

## 3113 METALS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY\*

## 3113 A. Introduction

## 1. Applications

Electrothermal atomic absorption permits determination of most metallic elements with sensitivities and detection levels from 20 to 1000 times better than those of conventional flame techniques without extraction or sample concentration. This increase in sensitivity results from an increase in atom density within the furnace as compared to flame atomic absorption. Many elements can be determined at concentrations of, or below, 1.0  $\mu\text{g/L}$ . An additional advantage of electrothermal atomic absorption is that only a very small volume of sample is required.

The electrothermal technique is used only at concentration levels below the optimum range of direct flame atomic absorption because it is subject to more interferences than the flame procedure and requires increased analysis time. The method of standard additions may be required to insure validity of data. Because of the high sensitivity of this technique, it is extremely susceptible to contamination; extra care in sample handling and analysis may be required.

## 2. Principle

Electrothermal atomic absorption spectroscopy is based on the same principle as direct flame atomization but an electrically heated atomizer or graphite furnace replaces the standard burner head. A discrete sample volume is dispensed into the graphite sample tube (or cup). Typically, determinations are made by heating the sample in three or more stages. First, a low current heats the tube to dry the sample. The second, or charring, stage destroys organic matter and volatilizes other matrix components at an intermediate temperature. Finally, a high current heats the tube to incandescence and, in an inert atmosphere, atomizes the element being determined. Additional stages frequently are added to aid in drying and charring, and to clean and cool the tube between samples. The resultant ground-state atomic vapor absorbs monochromatic radiation from the source. A photoelectric detector measures the intensity of transmitted radiation. The inverse of the transmittance is related logarithmically to the absorbance, which is directly proportional to the number density of vaporized ground-state atoms (the Beer-Lambert law) over a limited concentration range.

## 3. Interferences

Electrothermal atomization determinations may be subject to significant interferences from molecular absorption as well as chemical and matrix effects. Molecular absorption may occur

when components of the sample matrix volatilize during atomization, resulting in broadband absorption. Several background correction techniques are available commercially to compensate for this interference. A continuum source such as a deuterium arc can correct for background up to absorbance levels of about 0.8. Continuum lamp intensity diminishes at long wavelengths and use of continuum background correction is limited to analytical wavelengths below 350 nm. Zeeman effect background correctors can handle background absorbance up to 1.5 to 2.0. The self-reversal (e.g., Smith-Hieftje) correction technique can accommodate background absorbance levels as large as 2.5 to 3.0 (see Section 3111A.3b). Both Zeeman and self-reversal background corrections are susceptible to rollover (development of a negative absorbance-concentration relationship) at high absorbances. The rollover absorbance for each element should be available in the manufacturer's literature. Curvature due to rollover should become apparent during calibration; dilution produces a more linear calibration plot. Use background correction when analyzing samples containing high concentrations of acid or dissolved solids and in determining elements for which an absorption line below 350 nm is used.

Matrix modification can be useful in minimizing interference and increasing analytical sensitivity. Determine need for a modifier by evaluating recovery of a sample with a known addition. Recovery near 100% indicates that sample matrix does not affect analysis. Chemical modifiers generally modify relative volatilities of matrix and metal. Some modifiers enhance matrix removal, isolating the metal, while other modifiers inhibit metal volatilization, allowing use of higher ashing/charring temperatures and increasing efficiency of matrix removal. Chemical modifiers are added at high concentration (percent level) and can lead to sample contamination from impurities in the modifier solution. Heavy use of chemical modifiers may reduce the useful life (normally 50 to 100 firings) of the graphite tube. Nonetheless, the use of matrix modifiers is encouraged. Some specific chemical modifiers and approximate concentrations are listed in Table 3113:I.

Addition of a chemical modifier directly to the sample before analysis is restricted to inexpensive additives (e.g., phosphoric acid). Use of palladium salts for matrix modification normally requires methods of co-addition, in which sample and modifier are added consecutively to the furnace either manually or, preferably, with an automatic sampler. Palladium salts (nitrate is preferred, chloride is acceptable) are listed in Table 3113:I as a modifier for many metals. The palladium solution (50 to 2000 mg/L) generally includes citric or ascorbic acid, which aids reduction of palladium in the furnace. Citric acid levels of 1 to 2% are typical. Use of hydrogen (5%) in the purge gas (available commercially as a mixture) also reduces palladium, eliminating need for organic reducing acids. **CAUTION: Do not mix hydrogen and other gases in the laboratory; hydrogen gas is very flammable—handle with caution.** Use low levels of pal-

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Joint Task Group: 20th Edition—Raymond J. Lovett (chair), David J. Kaptain.

