

**Compendium of Methods
for the Determination of
Inorganic Compounds
in Ambient Air**

Compendium Method IO-3.2

**DETERMINATION OF METALS
IN AMBIENT PARTICULATE MATTER
USING ATOMIC ABSORPTION (AA)
SPECTROSCOPY**

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Method IO-3.2

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Method IO-3.2
Determination of Metals in Ambient
Particulate Matter Using Atomic Absorption (AA) Spectroscopy

TABLE OF CONTENTS

	<u>Page</u>
1. Scope	3.2-1
2. Applicable Documents	3.2-2
2.1 ASTM Standards	3.2-2
2.2 Other Documents	3.2-2
3. Summary of Method	3.2-2
3.1 Collection of Sample	3.2-2
3.2 Sample Extraction	3.2-2
3.3 Sample Analysis	3.2-3
4. Significance	3.2-3
5. Definitions	3.2-3
6. Interferences	3.2-4
7. Apparatus	3.2-5
7.1 Glassware	3.2-5
7.2 Analysis Equipment	3.2-5
8. Reagents	3.2-6
8.1 Nitric Acid (HNO ₃) Concentrated	3.2-6
8.2 Hydrochloric Acid (HCl) Concentrated	3.2-6
8.3 Water	3.2-6
8.4 Standard stock solutions (1,000 Fg/mL)	3.2-6
8.5 Working Standards	3.2-7
8.6 Ionization and Chemical Interference Suppressants	3.2-8
9. Determination of Background Concentration of Metals in Filters	3.2-8
10. Analysis	3.2-8
10.1 Receiving of Sample From Extraction Laboratory	3.2-8
10.2 Flame Procedure	3.2-9
10.3 Furnace Procedure	3.2-10
10.4 Method of Standard Additions	3.2-10
10.5 Background Correction Methods	3.2-11
11. Spectrometer Calibration Curve	3.2-12
12. Calculations	3.2-13
12.1 Sample Air Volume	3.2-13
12.2 Metal Concentration	3.2-13
13. Maintenance	3.2-14
13.1 Scheduled Maintenance	3.2-14
13.2 Light Source	3.2-15
13.3 No Absorbance Response	3.2-15
13.4 Readout Noisy, Flame On	3.2-15
13.5 Poor Sensitivity	3.2-15
14. Quality Assurance (QA) and Performance Criteria	3.2-15
14.1 QA Program	3.2-15
14.2 Performance Criteria	3.2-18
15. Method Safety	3.2-18
16. References	3.2-19

Chapter IO-3
CHEMICAL SPECIES ANALYSIS
OF FILTER COLLECTED SPM

Method IO-3.2
DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER
USING ATOMIC ABSORPTION (AA) SPECTROSCOPY

1. Scope

1.1 Suspended particulate matter (SPM) in air generally is a complex multi-phase system of all airborne solid and low vapor pressure liquid particles having aerodynamic particle sizes from below 0.01-100 μm and larger. Historically, SPM measurement has concentrated on total suspended particulates (TSP), with no preference to size selection.

1.2 Research on the health effects of TSP in ambient air has focused increasingly on particles that can be inhaled into the respiratory system, i.e., particles of aerodynamic diameter less than 10 μm . Researchers generally recognize that these particles may cause significant, adverse health effects. Recent studies involving particle transport and transformation strongly suggest that atmospheric particles commonly occur in two distinct modes: the fine (<2.5 μm) mode and the coarse (2.5 to 10.0 μm) mode. The fine or accumulation mode (also termed the respirable particulate matter) is attributed to growth of particles from the gas phase and subsequent agglomeration, while the coarse mode is made of mechanically abraded or ground particles. Because of their initially gaseous origin, particle sizes in this range include inorganic ions such as sulfate, nitrate, ammonia, combustion-form carbon, organic aerosols, metals, and other combustion products. Coarse particles, on the other hand, are produced mainly by mechanical forces such as crushing and abrasion. Coarse particles of soil or dust result primarily from entrainment by the motion of air or from other mechanical action within their area. Since the size of these particles is normally >2.5 μm , their retention time in the air parcel is shorter than the fine particle fraction.

1.3 Several methods are available for measuring SPM in ambient air. The most commonly used device is the high volume sampler, which consists essentially of a blower and a filter, and which is usually operated in a standard shelter to collect a 24-h sample. The sample is weighed to determine concentration and is usually analyzed chemically. The high volume is considered a reliable instrument for measuring the weight of TSP in ambient air.

1.4 The procedures for determining toxic metals in particulate matter in ambient air is described in this method. The method is based on active sampling with a high-volume sampler. Analysis is done by atomic absorption (AA) spectrometry. This method describes both flame atomic absorption (FAA) spectroscopy and graphite furnace atomic absorption (GFAA) spectroscopy. Of the two methods, the detection limit for GFAA is about two orders of magnitude better than FAA.

1.5 The trace metal to be detected is dissociated from its chemical bonds by flame or in a furnace and is put into an unexcited or "ground" state. The metal is then capable of absorbing radiation at discrete lines of narrow bandwidth. A hollow cathode or electrode less discharge lamp for the determined metal provides a source of the characteristic radiation energy for that particular metal. The absorption of this characteristic energy by the atoms of interest in the flame or furnace is measured and is related to the concentration of the metal in the aspirated sample.

1.6 The sensitivity, detection limit, and optimum working range for each metal detected by this methodology are given in Table 1.

2. Applicable Documents

2.1 ASTM Standards

- D1356 *Definition of Terms Related to Atmospheric Sampling and Analysis.*
- D1357 *Planning the Sampling of the Ambient Atmosphere.*
- D4185-83 *Standard Test Methods for Metals in Workplace Atmosphere by Atomic Absorption Spectrophotometry.*

2.2 Other Documents

- Federal Regulations (1,2).
- Laboratory and Ambient Air Documents (3-14).

3. Summary of Method

3.1 Collection of Sample

3.1.1 Particulate matter from ambient air may be collected on glass fiber filters using a high-volume sampler. The high-volume sampler must be capable of sampling at an average flow rate of 1.70 m³/min (60 ft³/min). Constant air flow is maintained by a mass flow controller over a 24-hr period.

