Standard Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy[1]

This standard is issued under the fixed designation D1976; 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 This test method covers the determination of dissolved, total-recoverable, or total elements in drinking water, surface water, domestic, or industrial wastewaters.[2, 3]

1.2 It is the user's responsibility to ensure the validity of the test method for waters of untested matrices.

1.3 Table 1 lists elements for which this test method applies, with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization.[4] Actual working detection limits are sample dependent and as the sample matrix varies, these detection limits may also vary. In time, other elements may be added as more information becomes available and as required.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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 specific hazard statements, see Note 2 and Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[5]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

3.1 *Definitions*—For definitions of other terms used in this test method, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *calibration blank, n*—a volume of water containing the same acid matrix as the calibration standards (see 11.1).

3.2.2 *calibration standards, n*—a series of known standard solutions used by the analyst for calibration of the instrument (preparation of the analytical curve) (see 8.11).

3.2.3 *instrumental detection limit, n*—the concentration equivalent to a signal, due to the analyte, that is equal to three times the standard deviation of a series of ten replicate measures of a reagent-blank signal at the same wavelength.

3.2.4 *laboratory control sample, n*—a solution with the certified concentration(s) of the analytes.

3.2.5 *reagent blank, n*—a volume of water containing the same matrix as the calibration standards, carried through the entire analytical procedure.

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] The detailed report of EPA Method Study 27, Method 200.7 is available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA. A summary of the project is available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH.

[3] Fishman, M. J. and Friedman, L., "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments", *U.S. Geological Survey Techniques of Water-Resources Investigations*, Book 5, Chapter D1066, Open File Report 85-495, 1985, p. 659–671.

[4] Winge, R. K., Fassel, V. A., Peterson, V. J. and Floyd, M. A., "Inductively Coupled Plasma-Atomic Emission Spectroscopy," *An Atlas of Spectral Information*, Elsevier Science Publishing Co., Inc., New York, NY, 1985.

[5] 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.

***A Summary of Changes section appears at the end of this standard**

TABLE 1 Suggested Wavelengths and Estimated Detection Limits[4]

Element	Wavelength, nm[A]	Estimated detection limit, μg/L[B]
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Selenium	196.026	75
Silver	328.068	7
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[A] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see 6.1.1).
[B] The estimated detection limits as shown are taken from Winge, Fassel, et al.[4] They are given as a guide for approximate detection limits for the listed wavelengths. The actual test method instrumental detection limits are sample-dependent and may vary as the sample matrix varies (see 3.2.3).

3.2.6 *total, n*—the concentration determined on an unfiltered sample following vigorous digestion (see 12.3).

3.2.7 *total-recoverable, adj*—a term relating to element forms that are determinable by the digestion method that is included in this procedure (see 12.2).

4. Summary of Test Method

4.1 Elements are determined, either sequentially or simultaneously, by inductively-coupled argon plasma optical emission spectroscopy.

4.2 A background correction technique may be used to compensate for variable background contribution from high concentrations of major and trace elements.

5. Significance and Use

5.1 This test method is useful for the determination of element concentrations in many natural waters and wastewaters. It has the capability for the simultaneous determination of up to 20 elements. High sensitivity analysis can be achieved for some elements that are difficult to determine by other techniques such as Flame Atomic Absorption.

6. Interferences

6.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. These interferences can be summarized as follows:

6.1.1 Spectral interferences can be categorized as (*1*) overlap of a spectral line from another element; (*2*) unresolved overlap of molecular band spectra; (*3*) background contribution from continuous or recombination phenomena; and (*4*) background contribution from stray light from line emission of high concentration elements.

6.1.1.1 The effects described in 6.1.1 can be compensated for by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated for by a background correction adjacent to the analyte line.

6.1.1.2 Table 2 lists some interference effects for the rec-

TABLE 2 Analyte Concentration Equivalents, mg/L, Arising from Interferents at the 100 mg/L Level[A]