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TABLE 3113:I. POTENTIAL MATRIX MODIFIERS FOR ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY\*

Modifier	Analyses for Which Modifier May Be Useful
1500 mg Pd/L + 1000 mg Mg(NO <sub>3</sub> ) <sub>2</sub> /L <sup>1</sup>	Ag, As, Au, Bi, Cu, Ge, Mn, Hg, In, Sb, Se, Sn, Te, Tl
500–2000 mg Pd/L + reducing agent <sup>2†</sup>	Ag, As, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb
5000 mg Mg(NO <sub>3</sub> ) <sub>2</sub> /L <sup>1</sup>	Be, Co, Cr, Fe, Mn, V
100–500 mg Pd/L <sup>2</sup>	As, Ga, Ge, Sn
50 mg Ni/L <sup>2</sup>	As, Se, Sb
2% PO <sub>4</sub> <sup>3-</sup> + 1000 mg Mg (NO <sub>3</sub> ) <sub>2</sub> /L <sup>1</sup>	Cd, Pb

\* Assumes 10 μL modifier/10 μL sample.

† Citric acid (1–2%) preferred; ascorbic acid or H<sub>2</sub> acceptable.

ladium (50 to 250 mg/L) for normal samples and higher levels for complex samples. Addition of excess palladium modifier may widen atomization peaks; in such cases peak area measurements may provide higher quality results. The recommended mode of modifier use is through co-addition to the furnace of about 10 μL of the palladium (or other) modifier solution. Palladium may not be the best modifier in all cases and cannot be recommended unconditionally. Test samples requiring a modifier first with palladium; test other modifiers only if palladium is unsuccessful or to minimize modifier cost. See 3113B.3d for preparation of modifier solution.

Temperature ramping, i.e., gradual heating, can be used to decrease background interferences and permits analysis of samples with complex matrices. Ramping permits a controlled, continuous increase of furnace temperature in any of the various steps of the temperature sequence. Ramp drying is used for samples containing mixtures of solvents or for samples with a high salt content (to avoid spattering). If spattering is suspected, develop drying ramp by visual inspection of the drying stage, using a mirror. Samples that contain a complex mixture of matrix components sometimes require ramp charring to effect controlled, complete thermal decomposition. Ramp atomization may minimize background absorption by permitting volatilization of the element being determined before the matrix. This is especially applicable in the determination of such volatile elements as cadmium and lead. Use of time-resolved absorbance profiles (available on most modern instruments) greatly aids method development. Changes in atomization, notably the element peak appearance time and magnitude of background and metal absorbances, can be monitored directly.

Improve analysis by using a graphite platform, inserted into the graphite tube, as the atomization site. The platform is not heated as directly by the current flowing through the graphite tube; thus the metal atomizes later and under more uniform conditions.

Use standard additions to compensate for matrix interferences. When making standard additions, determine whether the added metal and that in the sample behave similarly under the specified conditions. [See 3113B.4d2)]. In the extreme, test every sample for recovery (85 to 115% recovery desired) to determine whether modification of the temperature program or use of the method of standard additions is needed. Test every new sample type for

TABLE 3113:II. DETECTION LEVELS AND CONCENTRATION RANGES FOR ELECTROTHERMAL ATOMIZATION ATOMIC ABSORPTION SPECTROMETRY

Element	Wavelength nm	Estimated Detection Level μg/L	Optimum Concentration Range μg/L
Al	309.3	3	20–200
Sb	217.6	0.8	20–300
As	193.7	0.5	5–100
Ba	553.6	2	10–200
Be	234.9	0.02	1–30
Cd	228.8	0.05	0.5–10
Cr	357.9	0.1	5–100
Co	240.7	0.7	5–100
Cu	324.7	0.7	5–100
Fe	248.3	1	5–100
Pb*	283.3	0.7	5–100
Mn	279.5	0.2	1–30
Mo	313.3	1	3–60
Ni	232.0	0.6	5–100
Se	196.0	0.6	5–100
Ag	328.1	0.2	1–25
Sn	224.6	1.7	20–300