3.1.2 Air is drawn into a covered housing and through a filter by means of a high-flow rate blower at a flow rate [1.13 to 1.70 m³/min. (40 to 60 ft³/min)] that allows suspended particles having diameters <100 μm (Stokes equivalent diameter) to pass to the filter surface. Particles 100-0.1 μm diameter are ordinarily collected on glass fiber filters. The mass concentration (μg/m³) of suspended particulates in the ambient air is computed by measuring the mass of collected particulates and the volume of air sampled. After the mass is measured, the filter is ready for extraction to determine metal concentration.

3.2 Sample Extraction

3.2.1 Samples collected on glass fiber filters may be extracted by either hot acid procedure or by microwave extraction (see Method IO-3.1).

3.2.2 The preferred method of extraction is by microwave extraction. In operation, a 1" x 8" strip is cut from the 8" x 10" filter as described in the Federal Reference Method for Lead. The metals are extracted from the filter strip by a hydrochloric/nitric acid solution using a laboratory microwave digestion system. After cooling, the digestate is mixed and filtered with Acrodisc syringe filters to remove any insoluble material.

3.3 Sample Analysis

3.3.1 The trace element concentrations in each sample are determined by atomic absorption spectrometry. This technique operates by measuring energy changes in the atomic state of the analyte. The sample is vaporized and dissociates into its elements in the gaseous state. The element being measured is aspirated into

a flame or injected into a graphite furnace and atomized. The atoms in the unionized or "ground" state absorb energy, become excited, and advance to a higher energy level.

3.3.2 A light beam containing the corresponding wavelength of the energy required to raise the atoms of the analyte from the ground state to the excited state is directed through the flame or furnace. This wavelength is observed by a monochromator and a detector that measures the amount of light absorbed by the element, hence the number of atoms in the ground state in the flame or furnace. A hollow cathode or electrode less discharge lamp for the element being determined provides a source of that metal's particular absorption wavelength.

3.3.3 The data output from the spectrometer can be recorded on a strip chart recorder or processed by computer. Determination of metal concentrations is performed from prepared calibration curves or read directly from the instrument.

4. Significance

4.1 The area of toxic air pollutants has been the subject of interest and concern for many years. Exposure to metal containing particulate can cause adverse health effects. For example, high levels of lead in the body can cause motor nerve paralysis, anaemia, and, in children, inhibition of the nervous system's development. High cadmium levels can cause cardiovascular problems and bone thinning. Effects of long-term exposure to subacute levels of toxic metals in air pollution is, as yet, not well known.

4.2 Atomic absorption spectrophotometry is capable of quantitatively determining most metals at levels that are required by federal, state, and local regulatory agencies. Sensitivity and detection limits may vary from instrument to instrument.

5. Definitions

[Note: Definitions used in this document are consistent with ASTM methods. All pertinent abbreviations and symbols are defined within this document at point of use.]

5.1 Analysis Spike Sample. An analytical sample taken through the analytical preparation method and then spiked prior to analysis.

5.2 Analyte. The element or icon an analysis seeks to determine; the element of interest.

5.3 Analytical Preparation. An analytical sample taken through the analytical preparation method. Also referred to as preparation or sample preparation.

5.4 Analytical Preparation Method. A method (digestion, dilution, extraction, fusion, etc.) used to dissolve or otherwise release the analyte(s) of interest from its matrix and provide a final solution containing the analyte which is suitable for instrumental or other analysis methods.

5.5 Analytical Sample. Any solution or media introduced into an instrument on which an analysis is performed excluding instrument calibration, initial calibration verification, initial calibration blank, continuing calibration verification and continuing calibration blank.

5.6 Calibration. The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards.

5.7 Calibration Standards. A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions are not subject to the preparation method but contain the same matrix as the sample preparations to be analyzed.

5.8 Field Blank. Any sample submitted from the field identified as a blank.

5.9 Field Sample. A portion of material received to be analyzed that is contained in a single or multiple containers and identified by a unique sample number.

5.10 Flame Atomic Absorption (FAA). Atomic absorption which utilizes flame for excitation.

5.11 Graphite Furnace Atomic Absorption (GFAA). Atomic absorption which utilizes a graphite cell for excitation.

6. Interferences

6.1 In atomic absorption spectrometry, interferences, though less common than in other analytical methods, can occur. In flame atomic absorption analysis of some elements, the type and temperature of the flame used is critical; with improper conditions, chemical and ionization interferences can occur. In furnace atomic absorption analysis, the advantages of enhanced sensitivity may be offset by the fact that interference is also more of a problem. The categories of interference are discussed below.

6.1.1 Background or nonspecific absorption can occur from particles produced in the flame that 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 that can absorb light. The background absorption can be accounted for by using background correction techniques as discussed in Section 10.5.

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

6.1.3 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 that will buffer the electron concentration in the flame. The addition of sodium or potassium to the standards and samples is frequently used as an ionization suppressant.

6.1.4 Chemical interferences occur in AA 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. For example, calcium phosphate does not dissociate completely in the flame. Lanthanum may be added to bind the phosphate and allow the calcium to be ionized.

6.1.5 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, the method of standard additions, or both, are used to correct such interferences. High concentrations of silica in the sample can cause aspiration problems. If large amounts of silica are extracted from the samples, they should be allowed to stand for several hours and centrifuged or filtered to remove the silica. The matrix

components of the sample should match those of the standards. Any reagent added during extraction should be added to the standards.

6.2 Matching the matrix of the samples to the matrix of the standards minimizes interference. The method of standard additions in Section 10.4 and the use of background correction techniques in Section 10.5 should identify and correct for interference.

6.3 The known interferences and correction methods for each metal are indicated in Table 2.

7. Apparatus

7.1 Glassware

[Note: All glassware should be Class A borosilicate glass and should be cleaned with laboratory detergent, rinsed, soaked for 4 hr in a 20% (w/w) HNO₃, and rinsed several times with distilled water.]

7.1.1 Beakers. Borosilicate glass, including 30 mL, 125 mL, 150 mL Phillips or Griffin.

7.1.2 Volumetric flasks. 10 mL, 100 mL, 1 L.

7.1.3 Pipettes. Volumetric, including 1, 2, 4, 8, 15, 30, 50 mL.

7.1.4 Additional glassware. As required depending on dilution required to obtain concentrations above the detection limit, in the response range.