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	...	...	...	...	...	...	0.21	...	...	1.4
Antimony	206.833	0.47	...	2.9	...	0.08	...	...	...	0.25	0.45
Arsenic	193.696	1.3	...	0.44	...	...	...	...	...	...	1.1
Barium	455.403	...	...	...	...	...	...	...	...	...	...
Beryllium	313.042	...	...	...	...	...	...	...	...	0.04	0.05
Boron	249.773	0.04	...	...	...	0.32	...	...	...	...	...
Cadmium	226.502	...	...	...	...	0.03	...	...	0.02	...	...
Calcium	317.933	...	...	0.08	...	0.01	0.01	0.04	...	0.03	0.03
Chromium	267.716	...	...	...	...	0.003	...	0.04	...	...	0.04
Cobalt	228.616	...	...	0.03	...	0.005	...	...	0.03	0.15	...
Copper	324.754	...	...	...	...	0.003	...	...	...	0.05	0.02
Iron	259.940	...	...	...	...	...	0.12	0.12	...	...	...
Lead	220.353	0.17	...	...	...	...	...	...	...	...	...
Magnesium	279.079	...	0.02	0.11	...	0.13	0.002	0.25	...	0.07	0.12
Manganese	257.610	0.005	...	0.01	...	0.002	...	...	...	...	...
Molybdenum	202.030	0.05	...	...	...	0.03	...	...	...	...	...
Nickel	231.604	...	...	...	...	...	...	...	...	...	...
Selenium	196.026	0.23	...	...	...	0.09	...	...	...	...	...
Silicon	288.158	...	...	0.07	...	...	...	...	...	...	0.01
Sodium	588.995	...	...	...	...	...	...	...	...	0.08	...
Thallium	190.864	0.30	...	...	...	...	...	...	...	...	...
Vanadium	292.402	...	...	0.05	...	0.005	...	...	...	0.02	...
Zinc	213.856	...	...	...	0.14	...	...	...	0.29	...	...

[A] See Table 3 for concentrations used.

ommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

6.1.1.3 Only those interferents listed in Table 2 were investigated. The blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were considered as discernible if the interferent produced interference peaks or background shifts that corresponded to 2 to 5 % of the peaks generated by the analyte concentrations also listed in Table 3.

6.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies, especially in samples that may contain high dissolved solids or acid concentrations, or both. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of these samples or utilization of standard addition techniques, or both.

6.1.2.1 Salt buildup at the tip of the nebulizer is another problem that can occur from high dissolved solids. This salt buildup affects aerosol flow rate that can cause instrumental drift. To control this problem, wet the argon prior to nebulization, use a tip washer, or dilute the sample.

NOTE 1—Periodic inspection and cleaning of the nebulizer and torch components are highly recommended.

6.1.2.2 Reports indicate that better control of the argon flow rate improves instrument performance. This control of the argon flow rate can be accomplished with the use of mass flow controllers.

6.1.3 Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not pronounced with the ICP technique; however, if observed, they can be minimized by careful selection of operating conditions (incident power, plasma observation position, and so forth), by buffering the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte.

TABLE 3 Interferent and Analyte Elemental Concentrations[A]

Analytes	mg/L	Interferents	mg/L
Al	10	Al	1 000
As	10	Ca	1 000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1 000
Ca	1	Mg	1 000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

[A] This table indicates concentrations used for interference measurements in Table 2.

7. Apparatus

7.1 See the manufacturer's instruction manual for installation and operation of inductively-coupled argon plasma spectrometers.

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 reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[6] The high sensitivity of inductively-coupled argon plasma atomic emission spectrometry may require reagents of higher purity. Stock standard solutions are prepared from high purity metals, oxides, or nonhydroscopic reagent grade salts using Types I, II, and III reagent water, and ultrapure acids. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type I, II, or III of Specification D1193. It is the analyst's responsibility to assure that water is free of interferences. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the precision and bias of the test method. Type II water was specified at the time of round robin testing of this test method.

8.3 *Aqua Regia*—Mix three parts hydrochloric acid (sp gr 1.19) and one part concentrated nitric acid (sp gr 1.42) just before use.

NOTE 2—Exercise caution when mixing this reagent.

8.4 *Argon*—Welding grade equivalent or better.

8.5 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid, ultrapure or equivalent.

8.6 *Hydrochloric Acid* (1 + 1)—Add 1 vol of hydrochloric acid (sp gr 1.19) to 1 vol of water.

8.7 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid, ultrapure or equivalent.

8.8 *Nitric Acid* (1 + 1)—Add 1 vol of nitric acid (sp gr 1.42) to 1 vol of water.

8.9 *Nitric Acid* (1 + 499)—Add 1 vol of nitric acid (sp gr 1.42) to 499 vol of water.

[6] *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 *Annual 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.

8.10 *Stock Solutions*—Preparation of stock solutions for each element is listed in Table 4.

