Standard Test Methods for
Analyses of Metals in Refuse-Derived Fuel by Atomic Absorption Spectroscopy[1]

This standard is issued under the fixed designation E 885; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the determination of metals in solution by atomic absorption spectroscopy (AAS).

1.2 The following sections outline the operating parameters for the individual metals:

1.3 Detection limits, sensitivity, and optimum ranges of the test methods will vary with the various makes and models of atomic absorption spectrophotometers. The data shown in Table 1 provide some indication of the actual concentration ranges measurable by direct aspiration and using furnace techniques. In the majority of instances, the concentration range shown in the table by direct aspiration may be extended much lower with scale expansion and conversely extended upwards by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample or through solvent extraction techniques, or both. Lower concentrations may also be determined using the furnace techniques. The concentration ranges given in Table 1 are somewhat dependent on equipment such as the type of spectrophotometer and furnace accessory, the energy source, and the degree of electrical expansion of the output signal.

1.4 When using the furnace techniques, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures that may result in either suppression or enhancement of the analysis element. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see 6.2) and if detected, treat accordingly using either successive dilution, matrix modification or method of standard additions (see 10.5).

1.5 Where direct aspiration atomic absorption techniques do not provide adequate sensitivity, in addition to the furnace procedure, reference is made to specialized procedures such as gaseous hydride method for arsenic and selenium, the cold-vapor technique for mercury and the chelation-extraction procedure for selected metals.

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[1] These test methods are under the jurisdiction of ASTM Committee D34 on Waste Management and are the direct responsibility of Subcommittee D34.03 on Treatment.

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1.6 *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.* For hazard statement, see 8.4 and 17.2.2.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 1193 Specification for Reagent Water

D 3223 Test Method for Total Mercury in Water

E 926 Test Methods of Preparing Refuse-Derived Fuel (RDF) Samples for Analyses of Metals

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *detection limit*—detection limits can be expressed as either an instrumental or method parameter. The limiting factor of the former using acid water standards would be the signal to noise ratio and degree of scale expansion used; while the latter would be more affected by the sample matrix and preparation procedure used.

3.1.1.1 The Scientific Apparatus Makers Association (SAMA) has approved the following definition: The detection limit is that concentration of an element which would yield an absorbance equal to twice the standard deviation of a series of measurements of a solution, the concentration of which is distinctly detectable above, but close to blank absorbance measurement.

3.1.1.2 The detection limit values listed in Table 1 and on individual metal methods are to be considered minimum working limits achievable with the procedures outlined in these test methods.

3.1.2 *optimum concentration range*—a range defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. The range will vary with the sensitivity of the instrument and the operating condition employed.

3.1.3 *sensitivity*—the concentration in milligrams of metal per litre that produces an absorption of 1 %.

4. Summary of Test Methods

4.1 In direct aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. The light beam from a hollow cathode lamp whose cathode is made of the element to be determined is directed through the flame into a monochromator, and into a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal

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

TABLE 1 Atomic Absorption Concentrations[A]

Metal	Direct Aspiration			Furnace Technique[B,C]	
	Detection Limit, mg/L	Sensitivity, mg/L	Optimum Concentration Range, mg/L	Detection Limit, µg/L	Optimum Concentration Range, µg/L
Aluminum	0.1	1	5 to 50	3	20 to 200
Antimony	0.2	0.5	1 to 40	3	20 to 300
Arsenic[D]	0.002	...	0.002 to 0.02	1	5 to 100
Barium (*P*)	0.1	0.4	1 to 20	2	10 to 200
Beryllium	0.005	0.025	0.05 to 2	0.2	1 to 30
Cadmium	0.005	0.025	0.05 to 2	0.1	0.5 to 10
Calcium	0.01	0.08	0.2 to 7	...	...
Chromium	0.05	0.25	0.5 to 10	1	5 to 100
Cobalt	0.05	0.2	0.5 to 5	1	5 to 100
Copper	0.02	0.1	0.2 to 5	1	5 to 100
Iron	0.03	0.12	0.3 to 5	1	5 to 100
Lead	0.1	0.5	1 to 20	1	5 to 100
Lithium	...	0.035	...	...	...
Magnesium	0.001	0.007	0.02 to 0.5	...	...
Manganese	0.01	0.05	0.1 to 3	0.2	1 to 30
Mercury[E]	0.0002	...	0.0002 to 0.01	...	...
Molybdenum (*P*)	0.1	0.4	1 to 40	1	3 to 60
Nickel (*P*)	0.04	0.15	0.3 to 5	1	5 to 100
Potassium	0.01	0.04	0.1 to 2	...	...
Selenium[D]	0.002	...	0.002 to 0.02	2	5 to 100
Silver	0.01	0.06	0.1 to 4	0.2	1 to 25
Sodium	0.002	0.015	0.03 to 1	...	...
Tin	0.8	4	10 to 300	5	20 to 300
Titanium (*P*)	0.4	2	5 to 100	10	50 to 500
Vanadium (*P*)	0.2	0.8	2 to 100	4	10 to 200
Zinc	0.005	0.02	0.05 to 1	0.05	0.2 to 4

[A] The concentrations shown are not contrived values and should be obtainable with any satisfactory atomic absorption spectrophotometer.

[B] For furnace sensitivity values consult instrument operating manual.

[C] The listed furnace values are those expected when using a 20µ L injection and normal gas flow except in the case of arsenic and selenium where gas interrupt is used. The symbol (*p*) indicates the use of pyrolytic graphite with the furnace procedure.

[D] Gaseous hydride method.

[E] Cold vapor technique.

being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

4.2 Pretreatment of a solid sample is necessary for complete dissolution of the metals and complete breakdown of organic material prior to analysis (see Methods E 926). This process may vary because of the metals to be determined and the nature of the sample being analyzed.

4.3 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of the sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available atoms are vaporized and dissociated for absorption in the tube than the flame, the use of small sample volumes or detection of low concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor. The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp, and a photosensitive device measures the attenuated transmittal radiation.

5. Significance and Use

5.1 Metals in solution may be readily determined by atomic absorption spectroscopy (AAS). The method is simple, rapid, and applicable to a large number of metals in solution. Solid type samples may be analyzed after proper treatment.

6. Interferences

6.1 *Direct Aspiration*:

6.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination to the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

6.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are primarily employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

6.1.3 Highly dissolved solids in the sample being aspirated may result in an interference from nonatomic absorbance such as light scattering. If background correction is not available, a nonabsorbing wavelength should be checked. Preferably, high solid content solutions should be extracted (see 6.1.1 and 11.2).

6.1.4 Ionization interferences occur where the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positive charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess of an easily ionized element.

6.1.5 Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-element lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

6.2 *Flameless Atomization*:

6.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects that must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, use the following procedure. Withdraw from the sample two equal aliquots. To one of the aliquots, add a known amount of analyte and dilute both aliquots to the same predetermined volume. (The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4 while keeping in mind the optimum concentration range of the analysis. Under no circumstances should the dilution be less than 1:1). The diluted aliquots should then be analyzed and the unspiked results multiplied by the dilution factor should be compared to the original determination. Agreement of the results (within ± 10 %) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis. Those samples that indicate the presence of interference should be treated in one or more of the following ways.

6.2.1.1 The samples should be successively diluted and reanalyzed to determine if the interference can be eliminated.

6.2.1.2 The matrix of the sample should be modified in the furnace. Examples are the addition of ammonium nitrate to remove alkali chlorides, ammonium phosphate to retain cadmium, and nickel nitrate for arsenic and selenium analysis (**1**).[3] The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

6.2.1.3 Analyze the sample by method of standard additions while noting the precautions and limitations of its use (see 10.5).

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[3] The boldface numbers in parentheses refer to the list of references at the end of these test methods.

6.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either the use of background correction or choosing an alternate wavelength outside the absorption band should eliminate this interference. Background correction can also compensate for nonspecific broad band absorption interference.

6.2.3 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or using an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analysis element.

6.2.4 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way, broad-band absorption will be minimized.

6.2.5 From anion-interference studies in the graphite furnace it is generally accepted that nitrate is the preferred anion. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to HNO_3 is required, a minimum amount should be used. This applies particularly to hydrochloric and to a lesser extent to sulfuric and phosphoric acids.

6.2.6 Carbide formation resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. Molybdenum may be cited as an example. When this takes place, the metal will be released very slowly from the carbide as atomization continues. For molybdenum, one may be required to atomize for 30 s or more before the signal returns to baseline levels. This problem is greatly reduced, and the sensitivity increased with the use of pyrolytically-coated graphite.

6.2.7 Ionization interferences have to date not been reported with furnace techniques.

6.2.8 For comments on spectral interference see 6.1.5.

6.2.9 Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. The sample-preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed. Pipet tips have been known to be a source of contamination. If suspected, they should be acid soaked with 1:5 HNO_3 and rinsed thoroughly with tap and deionized water. The use of a better grade pipet tip can greatly reduce this problem. It is very important that special attention be given to reagent blanks in both analysis and the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to possibly ten high temperature burns may be required to clean the tube before use.

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*—Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range from 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

7.2 *Burner*—The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

7.3 *Hollow Cathode Lamps*—Single-element lamps are to be preferred but multi-element lamps may be used. Electrodeless discharge lamps may also be used when available.

7.4 *Graphite Furnace*—Any furnace device capable of reaching the specified temperatures is satisfactory.

7.5 *Strip Chart Recorder*—A recorder is strongly recommended for furnace work so that there will be a permanent record, and any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can be easily recognized.

7.6 *Pipets*—Microliter with disposable tips. Sizes can range from 5 to 100 μL as required.

7.7 *Pressure-reducing Valves*—The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

7.8 *Separatory Flasks*—250 mL, or larger, for extraction with organic solvents.

7.9 *Glassware*—All glassware, linear polyethylene, polypropylene or Teflon containers, including sampling bottles, should be washed and rinsed in the following order: washed with detergent; rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloride acid, tap water, and deionized distilled water.

7.10 *Borosilicate Glass Distillation Apparatus*.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

8.3 *Deionized Distilled Water*—Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

8.4 *Nitric Acid* (concentrated)—If metal impurities are found to be present, distill reagent grade nitric acid in a borosilicate glass distillation apparatus, or use a spectrograde acid. **Warning**—Perform distillation in hood with protective sash in place.

8.4.1 *Nitric Acid* (1:1)—Prepare a 1:1 dilution with deionized, distilled water by adding the concentrated acid to an equal volume of water.

8.5 *Hydrochloric Acid* (1:1)—Prepare a 1:1 solution of reagent grade hydrochloric acid and deionized distilled water.

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

If metal impurities are found to be present, distill this mixture from a borosilicate glass distillation apparatus or use a spectrograde acid.

8.6 *Stock Standard Metal Solutions*—Prepare as directed in 10.1 and under the individual metal procedures. Commercially available stock standard solutions may be used.

8.7 *Calibration Standards*—Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

8.8 *Fuel and Oxidant*—Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

8.9 *Special Reagents for the Extraction Procedure*:

8.9.1 *Pyrrolidine Dithiocarbamic Acid (PDCA)*[5]—Prepare by adding 18 mL of analytical reagent grade pyrrolidine to 500 mL of chloroform in a litre flask.[6] Cool and add 15 mL of carbon disulfide in small portions and with swirling. Dilute to 1 L with chloroform. The solution can be used for several months if stored in a brown bottle in a refrigerator.

8.9.2 *Ammonium Hydroxide*, 2*N*—Dilute 3 mL concentrated NH_4OH to 100 mL with deionized distilled water.

8.9.3 *Bromphenol Blue Indicator* (1 g/L)—Dissolve 0.1 g bromphenol blue in 100 mL of 500 % ethanol or isopropanol.

8.9.4 *HCL* (2.5 % v/v)—Dilute 2 mL redistilled HCl to 40 mL with deionized distilled water.

9. Sample Handling and Preservation

9.1 See Test Methods E 926 for sample handling and preservation procedures.

10. Preparation of Standards and Calibration

10.1 *Stock Standard Solutions*, are prepared from high purity metals, oxides, or nonhygroscopic reagent grade salts using deionized distilled water and redistilled nitric or hydrochloric acids. (See individual analysis sheets for specific instruction.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1000 mg of the metal per litre. Commercially available standard solutions may also be used.

10.2 *Calibration Standards*, are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least four calibration standards in graduated amounts in the appropriate range. The *calibration standards* should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal.

10.3 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition must be used. This technique relies on the addition of small, known amounts of the analysis element to portions of the sample, the absorbance difference between those, and the original solution giving the slope of the calibration curve. The method of standard addition is described in greater detail in 10.5.

10.4 For those instruments that do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards that produce an absorption of 0 to 80 %. The correct method is to convert the percent absorption readings to absorbance and plot that value against concentration. The following relationship is used to convert absorption values to absorbance:

$$\text{absorbance} = \log (100/\% \ T) = 2 - \log(\% \ T) \qquad (1)$$

where:
$\% \ T = 100 - \%$ absorption

As the curves are frequently nonlinear, especially at high absorption values, the number of standards should be increased in that portion of the curve.

10.5 *Method of Standard Additions*:

10.5.1 In this test method, equal volumes of sample are added to a deionized distilled water blank and to three standards containing different known amounts of the test element. The volume of the blank and the standards must be the same. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Fig. 1.