7.2 Analysis Equipment

7.2.1 Atomic Absorption Spectrometer. Equipped with air/acetylene and nitrous oxide/acetylene burner heads or graphite furnace.

7.2.2 Hollow cathode or electrode less discharge lamp. For each element to be determined.

7.2.3 Acetylene gas and regulator. Cylinder of acetylene equipped with two gauge, two stage pressure reducing regulator with hose connections.

7.2.4 Nitrous oxide gas and regulator. Cylinder of nitrous oxide equipped with 2 two gauge, two-stage pressure reducing regulator with hose connections.

7.2.5 Heating tape and rheostat. May be required to heat second stage of nitrous oxide gas cylinder regulator and hose to prevent freeze-up of line.

7.2.6 Air supply. Clean, dry compressed air with a two-stage regulator.

7.2.7 Parafilm M sealing film. A pliable, self-sealing, moisture-proof, thermoplastic sheet material, substantially colorless is recommended for use in sealing the acidified sample beakers. Commercially available Parafilm M satisfies this requirement.

8. Reagents

8.1 Nitric Acid (HNO₃) Concentrated. ACS reagent grade HNO₃ and commercially available redistilled HNO₃ which have sufficiently low metal concentrations.

8.2 Hydrochloric Acid (HCl) Concentrated. ACS reagent grade.

8.3 Water. ASTM Type I (ASTM D193) or equivalent. The same source or batch of distilled, deionized water must be used for all purposes in the analysis.

8.4 Standard Stock Solutions (1,000 Fg/mL)

[Note: For each metal that is to be determined, standards of known quality and concentration must either be made or acquired commercially. These solutions are stable for 1 yr when stored in polyethylene bottles, except as noted. Instructions for laboratory preparation are described below.]

[Note: Nitric acid fumes are toxic. Prepare in a well-ventilated fume hood]

8.4.1 Stock Aluminum Solution. Dissolve 1.00 g of aluminum wire in a minimum volume of 1 + 1 HCl. Dilute to volume in a 1-L flask with distilled water.

8.4.2 Stock Barium Solution. Dissolve 1.779 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water. Dilute to volume in a 1-L flask with distilled water.

8.4.3 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 .

8.4.4 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 .

8.4.5 Stock Calcium Solution. To 2.497 g of primary standard calcium carbonate (CaCO_3), add 50 mL of distilled water. Add drop wise a minimum volume of HCl (approximately 10 mL) to dissolve the CaCO_3 . Dilute to volume in a 1-L flask with distilled water.

8.4.6 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 distilled water.

8.4.7 Stock Cobalt Solution. Dissolve 1.000 g of cobalt metal in a minimum volume of HCl (1+1). Dilute to volume in a 1-L flask with 2% (v/v) HNO_3 .

8.4.8 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 .

8.4.9 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 .

8.4.10 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 .

8.4.11 Stock Lead Solution. Dissolve 1.598 g of lead nitrate [$\text{Pb}(\text{NO}_3)_2$] in 2% (v/v) HNO_3 . Dilute to volume in a 1-L flask with 2% (v/v) HNO_3 .

8.4.12 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 distilled water.

8.4.13 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 .

8.4.14 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 .

8.4.15 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 .

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

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

8.4.18 Stock Silver Solution. Dissolve 1.575 g of silver nitrate (AgNO_3) in 100 mL of distilled 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.

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

8.4.20 Stock Strontium Solution. Dissolve 2.415 g of strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) in distilled water. Dilute to volume in a 1-L flask with distilled water.

8.4.21 Stock Thallium Solution. Dissolve 1.303 g of thallium nitrate (TlNO_3) in a 10% (v/v) HNO_3 . Dilute to volume in a 1-L flask with 2% (v/v) HNO_3 .

8.4.22 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 .

8.4.23 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 .

8.5 Working Standards

8.5.1 Working Standards. Working standards are prepared by appropriate single or multiple dilutions of the standard solutions listed in Section 8.4. Mixed standards should be prepared with any chemical incompatibilities in mind. For those metals in Table 2 that indicate chemical or ionization interferences, the final dilution shall contain 2% (v/v) of the 50-mg/mL cesium and lanthanum solutions.

8.5.2 Match Matrices. The acid concentration of the working standards should be matrix-matched to that of the final sample extract. The final sample extract acid concentration is 3% HNO_3 /8% HCl . When using those atomic absorption spectrometers equipped with concentration read-out, follow the manufacturer's suggestions as to the spacing of the standard concentrations over the range of interest.

8.6 Ionization and Chemical Interference Suppressants

8.6.1 Cesium Solution (50 mg/mL). Dissolve 73.40 g of cesium nitrate (CsNO_3) in distilled water. When stored in a polyethylene bottle, this solution is stable for at least 1 yr.

8.6.2 Lanthanum Solution (50 mg/mL). Dissolve 156.32 g of lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) in a 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 1 yr.

9. Determination of Background Concentration of Metals in Filters

9.1 Use glass fiber filters to collect particulate matter with the high volume sampler. High quality filters with reproducible properties must be used in sampling for metals in ambient air. Analyze 5% of the total number of filters for the presence of specific metals, prior to sample collection, to verify reproducibility and low background metal concentrations.

9.2 Cut one 1" x 8" strip from each filter. Extract and analyze all strips separately, according to the directions given as delineated in Inorganic Compendium Method IO-3.1.

9.3 Calculate the total metal in each filter as:

$$F_b = \mu\text{g metal/mL} \times (20 \text{ mL/strip}) \times (9)$$

where:

F_b = Amount of metal per 72 square inches of filter, μg .

$\mu\text{g metal/mL}$ = metal concentration determined from Section 11.2.

20 mL/strip = total sample volume from extraction procedure.

9 = $464.52 \text{ cm}^2/51.61 \text{ cm}^2$.

9.4 Calculate the mean, F_m , of the values and the relative standard deviation (standard deviation/mean x 100). If the relative standard deviation is high enough so that, in the analyst's opinion, subtraction of F_m may result in a significant error in the $\mu\text{g metal/m}^3$, the batch should be rejected.