8.11 *Mixed Calibration Standard Solutions*—Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Note 3). Prior to preparing mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure the elements are compatible and stable.

NOTE 3—Mixed calibration standards will vary depending on the number of elements being determined. An example of mixed calibration standards for the simultaneous determination of 20 elements is as follows:

Mixed Standard Solution I—manganese, beryllium, cadmium, lead, and zinc
Mixed Standard Solution II—copper, vanadium, iron, and cobalt
Mixed Standard Solution III—molybdenum, arsenic, and selenium
Mixed Standard Solution IV—aluminum, chromium, and nickel
Mixed Standard Solution V—antimony, boron, magnesium, silver, and thallium

8.12 *Reagent Blank*—This must contain all the reagents and be the same volume as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

9. Hazards

9.1 The toxicity or carcinogenicity of each reagent used in this test method has not been precisely defined; however, each chemical should be treated as a potential health hazard. Adequate precautions should be taken to minimize personnel exposure to chemicals used in this procedure.

10. Sampling

10.1 Collect the samples in accordance with Practices D1066 or D3370 as applicable.

TABLE 4 Preparation of Metal Stock Solutions[A,B]

Element (Compound)	Weight, g	Solvent
Al	0.1000	HCl (1 + 1)
Sb	0.1000	Aqua regia
As_2O_3 [C]	0.1320	Water + 0.4 g NaOH
Be	0.1000	Aqua regia
H_3BO_3	0.5716	Water
Cd	0.1000	HNO_3 (sp gr 1.42)
Cr	0.1000	HCl (1 + 1)
Co	0.1000	HNO_3 (1 + 1)
Cu	0.1000	HNO_3 (1 + 1)
Fe	0.1000	HNO_3 (sp gr 1.42)
Pb	0.1000	HNO_3 (sp gr 1.42)
Mg	0.1000	HNO_3 (1 + 1)
Mn	0.1000	HNO_3 (1 + 1)
Ni	0.1000	HNO_3 (sp gr 1.42)
$(NH_4)_2MoO_4$	0.2043	Water
Na_2SeO_4 [D]	0.2393	Water
Ag	0.1000	HNO_3 (sp gr 1.42)
$TlNO_3$	0.1303	Water
NH_4VO_3	0.2297	HNO_3 (1 + 1)
Zn	0.1000	HNO_3 (1 + 1)

[A] Metal stock solutions, 1.00 mL = 100 µg of metal. Dissolve the listed weights of each compound or metal in 20 mL of specified solvent and dilute to 1 L. The metals may require heat to increase rate of dissolution.
[B] Where water is used as the solvent, acidify with 10 mL of HNO_3 (sp gr 1.42) and dilute to 1 L. See Section 8 for concentration of acids. Commercially available standards may be used. Alternative salts or oxides may also be used.
[C] Add 2 mL of HNO_3 (sp gr 1.42) and dilute to 1 L.
[D] Add 1 mL of HNO_3 (sp gr 1.42) and dilute to 1 L.

10.2 Preserve the samples by immediately adding nitric acid to adjust the pH to 2 at the time of collection. Normally, 2 mL of HNO_3 is required per L of sample. If only dissolved elements are to be determined, filter the sample through a 0.45-µm membrane filter before acidification (see Note 4). The holding time for the sample may be calculated in accordance with Practice D4841.

NOTE 4—Depending on the manufacturer, some filters have been found to be contaminated to various degrees with heavy metals. Care should be exercised in selecting a source for these filters. It is good practice to wash the filters with dilute nitric acid and a small portion of the sample before filtering.

11. Calibration and Standardization

11.1 Calibrate the instrument over a suitable concentration range for the elements chosen by atomizing the calibration blank and mixed standard solutions and recording their concentrations and signal intensities. Because the precision and bias for this test method was obtained using a two-point calibration, it is recommended that the instrument be calibrated using this procedure as outlined in the test method. Multiple-point calibration standards may be used, but it is the user's responsibility to ensure the validity of the test method. Regardless of the calibration procedure used, appropriate quality control (QC) is required to verify the calibration curve at the anticipated concentration range(s) before proceeding to the sample analysis. It is recommended that the calibration blank and standard be matrix matched with the same acid concentration contained in the samples.

12. Procedure

12.1 To determine dissolved elements, proceed with 12.4.

12.2 When determining total-recoverable elements, choose a volume of a well mixed, acid-preserved sample appropriate for the expected level of elements.

