Ca	Air-C_2H_2 (oxidizing)	422.7	ionization (slight) and chemical ionization	[D,E]	(1,4)
	N_2O-C_2H_2 (reducing)				
Cd	Air-C_2H_2 (oxidizing)	228.8	none known		
Co[C]	Air-C_2H_2 (oxidizing)	240.7	none known		
Cr[C]	Air-C_2H_2 (reducing)	357.9	Fe, Ni, oxidation state of Cr	[B]	(4)
Cu	Air-C_2H_2 (oxidizing)	324.8	none known		
Fe	Air-C_2H_2 (oxidizing)	248.3	high Ni concentration, Si	[B]	(1,4)
In	Air-C_2H_2 (oxidizing)	303.9	Al, Mg, Cu, Zn, $H_xPO_4^{x-3}$	[B]	(11)
K	Air-C_2H_2 (oxidizing)	766.5	ionization	[D]	(1,4)
Li	Air-C_2H_2 (oxidizing)	670.8	ionization	[D]	(12)
Mg	Air-C_2H_2 (oxidizing)	285.2	chemical ionization	[D,E]	(1,4)
	N_2O-C_2H_2 (reducing)				
Mn	Air-C_2H_2 (oxidizing)	279.5	SI		
Na	Air-C_2H_2 (oxidizing)	589.6	ionization	[E]	(1,4)
Ni	Air-C_2H_2 (oxidizing)	232.0	none known		
Pb	Air-C_2H_2 (oxidizing)	217.0	Ca, high concentration SO_4^{-2}	[B]	(9)
		283.3			
Rb	Air-C_2H_2 (oxidizing)	780.0	ionization	[D]	(1,10)
Sr	Air-C_2H_2 (oxidizing)	460.7	ionization and chemical ionization	[D,E]	(1,10)
	N_2O-C_2H_2 (reducing)				
Tl	Air-C_2H_2 (oxidizing)	276.8	none known		
Va	N_2O-C_2H_2 (reducing)	318.4	ionization		
Zn	Air-C_2H_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.

7.2.2 *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.[5] 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.

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 (HNO_3)*—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

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[5] *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.

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 ($BaCl_2 \cdot 2H_2O$) 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 $6 N$ HNO_3. Dilute to volume in a 1-L flask with 2 % (v/v) HNO_3.

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) HNO_3.

8.5.5 *Stock Calcium Solution*—To 2.497 g of primary standard calcium carbonate ($CaCO_3$) add 50 mL of distilled water. Add dropwise a minimum volume of HCl (approximately 10 mL) to dissolve the $CaCO_3$. Dilute to volume in a 1-L flask with purified water.

8.5.6 *Stock Chromium Solution*—Dissolve 3.735 g of potassium chromate (K_2CrO_4) 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) HNO_3.

8.5.8 *Stock Copper Solution*—Dissolve 1.000 g of copper metal in a minimum volume of $6 N$ HNO_3. Dilute to volume in a 1-L flask with 2 % (v/v) HNO_3.

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 HNO_3 and mild heating will aid in dissolving the metal. Dilute to volume in a 1-L flask with 2 % (v/v) HNO_3.

8.5.10 *Stock Iron Solution*—Dissolve 1.000 g of iron wire in 50 mL of $6 N$ HNO_3. Dilute to volume in a 1-L flask with 2 % (v/v) HNO_3.

8.5.11 *Stock Lead Solution*—Dissolve 1.598 g of lead nitrate ($Pb(NO_3)_2$) in 2 % (v/v) HNO_3. Dilute to volume in a 1-L flask with 2 % (v/v) HNO_3.

8.5.12 *Stock Lithium Solution*—Dissolve 5.324 g of lithium carbonate (Li_2CO_3) 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) HNO_3.

8.5.14 *Stock Manganese Solution*—Dissolve 1.000 g of manganese metal in a minimum volume of $6 N$ HNO_3. Dilute to volume in a 1-L flask with 2 % (v/v) HNO_3.

8.5.15 *Stock Nickel Solution*—Dissolve 1.000 g of nickel metal in a minimum volume of $6 N$ HNO_3. Dilute to volume in a 1-L flask with 2 % (v/v) HNO_3.