9.5 For acceptable metal/batches, use the value of F_m to correct all metal/analyses of particulate matter collected using that batch of filters. If the analyses are below the method detection limit (MDL) from Table 1, no correction is necessary.

10. Analysis

10.1 Receiving of Sample From Extraction Laboratory

10.1.1 The sample should be received by the atomic absorption spectroscopist in a centrifuge tube from the extraction procedure outlined in Method IO-3.1.

[Note: The entire extract volume of filter digestate was not received from extraction laboratory. The total volume should have been 20 mL \pm 0.5 mL, but only 10 mL may have been sent for analysis.]

10.1.2 The 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.

10.1.3 Filter blanks must be subject to the entire extraction and analytical procedure and processed as described.

10.1.4 Some relatively rare chemical forms of some of the elements listed in Table 2 may not be dissolved by the procedures stated in this method. If such chemical forms are suspected, results of their procedure should be compared to results of a non-destructive technique, which does not require sample dissolution, such as X-ray fluorescence.

10.1.5 Because of the differences between makes and models of atomic absorption spectrometers, formulating detailed instructions applicable to every instrument is difficult. Consequently, the user should follow manufacturer's operating instructions.

10.2 Flame Procedure

10.2.1 Set the atomic absorption spectrometer for the standard conditions as follows: choose the correct hollow cathode lamp or electrode less discharge lamp, install, and align in the instrument; position the monochromator at the value recommended by the manufacturer; select the proper monochromator slit width; set the light source current according to the manufacturer's recommendation; light the flame and regulate the flow of fuel and oxidant; adjust the burner for maximum absorption and stability; and balance the meter.

10.2.2 If using a chart recorder, set the chart speed at 8-15 cm/min and turn on the power, servo, and chart drive switches. Adjust the chart pen to the 5% division line. Also adjust instrument span using highest calibration standard. While aspirating the standard sample, span instrument to desired response.

10.2.3 Run a series of standards of the metal of interest and construct a calibration curve as in Section 11.3. Set the curve corrector of a direct reading instrument to read the proper concentration.

10.2.4 To evaluate the contribution to the absorbance from the filters and reagents used, blank samples must be analyzed. Usually blanks will be provided with each set of samples (see Section 9.2). Subject the blank to the entire analysis procedure. The absorbance obtained from the aspiration of the blank solution is subtracted from the sample absorbance.

10.2.5 The sample can be analyzed from the centrifuge tube or an appropriate amount of sample decanted into a sample analysis tube. At least the minimum sample volume required by the instrument should be available for each aspiration.

10.2.6 Aspirate samples, standards, and blank into the flame and record the absorbance. Aspirate distilled water after each sample or standard. If using a recorder, wait for response to stabilize before recording absorbance.

10.2.7 To the extent possible, all determinations should be based on replicate analyses.

10.2.8 Determine the average absorbance value for each known concentration and correct all absorbance values by subtracting the blank absorbance value. Determine the metal concentration in $\mu\text{g metal/mL}$ from the calibration curve as presented in Section 11.3 or by direct reading from the instrument.

10.2.8.1 Dilute samples that exceed the calibration range by taking an aliquot of the sample and diluting the sample to a known volume with a solution of the same acid concentration and ionization and chemical suppressants as the calibration standards and reanalyzed.

10.2.8.2 Check for drift of the zero point resulting from possible nebulizer clogging, especially when dealing with samples of low absorbance.

10.2.8.3 Aspirate a mid-range standard with sufficient frequency (once every 10 samples, after every 5 full MSAs or every 2 hr) to verify the continuing accuracy of the calibration curve.

10.3 Furnace Procedure

10.3.1 In graphite furnace atomic absorption, only a few microliters of the sample are placed in the furnace. Within seconds or fractions of a second, the sample is atomized. Graphite furnace analysis is more sensitive for trace element determination than the flame detection limit because it requires a smaller sample volume. As a general rule, samples that can be analyzed by flame or furnace may be more conveniently run with flame since flame atomic absorption is faster, simpler, and has fewer interference problems.

10.3.2 When some samples are atomized, they may absorb or scatter light causing sample absorbance to be greater than it should be, necessitating background correction. If some sample remains unburned, memory effects can occur. Blank burns should be run, and the graphite furnace should be cleaned by running at full power at intervals during determination series.

10.3.3 Inject a measured μL aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. Multiple injections can improve accuracy and help detect furnace pipetting errors.

10.3.4 Run a mid level check standard and a blank standard after every 10 sample injections, after 5 full MSAs, or at 2-hr intervals. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Tube life depends on sample matrix and atomization temperature. A conservative estimate of tube life is about 50 firings. A pyrolytic coating will extend that estimated life by a factor of three.

10.3.5 To determine the metal concentration by direct aspiration and furnace, read the metal value in $\mu\text{g/L}$ from the calibration curve or directly from the read-out of the instrument.

10.3.6 If sample dilution was required, calculate the final concentration using the following formula:

$$\mu\text{g/L metal in sample} = A \times (C + B) / C$$

where:

A = $\mu\text{g/L}$ of metal in diluted aliquot from calibration curve.

B = Acid blank matrix used for dilution, mL.

C = Sample aliquot, mL.

10.4 Method of Standard Additions

10.4.1 If chemical interferences are suspected, the method of standard additions may be used to evaluate them; and if deemed desirable, the method may be used to make an accurate determination of metal concentration in the presence of an interference.

10.4.2 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 micro liter pipets.

10.4.3 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.

10.4.4 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 curve.

10.4.5 If the slope of the spiked sample curve is not parallel to the original calibration curve, an interference may be present. Standard additions may allow metal concentration to be determined in the presence of interference by using the standard addition curve as the calibration. This method can give incorrect values if the interferant does not associate with the additions to the same extent as in the original analyte.

10.5 Background Correction Methods

10.5.1 Spurious absorption, absorption not due to the atoms of the metal being determined, can be caused by the presence of small particles in the resonance beam, 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 in the noise component of the signal. The final results may be considerably higher than the true value and a loss of sensitivity because of the increased noise. Various correction systems exist as indicated in the following sections.