12.2.1 Transfer the sample to a beaker and add 2 mL of HNO_3 (1 + 1) and 10 mL of HCl (1 + 1) and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL, making certain the sample does not boil. Cool the sample, and if necessary filter or let insoluble material settle to avoid clogging of the nebulizer. Adjust to the original sample volume. To determine total-recoverable elements, proceed with 12.4.

12.3 When determining total elements, choose a volume of well mixed, acid-preserved sample appropriate for the expected level of elements.

12.3.1 Transfer the sample to a beaker. Add 3 mL of HNO_3 (sp gr 1.42). Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add 5 mL of HNO_3 (sp gr 1.42). Cover the beaker with a watch glass and return it to the hot plate. Increase the temperature of the hot plate so a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add 10 mL of HCl (1 + 1) and 15 mL of water per 100 mL of final solution and warm the beaker gently for 15 min to dissolve any precipitate or residue resulting from evaporation. Allow the sample to cool, wash the beaker walls and watch glass with water, and if necessary, filter or let insoluble material settle to avoid clogging the nebulizer. Adjust to the original sample volume. To determine total elements, proceed with 12.4.

NOTE 5—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

12.4 Atomize each solution to record its emission intensity or concentration. A sample rinse of HNO_3 (1 + 499) is recommended between samples.

13. Calculation

13.1 Subtract reagent blanks (see 8.12) from all samples. This subtraction is particularly important for digested samples requiring large quantities of acids to complete the digestion.

13.2 If dilutions are required, apply the appropriate dilution factor to sample values.

13.3 Report results in the calibration concentration units.

14. Precision and Bias[7]

14.1 The precision and bias data for this test method are based on an interlaboratory study conducted by the U.S. Environmental Protection Agency.[2]

14.2 The test design of the study meets the requirements of Practice D2777-86 for elements listed in this test method. Barium, calcium, lithium, potassium, silica, and sodium did not meet the requirements of Practice D2777-86 and are outlined in Appendix X1.

14.2.1 The test design is based on a form of the analysis of variance applying the approach and methods of the Youden Unit block design. In the Youden nonreplicate approach to determining the precision and bias of the analytical method, pairs of samples of similar but different concentrations are analyzed. The key in the Youden approach is to estimate precision from analyses of Youden pairs rather than through replicate analyses. In the referenced study, five Youden pairs of spike materials were prepared (Guide D5810). Six water types were included. Only the data from reagent water and surface water are presented here. Each water type was spiked with three of the five Youden pairs with the exception of reagent water, which was spiked with all five Youden pairs. Each water sample was prepared for analysis by both a total and a total-recoverable digestion procedure. A total of twelve laboratories participated in the study.

14.2.2 Type II water was specified for this round robin.

14.2.3 Twenty-seven different elements were included in the study and individual measurements of precision and bias were developed for each. Bias was related to mean recovery of the analyte. The equation used to summarize accuracy data over concentration for each water type/digestion type/element was:

$$X = a + b \times C$$

where:

X = mean recovery of the element,
a = intercept,
b = slope, and
C = concentration level of the element.

14.2.4 The precision of the test method has been related to the overall and single analyst variation of the test method.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1144. Contact ASTM Customer Service at service@astm.org.

TABLE 5 Regression Equations for Bias and Precision, µg/L, Reagent Water versus Surface Water (Aluminum, Antimony, Arsenic, Beryllium)

NOTE 1—X = mean recovery; C = true value for the concentration.