10.5.2 The method of standard additions can be very useful. For the results to be valid, the following limitations must be taken into consideration:

10.5.2.1 The absorbance plot of sample and standards must be linear over the concentration range of concern. For best results the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20 %) caution should be exercised.

10.5.2.2 The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

10.5.2.3 The determination must be free of spectral interference and corrected for nonspecific background interference.

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[5] The name pyrrolidine dithiocarbamic acid (PDCA), although commonly referenced in the scientific literature is ambiguous. From the chemical reaction of pyrrolidine and carbon disulfide a more proper name would be 1-pyrrolidine carbodithioic acid, PCDA (CAS Registry No. 25769-03-3).

[6] An acceptable grade of pyrrolidine may be obtained from the Aldrich Chemical Co., 940 West St. Paul Ave., Milwaukee, WI 53233.
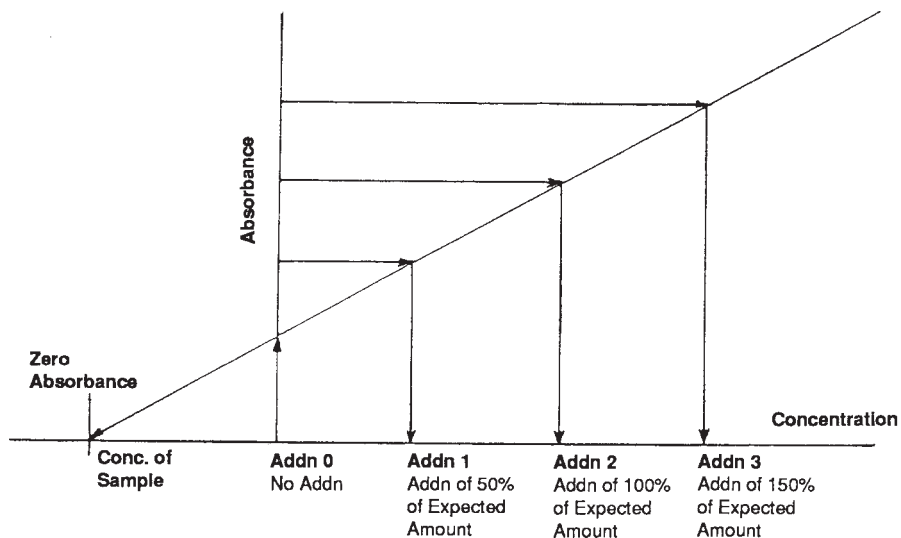
FIG. 1 Standard Addition Plot

11. General Procedure for Analysis by Atomic Absorption

11.1 *Direct Aspiration*—Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for his particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, allow the lamp to warm up for a minimum of 15 min unless operated in a double beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis and construct a calibration curve by plotting the concentrations of the standards against the absorbance. For those instruments which read directly in concentration set the curve corrector to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples are run.

11.1.1 *Calculation for Direct Determination of Liquid Samples*—Read the metal value in mg/L from the calibration curve or directly from the readout system of the instrument.

11.1.1.1 If dilution of sample was required:

$$\text{mg/L metal in sample} = A\left(\frac{C + B}{C}\right) \qquad (2)$$

where:
A = mg/L of metal in diluted aliquot from calibration curve,
B = mL of deionized distilled water used for dilution, and
C = mL of sample aliquot.

11.1.2 For solid samples: report all concentrations as mg/kg dry weight.

11.1.2.1 Dry sample:

$$\text{mg metal/kg sample} = \frac{A \times V}{D} \qquad (3)$$

where:
A = mg/L of metal in processed sample from calibration curve,
V = final volume of the processed sample in mL, and
D = weight of dry sample in grams.

11.1.2.2 Wet sample:

$$\text{mg metal/kg sample} = \frac{A \times V}{W \times P} \qquad (4)$$

where:
A = mg/L of metal in processed sample from calibration curve,
V = final volume of the processed sample in mL,
W = weight of wet sample in grams, and
P = percent solids.

11.2 *Special Extraction Procedure*—When the concentration of the metal is not sufficiently high to determine directly, or when considerable dissolved solids are present in the sample, certain metals may be chelated and extracted with organic solvents. Ammonium pyrrolidine dithiocarbamate (APDC)[7] in methyl isobutyl ketone (MIBK) is widely used for this purpose and is particularly useful for zinc, cadmium, iron, manganese, copper, silver, lead and chromium[+6]. Trivalent chromium does not react with APDC unless it has first been converted to the hexavalent form (2). This procedure is described under method for chromium (chelation extraction). Aluminum, beryllium, barium and strontium also do not react with APDC. While the APDC-MIBK chelating-solvent system can be used satisfactorily, it is possible to experience difficulties.

NOTE 1—Certain metal chelates, manganese-APDC in particular, are not stable in MIBK and will redissolve into the aqueous phase on

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[7] The name ammonium pyrrolidine dithiocarbamate (APDC) is somewhat ambiguous and should more properly be called ammonium, 1-pyrrolidine carbodithioate (APCD), CAS Registry No. 5108-96-3.

standing. The extraction of other metals is sensitive to both shaking rate and time. As with cadmium, prolonged extraction beyond 1 min, will reduce the extraction efficiency, whereas 3 min of vigorous shaking is required for chromium. Also, when multiple metals are to be determined either larger sample volumes must be extracted or individual extractions made for each metal being determined. The acid form of APDC-pyrrolidine dithiocarbamic acid prepared directly in chloroform as described by Lakanen has been found to be most advantageous (**3**). In this procedure the more dense chloroform layer allows for easy combination of multiple extractions which are carried out over a broader pH range favorable to multielement extraction. Pyrrolidine dithiocarbamic acid in chloroform is very stable and may be stored in a brown bottle in the refrigerator for months. Because chloroform is used as the solvent, it may not be aspirated into the flame. The procedure described in 11.2.1 is suggested.

11.2.1 *Extraction Procedure with Pyrrolidine Dithiocarbamic Acid (PDCA) in Chloroform*:

11.2.1.1 Transfer 200 mL of sample into a 250-mL separatory funnel, add 2 drops bromphenol blue indicator solution (8.9.3) and mix.

11.2.1.2 Prepare a blank and sufficient standards in the same manner and adjust the volume of each to approximately 200 mL with deionized distilled water. All of the metals to be determined may be combined into single solutions at the appropriate concentration levels.

11.2.1.3 Adjust the pH by addition of 2N NH_4OH solution (8.9.2) until a blue color persists. Add HCl (8.9.4) dropwise until the blue color just disappears; then add 2.0 mL HCl (8.9.4) in excess. The pH at this point should be 2.3. (The pH adjustment may be made with a pH meter instead of using indicator.)

11.2.1.4 Add 5 mL of PDCA-chloroform reagent (8.9.1) and shake vigorously for 2 min. Allow the phases to separate and drain the chloroform layer into a 100-mL beaker.

NOTE 2—If hexavalent chromium is to be extracted, the aqueous phase must be readjusted back to a pH of 2.3 after the addition of PDCA-chloroform and maintained at that pH throughout the extraction. For multielement extraction, the pH may be adjusted upward after the chromium has been extracted.

11.2.1.5 Add a second portion of 5 mL PDCA-chloroform reagent (8.7.1) and shake vigorously for 2 min. Allow the phases to separate and combine the chloroform phase with that obtained in 11.2.1.4.

11.2.1.6 Determine the pH of the aqueous phase and adjust to 4.5.

11.2.1.7 Repeat 11.2.1.4 again combining the solvent extracts.

11.2.1.8 Readjust the pH to 5.5, and extract a fourth time. Combine all extracts and evaporate to dryness on a steam bath.

11.2.1.9 Hold the beaker at a 45° angle, and slowly add 2 mL of concentrated distilled nitric acid, rotating the beaker to effect thorough contact of the acid with the residue.

11.2.1.10 Place the beaker on a low temperature hotplate or steam bath and evaporate just to dryness.

11.2.1.11 Add 2 mL of nitric acid (1:1) to the beaker and heat for 1 min. Cool, quantitatively transfer the solution to a 10-mL volumetric flask and bring to volume with distilled water. The sample is now ready for analysis.

11.2.2 Prepare a calibration curve by plotting absorbance versus the concentration of the metal standard (µg/L) in the 200-mL extracted standard solution. To calculate sample concentration read the metal value in µg/L from the calibration curve or directly from the readout system of the instrument. If dilution of the sample was required use the following equation:

$$\text{mg/L metal in sample} = Z\left(\frac{C + B}{C}\right) \qquad (5)$$

where:
Z = µg/L of metal in diluted aliquot from calibration curve,
B = mL of deionized distilled water used for dilution, and
C = mL of sample aliquot.

11.3 *Furnace Procedure*—Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of his particular instrument and use as a guide the temperature settings and other instrument conditions listed on the individual analysis sheets which are recommended for the Perkin-Elmer HGA-2100.[8] In addition, the following points may be helpful.

11.3.1 With flameless atomization, background correction becomes of high importance especially below 350 nm. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. It can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

11.3.2 If during atomization all the analyte is not volatilized and removed from the furnace, memory effects will occur. This condition is dependent on several factors such as the volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization and furnace design. If this situation is detected through blank burns, the tube should be cleaned by operating the furnace at full power for the required time period as needed at regular intervals in the analytical scheme.

11.3.3 Some of the smaller size furnace devices, or newer furnaces equipped with feedback temperature control employing faster rates of atomization, can be operated using lower atomization temperatures for shorter time periods than those listed in this manual.[9]

11.3.4 Although prior digestion of the sample in many cases is not required providing a representative aliquot of sample can be pipeted into the furnace, it will provide for a more uniform matrix and possibly lessen matrix effects.

11.3.5 Inject a measured microlitre 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

[8] The Perkin-Elmer HGA-2100 available from Perkin-Elmer Corp., Instruments Division, Main Ave., Norwalk, CT 06858 has been found suitable.

[9] Instrumentation Laboratories Model 555 available from Instrumentation Laboratory, Inc., Analytical Instrumentation Division, Jonspin Road, Wilmington, MA 01887; Perkin-Elmer Models HGA2200 and HGA7613; and Varian Model CRA-90 available from Varian Associates, Inc., 611 Hansen Way, Palo Alto, CA 94303 have been found suitable.

same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

11.3.6 To verify the absence of interference, follow the procedure as given in part 6.2.1.

11.3.7 A check standard should be run approximately after every 10 sample injections. 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. Even though tube life depends on sample matrix and atomization temperature, a conservative estimate would be that a tube will last at least 50 firings. A pyrolytic-coating would extend that estimate by a factor of 3.

11.3.8 *Calculation*—For determination of metal concentration by the furnace: Read the metal value in µg/L from the calibration curve or directly from the readout system of the instrument.

11.3.8.1 If different size furnace injection volumes are used for samples rather than for standards, calculate as follows:

$$\text{µg/L of metal in sample} = Z\left(\frac{S}{U}\right) \qquad (6)$$

where:
Z = µg/L of metal read from calibration curve or readout system,
S = µL volume standard injected into furnace for calibration curve, and
U = µL volume of sample injected for analysis.

11.3.8.2 If dilution of sample was required but sample injection volume was the same as for the following standard:

$$\text{µg/L of metal in sample} = Z\left(\frac{C + B}{C}\right) \qquad (7)$$

where:
Z = µg/L metal in diluted aliquot from calibration curve,
B = mL of deionized distilled water used for dilution, and
C = mL of sample aliquot.

11.3.9 For solid samples, report all concentrations as mg/kg dry weight.

11.3.9.1 *Dry sample*:

$$\text{mg metal/kg sample} = \frac{\left(\dfrac{Z}{1\ 000}\right)V}{D} \qquad (8)$$

where:
Z = µg/L of metal in processed sample from calibration curve (see 11.3.8.1),
V = final volume of processed sample in millilitres, and
D = weight of dry sample in grams.

11.3.10 *Wet sample*:

$$\text{mg metal/kg sample} = \frac{\left(\dfrac{Z}{1\ 000}\right)V}{W \times P} \qquad (9)$$

where:
Z = µg/L of metal in processed sample from calibration curve (see 11.3.8.1),

V = final volume of processed sample in millilitres,
W = weight of wet sample in grams, and
P = percent solids.

12. Aluminum—Direct Aspiration

12.1 *Requirements*:

12.1.1 *Optimum Concentration Range*, 5 to 50 mg/L using a wavelength of 309.3 nm (see Note 3 and Note 4).

12.1.2 *Sensitivity*, 1 mg/L.

12.1.3 *Detection Limit*, 0.1 mg/L.

NOTE 3—The following lines may also be used:

308.2 nm Relative Sensitivity 1
396.2 nm Relative Sensitivity 2
394.4 nm Relative Sensitivity 2.5

NOTE 4—For concentrations of aluminum below 0.3 mg/L, the furnace procedure is recommended.

12.2 *Preparation of Standard Solution*:

12.2.1 *Stock Solution*—Carefully weigh 1.000 g of aluminum metal (analytical reagent grade). Add 15 mL of concentrated HCl to the metal, cover the beaker, and warm gently. When solution is complete, transfer quantitatively to a 1 L-volumetric flask and make up to volume with deionized distilled water. 1 mL = 1 mg Al (1000 mg/L).