10.5.2 The deuterium arc automatic correction system operates by rapidly alternating light from a deuterium arc and the hollow cathode tube through the sample. The light from the arc is essentially unabsorbed by the element, but absorbed by the background. The difference is the element's actual absorbance. Most deuterium arc systems correct up to 0.5 absorbance (about 70% absorption) at wavelengths as high as that of copper (324.7 nm). Improved optical designs can extend this performance.

10.5.3 The Zeeman effect automatic correction system operates by placing the light source or atomizer between the poles of a strong magnet, thus splitting the spectral line emitted or absorbed by the atoms of interest into a central B component having the original wavelength and two sideband F components, which are shifted in wavelength. The components are polarized in different planes relative to the magnetic field. Various magnet

and polarizer configurations are employed in various instrument designs, all ultimately allowing subtraction of the F signal from the B signal to produce background correction. The Zeeman system, though expensive, overcomes some weaknesses inherent in the deuterium arc system.

10.5.4 The Smith-Hieftje automatic correction system operates on the principle of self-reversal: when excessive current is passed through a hollow cathode lamp, the emission line is broadened and absorbance from the analyte is reduced. Correction is accomplished by comparing low current absorption where the sample and the background absorb light to a brief pulse of much higher current causing self-reversal and greatly reducing the sample's absorption, while background absorption remains proportional. The background correction is determined by the difference between the two signals. The Smith-Hieftje system also overcomes some weaknesses inherent in the deuterium arc system and is comparable to the Zeeman system.

10.5.5 For atomic absorption spectrometers without automatic background correction devices, background correction can be accomplished by using a deuterium continuum lamp.

10.5.5.1 Measure the absorbance of a sample and a suitable standard in the usual manner.

10.5.5.2 Remove the hollow cathode lamp and replace with the continuum lamp; without changing the flame conditions or any other parameters, adjust the output of the amplifier to read 0 absorbance.

10.5.5.3 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.

11. Spectrometer Calibration Curve

[Note: Calibration is one of the most important factors in maintaining good quality data. Equipment must be calibrated regularly, when first purchased, after maintenance, and whenever audit checks indicate greater than acceptable deviation.]

11.1 The analytical application of atomic absorption, like other analytical methods, has a lower detection limit, which is specific for each individual instrument. Therefore, calibration curves must be constructed using not only standard solutions, but also standard conditions for each individual instrument. The standard conditions include instrumental parameters, burner gas flames, and aspiration rates. In routine sample analysis, several standards must be run with each set of samples so that the operating parameters are exactly the same for sample and standard. Standard procedures for analysis are supplied with most commercially available atomic absorption instruments. Standard curves must be constructed for each element, and standards must be analyzed each time a set of samples are run. The standard curves should list all parameters of the instrument, as well as sample preparation methods.

11.2 Prepare standard solutions from the solutions listed in Sections 8.4 and 8.5 to bracket the estimated concentration of the metal in the samples. Select at least three standards (plus the reagent blank) to cover the linear range indicated by the instrument manufacturer's instructions. Aspirate the standards into the flame (or inject the standards into the furnace as appropriate) and record the absorbance. Repeat until good agreement is obtained between replicates. Prepare a calibration graph by plotting absorbance (y-axis) versus the metal concentration in $\mu\text{g metal/mL}$ (x-axis). Calculate the best fit straight line for the data points by the method of least squares (see Section 11.3), and draw it in. Use the best fit line or its equation to obtain the metal concentration in the samples to be analyzed.

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

$$y = mx + c$$

where:

$$m = n[E \ x \ y] \ Ex(Ey) / [n(Ex^2) - (Ex)^2].$$

$$c = y - mx.$$

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.

Exy = the sum of the products of the x-coordinate times the y-coordinate for the n points.

Ex = the sum of the x-coordinates of n points.

Ey = the sum of the y-coordinates of n points.

Ex² = the sum of the squares of the x-coordinates of n points.

(Ex)² = the square of the sum of the x-coordinates of n points.

12. Calculations

12.1 Sample Air Volume

At standard temperature and pressure (stp) [25°C and 760 mm Hg] for sample air volume rotameter, use the following equation:

$$V_{std} = [(Q_i + Q_f) / 2] t$$

where:

V_{std} = air volume sampled, m³.

Q_i = initial air flow rate, m³/min at stp.

Q_f = final air flow rate, m³/min at stp.

t = sampling period (elapsed time), min.

For samplers equipped with flow recorders:

$$V = (Q) (t)$$

where:

Q = average sampling rate, m³/min at stp.

12.2 Metal Concentration

12.2.1 Estimation of Metal of Interest Concentration of the Blank Filter. For testing large batches of filters (>500 filters), select at random 20 to 30 filters from a given batch. For small batches (<500 filters) a lesser number of filters may be taken. Cut a 2.5 x 20.3 cm (1" x 8") strip from each filter. Analyze all strips separately.

12.2.2 Calculate total metal of interest in each filter as:

$$F_{bi} = (\mu\text{g metal/mL}) \times (\text{final extraction volume [i.e., 20 mL]/strip}) \times (9)$$

where:

F_{bi} = amount of metal per 465 square cm (72 square in.) of blank filter, μg .

$\mu\text{g metal/mL}$ = metal concentration determined from Section 11.2.

final extract volume (mL)/strip = total sample extraction volume from extraction procedure (i.e., 20 mL).

9 = $464.52 \text{ cm}^2/51.61 \text{ cm}^2$.

12.2.3 Calculate the mean, F_m , and the relative standard deviation (100 x standard deviation/mean).

$$F_m = \sum F_{bi} / n$$

where:

F_m = average amount of metal per 72 in.^2 of filter, μg

F_{bi} = amount of metal per 72 in.^2 for each filter, μg

n = number of blank filters analyzed.

12.2.4 The standard deviation (SD) of the analyses for the blank filters is given by equation

$$SD = [\sum (F_{bi} - F_m)^2 / n - 1]^{1/2}$$

The relative standard deviation (RSD) is given by the following equation:

$$RSD = (100) (SD) / F_m$$

If the relative standard deviation is high enough so that in the analyst's opinion subtraction of F_m the mean may result in a significant error in the $\mu\text{g metal/m}^3$, the batch should be rejected. For acceptable batches, use the value of F_m to correct all analyses (see Section 12.2.3) collected using that batch of filters. If F_m is below the lower detectable limit (LDL), no correction is necessary.