\* The more sensitive 217.0-nm wavelength is recommended for instruments with background correction capabilities.

recovery. Recovery of only 40 to 85% generally indicates that standard addition is required. Often, as long as the samples are from sources of consistent properties, a representative recovery can be used to characterize the analysis and determine the necessity of standard addition. Test samples of unknown origin or of complex composition (digestates, for example) individually for metal recovery. Ideally, chemical modifiers and graphite platforms render the sample fit to be analyzed using a standard analytical calibration curve. Always verify this assumption; however, a properly developed method with judicious use of chemical modifiers should eliminate the necessity for standard addition in all but the most extreme samples.

Chemical interaction of the graphite tube with various elements to form refractory carbides occurs at high charring and atomization temperatures. Elements that form carbides are barium, molybdenum, nickel, titanium, vanadium, and silicon. Carbide formation is characterized by broad, tailing atomization peaks and reduced sensitivity. Using pyrolytically coated tubes for these metals minimizes the problem.

#### 4. Sensitivity, Detection Levels, and Optimum Concentration Range

Estimated detection levels and optimum concentration ranges are listed in Table 3113:II. These values may vary with the chemical form of the element being determined, sample composition, or instrumental conditions.

For a given sample, increased sensitivity may be achieved by using a larger sample volume or by reducing flow rate of the purge gas or by using gas interrupt during atomization. Note, however, that these techniques also will increase the effects of any interferences present. Sensitivity can be de-

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creased by diluting the sample, reducing sample volume, increasing purge-gas flow, or using a less sensitive wavelength. Use of argon, rather than nitrogen, as the purge gas generally improves sensitivity and reproducibility. Hydrogen mixed with the inert gas may suppress chemical interference and increase sensitivity by acting as a reducing agent, thereby aiding in producing more ground-state atoms. Pyrolytically coated graphite tubes can increase sensitivity for the more refractory elements and are recommended. The optical pyrometer/maximum power accessory available on some instruments also offers increased sensitivity with lower atomization temperatures for many elements.

Using the Stabilized Temperature Platform Furnace (STPF) technique, which is a combination of individual techniques, also offers significant interference reduction with improved sensitivity. Sensitivity changes with sample tube age. Discard graphite tubes when significant variations in sensitivity or poor reproducibility are observed. The use of high acid concentrations, brine samples, and matrix modifiers often drastically reduces tube life. Preferably use the graphite platform in such situations.

## 5. References

1. PERKIN-ELMER CORP. 1991. Summary of Standard Conditions for Graphite Furnace. Perkin-Elmer Corp., Norwalk, Conn.
2. ROTHERY, E., ed. 1988. Analytical Methods for Graphite Tube Atomizers. Varian Techtron Pty, Ltd., Mulgrave, Victoria, Australia.

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## 3113 B. Electrothermal Atomic Absorption Spectrometric Method

### 1. General Discussion

This method is suitable for determination of micro quantities of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin.

### 2. Apparatus

*a. Atomic absorption spectrometer:* See Section 3111A.6a. The instrument must have background correction capability.

*b. Source lamps:* See Section 3111A.6d.

*c. Graphite furnace:* Use an electrically heated device with electronic control circuitry designed to carry a graphite tube or cup through a heating program that provides sufficient thermal energy to atomize the elements of interest. Furnace heat controllers with only three heating steps are adequate only for fresh waters with low dissolved solids content. For salt waters, brines, and other complex matrices, use a furnace controller with up to seven individually programmed heating steps. Fit the furnace into the sample compartment of the spectrometer in place of the conventional burner assembly.

Use argon as a purge gas to minimize oxidation of the furnace tube and to prevent the formation of metallic oxides. Use graphite tubes with platforms to minimize interferences and to improve sensitivity.

*d. Readout:* See Section 3111A.6c.

*e. Sample dispensers:* Use microliter pipets (5 to 100  $\mu\text{L}$ ) or an automatic sampling device designed for the specific instrument.

*f. Vent:* See Section 3111A.6f.

*g. Cooling water supply:* Cool with tap water flowing at 1 to 4 L/min or use a recirculating cooling device.

*h. Membrane filter apparatus:* Use an all-glass filtering device and 0.45- $\mu\text{m}$  or smaller-pore-diameter membrane filters. For trace analysis of aluminum, use polypropylene or TFE devices.