12.2.2 *Potassium Chloride Solution*—Dissolve 95 g potassium chloride (KCl) in deionized distilled water and make up to 1 L.

12.2.3 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing. To each 100 mL of standard and sample alike add 2.0 mL potassium chloride solution.

12.3 *General Instrumental Parameters*:

12.3.1 *Aluminum Hollow Cathode Lamp*.

12.3.2 *Wavelength*—309.3 nm.

12.3.3 *Fuel*—Acetylene.

12.3.4 *Oxidant*—Nitrous oxide.

12.3.5 *Type of flame*—Fuel rich.

12.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

12.5 *Interferences*—Aluminum is partially ionized in the nitrous oxide-acetylene flame. This problem may be controlled by the addition of an alkali metal (potassium, 1000 µg/mL) to both sample and standard solutions.

13. Aluminum—Furnace Technique

13.1 *Requirements*:

13.1.1 *Optimum Concentration Range*, 20–200 µg/L (see Note 5).

13.1.2 *Detection Limit*, 3 µg/L.

NOTE 5—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection, continuous flow purge gas and nonpyrolytic graphite.

13.2 *Preparation of Standard Solution*:

13.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

13.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Also use these solutions for "standard additions."

13.2.3 Dilute the calibration standard to contain 0.5 % (v/v) HNO_3.

13.3 *General Instrument Parameters*:

13.3.1 *Drying Time and Temperature*—30 s at 125°C.

13.3.2 *Ashing Time and Temperature*—30 s at 1300°C.

13.3.3 *Atomizing Time and Temperature*—10 s at 2700°C.

13.3.4 *Purge Gas Atmosphere*—Argon.

13.3.5 *Wavelength*—309.3 nm.

13.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer (see Note 6 and Note 7).

NOTE 6—Background correction may be required if the sample contains high dissolved solids.

NOTE 7—It has been reported that chloride ion and that nitrogen used as a purge gas suppress the aluminum signal. Therefore, the use of halide acids and nitrogen as a purge gas should be avoided.

13.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure" 11.3 (see Note 8 and Note 9).

NOTE 8—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 9—If the method of standard additions is required, follow the procedure given earlier in 10.5.

14. Antimony—Direct Aspiration

14.1 *Requirements*:

14.1.1 *Optimum Concentration Range*, 1 to 40 mg/L using a wavelength of 217.6 nm (see Note 10).

14.1.2 *Sensitivity*, 0.5 mg/L.

14.1.3 *Detection Limit*, 0.2 mg/L.

NOTE 10—For concentrations of antimony below 0.35 mg/L, the furnace procedure is recommended.

14.2 *Preparation of Standard Solution*:

14.2.1 *Stock Solution*—Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 L with deionized distilled water. 1 mL = 1 mg Sb (1000 mg/L).

14.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

14.3 *General Instrumental Parameters*:

14.3.1 *Antimony Hollow Cathode Lamp*.

14.3.2 *Wavelength*—217.6 nm.

14.3.3 *Fuel*—Acetylene.

14.3.4 *Oxidant*—Air.

14.3.5 *Type of Flame*—Fuel Lean.

14.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

14.5 *Interferences*:

14.5.1 In the presence of lead (1000 mg/L), a spectral interference may occur at the 217.6-nm resonance line. In this case the 231.1-nm antimony line should be used.

14.5.2 Increasing acid concentrations decrease antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards should be matched.

15. Antimony—Furnace Technique

15.1 *Requirements*:

15.1.1 *Optimum Concentration Range*, 20–300 μg/L (see Note 11).

15.1.2 *Detection Limit*, 3 μg/L.

NOTE 11—The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, continuous flow purge gas and non-pyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the recommended settings.

15.2 *Preparation of Standard Solution*:

15.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

15.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Also use these solutions for "standard additions."

15.2.3 Dilute the calibration standard to contain 0.2 % (v/v) HNO_3.

15.3 *General Instrument Parameters*:

15.3.1 *Drying Time and Temperature*—30 s at 125°C.

15.3.2 *Ashing Time and Temperature*—30 s at 800°C.

15.3.3 *Atomizing Time and Temperature*—10 s at 2700°C.

15.3.4 *Purge Gas Atmosphere*—Argon.

15.3.5 *Wavelength*—217.6 nm.

15.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer (see Note 12 and Note 13).

NOTE 12—The use of background correction is recommended.

NOTE 13—Nitrogen may also be used as the purge gas.

15.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure" 11.3 (see Note 14, Note 15, and Note 16).

NOTE 14—If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess of 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.

NOTE 15—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 16—If the method of standard additions is required, follow the procedure given in 10.5.

16. Arsenic—Furnace Technique

16.1 *Requirements*:

16.1.1 *Optimum Concentration Range*, 5–100 μg/L (see Note 17).

16.1.2 *Detection Limit*, 1 μg/L.

NOTE 17—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

16.2 *Preparation of Standard Solution*:

16.2.1 *Stock Solution*—Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 mL of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 L. 1 mL = 1 mg As (1000 mg/L).

16.2.2 *Nickel Nitrate Solution*, 5 %—Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 mL.

16.2.3 *Nickel Nitrate Solution*, 1 %—Dilute 20 mL of the 5 % nickel nitrate to 100 mL with deionized distilled water.

16.2.4 *Working Arsenic Solutions*—Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30 % H_2O_2 and 2 mL of the 5 % nickel nitrate solution. Dilute to 100 mL with deionized distilled water.

16.3 *Sample Preparation*:

16.3.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker. Add 2 mL of 30 % H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1 % (v/v). Heat for 1 h at 95°C or until the volume is slightly less than 50 mL.

16.3.2 Cool and bring back to 50 mL with deionized distilled water.

16.3.3 Pipet 5 mL of this digested solution into a 10 mL volumetric flask, add 1 mL of the 1 % nickel nitrate solution and dilute to 10-mL with deionized distilled water. The sample is now ready for injection into the furnace.

NOTE 18—If solubilization or digestion is not required, adjust the HNO_3 concentration of the sample to 1 % (v/v) and add 2 mL of 30 % H_2O_2 and 2 mL of 5 % nickel nitrate to each 100 mL of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

16.4 *General Instrument Parameters*:

16.4.1 *Drying Time and Temperature*—30 s at 125°C.

16.4.2 *Ashing Time and Temperature*—30 s at 1100°C.

16.4.3 *Atomizing Time and Temperature*—10 s at 2700°C.

16.4.4 *Purge Gas Atmosphere*—Argon.

16.4.5 *Wavelength*—193.7 nm.

16.4.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE 19—The use of background correction is recommended.

16.5 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure" 11.3.

NOTE 20—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 21—If the method of standard additions is required, follow the procedure given in 10.5.

17. Arsenic Gaseous Hydride Method

17.1 *Scope and Application:* The gaseous hydride method determines inorganic arsenic when present in concentrations at or about 2 µg/L. The method is applicable to drinking water and most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver.

17.2 *Summary of Test Method*:

17.2.1 Arsenic in the sample is first reduced to the trivalent form using $SnCl_2$ and converted to arsine, AsH_3, using zinc metal. The gaseous hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the method is 2 to 20 µg/L. The 193.7 nm wavelength is used.

17.2.2 Organic arsenic must be converted to inorganic compounds. **Warning**—Arsine is a toxic gas. Precautions should be made to keep the system closed to the atmosphere.

17.3 Except for the perchloric acid step, the procedure to be used for this determination is found in Standard Methods for the Examination of Water and Wastewater **(4).**

18. Barium—Direct Aspiration

18.1 *Requirements*:

18.1.1 *Optimum Concentration Range*, 1–20 mg/L using a wavelength of 553.6 nm (see Note 22).

18.1.2 *Sensitivity*, 0.4 mg/L.

18.1.3 *Detection Limit*, 0.1 mg/L.

NOTE 22—For concentrations of barium below 0.2 mg/L, the furnace procedure is recommended.

18.2 *Preparation of Standard Solution*:

18.2.1 *Stock Solution*—Dissolve 1.7787 g barium chloride ($BaCl_2 \cdot 2H_2O$, analytical reagent grade) in deionized distilled water and dilute to 1 L. 1 mL = 1 mg Ba (1000 mg/L).

18.2.2 *Potassium Chloride Solution*—Dissolve 95 g potassium chloride, KCl, in deionized distilled water and make up to 1 L.

18.2.3 Prepare dilutions of the stock barium solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike, add 2.0 mL potassium chloride solution. The *calibration standards* should be prepared using the same type of acid and the same concentration as that of the sample being analyzed either directly or after processing.

18.3 *General Instrumental Parameters*:

18.3.1 *Barium hollow cathode lamp*.

18.3.2 *Wavelength*—553.6 nm.

18.3.3 *Fuel*—Acetylene.

18.3.4 *Oxidant*—Nitrous oxide.

18.3.5 *Type of Flame*—Fuel rich.

18.4 *Analysis of Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

18.5 *Interferences*:

18.5.1 The use of nitrous oxide-acetylene flame virtually eliminates chemical interference. However, barium is easily ionized in this flame, and potassium must be added (1000 mg/L) to standards and samples alike to control this effect.

18.5.2 If the nitrous oxide flame is not available and acetylene-air is used, phosphate, silicon and aluminum will severely depress the barium absorbance. This may be overcome by the addition of 2000 mg/L lanthanum.

19. Barium—Furnace Technique

19.1 *Requirements*:

19.1.1 *Optimum Concentration Range*, 10 to 200 µg/L (see Note 23).

19.1.2 *Detection Limit*, 2 µg/L.

NOTE 23—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection, continuous flow purge gas and pyrolytic graphite.

19.2 *Preparation of Standard Solution*:

19.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

19.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

19.2.3 The calibration standard should be diluted to contain 0.5 % (v/v) HNO_3.

NOTE 24—The use of halide acid should be avoided.

19.3 *General Instrument Parameters*:

19.3.1 *Drying Time and Temperature*—30 s at 125°C.

19.3.2 *Ashing Time and Temperature*—30 s at 1200°C.

19.3.3 *Atomizing Time and Temperature*—10 s at 2800°C.

19.3.4 *Purge Gas Atmosphere*—Argon.

NOTE 25—Because of possible chemical interaction, nitrogen should not be used as a purge gas.

19.3.5 *Wavelength*—553.6 nm.

19.3.6 *Other Operating Parameters*, should be set as specified by the particular instrument manufacturer.

19.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure" 11.3.

NOTE 26—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 27—If the method of standard additions is required, follow the procedure given in 10.5.

20. Beryllium—Direct Aspiration

20.1 *Requirements*:

20.1.1 *Optimum Concentration Range*, 0.05 to 2 mg/L using a wavelength of 234.9 nm (see Note 28 and Note 29).

20.1.2 *Sensitivity*, 0.025 mg/L.

20.1.3 *Detection Limit*, 0.005 mg/L.

NOTE 28—The "aluminon colorimetric method" may also be used (6). The minimum detectable concentration by this method is 5 µg/L.

NOTE 29—For concentrations of beryllium below 0.02 mg/L, the furnace procedure is recommended.

20.2 *Preparation of Standard Solution*:

20.2.1 *Stock solution*—Dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in deionized distilled water containing 2 mL concentrated nitric acid and dilute to 1 L. 1 mL = 1 mg Be (1000 mg/L).

20.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

20.3 *General Instrumental Parameters*:

20.3.1 *Beryllium Hollow Cathode Lamp*.

20.3.2 *Wavelength*—234.9 nm.

20.3.3 *Fuel*—Acetylene.

20.3.4 *Oxidant*—Nitrous oxide.

20.3.5 *Type of Flame*—Fuel-rich.

20.4 *Analysis Procedure*:

20.4.1 For analysis procedure and calculation, see "Direct Aspiration," 11.3.

20.5 *Interferences*:

20.5.1 Sodium and silicon at concentrations in excess of 1000 mg/L have been found to severely depress the beryllium absorbance.

20.5.2 Bicarbonate ion is reported to interfere; however, its effect is eliminated when samples are acidified to a pH of 1.5.

20.5.3 Aluminum at concentrations of 500 µg/L is reported to depress the sensitivity of beryllium (5).

21. Beryllium—Furnace Technique

21.1 *Requirements*:

21.1.1 *Optimum Concentration Range*, 1 to 30 µg/L (see Note 30).

21.1.2 *Detection Limit*, 0.2 µg/L.

NOTE 30—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection, continuous flow purge gas and non-pyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

21.2 *Preparation of Standard Solution*:

21.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

21.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Also use these solutions for "standard additions."

21.2.3 The calibration standard should be diluted to contain 0.5 % (v/v) HNO_3.

21.3 *General Instrumental Parameters*:

21.3.1 *Drying Time and Temperature*—30 s at 125°C.

21.3.2 *Ashing Time and Temperature*—30 s at 1000°C.

21.3.3 *Atomizing Time and Temperature*—10 s at 2800°C.

21.3.4 *Purge Gas Atmosphere*—Argon.

21.3.5 *Wavelength*—234.9 nm.

21.3.6 The operating parameters should be set as specified by the particular instrument manufacturer.

NOTE 31—The use of background correction is recommended.

NOTE 32—Because of possible chemical interaction and reported lower sensitivity, nitrogen should not be used as the purge gas.