Water Type	Aluminum	Antimony	Arsenic	Beryllium
Total Digestion				
Applicable concentration range	(83 to 1434)	(411 to 1406)	(83 to 943)	(17 to 76)
Reagent water, hard				
Single-analyst precision	S_o = 0.05X + 3.72	S_o = 0.23X – 50.17	S_o = 0.07X + 8.28	S_o = 0.02X + 0.18
Overall precision	S_t = 0.07X + 9.34	S_t = 0.21X – 24.02	S_t = 0.11X + 2.96	S_t = 0.02X + 0.91
Bias	X = 0.91C + 6.62	X = 0.74C + 2.27	X = 1.03C – 12.03	X = 1.02C – 1.92
Surface water, hard				
Single-analyst precision	S_o = 0.00X + 40.75	S_o = 0.11X – 0.14	S_o = 0.05X + 7.79	S_o = 0.00X + 0.85
Overall precision	S_t = 0.10X + 67.23	S_t = 0.07X + 35.71	S_t = 0.10X + 10.55	S_t = 0.09X – 0.47
Bias	X = 0.98C + 90.54	X = 0.88C – 55.19	X = 1.00C – 16.02	X = 1.00C – 0.89
Total-Recoverable Digestion				
Applicable concentration range	(83 to 1434)	(411 to 1406)	(83 to 943)	(17 to 76)
Reagent water, soft				
Single-analyst precision	S_o = 0.05X + 25.05	S_o = 0.06X + 7.85	S_o = 0.07X + 6.12	S_o = 0.04X + 0.14
Overall precision	S_t = 0.10X + 28.72	S_t = 0.05X + 20.10	S_t = 0.12X + 2.99	S_t = 0.07X – 0.47
Bias	X = 0.93C + 28.40	X = 0.92C – 22.46	X = 1.01C – 2.08	X = 1.03C – 0.73
Reagent water, soft				
Single-analyst precision	S_o = 0.01X + 34.72	S_o = 0.06X + 0.97	S_o = 0.05X + 9.29	S_o = 0.02X + 0.43
Overall precision	S_t = 0.10X + 74.75	S_t = 0.07X + 14.28	S_t = 0.11X + 1.82	S_t = 0.01X + 15.4
Bias	X = 1.02C + 40.42	X = 0.95C – 34.50	X = 1.06C – 7.00	X = 1.04C – 2.08

Equations used to summarize precision data over concentration for each water type/digestion type/element were:

$$S_t = d + e \times X$$

where:

S_t = overall standard deviation, and

$$S_o = f + g \times X$$

where:

S_o = single analyst standard deviation,
f = intercept, and
g = slope.

The results for reagent water and surface water for these equations are presented in Tables 5-9.

14.2.5 These data may not apply to waters of other matrices; therefore, it is the responsibility of the analyst to ensure the validity of the test method in a particular matrix. Matrix effects and potential contamination encountered in this study can be found in Appendix X2.

14.3 Precision and bias for this test method conforms to Practice D2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777-08, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

15. Quality Control (QC)

15.1 The following quality control information is recommended for measuring elements in water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy.

15.2 The instrument shall be calibrated using a minimum of four calibration standards and a calibration blank. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

15.3 An instrument check standard shall be analyzed at a minimum frequency of 10 % throughout the batch analysis. The value of the instrument check standard shall fall between 80 % and 120 % of the true value.

15.4 Two method blanks shall be prepared ensuring that an adequate method blank volume is present for a minimum of seven repetitive analyses. The standard deviation of the method blank is used to determine the minimum detectable concentration of each sample and control in the batch.

15.5 A laboratory control sample should be analyzed with each batch of samples at a minimum frequency of 10 %.

15.6 If the QC for the sample batch is not within the established control limits, reanalyze the samples or qualify the results with the appropriate flags, or both (Practice D5847).

15.7 Blind control samples should be submitted by an outside agency in order to determine the laboratory performance capabilities.

16. Keywords

16.1 elements; inductively-coupled argon plasma atomic emission spectroscopy; simultaneous determination

TABLE 6 Regression Equations for Bias and Precision, µg/L, Reagent Water versus Surface Water (Boron, Cadmium, Chromium, Cobalt)

NOTE 1—X = mean recovery; C = true value for the concentration.