### 3. Reagents

*a. Metal-free water:* See Section 3111B.3c.

*b. Hydrochloric acid, HCl, 1 + 1 and conc.*

*c. Nitric acid, HNO<sub>3</sub>, 1 + 1 and conc.*

*d. Matrix modifier stock solutions:*

1) *Magnesium nitrate*, 10 000 mg Mg/L: Dissolve 10.5 g Mg(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O in water. Dilute to 100 mL.

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2) *Nickel nitrate*, 10 000 mg Ni/L: Dissolve 4.96 g  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in water. Dilute to 100 mL.

3) *Phosphoric acid*, 10% (v/v): Add 10 mL conc  $\text{H}_3\text{PO}_4$  to water. Dilute to 100 mL.

4) *Palladium nitrate*, 4000 mg Pd/L: Dissolve 9.34 g  $\text{Pd}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  in water. Dilute to 1 L.

5) *Citric acid*, 4%: Dissolve 40 g citric acid in water. Dilute to 1 L.

NOTE: All of the modifier solutions recommended in Table 3113:I can be prepared with volumetric combination of the above solutions and water. For preparation of other matrix modifiers, see references or follow manufacturers' instructions.

*e. Stock metal solutions*: Refer to Sections 3111B.3j and 3114.

*f. Chelating resin*: 100 to 200 mesh\* purified by heating at 60°C in 10N NaOH for 24 h. Cool resin and rinse 10 times each with alternating portions of 1N HCl, metal-free water, 1N NaOH, and metal-free water.

*g. Metal-free seawater (or brine)*: Fill a 1.4-cm-ID  $\times$  20-cm-long borosilicate glass column to within 2 cm of the top with purified chelating resin. Elute resin with successive 50-mL portions of 1N HCl, metal-free water, 1N NaOH, and metal-free water at the rate of 5 mL/min just before use. Pass salt water or brine through the column at a rate of 5 mL/min to extract trace metals present. Discard the first 10 bed volumes (300 mL) of eluate.

#### 4. Procedures

*a. Sample pretreatment*: Before analysis, pretreat all samples as indicated below. Rinse all glassware with 1 + 1  $\text{HNO}_3$  and water. Carry out digestion procedures in a clean, dust-free laboratory area to avoid sample contamination. For digestion of trace aluminum, use polypropylene or TFE utensils to avoid leachable aluminum from glassware.

1) Dissolved metals and metals where sample turbidity is  $<1$  NTU—See Section 3030B. For samples requiring arsenic and/or selenium analysis add 3 mL 30% hydrogen peroxide/100 mL sample and an appropriate volume of nickel nitrate solution (see Table 3113:I) before analysis. Nickel may be deleted if palladium is co-added during analysis. For all other metals no further pretreatment is required except for adding a matrix modifier when necessary.

2) Total recoverable metals (Al, Sb, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, and Sn)—NOTE: Sb and Sn are not recovered unless HCl is used in the digestion. See Section 3030D. Quantitatively transfer digested sample to a 100-mL volumetric flask, add an appropriate amount of matrix modifier (see Table 3113:I), and dilute to volume with water.

3) Total recoverable metals (As, Se)—Transfer 100 mL of shaken sample, 1 mL conc  $\text{HNO}_3$ , and 2 mL 30%  $\text{H}_2\text{O}_2$  to a clean, acid-washed 250-mL beaker. Heat on a hot plate without allowing solution to boil until volume has been reduced to about 50 mL. Remove from hot plate and let cool to room temperature. Add an appropriate concentration of nickel (see Table 3113:I), and dilute to volume in a 100-mL volumetric flask with water. Substitution of palladium is uneconomical. Nickel may be de-

leted if palladium is co-added during analysis. Simultaneously prepare a digested blank by substituting water for sample and proceed with digestion as described above.

*b. Instrument operation*: Mount and align furnace device according to manufacturer's instructions. Turn on instrument and data collection system. Select appropriate light source and adjust to recommended electrical setting. Select proper wavelength and set all conditions according to manufacturer's instructions, including background correction. Background correction is important when elements are determined at short wavelengths or when sample has a high level of dissolved solids. Background correction normally is not necessary at wavelengths longer than 350 nm. If background correction above 350 nm is needed, deuterium arc background correction is not useful and other types must be used.