21.4 *Analysis Procedure*—For the analysis procedure and the calculation see "Furnace Procedure," 11.3.

NOTE 33—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 34—If the method of standard additions is required, follow the procedure given in 10.5.

22. Cadmium—Direct Aspiration

22.1 *Requirements*:

22.1.1 *Optimum Concentration Range*, 0.05 to 2 mg/L using a wavelength of 228.8 nm (see Note 35).

22.1.2 *Sensitivity*, 0.025 mg/L.

22.1.3 *Detection Limit*, 0.005 mg/L.

NOTE 35—For levels of cadmium below 20 µg/L, either the Special

Extraction Procedure given in 11.2 or the furnace technique is recommended.

22.2 *Preparation of Standard Solution*:

22.2.1 *Stock Solution*—Carefully weigh 2.282 g of cadmium sulfate ($3CdSO_4 \cdot 8H_2O$, analytical reagent grade) and dissolve in deionized distilled water. 1 mL = 1 mg Cd (1000 mg/L).

22.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

22.3 *General Instrumental Parameters*:

22.3.1 *Cadmium Hollow Cathode Lamp*.

22.3.2 *Wavelength*—228.8 nm.

22.3.3 *Fuel*—Acetylene.

22.3.4 *Oxidant*—Air.

22.3.5 *Type of Flame*—Oxidizing.

22.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

23. Cadmium—Furnace Technique

23.1 *Requirements*:

23.1.1 *Optimum Concentration Range*, 0.5 to 10 µg/L (see Note 36).

23.1.2 *Detection Limit*, 0.1 µg/L.

NOTE 36—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection, continuous flow purge gas and non-pyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

23.2 *Preparation of Standard Solution*:

23.2.1 *Stock Solution:* Prepare as described under "direct aspiration method."

23.2.2 *Ammonium Phosphate Solution* (40 %)—Dissolve 40 g of ammonium phosphate, $(NH_4)2HPO_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 mL.

23.2.3 Prepare dilutions of the stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL of the ammonium phosphate solution. The calibration standards should be prepared to contain 0.5 % (v/v) HNO_3.

23.3 *General Instrument Parameters*:

23.3.1 *Drying Time and Temperature*—30 s at 125°C.

23.3.2 *Ashing Time and Temperature*—30 s at 500°C.

23.3.3 *Atomizing Time and Temperature*—10 s at 1900°C.

23.3.4 *Purge Gas Atmosphere*—Argon.

23.3.5 *Wavelength*—228.8 nm.

23.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE 37—The use of background correction is recommended.

23.4 *Analysis Procedure*—For the analysis procedure and the calculation see "Furnace Procedure," 11.3.

NOTE 38—Contamination from the work area is critical in cadmium analysis. Use of pipet tips which are free of cadmium is of particular importance.

NOTE 39—For every sample matrix analyzed, verification is necessary

to determine that the method of standard additions is not required (see 6.2.1).

NOTE 40—If the method of standard additions is required, follow the procedure given in 10.5.

24. Calcium—Direct Aspiration

24.1 *Requirements*:

24.1.1 *Optimum Concentration Range*, 0.2 to 7 mg/L using a wavelength of 422.7 nm (see Note 41 and Note 42).

24.1.2 *Sensitivity*, 0.08 mg/L.

24.1.3 *Detection Limit*, 0.01 mg/L.

NOTE 41—Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Since low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1000 mg/L also cause low calcium values. Concentrations of up to 500 mg/L each of sodium, potassium and nitrate cause no interference.

NOTE 42—The 239.9 nm line may also be used. This line has a relative sensitivity of 120.

24.2 *Preparation of Standard Solution*:

24.2.1 *Stock Solution*—Suspend 1.250 g of $CaCO_3$ (analytical reagent grade) dried at 180°C for 1 h before weighing, in deionized distilled water, and dissolve cautiously with a minimum of dilute HCl. Dilute to 1000 mL with deionized distilled water. 1 mL = 0.5 mg Ca (500 mg/L).

24.2.2 *Lanthanum Chloride Solution*—Dissolve 29 g of La_2O_3, slowly and in small portions, in 250 mL concentrated HCl (**Caution**—Reaction is violent). Dilute to 500 mL with deionized distilled water.

24.2.3 Prepare dilutions of the stock calcium solutions to be used as calibration standards at the time of analysis. To each 10 mL volume of calibration standard and sample alike, add 1.0 mL of the lanthanum chloride solution, that is, 20 mL of standard or sample + 2 mL $LaCl_3$ = 22 mL.

24.3 *General Instrumental Parameters*:

24.3.1 *Calcium Hollow Cathode Lamp*.

24.3.2 *Wavelength*—422.7 nm.

24.3.3 *Fuel*—Acetylene.

24.3.4 *Oxidant*—Air.

24.3.5 *Type of Flame*—Reducing.

24.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

NOTE 43—Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.

NOTE 44—The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame **(7).**

25. Chromium—Direct Aspiration

25.1 *Requirements*:

25.1.1 *Optimum Concentration Range:* 0.5 to 10 mg/L using a wavelength of 357.9 nm (see Note 45 and Note 46).

25.1.2 *Sensitivity*—0.25 mg/L.

25.1.3 *Detection Limit*—0.05 mg/L.

NOTE 45—The following wavelengths may also be used:
359.3 nm Relative Sensitivity 1.4,
425.4 nm Relative Sensitivity 2,

427.5 nm Relative Sensitivity 3, and

428.9 nm Relative Sensitivity 4.

NOTE 46—For levels of chromium between 50 and 200µ g/L, where the air-acetylene flame cannot be used or for levels below 50 µg/L, either the furnace procedure or the extraction procedure is recommended.

25.2 *Preparation of Standard Solution*:

25.2.1 *Stock Solution:* Dissolve 1.923 g of chromium trioxide (CrO_3, reagent grade) in deionized distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 L with deionized distilled water. 1 mL = 1 mg Cr (1000 mg/L).

25.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

25.3 *General Instrumental Parameters*:

25.3.1 *Chromium Hollow Cathode Lamp*.

25.3.2 *Wavelength*—357.9 nm.

25.3.3 *Fuel*—Acetylene.

NOTE 47—The fuel-rich air-acetylene flame provides greater sensitivity but is subject to chemical and matrix interference from iron, nickel, and other metals. If the analysis is performed in a lean flame the interference can be lessened but the sensitivity will also be reduced.

NOTE 48—The suppression of both Cr (III) and Cr (VI) absorption by most interfering ions in fuel rich air-acetylene flames is reportedly controlled by the addition of 1 % ammonium bifluoride in 0.2 % sodium sulfate (8). A 1 % oxine solution is also reported to be useful.

25.3.4 *Oxidant*—Nitrous oxide.

25.3.5 *Type of Flame*—Fuel rich.

25.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

26. Chromium—Furnace Technique

26.1 *Requirements*:

26.1.1 *Optimum Concentration Range*, 5 to 100 µg/L (see Note 49).

26.1.2 *Detection Limit*, 1 µg/L.

NOTE 49—The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of 20 µL injection, continuous flow purge gas and non-pyrolytic graphite.

26.2 *Preparation of Standard Solution*:

26.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

26.2.2 *Calcium Nitrate Solution*—Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade) in deionized distilled water and dilute to 100 mL. 1 mL = 20 mg Ca.

26.2.3 Prepare dilutions of the stock chromium solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared to contain 0.5 % (v/v) HNO_3. To each 100 mL of standard and sample alike, add 1 mL of 30 % H_2O_2 and 1 mL of the calcium nitrate solution.

NOTE 50—Hydrogen peroxide is added to the acidified solution to convert all chromium to the trivalent state. Calcium is added to a level above 200 mg/L where its suppressive effect becomes constant up to 1000 mg/L.

26.3 *General Instrument Parameters*:

26.3.1 *Drying Time and Temperature*—30 s at 125°C.

26.3.2 *Ashing Time and Temperature*—30 s at 1000°C.

26.3.3 *Atomizing Time and Temperature*—10 s at 2700°C.

26.3.4 *Purge Gas Atmosphere*—Argon.

26.3.5 *Wavelength*—357.9 nm.

26.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE 51—Background correction may be required if the sample contains high dissolved solids.

NOTE 52—Nitrogen should not be used as a purge gas because of possible CN band interference.

26.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure" 11.3.

NOTE 53—Pipet tips have been reported to be a possible source of contamination.

NOTE 54—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 55—If the method of standard additions is required, follow the procedure given in 10.5.

27. Chromium—Chelation-Extraction

27.1 *Scope*—This test method may be used to analyze samples containing from 1.0 to 25 µg of chromium per litre of solution.

27.2 *Summary of the Test Method*:

27.2.1 This test method is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) following oxidation of trivalent chromium. The chelate is extracted with methyl isobutyl ketone (MIBK) and aspirated into the flame of the atomic absorption spectrophotometer.

27.2.2 Hexavalent chromium may also be chelated with pyrrolidine dithiocarbamic acid in chloroform as described in 11.2.

27.3 *Interferences*—High concentrations of other reactive metals, as may be found in wastewaters, may interfere. The method is free from interferences from elements normally occurring in fresh water.

27.4 *General Instrumental Parameters*:

27.4.1 *Chromium Hollow Cathode Lamp*.

27.4.2 *Wavelength*—357.9 nm.

27.4.3 *Fuel*—Acetylene.

27.4.4 *Oxidant*—Air.

27.4.5 *Type of Flame*—Fuel rich (adjust for organic solvent).

27.5 *Reagents*:

27.5.1 *Ammonium Pyrrolidine Dithiocarbamate* (APDC) *Solution*—Dissolve 1.0 g APDC in dimineralized water and dilute to 100 mL. Prepare fresh daily.

27.5.2 *Bromphenol Blue Indicator Solution*—Dissolve 0.1 g bromphenol blue in 100 mL 50 % ethanol.

27.5.3 *Potassium Dichromate Standard Solution* (1.0 mL = 0.08 mg Cr)—Dissolve 0.2263 g dried analytical reagent grade $K_2Cr_2O_7$ in demineralized water, and make up to 1000 mL.

27.5.4 *Trivalent Chromium Stock Solution* (1.0 mL = 0.002 mg Cr^+3)—Pipet 5.00 mL of the potassium dichromate standard solution (5.3) into an Erlenmeyer flask. Add approximately 15 mg Na_2SO_3 and 0.5 mL concentrated HNO_3. Gently evaporate to dryness; strong heating reoxidizes the chromium. Add 0.5 mL concentrated HNO_3 and again evaporate to dryness to destroy any excess sulfite. Take up in 1 mL concentrated HNO_3 with warming and dilute to 200.00 mL with demineralized water.

27.5.5 *Trivalent Chromium Working Solution* (1.0 mL = 0.005 mg Cr^{+3})—Immediately before use, dilute 25.0 mL of trivalent chromium stock solution (27.5.4) to 100.0 mL with demineralized water.

27.5.6 *Potassium Permanganate* (0.1 N)—Dissolve 0.32 g potassium permanganate in 100 mL demineralized water.

27.5.7 *Sodium Azide* (0.1 %)—Dissolve 100 mg sodium azide in demineralized water and dilute to 100 mL.

27.5.8 *Methyl Isobutyl Ketone* (MIBK).

27.5.9 *Sodium Hydroxide Solution* (1 M)—Dissolve 40 g NaOH in demineralized water and dilute to 1 L.

27.5.10 *Sulfuric Acid* (0.12 M)—Slowly add 6.5 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

27.6 *Procedure*:

27.6.1 Pipet a volume of sample containing less than 2.5 µg chromium (100 mL maximum) into a 200 mL volumetric flask, and adjust the volume to approximately 100 mL. The pH must be 2.0 or less. Add concentrated HNO_3 if necessary.

27.6.2 Acidify a litre of demineralized water with 1.5 mL concentrated HNO_3. Prepare a blank and sufficient standards using trivalent chromium, and adjust volumes to approximately 100 mL with the acidified demineralized water.

27.6.3 Add 0.1 N $KMnO_4$ dropwise to both standards and samples until a faint pink color persists.

27.6.4 Heat on a steam bath for 20 min. If the color disappears, add additional $KMnO_4$ solution dropwise to maintain a slight excess.

27.6.5 While still on the steam bath, add sodium azide solution dropwise until the $KMnO_4$ color just disappears. Heat for about 2 min between each addition and avoid adding any excess. Continue heating for 5 min after adding the last drop of sodium azide solution.

27.6.6 Transfer the flasks to a water bath and cool to room temperature.

27.6.7 Remove from the water bath and filter (through Whatman No. 40 filter paper or equivalent) any sample that has a brownish precipitate or coloration which may interfere with the pH adjustment.

27.6.8 Add 2.0 mL of 1 M NaOH and 2 drops bromphenol blue indicator solution. Continue the addition of 1 M NaOH dropwise to all samples and standards in which the indicator change from yellow to blue has not occurred. Add 0.12 M H_2SO_4 dropwise until the blue color just disappears, then add 2.0 mL in excess. The pH at this point will be 2.4.

