This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

INTERNATIONAL

Designation: D1976 – 20

Standard Test Method for Elements in Water by Inductively-Coupled 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, ground water, surface water, domestic, commercial or industrial wastewaters,[2,3] within the following concentration ranges of Table 1.

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

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

1.4 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Note 2 and Section 9.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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2. Referenced Documents

2.1 *ASTM Standards:*[4]

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 Flowing Process Streams
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry
D5744 Test Method for Laboratory Weathering of Solid Materials Using a Humidity Cell
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D6234 Test Method for Shake Extraction of Mining Waste by the Synthetic Precipitation Leaching Procedure
D8006 Guide for Sampling and Analysis of Residential and Commercial Water Supply Wells in Areas of Exploration and Production (E&P) Operations
E1915 Test Methods for Analysis of Metal Bearing Ores and Related Materials for Carbon, Sulfur, and Acid-Base Characteristics
E2242 Test Method for Column Percolation Extraction of Mine Rock by the Meteoric Water Mobility Procedure

2.2 *USEPA Standards:*[2]

Method 200.7 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry

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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, http://www.epa.gov.

[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] 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**

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TABLE 1 Summary of Tested Concentration Ranges

Element	From	To	Unit
Aluminum	0.083	1.43	µg/mL
Antimony	0.411	1.41	µg/mL
Arsenic	0.083	0.943	µg/mL
Barium	0.030	250	µg/mL
Beryllium	0.017	0.076	µg/mL
Boron	0.330	1.18	µg/mL
Cadmium	0.018	0.776	µg/mL
Calcium	0.400	1100	µg/mL
Chromium	0.025	0.47	µg/mL
Cobalt	0.058	0.843	µg/mL
Copper	0.017	0.189	µg/mL
Iron	0.074	2.34	µg/mL
Lead	0.085	0.943	µg/mL
Lithium	0.800	450	µg/mL
Magnesium	0.073	4.62	µg/mL
Manganese	0.017	0.94	µg/mL
Molybdenum	0.073	1.09	µg/mL
Nickel	0.043	0.943	µg/mL
Phosphorus	10.0	310	µg/mL
Potassium	8.00	5200	µg/mL
Selenium	0.083	0.755	µg/mL
Silica	1.00	3000	µg/mL
Silver	0.017	0.189	µg/mL
Sodium	5.00	3500	µg/mL
Strontium	0.500	500	µg/mL
Sulfur	2.00	600	µg/mL
Thallium	0.126	0.953	µg/mL
Vanadium	0.041	1.877	µg/mL
Zinc	0.068	0.759	µg/mL

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, 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 8.9).

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 *method blank, n*—a volume of water carried through the entire sample preparation, preservation, and analytical procedure.

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

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

3.2.8 *total-recoverable, adj*—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 plasma atomic 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 29 elements. High sensitivity analysis and larger dynamic range can be achieved for some elements that are difficult to determine by other techniques such as Flame Atomic Absorption.

5.2 The test method is useful for multi-element analysis of domestic and commercial well produced drinking water for metals and nonmetals for use in baseline analysis and monitoring during exploration, hydraulic fracturing, production, closure and reclamation activities related to oil and gas operations (see Guide D8006).

5.2.1 Minimum analyses include arsenic, barium, iron, magnesium, sodium, calcium, manganese, and lead.

5.2.2 Boron, potassium, chromium, selenium, cadmium, and strontium may be required on a site specific basis.

5.2.3 The most abundant elements in oil and gas produced water are sodium, potassium, lithium, magnesium, calcium, strontium, iron, silica, phosphorus, and sulfur.

5.3 The test method is useful for multi-element analysis of acid rock drainage and other major and some trace elements in mining influenced water.

5.4 Where low quantitation limits are required, Test Method D5673 may be applicable.

5.5 The test method is also useful for testing leachates and effluents for ore and mining and metallurgical waste characterization tests including Test Methods D6234, E2242, D5744, and solutions from the Biological Acid Production Potential and Peroxide Acid Generation Methods in the Appendix of Test Methods E1915.