Water Type	Boron	Cadmium	Chromium	Cobalt
Total Digestion				
Applicable concentration range	(330 to 1179)	(18 to 776)	(25 to 470)	(58 to 843)
Reagent water, hard				
Single-analyst precision	$S_o = -0.02X + 62.67$	$S_o = 0.02X + 1.49$	$S_o = 0.01X + 3.74$	$S_o = 0.04X + 1.17$
Overall precision	$S_t = -0.02X + 75.99$	$S_t = 0.07X + 1.40$	$S_t = 0.02X + 4.72$	$S_t = 0.06X + 0.21$
Bias	$X = 0.97C - 39.09$	$X = 0.98C + 0.20$	$X = 0.98C - 0.96$	$X = 0.93C - 4.34$
Surface water, hard				
Single-analyst precision	$S_o = 0.02X + 73.05$	$S_o = 0.04X + 0.23$	$S_o = 0.01X + 2.83$	$S_o = 0.03X + 1.45$
Overall precision	$S_t = 0.11X + 38.83$	$S_t = 0.08X + 1.94$	$S_t = 0.07X + 2.77$	$S_t = 0.03X - 4.30$
Bias	$X = 0.94C + 0.99$	$X = 1.00C + 0.28$	$X = 0.98C + 2.18$	$X = 0.94C - 2.97$
Total-Recoverable Digestion				
Applicable concentration range	(330 to 1179)	(18 to 776)	(25 to 470)	(58 to 843)
Reagent water, soft				
Single-analyst precision	$S_o = 0.05X + 53.98$	$S_o = 0.03X + 1.07$	$S_o = 0.04X + 3.56$	$S_o = 0.05X - 0.22$
Overall precision	$S_t = 0.07X + 73.55$	$S_t = 0.05X + 1.36$	$S_t = 0.07X + 2.55$	$S_t = 0.06X + 2.29$
Bias	$X = 1.10C - 77.26$	$X = 1.01C + 0.45$	$X = 1.01C - 1.85$	$X = 0.93C - 1.01$
Reagent water, soft				
Single-analyst precision	$S_o = -0.02X + 62.90$	$S_o = 0.03X + 0.18$	$S_o = 0.02X + 5.18$	$S_o = 0.02X + 4.80$
Overall precision	$S_t = 0.06X + 32.16$	$S_t = 0.09X + 0.17$	$S_t = 0.05X + 6.83$	$S_t = 0.05X + 4.89$
Bias	$X = 1.07C - 2.83$	$X = 1.02C - 0.58$	$X = 0.98C + 0.30$	$X = 0.93C - 0.28$

TABLE 7 Regression Equations for Bias and Precision, µg/L, Reagent Water versus Surface Water (Copper, Iron, Lead, Magnesium)

NOTE 1—X = mean recovery; C = true value for the concentration.

Water Type	Copper	Iron	Lead	Magnesium
Total Digestion				
Applicable concentration range	(17 to 189)	(74 to 2340)	(85 to 943)	(73 to 4623)
Reagent water, hard				
Single-analyst precision	$S_o = 0.02X + 2.02$	$S_o = 0.04X + 2.34$	$S_o = 0.03X + 4.56$	$S_o = 0.03X + 0.24$
Overall precision	$S_t = 0.02X + 3.66$	$S_t = 0.04X + 17.09$	$S_t = 0.01X + 18.87$	$S_t = 0.04X + 17.24$
Bias	$X = 0.94C - 1.23$	$X = 0.99C - 11.50$	$X = 0.97C - 3.09$	$X = 1.01C - 5.94$
Surface water, hard				
Single-analyst precision	$S_o = 0.00X + 4.40$	$S_o = 0.11X + 3.13$	$S_o = 0.02X + 7.44$	$S_o = 0.02X + 58.13$
Overall precision	$S_t = 0.04X + 3.81$	$S_t = 0.14X + 26.28$	$S_t = 0.05X + 8.36$	$S_t = 0.10X + 41.28$
Bias	$X = 0.98C - 1.56$	$X = 0.98C\ \ 34.94$	$X = 0.98C - 4.58$	$X = 1.03C + 84.36$
Total-Recoverable Digestion				
Applicable concentration range	(17 to 189)	(74 to 2340)	(85 to 943)	(73 to 4623)
Reagent water, soft				
Single-analyst precision	$S_o = 0.03X + 1.73$	$S_o = 0.08X + 10.52$	$S_o = 0.05X + 4.18$	$S_o = 0.05X - 0.47$
Overall precision	$S_t = 0.05X + 2.55$	$S_t = 0.10X + 13.84$	$S_t = 0.10X + 3.09$	$S_t = 0.08X + 6.78$
Bias	$X = 0.98C - 4.68$	$X = 1.03C - 3.35$	$X = 0.99C + 11.21$	$X = 1.00C - 3.61$
Reagent water, soft				
Single-analyst precision	$S_o = 0.01X + 4.43$	$S_o = 0.01X + 53.15$	$S_o = 0.02X + 6.38$	$S_o = 0.15X + 0.24$
Overall precision	$S_t = 0.03X + 4.95$	$S_t = 0.05X + 51.00$	$S_t = 0.06X + 8.77$	$S_t = 0.19X + 109.84$
Bias	$X = 0.98C - 1.38$	$X = 1.01C + 10.13$	$X = 0.98C + 3.92$	$X = 0.96C + 104.38$

TABLE 8 Regression Equations for Bias and Precision, µg/L, Reagent Water versus Surface Water (Manganese, Molybdenum, Nickel, Selenium)

NOTE 1—X = mean recovery; C = true value for the concentration.