27.6.9 The pH adjustment to 2.4 may also be made with a pH meter instead of using an indicator.

27.6.10 Add 5.0 mL APDC solution and mix. The pH should then be approximately 2.8.

27.6.11 Add 10.0 mL MIBK and shake vigorously for 3 min.

27.6.12 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

27.6.13 Aspirate the ketone layer, record the instrument reading for each sample and standard against the blank. Repeat, and average the duplicate results.

27.7 *Calculations*:

27.7.1 Determine the µg/L Cr in each sample from a plot of the instrument readings of standards. A working curve must be prepared with each set of samples. Report Cr concentrations as follows:

27.7.1.1 Less than 10 µg/L, nearest µg/L, and

27.7.1.2 10 µg/L and above, two significant figures.

27.7.2 Calculate the mg metal per kg of samples as outlined in 11.2.

28. Chromium, Hexavalent—Chelation–Extraction

28.1 *Scope*:

28.1.1 This test method may be used to analyze samples containing from 1.0 to 25 µg of chromium per litre of solution.

28.2 *Summary of Test Method*:

28.2.1 This method is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the atomic absorption spectrophotometer.

28.2.2 Hexavalent chromium may also be chelated with pyrrolidine dithiocarbamic acid in chloroform as described in 11.2. A pH of 2.3 must be maintained throughout the extraction.

28.2.3 The diphenylcarbazide colorimetric procedure as found in "Standard Methods for the Examination of Water and Wastewater" may also be used **(9)**.

28.3 *Sample Handling and Preservation*:

28.3.1 Stability of hexavalent chromium is not completely understood at this time. Therefore, the chelation and extraction should be carried out as soon as possible.

28.3.2 To retard the chemical activity of hexavalent chromium, the sample should be transported and stored until time of analysis at 4°C.

28.4 *Interferences*:

28.4.1 High concentrations of other reactive metals, as may be found in wastewaters, may interfere. The method is free from interferences from elements normally occurring in fresh water.

28.5 *General Instrumental Parameters*:

28.5.1 *Chromium hollow cathode lamp*.

28.5.2 *Wavelength*—357.9 nm.

28.5.3 *Fuel*—Acetylene.

28.5.4 *Oxidant*—Air.

28.5.5 *Type of Flame:* Fuel-rich (adjust for organic solvent).

28.6 *Reagents*:

28.6.1 *Ammonium Pyrrolidine Dithiocarbamate (APDC) Solution*—Dissolve 1.0 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

28.6.2 *Bromphenol Blue Indicator Solution*—Dissolve 0.1 g bromphenol blue in 100 mL 50 % ethanol.

28.6.3 *Chromium Standard Solution I* (1.0 mL = 100 µg Cr)—Dissolve 0.2829 g pure, dried $K_2Cr_2O_7$ in demineralized water and dilute to 1000 mL.

28.6.4 *Chromium Standard Solution II* (1.0 mL = 10.0 µg Cr)—Dilute 100 mL chromium standard solution I to 1000 mL with demineralized water.

28.6.5 *Chromium Standard Solution III* (1.0 mL = 0.10 µg Cr)—Dilute 10.0 mL chromium standard solution II to 1000 mL with demineralized water.

28.6.6 *Methyl Isobutyl Ketone* (MIBK).

28.6.7 *Sodium Hydroxide Solution* (1 M)—Dissolve 40 g NaOH in demineralized water and dilute to 1 L.

28.6.8 *Sulfuric Acid* (0.12 M)—Slowly add 6.5 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

28.7 *Procedure*:

28.7.1 Pipet a volume of sample containing less than 2.5 µg chromium (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approximately 100 mL.

28.7.2 Prepare a blank and sufficient standards, and adjust the volume of each to approximately 100 mL.

28.7.3 Add 2 drops bromphenol blue indicator solution. (The pH adjustment to 2.4 may also be made with a pH meter instead of using an indicator.)

28.7.4 Adjust the pH by addition of 1 M NaOH solution dropwise until a blue color persists. Add 0.12 M H_2SO_4 dropwise until the blue color just disappears in both the standards and sample. Then add 2.0 mL of 0.12 M H_2SO_4 in excess. The pH at this point should be 2.4.

28.7.5 Add 5.0 mL APDC solution and mix. The pH should then be approximately 2.8.

28.7.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

28.7.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

28.7.8 Aspirate the ketone layer, and record the scale reading for each sample and standard against the blank. Repeat and average the duplicate results.

28.8 *Calculations*:

28.8.1 Determine the µg/L Cr^{+6} in each sample from a plot of scale readings of standards. A working curve must be prepared with each set of samples. Report Cr^{+6} concentrations as follows: Less than 10 µg/L, nearest µg/L; 10 µg/L and above, two significant figures.

28.8.2 Calculate the mg metal per kg of sample as outlined in 11.2.

29. Cobalt—Direct Aspiration

29.1 *Requirements*:

29.1.1 *Optimum Concentration Range*—0.5 to 5 mg/L using a wavelength of 240.7 nm (see Note 56).

29.1.2 *Sensitivity*—0.2 mg/L.

29.1.3 *Detection Limit*—0.05 mg/L.

Note 56—For levels of cobalt below 100 µg/L, either the special extraction procedure (11.2), or the furnace technique is recommended.

29.2 *Preparation of Standard Solution*:

29.2.1 *Stock Solution*—Dissolve 4.307 g of cobaltous chloride, $CoCl_2 \cdot 6H_2O$ (analytical reagent grade), in deionized distilled water. Add 10 mL of concentrated nitric acid and dilute to 1 L with deionized distilled water. 1 mL = 1 mg Co (1000 mg/L).

29.2.2 Prepare dilutions of the stock cobalt solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

29.3 *General Instrumental Parameters*:

29.3.1 *Cobalt Hollow Cathode Lamp*.

29.3.2 *Wavelength*—240.7 nm.

29.3.3 *Fuel*—Acetylene.

29.3.4 *Oxidant*—Air.

29.3.5 *Type of Flame*—Oxidizing.

29.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

30. Cobalt—Furnace Technique

30.1 *Requirements*:

30.1.1 *Optimum Concentration Range*, 5–100 µg/L (see Note 57).

30.1.2 *Detection Limit*, 1 µg/L.

Note 57—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 µL injection, continuous flow purge gas and nonpyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

30.2 *Preparation of Standard Solution*:

30.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

30.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

30.2.3 The calibration standard should be diluted to contain 0.5 % (v/v) HNO_3.

30.3 *General Instrument Parameters*:

30.3.1 *Drying Time and Temperature*—30 s at 125°C.

30.3.2 *Ashing Time and Temperature*—30 s at 900°C.

30.3.3 *Atomizing Time and Temperature*—10 s at 2700°C.

30.3.4 *Purge Gas Atmosphere*—Argon.

30.3.5 *Wavelength*—240.7 nm.

30.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

Note 58—The use of background correction is recommended.

Note 59—Nitrogen may also be used as the purge gas but with reported lower sensitivity.

30.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure" 11.3.

Note 60—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

Note 61—If the method of standard additions is required, follow the procedure given earlier in 10.5.

31. Copper—Direct Aspiration

31.1 *Requirements*:

31.1.1 *Optimum Concentration Range*, 0.2–5 mg/L using a wavelength of 324.7 nm (see Note 62 and Note 63).

31.1.2 *Sensitivity*, 0.1 mg/L.

31.1.3 *Detection Limit*, 0.02 mg/L.

NOTE 62—For levels of copper below 50 μg/L, either the Special Extraction Procedure, given in 11.2 or the furnace technique is recommended.

NOTE 63—Numerous absorption lines are available for the determination of copper. By selecting a suitable absorption wavelength, copper samples may be analyzed over a very wide range of concentration. The following lines may be used:

    327.4 nm Relative Sensitivity 2,

    216.5 nm Relative Sensitivity 7, and

    222.5 nm Relative Sensitivity 20.

31.2 *Preparation of Standard Solution*:

31.2.1 *Stock Solution*—Carefully weigh 1.00 g of electrolyte copper (analytical reagent grade). Dissolve in 5 mL redistilled HNO_3, and make up to 1 L with deionized distilled water. Final concentration is 1 mg Cu per mL (1000 mg/L).

31.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

31.3 *General Instrumental Parameters*:

31.3.1 *Copper Hollow Cathode Lamp*.

31.3.2 *Wavelength*—324.7 nm.

31.3.3 *Fuel*—Acetylene.

31.3.4 *Oxidant*—Air.

31.3.5 *Type of Flame*—Oxidizing.

31.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration", 11.1.

32. Copper—Furnace Technique

32.1 *Requirements*:

32.1.1 *Optimum Concentration Range*, 5 to 100 μg/L (see Note 64).

32.1.2 *Detection Limit*, 1 μg/L.

NOTE 64—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, continuous flow purge gas and non-pyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

32.2 *Preparation of Standard Solution*:

32.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

32.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

32.2.3 The calibration standard should be diluted to contain 0.5 % (v/v) HNO_3.

32.3 *General Instrument Parameters*:

32.3.1 *Drying Time and Temperature*—30 s at 125°C.

32.3.2 *Ashing Time and Temperature*—30 s at 900°C.

32.3.3 *Atomizing Time and Temperature*—10 s at 2700°C.

32.3.4 *Purge Gas Atmosphere*—Argon.

32.3.5 *Wavelength*—324.7 nm.

32.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE 65—Background correction may be required if the sample contains high dissolved solids.

NOTE 66—Nitrogen may also be used as the purge gas.

32.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure" 11.3.

NOTE 67—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 68—If the method of standard additions is required, follow the procedure given in 10.5.

33. Iron—Direct Aspiration

33.1 *Requirements*:

33.1.1 *Optimum Concentration Range*, 0.3 to 5 mg/L using a wavelength of 248.3 nm (see Note 69 and Note 70).

NOTE 69—The following lines may also be used:

248.8 nm relative sensitivity 2,

271.9 nm relative sensitivity 4,

302.1 nm relative sensitivity 5,

252.7 nm relative sensitivity 6, and

372.0 nm relative sensitivity 10.

NOTE 70—For concentrations of iron below 0.05 mg/L, either the Special Extraction Procedure given in 11.2 or the furnace procedure, is recommended.

33.1.2 *Sensitivity*, 0.12 mg/L.

33.1.3 *Detection Limit*, 0.03 mg/L.

33.2 *Preparation of Standard Solution*:

33.2.1 *Stock Solution*—Carefully weigh 1.000 g of pure iron wire (analytical reagent grade) and dissolve in 5 mL redistilled HNO_3, warming if necessary. When solution is complete, make up to 1 L with deionized distilled water. 1 mL = 1 mg Fe (1000 mg/L).

33.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

33.3 *General Instrumental Parameters*:

33.3.1 *Iron Hollow Cathode Lamp*.

33.3.2 *Wavelength*—248.3 nm.

33.3.3 *Fuel*—Acetylene.

33.3.4 *Oxidant*—Air.

33.3.5 *Type of Flame*—Oxidizing.

33.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

34. Iron—Furnace Technique

34.1 *Requirements*:

34.1.1 *Optimum Concentration Range*—5 to 100 μg/L (see Note 71).

34.1.2 *Detection Limit*—1 μg/L.

NOTE 71—The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 μL-injection, continuous flow purge gas, and nonpyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the recommended settings.

34.2 *Preparation of Standard Solution*:

34.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

34.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

34.2.3 The calibration standard should be diluted to contain 0.5 % (v/v) HNO_3.

34.3 *General Instrument Parameters*:

34.3.1 *Drying Time and Temperature*—30 s at 125°C.

34.3.2 *Ashing Time and Temperature*—30 s at 1000°C.

34.3.3 *Atomizing Time and Temperature*—10 s at 2700°C.

34.3.4 *Purge Gas Atmosphere*—Argon.

34.3.5 *Wavelength*—248.3 nm.

34.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

Note 72—The use of background correction is recommended.
Note 73—Nitrogen may also be used as the purge gas.

34.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure," 11.3.

Note 74—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).
Note 75—If the method of standard additions is required, follow the procedure given in 10.5.

35. Lead—Direct Aspiration

35.1 *Requirements*:

35.1.1 *Optimum Concentration Range*, 1–20 mg/L using a wavelength of 283.3 nm (see Note 76 and Note 77).

35.1.2 *Sensitivity*, 0.5 mg/L.

35.1.3 *Detection Limit*, 0.1 mg/L.

Note 76—For levels of lead below 200 µg/L, either the Special Extraction Procedure given in 11.2 or the furnace technique is recommended.
Note 77—The following lines may also be used:
217.0 nm Relative Sensitivity 0.4, and
261.4 nm Relative Sensitivity 10.

35.2 *Preparation of Standard Solution*:

35.2.1 *Stock Solution*—Carefully weigh 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete, acidify with 10 mL redistilled HNO_3 and dilute to 1 L with deionized distilled water. 1 mL = 1 mg Pb (1000 mg/L).

35.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

35.3 *General Instrumental Parameters*:

35.3.1 *Iron Hollow Cathode Lamp*.

35.3.2 *Wavelength*—283.3 nm.

35.3.3 *Fuel*—Acetylene.

35.3.4 *Oxidant*—Air.

35.3.5 *Type of Flame*—Oxidizing.

35.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

Note 78—The analysis of this metal is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust the burner to maximize the absorbance reading with a lead standard. Then, aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal.