12.2.5 Calculation of Metal of Interest Concentration of the Exposed Filter. Metal concentration in the air sample can be calculated from data tabulated on data record form as follows:

$$C = [(\mu\text{g metal/mL} \times (\text{final extraction volume [i.e., 20 mL]/strip})(9) - F_m) / V_{std}]$$

where:

C = concentration, $\mu\text{g metal/std. m}^3$.

$\mu\text{g metal/mL}$ = metal concentration determined from Section 10.

final extract volume (mL)/strip = total sample extraction volume from extraction procedure (i.e., 20 mL),

$$9 = \frac{[\text{Useable filter area, } 20 \text{ cm} \times 23 \text{ cm (8" x 9")}]}{[\text{Exposed area of one strip, } 2.5 \text{ cm} \times 20 \text{ cm (1" x 8")}]}$$

F_m = average concentration of blank filters, F_g .

V_{std} = air volume pulled through filter, std. m^3 .

13. Maintenance

13.1 Scheduled Maintenance

13.1.1 Scheduled maintenance of the sampling equipment and the atomic absorption spectrophotometer will reduce downtime and remedial maintenance. The major maintenance checks are summarized in Table 3. Record all maintenance activities in a maintenance log book. Normally, two to three remedial maintenance activities are required per year.

13.1.2 Major maintenance and calibration should be done by service engineers or qualified operators. The following general maintenance procedures should be carried out only after consulting the manufacturer's manual.

13.2 Light Source

13.2.1 When problems are suspected with a light source, check the hollow cathode lamp or electrode less discharge lamp mounting bracket and lamp connection. Make sure the instrument is plugged in, turned on, and warmed up. If line voltages are low, operate the power supply from a variac that is set to give maximum voltage. Lamp current meter fluctuation can be reduced by using a constant voltage sine wave transformer.

13.2.2 As the lamp is used, a loss of the element from the hollow cathode source occurs. Some lamps will evolve hydrogen, which will contaminate the element's spectrum and reduce sensitivity and calibration linearity. Hydrogen contamination may be reversed by running the lamp with reversed polarity at a few mill amperes for several minutes.

13.3 No Absorbance Response

Make sure that the lamp is lighted, properly aligned, and that the wavelength, slit, and range controls are properly adjusted. If the meter cannot be zeroed, adjust the level of the burner head to avoid intercepting the light beam and clean the lamp and window, or meter cover windows, with a diluted solution of a mild detergent; rinse several times with distilled water. Dirty windows or lenses are a major problem when operating the instrument below 2300 Å (230 nm).

13.4 Readout Noisy, Flame On

Check the lamp current setting, fuel, and oxidizer flow rates; the leviner to make sure it is draining properly; the nebulizer for corrosion around the tip; the adjustment of the nebulizer capillary; the burner head (it may need cleaning with razor blade); the acetylene cylinder pressure; the air pressure; and the air line filter.

13.5 Poor Sensitivity (Within 50% of That Suggested in the Analytical Method Book)

Check the sensitivity obtainable for several other elements to ascertain that the low sensitivity is not due to the lamp used. Check the slit width, wavelength, range setting, burner alignment, adjustment of the nebulizer capillary, and fuel/oxidant flow rate ratio to ascertain that it is optimized for the element to be analyzed. Make sure that the lamp current is not above the recommended value. Check the lamp alignment and the

concentration of the standard solution used. All other maintenance problems, such as cleaning of mirrors or gratings, should be discussed with the manufacturer or service representative.

14. Quality Assurance (QA) and Performance Criteria

14.1 QA Program

14.1.1 To achieve quality data, two essential considerations are necessary: the measurement process must be in a state of statistical control at the time of the measurement and the systematic errors, when combined with the random variation (errors of measurement), must result in an acceptable level of uncertainty. To produce good quality data, perform quality control checks and independent audits of the measurement process, document these data, and use materials, instruments, and measurement procedures that can be traced to an appropriate standard of reference. Repeat measurements of standard reference samples (primary, secondary, and/or working standards) aid in establishing a condition of process control. The working calibration standards should be traceable to standards of higher accuracy.

Several other procedures are usually necessary to ensure that the instrument is providing good quality data. Following the initial instrument calibration with a calibration blank and at least three calibration (standard reference) samples, a calibration verification sample is prepared at the midpoint of the calibration curve from certified stock solutions. The use of additional calibration standards and blanks during the sample analyses were discussed in Section 11. In addition to the standard and blank samples, laboratory control spike samples, matrix spike samples, and duplicate spike samples are prepared and analyzed with most sample batches. A summary of the quality control procedures for FAA and GFAA is provided in Table 4. Depending upon the specific requirements of the client, some of these procedures may be deleted, or additional procedures may be initiated to comply with specific analysis requirements.

14.1.2 The user should develop, implement, and maintain a quality assurance program to ensure that the sampling system is operating properly and collecting accurate data. Established calibration, operation, and maintenance procedures should be conducted on a regularly scheduled basis and should be part of the quality assurance program. The manufacturer's instruction manual should be followed and included in the QA program. Additional QA measures (e.g., troubleshooting) as well as further guidance in maintaining the sampling system are provided by the manufacturer.

14.1.2.1 Consult the latest copy of the *Quality Assurance Handbook for Air Pollution Measurement Systems* to determine the level of acceptance of zero and span errors.

14.1.2.2 For detailed guidance in setting up a quality assurance program, refer to the *EPA Quality Assurance Handbook* and the *Code of Federal Regulations*.

14.1.3 Sampling Quality Assurance

14.1.3.1 Select a site with the highest expected geometric mean concentrations.

14.1.3.2 Locate two high-volume samplers within 4 m of each other, but at least 2 m apart, to preclude air flow interference.

14.1.3.3 Identify one of the two samplers at the time of installation as the sampler for normal routine monitoring; identify the other as the duplicate sampler.

14.1.3.4 Be sure that the calibration, sampling, and analysis are the same for the collocated sampler as for all other samplers in the network.

14.1.3.5 Operate the collocated sampler whenever the routine sampler is operated.

14.1.3.6 Use the differences in the concentrations (F_g metal/std. m^3) between the routine and duplicate samplers to calculate precision.