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 ($AgNO_3$) in 100 mL of purified water. Dilute to volume in a 1-L volumetric flask with 2 % (v/v) HNO_3. 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 ($Sr(NO_3)_2$) 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 ($TINO_3$) in 10 % (v/v) HNO_3. Dilute to volume in a 1-L flask with 2 % (v/v) HNO_3.

8.5.22 *Stock Vanadium Solution*—Dissolve 1.000 g of vanadium metal in a minimum volume of $6 N$ HNO_3. Dilute to volume in a 1-L flask with 2 % (v/v) HNO_3.

8.5.23 *Stock Zinc Solution*—Dissolve 1.000 g of zinc metal in a minimum volume of $6 N$ HNO_3. Dilute to volume in a 1-L flask with 2 % (v/v) HNO_3.

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) HNO_3 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 ($CsNO_3$) 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 ($La(NO_3)_3 \cdot 6H_2O$) in 2 % (v/v) HNO_3. Dilute to volume in a 1-L flask with 2 % (v/v) HNO_3. 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 manual has been read and completely understood. Follow all safety instructions in the manual and the safety requirements pertaining to the handling, storage, and use of compressed gases.

9.2 Hazards to personnel exist in all operations in which hot, concentrated mineral acids are used. The appropriate laboratory procedures for working with reagents of this nature shall be observed.

9.3 Many of the metals that can be determined by AAS are health hazards (for example, cadmium, arsenic, beryllium,

mercury) and must be handled in a manner consistent with the danger they present.

9.4 The instrument exhaust gases contain the combustion products of the flame as well as metal vapor from the sample. Both the combustion products and the metal vapor (see 9.3) are definite personnel hazards. The instrument combustion gases shall be mechanically exhausted from the laboratory (see instrument manufacturer's instructions).

10. Sampling

10.1 For general information on sampling, refer to Practice D 1357.

10.2 Air samples are collected on a 0.8-μm cellulose ester or cellulose nitrate membrane filter at a flow rate of 2 L/min. Measure and record the beginning and ending flow rates. Sampling time shall be representative of average or peak exposures as needed. Sampling times might coincide with shift changes or be for shorter periods. However, the sampling time shall be limited so that overloading of the filter will not occur. Overloading the filter can seriously change the flow rate and may result in some of the sample falling off the surface of the filter.

10.3 One blank sample shall be provided with every ten actual samples. No air is drawn through the blank filter but it is subjected to the same handling and shipping manipulations as the actual samples are.

10.4 General area samples can be collected with suitable air sampling equipment.

11. Calibration and Standardization

11.1 *Air Sampling Pumps*—All air sampling pumps must be calibrated in the laboratory before use. For an accurate calibration, attach filters to be used for collecting the samples to the pump during the calibration. Calibration may be effected by drawing air through a calibrated rotameter or through a soap-bubble flowmeter. Refer to Practice D 3195 for the exact procedure for calibrating a rotameter. A primary standard practice is given for the calibration of low flow-rate pumps in Annex A1 and Fig. A1.1 of this practice.

11.2 Prepare standard solutions from the solutions listed in 8.5 and 8.6 to bracket the estimated concentration of the metal in the samples. Aspirate the standards into the flame and record the absorbance. Prepare a calibration graph by plotting absorbance versus the metal concentration. Calculate the best fit straight line for the data points by the method of least squares (see 13.2) and draw it in. Use the best fit line or its equation to obtain the metal concentration in the samples to be analyzed.

12. Procedure

12.1 Use borosilicate glassware for this procedure. Before use, clean all glassware with a detergent wash, rinse with distilled water, soak 4 h in 1 + 1 HNO_3, rinse in distilled water, and dry.

12.2 Transfer the samples and blanks (minimum of 1 filter blank for every 10 filter samples) to clean 125-mL Phillips or Griffin beakers and add sufficient concentrated HNO_3 to cover the sample. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until the sample dissolves and a slightly yellow solution is produced. Approximately 30 min of heating will be sufficient for most air samples. However, subsequent additions of HNO_3 may be needed to completely ash and destroy high concentrations of organic material, and under these conditions longer ashing times will be required. Do not permit the sample to evaporate to dryness.