36. Lead—Furnace Technique

36.1 *Requirements*:

36.1.1 *Optimum Concentration Range*, 5 to 100 µg/L (see Note 79).

36.1.2 *Detection Limit*, 1 µg/L.

Note 79—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection, continuous flow purge gas and nonpyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

36.2 *Preparation of Standard Solution*:

36.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

36.2.2 *Lanthanum Nitrate Solution*—Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 mL concentrated HNO_3, and dilute to 1000 mL with deionized distilled water. 1 mL = 50 mg La.

36.2.3 *Working Lead Solution*—Prepare dilutions of the stock lead solution to be used as calibration standards at the time of analysis. Each calibration standard should contain 0.5 % (v/v) HNO_3. To each 100 mL of diluted standard, add 10 mL of the lanthanum nitrate solution.

36.3 *General Instrument Parameters*:

36.3.1 *Drying Time and Temperature*—30 s at 125°C.

36.3.2 *Ashing Time and Temperature*—30 s at 500°C.

36.3.3 *Atomizing Time and Temperature*—10 s at 2700°C.

36.3.4 *Purge Gas Atmosphere*—Argon.

36.3.5 *Wavelength*—283.3 nm.

Note 80—Greater sensitivity can be achieved using the 217.0-nm line, but the optimum concentration range is reduced. The use of a lead electrodeless discharge lamp at this lower wavelength has been found to be advantageous. Also a lower atomization temperature (2400°C) may be preferred.

36.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

Note 81—The use of background correction is recommended.

36.4 *Analysis Procedure*—For the analysis procedure in the calculation see "Furnace Procedure," 11.3.

Note 82—To suppress sulfate interference (up to 1500 ppm) lanthanum is added as the nitrate to both samples and calibration standards (**10**).
Note 83—Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.
Note 84—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).
Note 85—If the method of standard additions is required, follow the procedure given in 10.5.

37. Lithium—Direct Aspiration

37.1 *Requirements*:

37.1.1 *Optimum Concentration Range*—to 0.2 mg/L using a wavelength of 670.8 nm (see Note 86).

37.1.2 *Sensitivity*—0.035 mg/L.

NOTE 86—The following lines may also be used:
323.3 nm relative sensitivity 235, and
610.4 nm relative sensitivity 3600.

37.2 *Preparation of Standard Solution*:

37.2.1 *Stock Solution*—Dissolve 5.324 g of lithium carbonate, Li_2CO_3 in a minimum volume of (1 + 1) HCl and dilute to 1 L with deionized water. 1 mL = 1.00 mg Li (1000 mg/L).

37.2.2 Prepare dilutions of the stock lithium solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

37.3 *General Instrumental Parameters*:

37.3.1 *Lithium Hollow Cathode Lamp*.

37.3.2 *Wavelength*—670.8 nm.

37.3.3 *Fuel*—Acetylene.

37.3.4 *Oxidant*—Air.

37.4 *Analysis Procedure*—For analysis procedure and calculations, see "Direct Aspiration," 11.1.

38. Magnesium—Direct Aspiration

38.1 *Requirements*:

38.1.1 *Optimum Concentration Range*, 0.02 to 0.5 mg/L using a wavelength of 285.2 nm (see Note 87 and Note 88).

38.1.2 *Sensitivity*, 0.007 mg/L.

38.1.3 *Detection Limit*, 0.001 mg/L.

NOTE 87—The following line may also be used: 202.5 nm relative sensitivity 25.

NOTE 88—To cover the range of magnesium values normally observed in surface waters (0.1 to 20 mg/L), it is suggested that either the 202.5 nm line be used or the burner head be rotated. A 90° rotation of the burner head will produce approximately one-eighth the normal sensitivity.

38.2 *Preparation of Standard Solution*:

38.2.1 *Stock Solution*—Dissolve 0.829 g of magnesium oxide, MgO (analytical reagent grade), in 10 mL of redistilled HNO_3, and dilute to 1 L with deionized distilled water. 1 mL = 0.50 mg Mg (500 mg/L).

38.2.2 *Lanthanum Chloride Solution*—Dissolve 29 g of La_2O_3, slowly and in small portions in 250 mL concentrated HCl, (**Caution**—Reaction is violent), and dilute to 500 mL with deionized distilled water.

38.2.3 Prepare dilutions of the stock magnesium solution to be used as calibration standards at the time of analysis. These *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed directly or after processing. To each 10-mL volume of *calibration standard* and sample alike add 1.0 mL of the lanthanum chloride solution, that is, 20 mL of standard or sample + 2 mL $LaCl_3$ = 22 mL.

38.3 *General Instrumental Parameters*:

38.3.1 *Magnesium Hollow Cathode Lamp*.

38.3.2 *Wavelength*—285.2 nm.

38.3.3 *Fuel*—Acetylene.

38.3.4 *Oxidant*—Air.

38.3.5 *Type of Flame*—Oxidizing.

38.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

NOTE 89—The interference caused by aluminum at concentrations greater than 2 mg/L is masked by addition of lanthanum. Sodium, potassium and calcium cause no interference at concentrations less than 400 mg/L.

39. Manganese—Direct Aspiration

39.1 *Requirements*:

39.1.1 *Optimum Concentration Range*, 0.1 to 3 mg/L using a wavelength of 279.5 nm (see Note 90).

39.1.2 *Sensitivity*, 0.05 mg/L.

39.1.3 *Detection Limit*, 0.01 mg/L.

NOTE 90—The following line may also be used: 403.1 nm Relative Sensitivity 10.

39.2 *Preparation of Standard Solution*:

39.2.1 *Stock Solution*—Carefully weigh 1.000 g of manganese metal (analytical reagent grade), and dissolve in 10 mL of redistilled HNO_3. When solution is complete, dilute to 1 L with 1 % (v/v) HCl. 1 mL = 1 mg Mn (1000 mg/L).

39.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

39.3 *General Instrumental Parameters*:

39.3.1 *Manganese hollow cathode lamp*.

39.3.2 *Wavelength*—279.5 nm.

39.3.3 *Fuel*—Acetylene.

39.3.4 *Oxidant*—air.

39.3.5 *Type of Flame*—oxidizing.

39.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

NOTE 91—For levels of manganese below 25 µg/L, either the furnace procedure or the Special Extraction Procedure given in 10.2 is recommended. The extraction is carried out at a pH of 4.5 to 5. The manganese chelate is very unstable and the analysis must be made without delay to prevent its solution in the aqueous phase.

40. Manganese—Furnace Technique

40.1 *Requirements*:

40.1.1 *Optimum Concentration Range*, 1 to 30 µg/L (see Note 92).

40.1.2 *Detection Limit*, 0.2 µg/L.

NOTE 92—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous flow purge gas and nonpyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

40.2 *Preparation of Standard Solution*:

40.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

40.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

40.2.3 The calibration standard should be diluted to contain 0.5 % (v/v) HNO_3.

40.3 *General Instrument Parameters*:

40.3.1 *Drying Time and Temperature*—30 s at 125°C.

40.3.2 *Ashing Time and Temperature*—30 s at 1000°C.

40.3.3 *Atomizing Time and Temperature*—10 s at 2700°C.

40.3.4 *Purge Gas Atmosphere*—Argon.

40.3.5 *Wavelength*—279.5 nm.

40.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE 93—The use of background correction is recommended.

NOTE 94—Nitrogen may also be used as the purge gas.

40.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure" 11.3.

NOTE 95—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 96—If the method of standard additions is required, follow the procedure given earlier in 10.5.

41. Mercury Cold Vapor Technique

41.1 *Scope and Application* (**11**)*:*

41.1.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100 % recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to ensure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.

41.1.2 The range of the test method may be varied through instrument or recorder expansion, or both. Using a 100-mL sample, a detection limit of 0.2 µg Hg/L can be achieved. Concentrations below this level should be reported as <0.2.

NOTE 97—If additional sensitivity is required, a 200 mL sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 µg/L, the standard deviations were ±0.027, ±0.006,± 0.01, and ±0.004. Percent recoveries at these levels were 107, 83, 84, and 96 %, respectively.

41.2 *Summary of Test Method*:

41.2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

41.3 *Sample Handling and Preservation*:

41.3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. If only dissolved mercury is to be determined, the sample should be filtered through an all glass apparatus before the acid is added. For total mercury, the filtration is omitted.

41.4 *Interference*:

41.4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

41.4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

41.4.3 High chloride concentrations require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

41.4.4 Interference from certain volatile organic materials that will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present.

NOTE 98—The possibility of absorption from certain organic substances actually being present in the sample does exist. This is mentioned only to caution the analyst of the possibility. A simple correction that may be used is as follows: If an interference has been found to be present, the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

41.5 *Apparatus*:

41.5.1 Atomic Absorption Spectrophotometer; (See Note 99) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 99—Instruments designated specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

41.5.2 *Mercury Hollow Cathode Lamp*—argon filled, or equivalent.[10]

41.5.3 *Recorder*—Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

41.5.4 *Absorption Cell*—Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1 outside diameter by 4½ in. The ends are ground perpendicular to the

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[10] Westinghouse WL-22847 available from any laboratory supply house has been found suitable.

longitudinal axis and quartz windows (1-in. diameter by $\frac{1}{16}$-in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2 by 2 in. cards. One-inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

41.5.5 *Air Pump*—Any peristaltic pump capable of delivering 1 L of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

41.5.6 *Flowmeter*—Capable of measuring an air flow of 1 L per minute.

41.5.7 *Aeration Tubing*—A straight-glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

41.5.8 *Drying Tube*—6 by $\frac{3}{4}$ in. diameter tube containing 20 g of magnesium perchlorate (see Note 100). The apparatus is assembled as shown in Fig. 2.

NOTE 100—In place of the magnesium perchlorate drying tube, a small reading lamp with 60 W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10.25°C above ambient.

41.6 *Reagents*:

41.6.1 *Sulfuric Acid, Concentrated*—Reagent grade.

41.6.1.1 *Sulfuric Acid,* 0.5 N—Dilute 14.0 mL of concentrated sulfuric acid to 1.0 L.

41.6.2 *Nitric Acid,* Concentrate—Reagent grade of low mercury content.

NOTE 101—If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

41.6.3 *Stannous Sulfate*—Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

41.6.4 *Sodium Chloride-Hydroxylamine Sulfate Solution*—Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

41.6.5 *Potassium Permanganate* (5 % solution, w/v)—Dissolve 5 g of potassium permanganate in 100 mL of distilled water.

41.6.6 *Potassium Persulfate* (5 % solution, w/v)—Dissolve 5 g of potassium persulfate in 100 mL of distilled water.

41.6.7 *Stock Mercury Solution*—Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL. 1 mL = 1 mg Hg.

41.6.8 *Working Mercury Solution*—Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15 % nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

41.7 *Calibration*:

41.7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0, and 10.0 mL aliquots of the working mercury solution containing 0 to 1.0 µg of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid to each bottle. Add 15 mL of $KMnO_4$ solution to each bottle, and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 h in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized wait 30 s, add 5 mL of the stannous sulfate solution and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L per minute, is allowed to run continuously. (An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.)

41.7.2 The absorbance will increase and reach maximum within 30 s. As soon as the recorder pen levels off, approximately 1 min, open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in
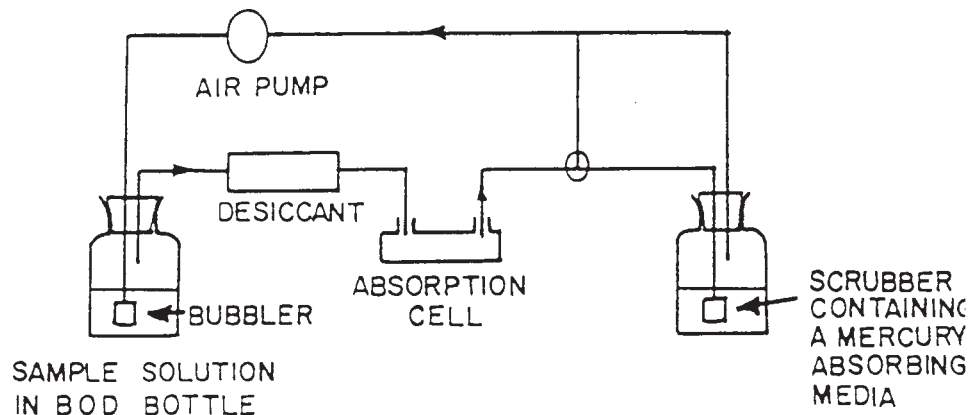

FIG. 2 Apparatus for Flameless Mercury Determination

the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media such as follows:

(a) (a) equal volumes of 0.1 M $KMnO_4$ and 10 % H_2SO_4, and

(b) (b) 0.25 % iodine in a 3 % KI solution.

NOTE 102—Directions for the disposal of mercury-containing wastes are given in Test Method D 3223.[11]

41.7.3 Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

41.8 *Procedure*:

41.8.1 Transfer 100 mL, or an aliquot diluted to 100 mL, containing not more than 1.0 µg of mercury, to a 300-mL BOD bottle. Add 5 mL of sulfuric acid and 2.5 mL of concentrated nitric acid mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. For sewage, sample additional permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 h in a water bath at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 s, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described in 41.7.

