Designation: D4190 – 15 (Reapproved 2023)

Standard Test Method for Elements in Water by Direct-Current Plasma Atomic Emission Spectroscopy[1]

This standard is issued under the fixed designation D4190; 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 and total recoverable elements in water, which includes drinking water, lake water, river water, sea water, snow, and Type II reagent water by direct current plasma atomic emission spectroscopy (DCP).

1.2 The information on precision and bias may not apply to other waters.

1.3 This test method is applicable to the 15 elements listed in Annex A1 (Table A1.1) and covers the ranges in Table 1.

1.4 This test method is not applicable to brines unless the sample matrix can be matched or the sample can be diluted by a factor of 200 up to 500 and still maintain the analyte concentration above the detection limit.

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

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E1097 Guide for Determination of Various Elements by Direct Current Plasma Atomic Emission Spectrometry

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *total recoverable element, n*—a descriptive term relating to the elemental forms recovered in the acid-digestion procedure specified in this test method.

4. Summary of Test Method

4.1 Elements are determined, either sequentially or simultaneously, by DCP.

4.2 Matrix enhancement or suppression of the emission signal can be minimized by the addition of 2000 mg/L of lithium ion to all standards, samples, and blanks.

4.3 Dissolved elements are determined by atomizing a filtered and acidified sample directly with no pretreatment.

4.4 If the sample is clear, total recoverable elements are determined in the same manner as dissolved elements except that sample is unfiltered and acidified.

4.5 If there are large particles (non-colloidal) the total recoverable elements are determined on a portion of the sample after a hydrochloric-nitric acid digestion (12.2 – 12.5). The same digestion procedure is used to determine all total recoverable elements in this test method.

[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] 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.

TABLE 1 Solutions for Analysis

Element	Concentration Range
Aluminum	50 to 200 µg/L
Beryllium	50 to 1000 µg/L
Boron	50 to 1000 µg/L
Cadmium	50 to 1000 µg/L
Chromium	50 to 1000 µg/L
Cobalt	50 to 1000 µg/L
Copper	50 to 1000 µg/L
Iron	50 to 1000 µg/L
Lead	200 to 1000 µg/L
Manganese	50 to 1000 µg/L
Mercury	50 to 1000 µg/L
Nickel	50 to 1000 µg/L
Strontium	50 to 1000 µg/L
Vanadium	50 to 1000 µg/L
Zinc	50 to 1000 µg/L

NOTE 1—The volatility of mercury[3, 4] compounds, especially the chlorides, makes it necessary to use considerable care in digesting samples containing these elements. The samples must not be boiled unless provision is made to prevent loss by volatilization.

5. Significance and Use

5.1 This test method is useful for the determination of element concentrations in many natural waters. It has the capability for the simultaneous determination of up to 15 separate elements. High analysis sensitivity can be achieved for some elements, such as boron and vanadium.

6. Interferences

6.1 For commonly occurring matrix elements the following spectral interferences have been observed:

6.1.1 Calcium, magnesium, and boron interfere with lead at 405.78 nm.

6.1.2 Calcium interferes with chromium at 425.43 nm.

6.1.3 Magnesium interferes with cadmium at 214.44 nm.

6.1.4 Iron interferes with cobalt at 345.35 nm and 240.73 nm.

6.1.5 Cobalt interferes with nickel at 341.48 nm.

NOTE 2—The exact magnitude of these interferences has not been determined since it depends on the concentration of the calibration standards used and the sample matrix.

6.2 Some additional possible interferences are listed in Annex A2 (Table A2.1) so that the analyst may be aware of and test for them.

7. Apparatus

7.1 See the manufacturer's instruction manual for installation and operation of DCP spectrometers, refer to Guide E1097 for information on DCP spectrometers.

8. Reagents

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] where such specifications are available. 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 of Specification D1193. 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 lessening the bias and precision of the determination. Type II water was specified at the time of round robin testing of this test method.

8.3 *Stock Solutions*—Preparation of stock solutions for each element is listed in Annex A3 (Table A3.1) or use commercially available, ICP Grade, stock standards.

8.4 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45 µm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.8.4

NOTE 3—Depending on the manufacturer, these filters have been found to be contaminated to various degrees with heavy metals. Care should be exercised in selecting a source of these filters. A good practice is to wash the filters with nitric acid and reagent water before filtering a sample.

8.5 *High Purity Hydrochloric Acid, (HCl),* (sp gr 1.19), concentrated hydrochloric acid.

8.6 *Hydrochloric Acid, (1 + 1)*—Add one volume of HCl (sp gr 1.19) to one volume of water.

8.7 *Lithium Carbonate,* ultrapure.

8.8 *Lithium Solution (40 000 mg/L)*—Dissolve 213 g of ultrapure lithium carbonate in a minimum amount of HCl (sp gr 1.19) and dilute to 1 L with water.

8.9 *Concentrated Nitric Acid, (HNO_3),* (sp gr 1.42)—High-purity acid can be prepared by distillation of concentrated nitric acid from a sub-boiling quartz still or it can be commercially purchased.

8.10 *Dilute Nitric Acid, (1+1)*—Add one volume of HNO_3 (sp. gr. 1.42) to one volume of water.

8.11 *Dilute Nitric Acid, (1 + 499)*—Add one volume of HNO_3 (sp gr 1.42) to 499 volumes of water.

NOTE 4—If a high reagent blank is obtained on either HNO_3 or HCl, distill the acid or use high purity acid. When HCl is distilled, an azeotropic mixture is obtained (approximately 6 N HCl); therefore, whenever concentrated HCl is specified in the preparation of a reagent or in the procedure, use double the amount if distilled acid is used.

9. Precautions

9.1 Emission intensities are affected by changing viscosity so it is important to control the viscosity of blanks, standards,

[3] *Standard Methods of Chemical Analysis*, Editor, N. H. Furman, Vol 1, Sixth Edition, pp. 107 and 657.

[4] Smith, G. F., *The Wet Chemical Oxidation of Organic Compositions*, The G. Frederick Smith Chemical Co., 1965.

[5] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.