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 recommended wavelengths given in Table 2. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose,

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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 4 for concentrations used.

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 for the analytes in Table 3. The blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 4. 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 listed in Table 3.

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TABLE 3 Analyte Elemental Concentrations Tested for Interferents[A]

Analytes	mg/L
Al	10
As	10
B	10
Ba	1
Be	1
Ca	1
Cd	10
Co	1
Cr	1
Cu	1
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.

TABLE 4 Interferent Elemental Concentrations for Analytes Tested[A]

Interferents	mg/L
Al	1000
Ca	1000
Cr	200
Cu	200
Fe	1000
Mg	1000
Mn	200
Ni	200
Ti	200
V	200

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

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 inductively coupled plasma (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.

6.2 Analysis for silica precludes the use of borosilicate glassware due to potential contamination.

7. Apparatus

7.1 See the manufacturer's instruction manual for installation and operation of inductively-coupled argon plasma spectrometers. Table 5 lists elements for which this test method applies, with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. 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.

7.1.1 Use of a vacuum or purged path is necessary for determination of sulfur.

7.1.2 Use of glass in the sample path may not be acceptable for silica, use of an inert material is recommended to avoid silica contamination.

TABLE 5 Suggested Wavelengths and Estimated Detection Limits[A]

Element	Wavelength, nm[B]	Estimated detection limit, µg/L[C]
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Lithium	670.784	4
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Phosphorous	214.914	76
Potassium	766.491	700
Selenium	196.026	75
Silica	288.158	27
Silver	328.068	7
Sodium	588.995	29
Strontium	421.552	0.77
Sulfur	182.037	3
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[A] 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.

[B] 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).

[C] The estimated detection limits as shown are taken from Winge et al.,[A] USEPA Method 200.7, or task group data. 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).

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.[5] 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.

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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, use of a fume hood is recommended.

8.4 *Argon*—Welding grade equivalent or better.

8.5 *Hydrochloric Acid* (1 + 1)—Add 1 volume of hydrochloric acid (sp gr 1.19) ultrapure or equivalent to 1 volume of water.

8.6 *Nitric Acid* (1 + 1)—Add 1 volume of nitric acid (sp gr 1.42) ultrapure or equivalent to 1 volume of water.

8.7 *Nitric Acid* (1 + 499)—Add 1 volume of nitric acid (sp gr 1.42) ultrapure or equivalent to 499 volumes of water.

8.8 *Stock Solutions*—Preparation of example stock solutions for each element is listed in Table 6. Use of commercially prepared certified stock solutions is recommended.

8.9 *Mixed Calibration Standard Solutions*—Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Note 3).

[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 *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.

TABLE 6 Preparation of Example Element 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
$BaCl_2$[E]	0.1516	HCl (1 + 1)
Be	0.1000	Aqua regia
H_3BO_3	0.5716	Water
Cd	0.1000	HNO_3 (sp gr 1.42)
$CaCO_3$[F]	0.2498	Water + HCl (1 + 1)
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)
Li_2CO_3	0.5323	HNO_3 (1 + 1)
Mg	0.1000	HNO_3 (1 + 1)
Mn	0.1000	HNO_3 (1 + 1)
Ni	0.1000	HNO_3 (sp gr 1.42)
$NH_4H_2PO_4$	0.3745	HCl (1 + 9)
KCl	0.1907	Water
$(NH_4)_2MoO_4$	0.2043	Water
Na_2SeO_4 [D]	0.2393	Water
$Na_2SiO_3{\cdot}5H_2O$	0.3531	Water
Ag	0.1000	HNO_3 (sp gr 1.42)
NaCl	0.2542	Water
$SrCO_3$	0.1685	HCl (1 + 9)
Na_2SO_4	0.4431	Water
$TlNO_3$	0.1303	Water
NH_4VO_3	0.2297	HNO_3 (1 + 1)
Zn	0.1000	HNO_3 (1 + 1)

[A] Example element 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.
[E] Dry for 1 h at 180°C.
[F] 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.

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. It is common practice to have all or nearly all elements in one mixed calibration standard.