14.1.4 Analysis Quality Assurance

14.1.4.1 Perform a linearity test on the atomic absorption spectrometer employing a series of standard metal solutions. This procedure should be done at regular intervals and when the analyst suspects erroneous readings. Refer to Table 3 and manufacturer's instructions for details on instrument performance checkout.

14.1.4.2 Obtain Standard Reference Materials (SRM) from National Institute of Standards Technology (NIST) and EPA reference standards. Analyze these standards at regular intervals along with samples and record accuracy.

14.1.5 Standard Operating Procedures (SOPs)

14.1.5.1 SOPs should be generated by the users to describe and document the following activities in their laboratory:

- assembly, calibration, leak check, and operation of the specific sampling system and equipment used;
- preparation, storage, shipment, and handling of the sampler system;
- purchase, certification, and transport of standard reference materials; and
- all aspects of data recording and processing, including lists of computer hardware and software used.

14.1.5.2 Provide specific instructions in the SOPs that are available and understood by the personnel conducting the monitoring work.

14.2 Performance Criteria

The sensitivity, detection limit, and optimum working range for each metal are given in Table 1. The values for the sensitivity and detection limits are instrument-dependent and may vary from instrument to instrument.

14.2.1 The sensitivity is defined as that concentration of a given element that will absorb 1% of the incident radiation (0.0044 absorbance units) when aspirated into the flame. The atomic absorption sensitivity for an element can be calculated using the absorbance of a known concentration and solving the equation below.

$$\text{conc of std} / \text{measured abs} = \text{sensitivity} / 0.0044$$

therefore:

$$\text{sensitivity} = (\text{conc of std} \times 0.0044) / \text{measured abs}$$

14.2.2 The detection limit is defined as that concentration of a given element that produces a signal-to-noise ratio of 2, which is the lowest limit of concentration that can be distinguished from zero.

[Note: The blank signal is defined as that signal that results from all added reagents and a clean filter that has been extracted exactly as the samples.]

14.2.3 The working range for an analytical precision better than 3% is generally defined as those sample concentrations that will absorb 10%-70% of the incident radiation (0.05-0.52 absorbance units.)

15. Method Safety

15.1 This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. The user must establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This requirement should be part of the user's SOP manual.

15.2 Hazards to personnel exist in the operation of the atomic absorption spectrometer. Atomic absorption units are potentially dangerous when using a nitrous oxide/acetylene flame. Do not operate these 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.

15.3 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 should be observed.

15.4 Many of the metals that can be determined by atomic absorption are health hazards (for example, cadmium, arsenic, beryllium, mercury) and must be handled in a manner consistent with the danger they present.

15.5 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 are definite personnel hazards. The instrument combustion gases should be mechanically exhausted from the laboratory.

16. References

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TABLE 1. SENSITIVITY, DETECTION LIMITS, AND OPTIMUM WORKING CONCENTRATION FOR 23 METALS USING FAA AND GFAA

Element	Sensitivity, µg/mL ^a	Optimum Range, µg/mL	Method Detection Limit ^b			TLV ^c mg/m ³
			µg/mL ^a	FAA ng/m ³	GFAA ng/m ³	
Ag	0.06	0.5-5.0	0.002	0.4	0.005	0.1 (metal)
Al	1.0	5-50	0.02	4.4	0.01	0.01 (soluble cmpds) ten (metal and oxide)
Ba	0.20	1-10	0.008	1.8	0.04	0.5 (soluble cmpds)
Bi	0.5	1-10	0.025	5.5	NA d	NL
Ca	0.08	0.1-1.0	0.0005	0.1	0.05	2 CAO
Cd	0.025	0.1-1.0	0.001	0.2	0.0003	0.05
Co	0.15	0.5-5.0	0.01	2.2	0.02	0.1 (metal fume and dust)
Cr	0.1	0.5-5.0	0.003	0.7	0.01	0.05 (chromic acid and chromates) 0.5 (soluble chromic, chromous salts)
Cu	0.09	0.5-5.0	0.002	0.4	0.02	0.2 (fume) 1 (dust and mists)
Fe	0.12	0.5-5.0	0.005	1.1	0.02	5 (iron oxide fume) 1 (soluble cmpds)
In	0.7	5-50	0.02	4.4	NA	0.1 (metal and cmpds)
K	0.04	0.1-1.0	0.002	0.4	0.02	2 (as KOH)
Li	0.035	0.1-1.0	0.0003	0.1	NA	0.025 (as Lithium Hydride)
Mg	0.004	0.05-0.5	0.0001	0.1	0.004	10 (as MgO fume)
Mn	0.055	0.5-5.0	0.002	0.4	0.01	5 (metals and cmpds)
Na	0.015	0.05-0.50	0.0002	0.1	0.01	2 (as NaOH)
Ni	0.15	0.5-5.0	0.005	1.1	0.10	0.1 (soluble cmpds)
Pb	0.5	1-10	0.01	2.2	0.05	0.150 (inorganic cmpds, fume dust)
Rb	0.1	0.5-5.0	0.002	0.4	NA	NL
Sr	0.12	0.5-5.0	0.002	0.4	0.20	NL
Tl	0.5	5-50	0.01	2.2	0.10	0.1 (soluble cmpds)
V	1.7	10-100	0.04	8.8	0.20	0.5 (V ₂ O ₅ dust as V) 0.05 (V ₂ O ₅ fume as V)
Zn	0.018	0.1-1.0	0.001	0.2	0.0001	1 (ZnCl ₂ fume) 5 (ZnO fume)

^aSensitivity and Detection Limit (GFAA) data are taken from "Analytical Methods for Atomic Absorption Spectrophotometry," Perkin-Elmer Corp., Norwalk, Conn., 1976. **Note: These detection limits represent the ultimate values since the blanks resulting from the reagents and the filter material have not been taken into account.**

^bAll values are expressed as elemental concentrations except as noted. Detection limits expressed as ng/m³ based upon sampling rate of 1.13 m³/min for 24-hr for a total sample volume of 1,627.2 m³; factors of 9 for partial filter analysis; digestion of 0.020 L/filter.

^cNL signifies No Limit for this element or its compounds.