Water Type	Manganese	Molybdenum	Nickel	Selenium
Total Digestion				
Applicable concentration range	(17 to 943)	(73 to 1094)	(43 to 943)	(83 to 755)
Reagent water, hard				
Single-analyst precision	$S_o = 0.02X + 0.50$	$S_o = 0.04X + 0.97$	$S_o = 0.00X + 9.15$	$S_o = 0.04X + 3.82$
Overall precision	$S_t = 0.04X + 0.93$	$S_t = 0.08X - 1.77$	$S_t = 0.04X + 6.46$	$S_t = 0.11X + 13.14$
Bias	$X = 0.97C - 1.46$	$X = 0.97C - 2.93$	$X = 0.98C - 2.93$	$X = 0.92C - 0.48$
Surface water, hard				
Single-analyst precision	$S_o = 0.01X + 3.44$	$S_o = 0.06X - 2.60$	$S_o = 0.01X + 3.39$	$S_o = 0.03X + 7.53$
Overall precision	$S_t = 0.03X + 4.69$	$S_t = 0.09X - 2.27$	$S_t = 0.03X + 6.43$	$S_t = 0.13X + 15.91$
Bias	$X = 0.95C + 2.06$	$X = 0.96C + 1.30$	$X = 0.98C + 1.17$	$X = 0.91C + 6.31$
Total-Recoverable Digestion				
Applicable concentration range	(17 to 943)	(73 to 1094)	(43 to 943)	(83 to 755)
Reagent water, soft				
Single-analyst precision	$S_o = 0.04X + 0.29$	$S_o = 0.06X + 0.58$	$S_o = 0.05X + 1.98$	$S_o = 0.06X + 4.00$
Overall precision	$S_t = 0.06X + 0.86$	$S_t = 0.06X + 6.49$	$S_t = 0.06X + 3.33$	$S_t = 0.14X + 15.64$
Bias	$X = 0.98C - 0.78$	$X = 0.99C - 6.78$	$X = 1.00C - 0.66$	$X = 0.97C + 0.36$
Reagent water, soft				
Single-analyst precision	$S_o = 0.04X + 2.90$	$S_o = 0.02X + 4.55$	$S_o = 0.04X + 0.35$	$S_o = 0.05X + 3.05$
Overall precision	$S_t = 0.07X + 5.85$	$S_t = 0.02X + 7.08$	$S_t = 0.05X + 3.29$	$S_t = 0.12X - 0.02$
Bias	$X = 0.97C - 0.02$	$X = 1.02C - 5.90$	$X = 0.96C + 4.20$	$X = 0.95C - 3.25$

TABLE 9 Regression Equations for Bias and Precision, µg/L, Reagent Water versus Surface Water (Silver, Thallium, Vanadium, Zinc)

NOTE 1—X = mean recovery; C = true value for the concentration.

Water Type	Silver	Thallium	Vanadium	Zinc
Total Digestion				
Applicable concentration range	(17 to 189)	(126 to 953)	(41 to 1877)	(68 to 759)
Reagent water, hard				
Single-analyst precision	$S_o = 0.22X - 2.05$	$S_o = 0.00X + 24.72$	$S_o = 0.03X - 0.28$	$S_o = 0.00X + 8.29$
Overall precision	$S_t = 0.64X - 6.71$	$S_t = 0.07X + 25.10$	$S_t = 0.05X + 3.80$	$S_t = 0.02X + 10.91$
Bias	$X = 0.29C + 9.78$	$X = 0.93C - 16.28$	$X = 0.97C - 1.85$	$X = 0.97C - 3.04$
Surface water, hard				
Single-analyst precision	$S_o = 0.16X - 0.33$	$S_o = 0.06X - 1.59$	$S_o = 0.02X + 4.71$	$S_o = -0.00X + 5.17$
Overall precision	$S_t = 0.46X - 3.07$	$S_t = 0.06X + 3.70$	$S_t = 0.06X + 3.10$	$S_t = 0.05X + 7.17$
Bias	$X = 1.02C - 4.12$	$X = 0.90C - 15.59$	$X = 1.00C - 2.07$	$X = 0.98C + 0.57$
Total-Recoverable Digestion				
Applicable concentration range	(17 to 189)	(126 to 953)	(41 to 1877)	(68 to 759)
Reagent water, soft				
Single-analyst precision	$S_o = 0.15X + 1.35$	$S_o = 0.02X + 33.81$	$S_o = 0.05X + 0.78$	$S_o = 0.06X + 2.52$
Overall precision	$S_t = 0.83X - 12.00$	$S_t = 0.07X + 30.95$	$S_t = 0.06X + 5.41$	$S_t = 0.05X + 7.98$
Bias	$X = 0.23C + 13.92$	$X = 0.87C + 12.93$	$X = 0.97C - 1.32$	$X = 1.02C - 8.32$
Reagent water, soft				
Single-analyst precision	$S_o = 0.07X + 0.17$	$S_o = 0.14X - 1.80$	$S_o = 0.01X + 1.86$	$S_o = 0.01X + 9.04$
Overall precision	$S_t = 0.08X + 1.45$	$S_t = 0.15X - 0.58$	$S_t = 0.05X + 4.97$	$S_t = 0.00X + 16.57$
Bias	$X = 0.79C + 3.44$	$X = 0.84C - 6.86$	$X = 0.98C - 1.14$	$X = 1.01C - 8.67$