Select proper inert- or sheath-gas flow. In some cases, it is desirable to interrupt the inert-gas flow during atomization. Such interruption results in increased sensitivity by increasing residence time of the atomic vapor in the optical path. Gas interruption also increases background absorption and intensifies interference effects, but modern background correction methods usually eliminate these problems. Consider advantages and disadvantages of this option for each matrix when optimizing analytical conditions.

To optimize graphite furnace conditions, carefully adjust furnace temperature settings to maximize sensitivity and precision and to minimize interferences. Follow manufacturer's instructions.

Use drying temperatures slightly above the solvent boiling point and provide enough time and temperature for complete evaporation without boiling or spattering.

Select atomization temperature by determining the lowest temperature providing maximum sensitivity without significantly eroding precision. Optimize by a series of successive determinations at various atomization temperatures using a standard solution giving an absorbance of 0.2 to 0.5.

The charring temperature must be high enough to maximize volatilization of interfering matrix components yet too low to volatilize the element of interest. With the drying and atomization temperatures set to their optimum values, analyze a standard solution at a series of charring temperatures in increasing increments of 50 to 100°C. When the optimum charring temperature is exceeded, there will be a significant drop in sensitivity. Plot charring temperature versus sample absorbance: the optimum charring temperature is the highest temperature without reduced sensitivity. Verify optimization with major changes in sample matrix.

*c. Instrument calibration*: Prepare standard solutions for instrument calibration by diluting metal stock solutions. Prepare standard solutions every 2 weeks, or more frequently as needed if standard response indicates degradation of standard. A decrease in signal of more than 10% requires investigation and indicates the possible need for fresh standards.

Prepare a blank and at least three calibration standards in the appropriate concentration range (see Table 3113:II) for correlating element concentration and instrument response. Match the matrix of the standard solutions to those of the samples as closely as possible. In most cases, this simply requires matching the acid background of the samples. For seawaters or brines, however, use the metal-free matrix (3113B.3g) as the standard solution diluent. In addition, add the same concentration of matrix modifier (if required for sample analysis) to the standard solutions.

\* Chellex 100, or equivalent, available from Bio-Rad Laboratories, Richmond, CA.



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Inject a suitable portion of each standard solution, in order of increasing concentration. Analyze each standard solution in duplicate to verify method precision.

Construct an analytical curve by plotting the average peak absorbances or peak areas of the standard solution versus concentration on linear graph paper. Alternatively, use electronic instrument calibration if the instrument has this capability.

*d. Sample analysis:* Analyze all samples except those demonstrated to be free of matrix interferences (based on recoveries of 85 to 115% for known additions) using the method of standard additions. Analyze all samples at least in duplicate or until reproducible results are obtained. A variation of  $\leq 10\%$  is considered acceptable reproducibility. Average replicate values.

1) Direct determination—Inject a measured portion of pretreated sample into the graphite furnace. Use the same volume as was used to prepare the calibration curve. Usually add modifier immediately after the sample, preferably using an automatic sampler or a micropipet. Some methods require modifier to be injected before the sample. Co-addition of the modifier is acceptable. Use the same volume and concentration of modifier for all standards and samples. Dry, char, and atomize according to the preset program. Repeat until reproducible results are obtained.

Compare the average absorbance value or peak area to the calibration curve to determine concentration of the element of interest. Alternatively, read results directly if the instrument is equipped with this capability. If absorbance (or concentration) or peak area of the sample is greater than absorbance (concentration) or peak area of the most concentrated standard solution, dilute sample and reanalyze. If very large dilutions are required, another technique (e.g., flame AA or ICP) may be more suitable for this sample. Large dilution factors magnify small errors on final calculation. Keep acid background and concentration of matrix modifier (if present in the solutions) constant. Dilute the sample in a blank solution of acid and matrix modifiers.

Proceed to 3113B.5a.

2) Method of standard additions—Refer to ¶ c above. The method of standard additions is valid only when it falls in the linear portion of the calibration curve. Once instrument sensitivity has been optimized for the element of interest and the linear range for the element has been established, proceed with sample analyses.

Inject a measured volume of sample into furnace device. Dry, char or ash, and atomize samples according to preset program. Repeat until reproducible results are obtained. Record instrument response in absorbance or concentration as appropriate. Add a known concentration of the element of interest to a separate portion of sample so as not to change significantly the sample volume. Repeat the determination.

