



Designation: D 1976 – 02

Standard Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy¹

This standard is issued under the fixed designation D 1976; 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 *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:

- D 1066 Practice for Sampling Steam⁵
- D 1129 Terminology Relating to Water⁵
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits⁵
- D 1193 Specification for Reagent Water⁵
- D 2777 Practice for Determination of Precision and Bias of

TABLE 1 Suggested Wavelengths and Estimated Detection Limits⁴

Element	Wavelength, nm ^A	Estimated detection limit, μ g/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 3.1.4).

- Applicable Test Methods of Committee D-19 on Water⁵
- D3370 Practices for Sampling Water from Closed Conduits⁵
- D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents⁵
- D 5810 Guide for Spiking into Aqueous Samples³
- D 5847 Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis⁶

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

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

3.1.2 *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).

⁶ Annual Book of ASTM Standards, Vol 11.02.

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.

Current edition approved May 10, 2002. Published June 2002. Originally published as D 1976 – 91. Last previous edition D 1976 – 96.

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 , 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 Annual Book of ASTM Standards, Vol 11.01.

3.1.3 *dissolved, adj*—those elements that will pass through a 0.45 µm membrane filter.

3.1.4 *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.

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

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

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

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

3.2 *Definitions*—For definitions of other terms used in this test method, refer to Terminology D 1129.

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 analysis sensitivity can be achieved for some elements that are difficult to determine by other techniques.

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 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

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.

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.

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.

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 Society⁷. 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 nonhygroscopic 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 D 1193. 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.

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

⁷ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

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 ₂ O ₃ ^C	0.1320	Water + 0.4 g NaOH
Be	0.1000	Aqua regia
H ₃ BO 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) ₂ MoO ₄	0.2043	Water
Na ₂ SeO ₄ ^D	0.2393	Water
Ag	0.1000	HNO ₃ (sp gr 1.42)
TiNO ₃	0.1303	Water
NH ₄ VO 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 HNO₃(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 HNO₃(sp gr 1.42) and dilute to 1 L.

^D Add 1 mL of HNO₃(sp gr 1.42) and dilute to 1 L.

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 Practice **D 1066** or **D 3370** or Specification **D 1192**, as applicable.

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 HNO₃ is required per litre 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 **D 4841**.

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 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 HNO₃(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 HNO₃(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 HNO₃(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**.

12.4 Atomize each solution to record its emission intensity or concentration. A sample rinse of HNO₃(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.