12.2.1 Some compounds of metals given in Table 2 may not be solubilized by the procedure described. Alternative ashing procedures include the use of hydrochloric acid, mixed nitric and sulfuric acids, or mixed nitric, sulfuric, and perchloric acids. Do not add perchloric acid to the sample preparation until all organic matter has been destroyed by either nitric or mixed nitric and sulfuric acids. When using perchloric acid, proper precautions for the handling of the acid fumes must be taken [6]. Also, if a sample to which perchloric acid has been added is taken to dryness, a potential explosion hazard must be recognized. References [7] and [8] may provide assistance in dissolving particularly troublesome samples. Whatever method is used to dissolve the sample, the standard solutions must be prepared in a similar mixture of acids. Also, the sample solution should be clear after the dissolution process.

12.3 Remove the beaker and quantitatively transfer the solution with purified water to a 10-mL volumetric flask. If any of the elements being determined require the ionization buffer, add 0.2 mL of 50 mg/mL cesium to the volumetric flask (see Table 2, footnote *D*). If any of the elements being determined require the releasing agent, add 0.2 mL of 50 mg/mL lanthanum solution to each volumetric flask (see Table 2, footnote *E*). Dilute the samples to volume with purified water.

12.3.1 If more than one metal is to be determined in the sample, dilution to a volume larger than 10 mL may be required. In such cases, maintain the acid, ionization buffer, and releasing agent concentrations by increasing proportionally the amount added. The amount of dilution permitted will depend upon the number and concentration of metals being determined.

12.4 The 10-mL solution may be analyzed directly for any elements of very low concentration in the sample. Aliquots of this solution may be then diluted to an appropriate volume for the other elements of interest present at higher concentrations. Approximately 2 mL of solution are required for each element being determined.

12.5 Adjust the operating parameters of the spectrophotometer (slit width, amplifier gain, lamp current, etc.) to the values recommended by the manufacturer of the instrument. Set the wavelength at the proper value and aspirate the sample solution into the proper flame. Record the absorbance. The use of a stripchart recorder or a data acquisition system to provide a permanent record to the absorbances is recommended. Aspirate purified water after each sample or standard. Should the absorbance be above the calibration range, dilute an appropriate aliquot to 10 mL. A mid-range standard must be aspirated with sufficient frequency (that is, once every 10 samples) to assure the accuracy of the sample determinations. To the extent possible, all determinations shall be based on replicate analyses.

12.6 In order to evaluate the contribution to the absorbance from the membrane filters and reagents used, blank samples must be analyzed. Usually blanks will be provided with each

set of samples. Subject the blank to the entire ashing and analysis procedure. The absorbance obtained from the aspiration of the blank solution is subtracted from the sample absorbance.

12.7 If chemical interferences are suspected, use the method of additions to evaluate them. Take three identical portions from a sample. Dilute the first portion to a known volume with the solvent used in the standard solutions. Add known but different amounts of the metal of interest to the second and third portions. The additions and dilutions should be kept as small as possible by using microlitre pipets. Aspirate each portion and measure the absorbance. Plot the absorbance values (Y-axis) against metal concentration (X-axis). Consider the first portion concentration to be 0 and that of the others as the known amount added to each. Draw the curve through these points. It should be a straight line. The metal concentration in the unknown is measured as the distance from the origin along the X-axis in the negative direction using the same concentration scale factor. Compare the values obtained for the same samples by direct comparison to the calibration curve. If the values are the same, no chemical interferences are present, and subsequent analyses can be made by direct comparison to the standard working graph.

12.8 Spurious absorption, that is, absorption not due to the atoms of the metal being determined, can be caused by the presence of small particles in the resonance beam or by the presence of radicals or molecular species resulting from components of the prepared sample or from combustion reactions of the flame itself. The effects of background absorption and scatter are an increase in the absorption signal and an increase in the noise component of the signal. The final effect is the reporting of results that may be considerably higher than the true value and a loss of sensitivity because of the increased noise. Background correction using the instrument's automatic deuterium background corrector is a necessity for those elements which absorb at wavelengths shorter than 250 nm. In addition, there are a number of different approaches to automatic background correction available on current instrumentation. For AAS units not equipped with background correction devices, background interferences can be evaluated in the following manner:

12.9 A deuterium continuum lamp is required for this procedure. First measure the absorbance of a sample and a suitable standard in the usual manner. Second, remove the hollow cathode lamp and replace with the continuum lamp, and without changing the flame conditions or any other parameters, adjust the output of the amplifier to read 0 absorbance. Third, measure the absorbance of the same sample and standard and subtract the continuum lamp values from the hollow cathode lamp values to get an absorbance value free of background absorbance interference.