41.9 *Calculation*:

41.9.1 Determine the peak height of the unknown from the chart, and read the mercury value from the standard curve.

41.9.2 Calculate the mercury concentration in the sample by the formula:

$$\mu g\ Hg/L = (\mu g\ Hg\ in\ aliquot) \left(\frac{1,000}{volume\ of\ aliquot\ in\ mL} \right) \quad (10)$$

41.9.3 Report mercury concentrations as follows: Below 0.2 µg/L, <0.2; between 1 and 10 µg/L, one decimal; above 10 µg/L, whole numbers.

42. Molybdenum—Direct Aspiration

42.1 *Requirements*:

42.1.1 *Optimum Concentration Range*, 1 to 40 mg/L using a wavelength of 313.3 nm (see Note 103).

42.1.2 *Sensitivity*, 0.4 mg/L.

42.1.3 *Detection Limit*, 0.1 mg/L.

NOTE 103—For concentrations of molybdenum below 0.2 mg/L, the furnace procedure is recommended.

42.2 *Preparation of Standard Solution*:

42.2.1 *Stock Solution*—Dissolve 1.840 g of ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (analytical reagent grade) in deionized distilled water and dilute to 1 L. 1 mL = 1 mg Mo (1000 mg/L).

42.2.2 *Aluminum Nitrate Solution*—Dissolve 139 g aluminum nitrate, $Al(NO_3)_3\cdot9H_2O$, in 150 mL of deionized distilled water; heat to effect solution. Allow to cool and make up to 200 mL.

42.2.3 Prepare dilutions of the stock molybdenum solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing. To each 100 mL of standard and sample alike, add 2 mL of the aluminum nitrate solution.

42.3 *General Instrumental Parameters*:

42.3.1 *Molybdenum Hollow Cathode Lamp*.

42.3.2 *Wavelength*—313.3 nm.

42.3.3 *Fuel*—Acetylene.

42.3.4 *Oxidant*—Nitrous Oxide.

42.3.5 *Type of Flame*—Fuel rich.

42.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

42.5 *Interferences*:

42.5.1 With the recommended nitrous oxide-acetylene flame, interferences of calcium and other ions may be controlled by adding 1000 mg/L of a refractory metal such as aluminum **(12).** This should be done to both samples and standards alike.

43. Molybdenum—Furnace Technique

43.1 *Requirements*:

43.1.1 *Optimum Concentration Range*, 3 to 60 µg/L (see Note 104).

43.1.2 *Detection Limit*, 1 µg/L.

NOTE 104—The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection, continuous flow purge gas and pyrolytic graphite.

43.2 *Preparation of Standard Solution*:

43.2.1 *Stock Solution*—Prepare as described under "direct aspiration method".

43.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".

43.2.3 The calibration standard should be diluted to contain 0.5 % (v/v) HNO_3.

43.3 *General Instrument Parameters*:

43.3.1 *Drying Time and Temperature*—30 s at 125°C.

43.3.2 *Ashing Time and Temperature*—30 s at 1400°C.

43.3.3 *Atomizing Time and Temperature*—15 s at 2800°C.

43.3.4 *Purge Gas Atmosphere*—Argon.

43.3.5 *Wavelength*—313.3 nm.

43.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE 105—Background correction may be required if the sample contains high dissolved solids.

NOTE 106—The use of nitrogen as a purge gas is not recommended.

43.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure," 11.3.

NOTE 107—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

[11] A specially treated charcoal that will absorb mercury vapor is also available from Barneby and Cheney, East 8th Ave. and North Cassidy St., Columbus, OH 43219, Catalog No. E580-13 or 580-22.

NOTE 108—If the method of standard additions is required, follow the procedure given in 10.5.

44. Nickel—Direct Aspiration

44.1 *Requirements*:

44.1.1 *Optimum Concentration Range*, 0.3 to 5 mg/L using a wavelength of 232.0 nm (see Note 109).

44.1.2 *Sensitivity*, 0.15 mg/L.

44.1.3 *Detection Limit*, 0.04 mg/L.

NOTE 109—For levels of nickel below 100 µg/L, either the Special Extraction Procedure, given in 11.2, or the furnace technique is recommended.

44.2 *Preparation of Standard Solution*:

44.2.1 *Stock Solution*—Dissolve 4.953 g of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ (analytical reagent grade) in deionized distilled water. Add 10 mL of concentrated nitric acid and dilute to 1 L with deionized distilled water. 1 mL = 1 mg Ni (1000 mg/L).

44.2.2 Prepare dilutions of the stock nickel solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

44.3 *General Instrumental Parameters*:

44.3.1 *Nickel Hollow Cathode Lamp*.

44.3.2 *Wavelength*—232.0 nm.

44.3.3 *Fuel*—Acetylene.

44.3.4 *Oxidant*—Air.

44.3.5 *Type of Flame*—Oxidizing.

44.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration", 11.1.

44.5 *Interferences*—The 352.4-nm wavelength is less susceptible to interference and may be used. The calibration curve is more linear at this wavelength; however, there is some loss of sensitivity.

45. Nickel—Furnace Technique

45.1 *Requirements*:

45.1.1 *Optimum Concentration Range*, 5 to 100 µg/L (see Note 110).

45.1.2 *Detection Limit*, 1 µg/L.

NOTE 110—The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection, continuous flow purge gas and pyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the recommended settings.

45.2 *Preparation of Standard Solution*:

45.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

45.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

45.2.3 The calibration standard should be diluted to contain 0.5 % (v/v) HNO_3.

45.3 *General Instrument Parameters*:

45.3.1 *Drying Time and Temperature*—30 s at 125°C.

45.3.2 *Ashing Time and Temperature*—30 s at 900°C.

45.3.3 *Atomizing Time and Temperature*—10 s at 2700°C.

45.3.4 *Purge Gas Atmosphere*—Argon.

45.3.5 *Wavelength*—232.0 nm.

45.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE 111—The use of background correction is recommended.
NOTE 112—Nitrogen may also be used as the purge gas.

45.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure", 11.3.

NOTE 113—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).
NOTE 114—If the method of standard additions is required, follow the procedure given in 10.5.

46. Potassium—Direct Aspiration

46.1 *Requirements*:

46.1.1 *Optimum Concentration Range*—0.1 to 2 mg/L using a wavelength of 766.5 nm (see Note 115).

46.1.2 *Sensitivity*—0.04 mg/L.

46.1.3 *Detection Limit*—0.01 mg/L.

NOTE 115—The 404.4-nm line may also be used. This line has a relative sensitivity of 500.

46.2 *Preparation of Standard Solution*:

46.2.1 *Stock Solution*—Dissolve 0.1907 g of KCl (analytical reagent grade), dried at 110°C, in deionized distilled water and make up to 1 L. 1 mL = 0.10 mg K (100 mg/L).

46.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

46.3 *General Instrumental Parameters*:

46.3.1 *Potassium Hollow Cathode Lamp*.

46.3.2 *Wavelength*—766.5 nm.

46.3.3 *Fuel*—Acetylene.

46.3.4 *Oxidant*—Air.

46.3.5 *Type of Flame*—Slightly oxidizing.

46.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration", 11.1.

NOTE 116—In air-acetylene or other high temperature flames (>2800°C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1000 µg/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks should be analyzed to correct for potassium impurities in the buffer stock.

NOTE 117—To cover the range of potassium values normally observed in surface waters (0.1 to 20 mg/L), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides approximately one-eighth the normal sensitivity.

47. Selenium—Furnace Technique

47.1 *Requirements*:

47.1.1 *Optimum Concentration Range*, 5 to 100 µg/L (see Note 118).

47.1.2 *Detection Limit*, 2 µg/L.

NOTE 118—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection, continuous flow purge gas and non-pyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

47.2 *Preparation of Standard Solution*:

47.2.1 *Stock Selenium Solution*—Dissolve 0.3453 g of selenous acid (actual assay 94.6 % H_2SeO_3) in deionized distilled water and make up to 200 mL. 1 mL = 1 mg Se (1000 mg/L).

47.2.2 *Nickel Nitrate Solution, 5 %*—Dissolve 24.780 g of ACS reagent grade Ni $(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 mL.

47.2.3 *Nickel Nitrate Solution, 1 %*—Dilute 20 mL of the 5 % nickel nitrate to 100 mL with deionized distilled water.

47.2.4 *Working Selenium Solution*—Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30 % H_2O_2 and 2 mL of the 5 % nickel nitrate solution. Dilute to 100 mL with deionized distilled water.

47.3 *Sample Preparation*:

47.3.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker, add 2 mL of 30 % H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1 % (v/v). Heat for 1 h at 95°C or until the volume is slightly less than 50 mL.

47.3.2 Cool and bring back to 50 mL with deionized distilled water.

47.3.3 Pipet 5 mL of this digested solution into a 10 mL volumetric flask, add 1 mL of the 1 % nickel nitrate solution and dilute to 10 mL with deionized distilled water. The sample is now ready for injection into the furnace.

NOTE 119—If solubilization or digestion is not required, adjust the HNO_3 concentration of the sample to 1 % (v/v) and add 2 mL of 30 % H_2O_2 and 2 mL of 5 % nickel nitrate to each 100 mL of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

47.4 *Instrument Parameters*:

47.4.1 *Drying Time and Temperature*—30 s at 125°C.

47.4.2 Charring Time and Temperature—30 s at 1200°C.

47.4.3 *Atomizing Time and Temperature*—10 s at 2700°C.

47.4.4 *Purge Gas Atmosphere*—Argon.

47.4.5 *Wavelength*—196.0 nm.

47.4.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE 120—The use of background correction is recommended.

47.5 *Analysis Procedure*—For the analysis procedure and the calculation see "Furnace Procedure," 11.3.

NOTE 121—Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/L, both samples and standards should be prepared to contain 1 % nickel.

NOTE 122—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 123—If the method of standard additions is required, follow the procedure given in 10.5.

48. Selenium—Gaseous Hydride

48.1 *Scope and Application*—The gaseous hydride method determines inorganic selenium when present in concentrations at or above 2 µg/L. The test method is applicable in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver.

48.2 *Summary of Test Method*—Selenium in the sample is reduced from the + 6 oxidation state to the + 4 oxidation state by the addition of $SnCl_2$. Zinc is added to the acidified sample, producing hydrogen and converting the selenium to the hydride, SeH_2. The gaseous selenium hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the test method is 2 to 20 µg/L using the 196.0-nm wavelength.

48.3 *Discussion*:

48.3.1 In analyzing drinking water and most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of selenium to establish adequate recovery.

48.3.2 Organic forms of selenium must be converted to an inorganic form and organic matter must be oxidized before beginning the analysis. The oxidation procedure given in Procedure 4.1 of Method 206.5 should be used **(13)**.

48.4 References

48.4.1 Except for the perchloric acid step, the procedure to be used for this determination is found in *Standard Methods for the Examination of Water and Wastewater* **(14).**

49. Silver—Direct Aspiration

49.1 *Requirements*:

49.1.1 Optimum Concentration Range, 0.1 to 4 mg/L using a wavelength of 328.1 nm (see Note 124 and Note 125).

49.1.2 *Sensitivity*, 0.06 mg/L.

49.1.3 *Detection Limit*, 0.01 mg/L.

NOTE 124—For levels of silver below 30 µg/L, either the Special Extraction Procedure, given in 11.2 or the furnace procedure is recommended.

NOTE 125—The 338.2-nm wavelength may also be used. This has a relative sensitivity of 2.

49.2 *Preparation of Standard Solution*:

49.2.1 *Stock Solution*—Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in deionized distilled water, add 10 mL concentrated HNO_3 and make up to 1 L. 1 mL = 1 mg Ag (1000 mg/L).

NOTE 126—Silver nitrate standards are light sensitive. Dilutions of the stock should be discarded after use as concentrations below 10 mg/L are not stable over long periods of time.

49.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using nitric acid and at the same concentration as that of the sample being analyzed either directly or after processing.

49.2.3 *Iodine Solution* (1 *N*)—Dissolve 20 g of potassium iodide, KI (analytical reagent grade) in 50 mL of deionized distilled water, add 12.7 g of iodine, I_2 (analytical reagent grade) and dilute to 100 mL. Store in a brown bottle.

49.2.4 *Cyanogen Iodide* (CNI) *Solution*—To 50 mL of deionized distilled water add 4.0 mL concentrated NH_4OH, 6.5 g KCN, and 5.0 mL of 1.0 N I_2 solution. Mix and dilute to 100 mL with deionized distilled water. Fresh solution should be prepared every 2 weeks.

49.3 *General Instrumental Parameters*:

49.3.1 *Silver Hollow Cathode Lamp*.

49.3.2 Wavelength—328.1 nm.

49.3.3 *Fuel*—Acetylene.

49.3.4 *Oxidant*—Air.

49.3.5 *Type of Flame*—Oxidizing.

49.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Direct Aspiration," 11.1.

NOTE 127—If absorption to container walls or the formation of AgCl is suspected, make the sample basic using concentrated NH_4OH and add 1 mL of (CNI) solution per 100 mL of sample. Mix the sample and allow to stand for 1 h before proceeding with the analysis.

50. Silver—Furnace Technique

50.1 *Requirements*:

50.1.1 *Optimum Concentration Range*—1 to 25 µg/L (see Note 128).