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

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 Practices D3370 as applicable.

10.1.1 Analysis for silica precludes the use of borosilicate glassware due to potential contamination.

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.

11.1.1 Multiple-point calibration standards may be used, and 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(s) be matrix matched with the same acid concentration contained in the samples.

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12. Procedure

12.1 To determine dissolved elements, proceed with 12.4.

12.2 When determining total-recoverable elements for a two-point calibration, 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 (use tetrafluoroethylene or equivalent for silica analysis) 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 (hard digestion), choose a volume of well mixed, acid-preserved sample appropriate for the expected level of elements.

NOTE 5—Addition of HF acid may be required in order to effect complete dissolution of all siliceous material, so this digestion method will result in low results for samples containing insoluble silica.

12.3.1 Transfer the sample to a beaker (use tetrafluoroethylene or equivalent for silica analysis). 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 (use tetrafluoroethylene or equivalent for silica analysis) 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 6—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 Include the blank in the calibration as the zero point.

NOTE 7—The original interlaboratory study subtracted reagent blanks from all samples. This subtraction was 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[6]

14.1 The original 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 during the original testing.

14.2.1 The original study test design was 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, from the original study but the data for the four other water types can be found in the original interlaboratory study report.[2] 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 original study and individual measurements of precision and bias were developed for each element and matrix tested. Bias was related to mean recovery of the analyte. The equation used

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1144 and RR:D19-1198. Contact ASTM Customer Service at service@astm.org.

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TABLE 7 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	$X = 0.93C + 28.40$	$X = 0.92C - 22.46$	$X = 1.01C - 2.08$	$X = 1.03C - 0.73$
Surface 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	$X = 1.02C + 40.42$	$X = 0.95C - 34.50$	$X = 1.06C - 7.00$	$X = 1.04C - 2.08$

to summarize accuracy data over concentration for each water type/digestion type/element was:

$$X = a + b \times C \qquad (1)$$

where:

X = mean recovery of the element,
a = intercept,
b = slope, and
C = reference 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. Equations used to summarize precision data over concentration for each water type/digestion type/element were:

$$S_t = d + e \times X \qquad (2)$$

where:

S_t = overall standard deviation,
d = intercept,
e = slope, and

$$S_o = f + g \times X \qquad (3)$$

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 7-11.

14.2.5 These data from the original study 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 the original study can be found in Appendix X1.

14.2.6 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, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

14.3 A second interlaboratory test was carried out to add barium, calcium, lithium, phosphorous, potassium, silica, sodium, strontium and sulfur to meet the requirements of Practice D2777 in the drinking water matrix of potable ground water wells. Eight laboratories participated, providing eight sets of data for dissolved elements and only five sets of data for total elements and total recoverable elements after digestion. Since six laboratories is the minimum to evaluate the results using Practice D2777, only the dissolved results were used to calculate the precision and bias statistics.

14.3.1 Eight laboratories cooperated in testing these test methods, providing eight sets of data and obtained the precision and bias data summarized in Tables 12-20 for the potable well impacted water matrix Youden Pairs and the bias for the base line potable well water matrix is shown in Table 21. Regression equations for the precision and bias are shown in Table 22 and Table 23.

15. Quality Control (QC)

15.1 The following quality control information is recommended for measuring elements in water by inductively-coupled plasma atomic emission spectroscopy.

15.2 The instrument shall be calibrated using a minimum of one-point calibration standard at the highest concentration level and shall include a calibration blank for a two-point calibration. If a multi-point calibration is used, one point must be at the quantification limit for the method. In addition to the initial calibration blank, a continuing calibration blank (CCB) shall be analyzed at a rate of 10 % of the batch run to ensure contamination was not a problem during the batch analysis.

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TABLE 8 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	$X = 1.10C - 77.26$	$X = 1.01C + 0.45$	$X = 1.01C - 1.85$	$X = 0.93C - 1.01$
Surface 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	$X = 1.07C - 2.83$	$X = 1.02C - 0.58$	$X = 0.98C + 0.30$	$X = 0.93C - 0.28$