Add a known concentration (preferably twice that used in the first addition) to a separate sample portion. Mix well and repeat the determination. NOTE: These steps must yield results within the linear range of the method.

Using linear graph paper, plot average absorbance or instrument response for the sample and the additions on the vertical axis against the concentrations of the added element on the horizontal axis, using zero as the concentration for the sample. Draw a straight line connecting the three points and extrapolate to zero absorbance. The intercept at the horizontal axis is the

negative of the element concentration in the sample. The concentration axis to the left of the origin should be a mirror image of the axis to the right.

Some instruments can perform and calculate methods of standard additions. Use of these capabilities is acceptable.

## 5. Calculations

### a. Direct determination:

$$\mu\text{g metal/L} = C \times F$$

where:

$C$  = metal concentration as read directly from the instrument or from the calibration curve,  $\mu\text{g/L}$ , and

$F$  = dilution factor.

### b. Method of additions:

$$\mu\text{g metal/L} = C \times F$$

where:

$C$  = metal concentration as read from the method of additions plot,  $\mu\text{g/L}$ , and

$F$  = dilution factor.

## 6. Precision and Bias

Data typical of the precision and bias obtainable are presented in Tables 3113:III, IV, and V.

## 7. Quality Control

The QC practices considered to be an integral part of each method can be found in Section 3020. Although previous indications were that very low optimum concentration ranges were attainable for most metals (see Table 3113:II), data in Table 3113:III using variations of these protocols show that this may not be so. Exercise extreme care when applying this method to the lower concentration ranges. Verify analyst precision at the beginning of each analytical run by making triplicate analyses. Verify autosampler precision by checking volumes (by weight) delivered by the autosampler at routinely used injection volume settings.

## 8. Reference

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TABLE 3113:III. INTERLABORATORY SINGLE-ANALYST PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS<sup>1</sup>

Element	Concentration $\mu\text{g/L}$	Single-Analyst Precision % RSD					
		Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28	66	108	70	—	—	66
	125	27	35	24	—	—	34
	11 000	11	—	—	22	—	—
	58 300	27	—	—	19	—	—
	460	9	—	—	—	30	—
	2 180	28	—	—	—	4	—
As	10.5	20	13	13	13	56	18
	230	10	18	13	21	94	14
	9.78	40	25	15	74	23	11
Ba	227	10	6	8	11	15	6
	56.5	36	21	29	59	23	27
Be	418	14	12	20	24	24	18
	0.45	18	27	15	30	2	11
Cd	10.9	14	4	9	7	12	12
	0.43	72	49	1	121	35	27
Cr	12	11	17	22	14	11	15
	9.87	24	33	10	23	15	10
	236	16	7	11	13	16	7
Co	29.7	10	17	10	19	24	12
	420	8	11	13	14	9	5
Cu	10.1	49	47	17	17	—	30
	234	8	15	6	21	—	11
	300	6	—	—	—	11	—
	1 670	11	—	—	—	6	—
Fe	26.1	144	52	153	—	—	124
	455	48	37	45	—	—	31
	1 030	17	—	—	30	—	—
	5 590	6	—	—	32	—	—
	370	14	—	—	—	19	—
	2 610	9	—	—	—	18	—
Pb	10.4	6	19	17	21	19	33
	243	17	7	17	18	12	16
Mn	0.44	187	180	—	—	—	275
	14.8	32	19	—	—	—	18
	91.0	15	—	—	48	—	—
	484.0	4	—	—	12	—	—
	111.0	12	—	—	—	21	—
Ni	666.0	6	—	—	—	20	—
	26.2	20	26	25	24	18	9
	461.0	15	11	9	8	11	4
Se	10.0	12	27	16	35	41	13
	235.0	6	6	15	6	13	14
Ag	8.48	10	—	—	15	27	16
	56.5	14	—	—	7	16	23
	0.45	27	166	48	—	—	—
	13.6	15	4	10	—	—	—

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## ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY (3113)/Electrothermal Atomic Absorption Spectrometric Method

TABLE 3113:IV. INTERLABORATORY OVERALL PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS<sup>1</sup>