TABLE 2. THE TYPE OF FLAME AND OPERATING CONDITIONS FOR EACH ELEMENT AND IDENTIFICATION OF INTERFERENCES

Element	Type of Flame	Analytical Wavelength nm	Interferences ^b	Remedy ^b
Ag	Air-C ₂ H ₂ (oxidizing)	328.1	IO ₃ ⁻ , WO ₄ ⁻² , MnO ₄ ⁻²	c
Al ^a	N ₂ O-C ₂ H ₂ (reducing)	309.3	Ionization, SO ₄ ⁻² , V	c,d,e
Ba	N ₂ O-C ₂ H ₂ (reducing)	553.6	Ionization, large concentration Ca	d,f
Bi	Air-C ₂ H ₂ (oxidizing)	223.1	None known	
Ca	Air-C ₂ H ₂ (reducing) N ₂ O-C ₂ H ₂	422.7	Ionization and chemical	d,e
Cd	Air-C ₂ H ₂ (oxidizing)	228.8	None known	
Co ^a	Air-C ₂ H ₂ (oxidizing)	240.7	None known	
Cr ^a	Air-C ₂ H ₂ (reducing)	357.9	Fe, Ni	c
Cu	Air-C ₂ H ₂ (oxidizing)	324.8	None known	
Fe	Air-C ₂ H ₂ (oxidizing)	248.3	High Ni concentration, Si	c
In	Air-C ₂ H ₂ (oxidizing)	303.9	Al, Mg, Cu, Zn	c
K	Air-C ₂ H ₂ (oxidizing)	766.5	Ionization	d
Li	Air-C ₂ H ₂ (oxidizing)	670.8	Ionization	d
Mg	Air-C ₂ H ₂ (oxidizing) N ₂ O-C ₂ H ₂ (oxidizing)	285.2	Ionization and chemical	d,e
Mn	Air-C ₂ H ₂ (oxidizing)	279.5	None known	
Na	Air-C ₂ H ₂ (oxidizing)	589.6	Ionization	e
Ni	Air-C ₂ H ₂ (oxidizing)	232.0	None known	
Pb	Air-C ₂ H ₂ (oxidizing)	217.0 283.3 283.3	Ca, high concentration SO ₄ ⁻²	c
Rb	Air-C ₂ H ₂ (oxidizing)	780.0	Ionization	d
Sr	Air-C ₂ H ₂ (oxidizing) N ₂ O-C ₂ H ₂ (oxidizing)	460.7	Ionization and chemical	d,e
Tl	Air-C ₂ H ₂ (oxidizing)	276.8	None known	
Va	N ₂ O-C ₂ H ₂ (oxidizing)	318.4	None known in N ₂ O-C ₂ H ₂ flame	
Zn	Air-C ₂ H ₂ (oxidizing)	213.9	None known	

^aSome 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.

^bHigh 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.

^cSamples 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 interferant is identified, it may be added to the standards.

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

^e1000-ppm solution of lanthanum as a releasing agent to all samples and standards.

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

TABLE 3. EXAMPLE OF ROUTINE MAINTENANCE CHECKS

Equipment	Acceptance Limits	Frequency and Method of Measurement	Action if Requirements Are Not Met
Sampler motor	400 hrs. operation of motor; absence of malfunction	Visually check upon receipt and after each 400 h of operation	Replace motor brushes, other maintenance as indicated
Facepiece gasket	Absence of leaks at filter seal	Visually check after each sampling period	Replace gasket
Rotameter	Absence of foreign materials; stable operations	Visually check for each sample	Clean; replace if damaged
Motor gaskets	Leak tight fit	Visually check each 400 h of operation	Replace gaskets
Sampling head	Absence of leaks	Visually check each 200 h of operation	Replace sampling head
Atomic Absorption spectrophotometer	Absence of dirt and/or contamination in light source systems; absence of current fluctuation; manufacturer's specifications on sensitivity achieved	Clean up and adjust trouble parts, visually check energy meter needle; visually check gauge, and adjust light passing systems, and clean up lamp and window and photometer cover window; check for possible troubled parts	Replace damaged parts; use constant voltage transformer; contact manufacturer

TABLE 4. SUGGESTED QUALITY CONTROL PROCEDURES FOR BOTH FAA AND GFAA

QC procedures ¹	Typical frequency	Acceptance criteria	Action, if outside criteria
Initial calibration	At the beginning of the analysis	Linear correlation coefficient ≥ 0.995	Terminate analysis and restart the run with initial calibration
ICV	Immediately after initial calibration	90%-110% of the actual concentration	Terminate analysis, recalibrate, and restart the run
ICB	Immediately after the ICV	< method detection limits	Terminate analysis, recalibrate, and restart the run
CCV	Analyzed before the first sample, after every 10 samples or 5 full MSAs, and at the end of the run	80%-120% of the actual concentration	Terminate analysis, recalibrate, and reanalyze samples from last acceptable CCV
CCB	Analyzed following each CCV	< method detection limits	Terminate analysis, recalibrate, and reanalyze samples from last acceptable CCB
Method blank	1 per 20 samples, a minimum of 1 per batch	< method detection limits	Redigest strips of the blank and all associated samples.
LCS	1 per 20 samples, a minimum of 1 per batch	80%-120% recovery, with the exception of Sb	Redigest strips of the LCS and all associated samples.
SD or MSD	1 per 20 samples per matrix type	RPD \neq 20%	Report and qualify results in analysis report
Matrix spike (MS)	1 per 20 sample per matrix type	Percent recovery of 75%-125%	Perform appropriate interference tests
Serial dilution	1 per matrix type, if MS/MSD criterion fails and if needed	\neq 10% Difference	Analysis by method of standard addition (MSA)
Post-digestion spike	1 per matrix type, if MS/MSD criterion fails and if needed	%R = 85%-115%	Analysis by MSA recommended
Sample dilution	Dilute sample beneath the upper calibration limit, minimizing the dilution factor	As needed	Not applicable

¹Legend of Abbreviations (alphabetical order):

CCB = Continuing Calibration Blank
 CCV = Continuing Calibration Verification
 ICB = Initial Calibration Blank
 ICV = Initial Calibration Verification
 LCS = Laboratory Control Spike
 SD = Sample Duplicate
 MSD = Matrix Spike Duplicate