APPENDIXES

(Nonmandatory Information)

X1. ADDITIONAL TEST ELEMENTS BY INDUCTIVELY-COUPLED ARGON PLASMA ATOMIC EMISSION SPECTROSCOPY

X1.1 Table X1.1 is provided as a guide for suggested wavelengths and detection limits.

X1.2 Table X1.2 is provided as a guide for preparation of metal stock solutions.

TABLE X1.1 Suggested Wavelengths and Estimated Detection Limits[5]

Element	Wavelength, nm[A]	Estimated detection limit, µg/L[B]
Barium	455.403	2
Calcium	317.933	10
Lithium	670.784	4
Potassium	766.491	[C]
Silica	288.158	27
Sodium	588.995	29

[A] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see 6.1.1).

[B] The estimated detection limits as shown are taken from Winge, Fassel, et al. They are given as a guide for approximate detection limits. The actual method instrumental detection limits are sample dependent and may vary as the sample matrix varies (see 3.2.3).

[C] Highly dependent on operating conditions and plasma position.

TABLE X1.2 Preparation of Metal Stock Solution[A,B]

Element (Compound)	Weight, g	Solvent
$BaCl_2$ [C]	0.1516	HCl (1 + 1)
$CaCO_3$ [D]	0.2498	Water + HCl (1 + 1)
Li_2CO_2	0.1907	HNO_3 (1 + 1)
KCl	0.5323	Water
$Na_2SiO_3{\cdot}5H_2O$	0.3531	Water
NaCl	0.2542	Water

[A] Metal stock solutions, 1.00 mL = 100 µg of metal. Dissolve the listed weights of each compound or metal in 20 mL of specified solvent and dilute to 1 L. The metals may require heat to increase rate of dissolution.
[B] Where water is used as the solvent, acidify with 10 mL of HNO_3 (sp gr 1.42) and dilute to 1 L. See Section 8 for concentration of acids. Commercially available standards may be used. Alternate salts or oxides may also be used.
[C] Dry for 1 h at 180°C.
[D] Dry for 1 h at 180°C. Add to approximately 600 mL of water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1 L with water.

X2. PRECISION AND BIAS

X2.1 Study data sets for potassium, lithium, sodium, thallium, and silicon were limited due to either the small number of laboratories reporting data for the element or to an unusually high percentage of rejected data. Regression equations and summary statistics for these elements must, therefore, be used with prudence.

X2.2 Low concentration level data for aluminum, boron, and silicon were affected by contamination of the spiking material from the borosilicate glass ampules used in the study. Precision and bias for low concentration spikes for these elements were poorer than expected due to this difficulty.

X2.3 High levels of some elements in specific effluents made evaluation of data for precision and bias difficult. This problem was inherent in the study design and selection of real world effluents.

X2.4 The following elements have shown some matrix effect of practical importance due to water type: aluminum, barium, beryllium, boron, cobalt, copper, iron, magnesium, manganese, nickel, selenium, silver, strontium, vanadium, and zinc.

X2.5 Digestion was shown to have an effect on accuracy or precision or both on some of the elements studied.

X2.6 High solids or MAK-type nebulization for high dissolved solids samples was less prone to difficulties than standard, fixed cross-flow or concentric nebulizers.

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D1976 – 07) that may impact the use of this standard. (Approved March 1, 2012.)

(1) Added SI statement to Section 1.
(2) Removed reference to D1192 from Sections 2 and 10.
(3) Added Note 5 to discuss the use of block digestion systems.