13. Calculations

13.1 Calculate the volume collected by the filter by averaging the beginning and ending sample flow rates, converting to cubic metres, and multiplying by the sample collection time, as follows:

$$V = (F_B + F_E)/(2 \times 1000) \times t \tag{1}$$

where:
V = sample volume, m^3,
F_B = sample flow rate at beginning of sample collection, L/min,
F_E = sample flow rate at end of sample collection, L/min, and
t = sample collection time, min.

13.2 Calculate the calibration line by the least squares regression procedure, as follows:

$$y = mx + c \tag{2}$$

where:

$$m = \frac{n\,(\Sigma xy) - \Sigma x\,(\Sigma y)}{n\,(\Sigma x^2) - (\Sigma x)^2} \tag{3}$$

c = $y - mx$,
n = number of points used to fit the curve,
y = arithmetic mean of the y–coordinates for n points,
x = arithmetic mean of the x–coordinates for n points,
Σxy = the sum of the products of the x-coordinate times the y-coordinate for the n points,
Σx = the sum of the x-coordinates of n points,
Σy = the sum of the y-coordinates of n points,
Σx^2 = the sum of the squares of the x-coordinates of n points, and
$(\Sigma x)^2$ = the square of the sum of the x-coordinates of n points.

13.3 Calculate the atmospheric concentration of the metal as follows:

$$\text{Metal concentration, } \mu g/m^3 = \left(C \times \frac{V_1}{F} - B\right) / (V) \tag{4}$$

where:
C = concentration of metal in solution aspirated obtained from calibration graph or instrument read-out,μ g/mL,
V_1 = final volume to which any aliquot of sample is diluted, mL,
B = total metal in the blank, μg,
F = dilution factor; volume of aliquot taken divided by original volume of sample, and
V = volume of air sample calculated from 13.1, m^3.

14. Keywords

14.1 air monitoring; atomic absorption spectrophotometry; metals analysis; sampling and analysis; workplace atmospheres

ANNEX

A1. METHOD FOR CALIBRATION OF SMALL VOLUME AIR PUMPS

A1.1 Using a 1-L buret, assemble the apparatus as shown in Fig. A1.1 using any good soap bubble solution as a source of the film. Make sure all connections are tight.

A1.1.1 It is advisable to check the volume of burets used for calibrating sampling pumps by weighing the volume of distilled water contained in the buret and calculating the true volume.
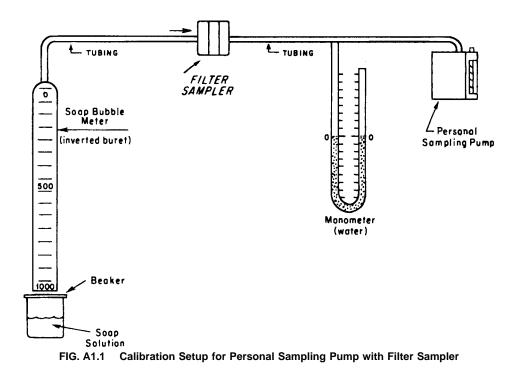
A1.1.2 Make sure the batteries of the pump are charged.

A1.2 Prime the surface of the cylinder with bubble solution by drawing repeated films up the tube until a single film travels to the desired mark.

A1.3 With a stop watch, time the travel of a single film from the zero mark to the selected volume mark. Note the time and repeat this procedure at least three times.

A1.4 Calculate the sampling rate of the pump, correcting the air volume to 25°C and 760 mmHg (101.3 kPa), using the ambient barometric pressure.

A1.5 Replace the filter sampler with another one selected at random, and repeat the calibration sequence.

FIG. A1.1   Calibration Setup for Personal Sampling Pump with Filter Sampler

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