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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:

	Sections
Aluminum, Direct Aspiration	12
Aluminum, Furnace Technique	13
Antimony, Direct Aspiration	14
Antimony, Furnace Technique	15
Arsenic, Furnace Technique	16
Arsenic, Gaseous Hydride Method	17
Barium, Direct Aspiration	18
Barium, Furnace Technique	19
Beryllium, Direct Aspiration	20
Beryllium, Furnace Technique	21
Cadmium, Direct Aspiration	22
Cadmium, Furnace Technique	23
Calcium, Direct Aspiration	24
Chromium, Direct Aspiration	25
Chromium, Furnace Technique	26
Chromium, Chelation-Extraction	27
Chromium, Hexavalent, Chelation-Extraction	28
Cobalt, Direct Aspiration	29
Cobalt, Furnace Technique	30
Copper, Direct Aspiration	31
Copper, Furnace Technique	32
Iron, Direct Aspiration	33
Iron, Furnace Technique	34
Lead, Direct Aspiration	35
Lead, Furnace Technique	36
Lithium, Direct Aspiration	37
Magnesium, Direct Aspiration	38
Manganese, Direct Aspiration	39
Manganese, Furnace Technique	40
Mercury, Cold Vapor Technique	41
Molybdenum, Direct Aspiration	42
Molybdenum, Furnace Technique	43
Nickel, Direct Aspiration	44
Nickel, Furnace Technique	45
Potassium, Direct Aspiration	46
Selenium, Furnace Technique	47
Selenium, Gaseous Hydride	48
Silver, Direct Aspiration	49
Silver, Furnace Technique	50
Sodium, Direct Aspiration	51
Tin, Direct Aspiration	52
Tin, Furnace Technique	53
Titanium, Direct Aspiration	54
Titanium, Furnace Technique	55
Vanadium, Direct Aspiration	56
Vanadium, Furnace Technique	57
Zinc, Direct Aspiration	58
Zinc, Furnace Technique	59

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.

[1] These test methods are under the jurisdiction of ASTM Committee D34 on Waste Management and are the direct responsibility of Subcommittee D34.06 on Recovery and Reuse.

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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 17.2.3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 3223 Test Method for Total Mercury in Water[2]

E 926 Test Methods of Preparing Refuse-Derived Fuel (RDF) Samples for Analyses of Metals[3]

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 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

[2] *Annual Book of ASTM Standards,* Vol 11.01.
[3] *Annual Book of ASTM Standards,* Vol 11.04.

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.

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material prior to analysis (see Methods E 926E 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**).[4] 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).

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

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

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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.[5] 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 1193D 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.

NOTE 1—**Precaution:** 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. If metal impurities are found to be present, distill this mixture from a borosilicate glass distillation apparatus or use a spectrograde acid.

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

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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)*[6]—Prepare by adding 18 mL of analytical reagent grade pyrrolidine to 500 mL of chloroform in a litre flask.[7] 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 926E 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:

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

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.

[6] 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).

[7] An acceptable grade of pyrrolidine may be obtained from the Aldrich Chemical Co., 940 West St. Paul Ave., Milwaukee, WI 53233.

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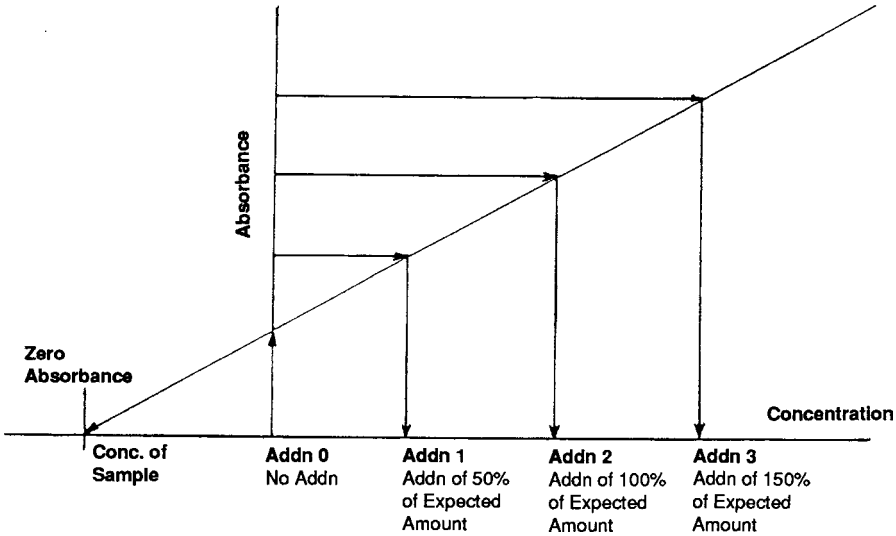

FIG. 1 Standard Addition Plot

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:

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

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:

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

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:

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

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)[8] 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 2—Certain metal chelates, manganese-APDC in particular, are not stable in MIBK and will redissolve into the aqueous phase on

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

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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 3—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:

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

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.[9] 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.[10]

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

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

[10] 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.

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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:

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

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:

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

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*:

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

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*:

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

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 4 and Note 5).

12.1.2 *Sensitivity*, 1 mg/L.

12.1.3 *Detection Limit*, 0.1 mg/L.

NOTE 4—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 5—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 6).

13.1.2 *Detection Limit*, 3 µg/L.

NOTE 6—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."

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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 7 and Note 8).

NOTE 7—Background correction may be required if the sample contains high dissolved solids.

NOTE 8—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 9 and Note 10).

NOTE 9—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 10—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 11).

14.1.2 *Sensitivity*, 0.5 mg/L.

14.1.3 *Detection Limit*, 0.2 mg/L.

NOTE 11—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 12).

15.1.2 *Detection Limit*, 3 µg/L.

NOTE 12—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 13 and Note 14).

NOTE 13—The use of background correction is recommended.

NOTE 14—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 15, Note 16, and Note 17).

NOTE 15—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 16—For every sample matrix analyzed, verification is necessary to determine that the method of standard additions is not required (see 6.2.1).

NOTE 17—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 18).

16.1.2 *Detection Limit*, 1 µg/L.

NOTE 18—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.

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