Element	Concentration $\mu\text{g/L}$	Overall Precision % RSD					
		Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28	99	114	124	—	—	131
	125	45	47	49	—	—	40
	11 000	19	—	—	43	—	—
	58 300	31	—	—	32	—	—
	460	20	—	—	—	47	—
	2 180	30	—	—	—	15	—
As	10.5	37	19	22	50	103	39
	230	26	16	16	17	180	21
	9.78	43	26	37	72	50	39
Ba	227	18	12	13	20	15	14
	56.5	68	38	43	116	43	65
Be	418	35	35	28	38	48	16
	0.45	28	31	15	67	50	35
Cd	10.9	33	15	26	20	9	19
	0.43	73	60	5	88	43	65
Cr	12	19	25	41	26	20	27
	9.87	30	53	24	60	41	23
	236	18	14	24	20	14	20
Co	29.7	13	26	17	18	21	17
	420	21	21	17	18	13	13
Cu	10.1	58	82	31	32	—	74
	234	12	33	19	21	—	26
	300	13	—	—	—	14	—
	1 670	12	—	—	—	13	—
Fe	26.1	115	93	306	—	—	204
	455	53	46	53	—	—	44
	1 030	32	—	—	25	—	—
	5 590	10	—	—	43	—	—
	370	28	—	—	—	22	—
	2 610	13	—	—	—	22	—
Pb	10.4	27	42	31	23	28	47
	243	18	19	17	19	19	25
Mn	0.44	299	272	—	—	—	248
	14.8	52	41	—	—	—	29
	91.0	16	—	—	45	—	—
	484.0	5	—	—	17	—	—
	111.0	15	—	—	—	17	—
Ni	666.0	8	—	—	—	24	—
	26.2	35	30	49	35	37	43
	461.0	23	22	15	12	21	17
Se	10.0	17	48	32	30	44	51
	235.0	16	18	18	17	22	34
Ag	8.48	23	—	—	16	35	34
	56.5	15	—	—	24	32	28
	0.45	57	90	368	—	—	—
	13.6	19	19	59	—	—	—

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ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY (3113)/Electrothermal Atomic Absorption Spectrometric Method

TABLE 3113:V. INTERLABORATORY RELATIVE ERROR DATA FOR ELECTROTHERMAL ATOMIZATION METHODS<sup>1</sup>

Element	Concentration <i>µg/L</i>	Relative Error %					
		Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28.0	86	150	54	—	—	126
	125.0	4	41	39	—	—	30
	11 000.0	2	—	—	14	—	—
	58 300.0	12	—	—	7	—	—
	460.0	2	—	—	—	11	—
	2 180.0	11	—	—	—	9	—
Sb	10.5	30	32	28	24	28	36
	230.0	35	14	19	13	73	39
As	9.78	36	1	22	106	13	16
	227.0	3	7	10	19	6	13
Ba	56.5	132	54	44	116	59	40
	418.0	4	0	0	13	6	60
Be	0.45	40	16	11	16	10	15
	10.9	13	2	9	7	8	8
Cd	0.43	58	45	37	66	16	19
	12.0	4	6	5	22	18	3
Cr	9.87	10	9	4	2	5	15
	236.0	11	0	9	13	5	8
Co	29.7	7	7	1	6	3	13
	420.0	12	8	8	11	5	18
Cu	10.1	16	48	2	5	—	15
	234.0	8	7	0	4	—	19
	300.0	4	—	—	—	21	—
	1 670.0	6	—	—	—	2	—
Fe	26.1	85	60	379	—	—	158
	455.0	43	22	31	—	—	18
	1 030.0	8	—	—	8	—	—
	5 590.0	2	—	—	12	—	—
	370.0	4	—	—	—	11	—
	2 610.0	35	—	—	—	2	—
Pb	10.4	16	10	17	1	34	14
	243.0	5	15	8	18	15	29
Mn	0.44	332	304	—	—	—	556
	14.8	10	1	—	—	—	36
	91.0	31	—	—	10	—	—
	484.0	42	—	—	4	—	—
	111.0	1	—	—	—	29	—
	666.0	6	—	—	—	23	—
Ni	26.2	9	16	10	7	33	54
	461.0	15	19	18	31	16	18
Se	10.0	12	9	6	36	17	37
	235.0	7	7	0	13	10	17
Ag	8.48	12	—	—	1	51	20
	56.5	16	—	—	8	51	22
	0.45	34	162	534	—	—	—
	13.6	3	12	5	—	—	—