50.1.2 *Detection Limit*—0.2 µg/L.

NOTE 128—The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection, continuous flow purge gas and nonpyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

50.2 *Preparation of Standard Solution* :

50.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

50.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

50.2.3 The calibration standard should be diluted to contain 0.5 % (v/v) HNO_3.

NOTE 129—The use of halide acids should be avoided.

50.3 *General Instrument Parameters*:

50.3.1 *Drying Time and Temperature*—30 s at 125°C.

50.3.2 *Ashing Time and Temperature*—30 s at 400°C.

50.3.3 *Atomizing Time and Temperature*—10 s at 2700°C.

50.3.4 *Purge Gas Atmosphere*—Argon.

50.3.5 *Wavelength*—328.1 nm.

50.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE 130—Background correction may be required if the sample contains high dissolved solids.

50.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure," 11.3 (see Note 2, Note 4, Note 5, and Note 6).

NOTE 131—If adsorption to container walls or formation of AgCl is suspected, see the Direct Aspiration Method.
NOTE 132—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).
NOTE 133—If the method of standard additions is required, follow the procedure given in 10.5.

51. Sodium—Direct Aspiration

51.1 *Requirements*:

51.1.1 *Optimum Concentration Range*, 0.03 to 1 mg/L using a wavelength of 589.6 nm (see Note 134).

51.1.2 *Sensitivity*, 0.015 mg/L.

51.1.3 *Detection Limit*, 0.002 mg/L.

NOTE 134—The 330.2 nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.

51.2 *Preparation of Standard Solution*:

51.2.1 *Stock Solution*—Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in deionized distilled water and make up to 1 L. 1 mL = 1 mg Na (1000 mg/L).

51.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

51.3 *General Instrumental Parameters*:

51.3.1 *Sodium Hollow Cathode Lamp*.

51.3.2 *Wavelength*—589.6 nm.

51.3.3 *Fuel*—Acetylene.

51.3.4 *Oxidant*—Air.

51.3.5 *Type of Flame*—Oxidizing.

NOTE 135—Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1000 mg/L) to both standards and samples.

51.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

52. Tin—Direct Aspiration

52.1 *Requirements*:

52.1.1 Optimum Concentration Range, 10 to 300 mg/L using a wavelength of 286.3 nm (see Note 136).

52.1.2 *Sensitivity*, 4 mg/L.

52.1.3 *Detection Limit*, 0.8 mg/L.

NOTE 136—For concentrations of tin below 2 mg/L, the furnace procedure is recommended.

52.2 *Preparation of Standard Solution*:

52.2.1 *Stock Solution*—Dissolve 1.000 g of tin metal (analytical reagent grade) in 100 mL of concentrated HCl and dilute to 1 L with deionized distilled water. 1 mL = 1 mg Sn (1000 mg/L).

52.2.2 Prepare dilutions of the stock tin solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

52.3 *General Instrumental Parameters*:

52.3.1 *Tin Hollow Cathode Lamp*.

52.3.2 *Wavelength*—286.3 nm.

52.3.3 *Fuel*—Acetylene.

52.3.4 *Oxidant*—Nitrous oxide.

52.3.5 *Type of Flame*—Fuel rich.

52.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Direct Aspiration," 11.1.

53. Tin—Furnace Technique

53.1 *Requirements*:

53.1.1 *Optimum Concentration Range*, 20 to 300 µg/L (see Note 137).

53.1.2 *Detection Limit*, 5 µg/L.

Note 137—The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 µL injection, continuous flow purge gas and non-pyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the recommended settings.

53.2 *Preparation of Standard Solution*:

53.2.1 *Stock Solution*—Prepare as described under "direct aspiration method".

53.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".

53.2.3 The calibration standard should be diluted to contain 2 % (v/v) HNO_3.

53.3 *Instrument Parameters*:

53.3.1 *Drying Time and Temperature*—30 s at 125°C.

53.3.2 *Ashing Time and Temperature*—30 s at 600°C.

53.3.3 *Atomizing Time and Temperature*—10 s at 2700°C.

53.3.4 *Purge Gas Atmosphere*—Argon.

53.3.5 *Wavelength*—224.6 nm.

53.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

Note 138—The use of background correction is recommended.

Note 139—Nitrogen may also be used as the purge gas.

53.4 *Analysis Procedure*—For the analysis procedure and the calculation see "Furnace Procedure," 11.3.

Note 140—Tin analysis is sensitive to chloride concentration. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess of 5 mg of ammonium nitrate to the furnace and ash using a ramp necessary or with incremental steps until the recommended ashing temperature is reached. Extended ashing times have been reported to improve precision.

Note 141—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

Note 142—If the method of standard additions is required, follow the procedure given in 10.5.

54. Titanium—Direct Aspiration

54.1 *Requirements*:

54.1.1 *Optimum Concentration Range*, 5 to 100 mg/L using a wavelength of 365.3 nm (see Note 143).

54.1.2 *Sensitivity*, 2 mg/L.

54.1.3 *Detection Limit*, 0.4 mg/L.

Note 143—For concentrations of titanium below 1.0 mg/L, the furnace procedure is recommended.

54.2 *Preparation of Standard Solution*:

54.2.1 *Stock Solution*—Dissolve 4.008 g of titanium sulfate, $Ti_2(SO_4)_3$, in dilute HCl and make up to 1 L with deionized distilled water. 1 mL = 1 mg Ti (1000 mg/L).

54.2.2 *Potassium Chloride Solution*—Dissolve 95 g potassium chloride, KCl, in distilled water and make up to 1 L.

54.2.3 Prepare dilutions of the stock titanium solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing. To each 100 mL of standard and sample alike, add 2 mL of potassium chloride solution.

54.3 *General Instrumental Parameters*:

54.3.1 *Titanium Hollow Cathode Lamp*.

54.3.2 *Wavelength*—365.3 nm.

54.3.3 *Fuel*—Acetylene.

54.3.4 *Oxidant*—Nitrous oxide.

54.3.5 *Type of Flame*—Fuel rich.

54.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Direct Aspiration," 11.1.

54.5 *Interferences*—A number of elements increase the sensitivity of titanium. To control this problem, potassium (1000 mg/L) must be added to standards and samples alike **(15)**.

55. Titanium Furnace Technique

55.1 *Requirements*:

55.1.1 *Optimum Concentration Range*, 50 to 500 µg/L (see Note 144).

55.1.2 *Detection Limit*, 10 µg/L.

Note 144—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection, continuous flow purge gas and pyrolytic graphite.

55.2 *Preparation of Standard Solution*:

55.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

55.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis.

55.2.3 The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

55.3 *General Instrument Parameters*:

55.3.1 *Drying Time and Temperature*—30 s at 125°C.

55.3.2 *Ashing Time and Temperature*—30 s at 1400°C.

55.3.3 *Atomizing Time and Temperature*—15 s at 2800°C.

55.3.4 *Purge Gas Atmosphere*—Argon.

55.3.5 *Wavelength*—365.4 nm.

55.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

Note 145—Background correction may be required if the sample contains high dissolved solids.

Note 146—Because of possible chemical interactions, nitrogen should not be used as the purge gas.

55.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure," 11.3.

Note 147—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

Note 148—If the method of standard additions is required, follow the procedure given in 10.5.

56. Vanadium—Direct Aspiration

56.1 *Requirements*:

56.1.1 *Optimum Concentration Range*—2 to 100 mg/L using a wavelength of 318.4 nm (see Note 149).

56.1.2 *Sensitivity*—0.8 mg/L.

56.1.3 *Detection Limit*—0.2 mg/L.

Note 149—For concentrations of vanadium below 0.5 mg/L, the furnace procedure is recommended.

56.2 *Preparation of Standard Solution*:

56.2.1 *Stock Solution*—Dissolve 1.7854 g of vanadium pentoxide, V_2O_5 (analytical reagent grade) in 10 mL of concentrated nitric acid and dilute to 1 L with deionized distilled water. 1 mL = 1 mg V (1000 mg/L).

56.2.2 *Aluminum Nitrate Solution*—Dissolve 139 g aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, in 150 mL of deionized distilled water; heat to effect solution. Allow to cool and make up to 200 mL.

56.2.3 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing. To each 100 mL of standard and sample alike, add 2 mL of the aluminum nitrate solution.

56.3 *General Instrumental Parameters*:

56.3.1 *Vanadium Hollow Cathode Lamp* .

56.3.2 *Wavelength*—318.4 nm.

56.3.3 *Fuel*—Acetylene.

56.3.4 *Oxidant*—Nitrous oxide.

56.3.5 *Type of Flame*—Fuel rich.

56.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Direct Aspiration," 11.1.

56.5 *Interferences*—It has been reported that high concentrations of aluminum and titanium increase the sensitivity of vanadium. This interference can be controlled by adding excess aluminum (1000 ppm) to both samples and standards **(16)**.

57. Vanadium—Furnace Technique

57.1 *Requirements*:

57.1.1 *Optimum Concentration Range*, 10 to 200 µg/L (see Note 150).

57.1.2 *Detection Limit*, 4 µg/L.

Note 150—The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection, continuous flow purge gas and pyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

57.2 *Preparation of Standard Solution*:

57.2.1 *Stock Solution*—Prepare as described under "direct aspiration method."

57.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

57.2.3 The calibration standard should be diluted to contain 0.5 % (v/v) HNO_3.

57.3 *General Instrument Parameters*:

57.3.1 *Drying Time and Temperature*—30 s at 125°C.

57.3.2 *Ashing Time and Temperature*—30 s at 1400°C.

57.3.3 *Atomizing Time and Temperature*—15 s at 2800°C.

57.3.4 *Purge Gas Atmosphere*—Argon.

57.3.5 *Wavelength*—318.4 nm.

57.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

Note 151—Background correction may be required if the sample contains high dissolved solids.

Note 152—Because of possible chemical interaction, nitrogen should not be used as the purge gas.

57.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure," 11.3.

Note 153—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

Note 154—If the method of standard additions is required, follow the procedure given in 10.5.

58. Zinc—Direct Aspiration

58.1 *Requirements*:

58.1.1 *Optimum Concentration Range*, 0.05 to 1 mg/L using a wavelength of 213.9 nm (see Note 155).

58.1.2 *Sensitivity*, 0.02 mg/L.

58.1.3 *Detection Limit*, 0.005 mg/L.

Note 155—For concentrations of zinc below 0.01 mg/L, either the Special Extraction Procedure or the Furnace Procedure, is recommended.

58.2 *Preparation of Standard Solution*:

58.2.1 *Stock Solution*—Carefully weigh 1.00 g of zinc metal (analytical reagent grade) and dissolve cautiously in 10 mL HNO_3. When solution is complete make up to 1 L with deionized distilled water. 1 mL = 1 mg Zn (1000 mg/L).

58.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid and at the same concentration as that of the sample being analyzed either directly or after processing.

58.3 *Instrumental Parameters*:

58.3.1 *Zinc Hollow Cathode Lamp*.

58.3.2 *Wavelength*—13.9 nm.

58.3.3 *Fuel*—Acetylene.

58.3.4 *Oxidant*—Air.

58.3.5 *Type of Flame*—Oxidizing.

58.4 *Analysis Procedure*—For analysis procedure and calculation, see "Direct Aspiration," 11.1.

Note 156—High levels of silicon may interfere.

Note 157—The air-acetylene flame absorbs about 25 % of the energy at the 213.9 nm line.

Note 158—The sensitivity may be increased by the use of low-temperature flames.

Note 159—Some sample container cap liners can be a source of zinc contamination. To circumvent or avoid this problem, the use of polypropylene caps is recommended.

59. Zinc—Furnace Technique

59.1 *Requirements*:

59.1.1 *Optimum Concentration Range*—0.2 to 4 µg/L (see Note 160).

59.1.2 *Detection Limit*—0.05 µg/L.

Note 160—The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-µL injection,

continuous flow purge gas and non-pyrolytic graphite. Smaller sized furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the recommended settings.

59.2 *Preparation of Standard Solution*:

59.2.1 *Stock Solution*—Prepare as described under "Direct Aspiration Method."

59.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

59.2.3 The calibration standard should be diluted to contain 0.5 % (v/v) HNO_3.

59.3 *General Instrument Parameters*:

59.3.1 *Drying Time and Temperature*—30 s at 125°C.

59.3.2 *Ashing Time and Temperature*—30 s at 400°C.

59.3.3 *Atomizing Time and Temperature*—10 s at 2500°C.

59.3.4 *Purge Gas Atmosphere*—Argon.

59.3.5 *Wavelength*—213.9 nm.

59.3.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE 161—The use of background correction is recommended.

NOTE 162—Nitrogen may also be used as a purge gas.

59.4 *Analysis Procedure*—For the analysis procedure and the calculation, see "Furnace Procedure," 11.3.

NOTE 163—The analysis of zinc by the graphite furnace is extremely sensitive and very subject to contamination from the work area, reagents, and pipet tips. Since all these factors affect the precision and accuracy, zinc should be analyzed by the direct aspiration procedure whenever possible.

NOTE 164—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 165—If the method of standard additions is required, follow the procedure given in 10.5.

60. Precision and Bias

60.1 Precision and bias data for the methods described on RDF are not available at this time.

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