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.

and samples within reasonable limits. Reagent water standards should not be used to analyze oil field brines. Alternatively, matrix matching or the method of additions can be used.

9.2 Organic solvents, such as alcohol, acetone, and methyl ethyl ketone have been observed to enhance emission intensity. This enhancement effect must be compensated for when organic solvents are known to be present. Alternatively, matrix matching or the method of additions can be used.

10. Sampling

10.1 Collect the samples in accordance with the applicable standards, Practice D1066 or Practices D3370.

10.2 Preserve the samples by immediately adding high purity nitric acid to adjust the pH to two at the time of collection. Normally 2 mL of HNO_3 is required per liter of sample. If only dissolved elements are to be determined, (Note 5) filter the sample through a 0.45 µm membrane filter before acidification. The holding time for the sample may be calculated in accordance with Practice D4841.

NOTE 5—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. However, acid must be added at least 24 h before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

11. Calibration and Standardization

11.1 Prepare 100 mL of a blank and at least four standard solutions to bracket the expected concentration range of the samples to be analyzed by diluting 5.0 mL of lithium solution (see 8.8) and an appropriate volume of stock solution with HNO_3 (1 + 499). Prepare the blank and standards each time the test is to be run or as determined by Practice D4841.

11.2 Analyze at least four working standards containing concentrations of each element that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. Atomize the blank and standards and record the emission intensity or concentration. Atomize HNO_3 (1 + 499) between each standard.

11.3 Using the instrument software verify that the instrument calibration is within user acceptable QC limits.

12. Procedure

12.1 To determine dissolved elements, add 5.0 mL of lithium solution (see 8.8) to a 100.0 mL volumetric flask and bring to volume with the well-mixed acidified sample. Proceed with 12.6.

12.2 When determining total recoverable elements in solutions containing suspended matter or large particles (that is, noncolloidal), add 5.0 mL of HNO_3 (sp. gr. 1.42) (8.9) and 5.0 mL of lithium solution (8.8) to a 100.0 mL sample.

NOTE 6—When digestion is necessary, subject the standards, sample, and blank to the same procedure.

12.3 Add 5.0 mL of HCl (sp. gr. 1.19) (8.5) to each sample.

12.4 Heat the samples in a covered beaker on a steam bath or hot plate until the volume has been reduced to 15 mL or 20 mL. Take care to see that the samples do not boil. Loss of sample could result from bumping or spattering.

NOTE 7—For samples with high levels of dissolved solids, the amount of reduction in volume is left to the discretion of the analyst.

NOTE 8—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.

12.5 Cool and filter (8.4) the samples, if necessary, through a fine ashless filter paper into 100.0 mL volumetric flasks. Wash the filter paper three times with water and adjust to volume.

12.6 Atomize each solution and record its emission intensity or concentration. Atomize HNO_3 (1 + 499) (8.11) between samples.

13. Calculation

13.1 Calculate the concentration of elements in each sample, in µg/L, using the calibrations established in 11.3. Modern DCP instruments will provide the results in the calibrated concentration units.

13.2 Multiply the results for dissolved elements by the dilution factor of 1.05 to correct for the required addition of lithium solution (12.1).

NOTE 9—The correction does not need to be applied to samples analyzed using the total recoverable process because those samples are adjusted to volume. If the block digestion systems reflux the samples without any loss of volume the dilution factor will need to be applied.

14. Precision and Bias[6]

14.1 To facilitate handling and distribution for round robin testing, three concentrated solutions were prepared. These were acidified solutions of 15 elements.

14.2 The concentrated solutions, when diluted according to directions, yielded solutions for analysis with the composition as shown in Table 2. A total of eight laboratories and thirteen operators participated in this study.

14.2.1 Type II water was specified at the time of round robin testing of this test method.

14.3 *Precision*—The precision of this test method for the elements tested within their respective ranges of concentration given in Table 2 may be expressed as given in Table 3.

14.4 *Bias*—See Table 4.

14.5 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1079. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Solutions for Round Robin Analysis

Element P	Solutions for Analysis, µg/L		
	1	2	3
Al	50	100	190
Be	50	500	1000
B	50	500	1000
Cd	1000	50	500
Cr	500	1000	50
Co	50	500	1000
Cu	1000	50	500
Fe	500	1000	50
Pb	500	200	1000
Mn	800	50	300
Hg	500	1000	200
Ni	50	300	800
Sr	600	50	300
V	1000	50	400
Zn	500	1000	50

TABLE 3 Precision

Element	Reagent Water	Water of Choice
Al	$S_T = 0.093X - 0.301$	$S_T = 0.108X + 0.424$
	$S_O = 0.051X + 0.497$	$S_O = 0.044X + 3.18$
Be	$S_T = 0.066X + 0.354$	$S_T = 0.059X + 2.15$
	$S_O = 0.025X - 0.250$	$S_O = 0.042X\ 1.43$
B	$S_T = 0.045X + 9.34$	$S_T = 0.045X + 2.87$
	$S_O = 0.022X + 3.70$	$S_O = 0.021X + 5.12$
Cd	$S_T = 0.044X + 6.08$	$S_T = 0.066X + 2.99$
	$S_O = 0.025X + 4.96$	$S_O = 0.037X + 7.99$
Cr	$S_T = 0.060X + 2.13$	$S_T = 0.038X + 4.56$
	$S_O = 0.032X + 1.20$	$S_O = 0.027X + 3.86$
Co	$S_T = 0.062X + 4.59$	$S_T = 0.085X + 9.55$
	$S_O = 0.032X + 4.11$	$S_O = 0.040X + 3.99$
Cu	$S_T = 0.038X + 5.58$	$S_T = 0.049X + 2.75$
	$S_O = 0.031X + 0.956$	$S_O = 0.039X + 0.644$
Fe	$S_T = 0.051X + 14.3$	$S_T = 0.053X + 15.7$
	$S_O = 0.013X + 10.7$	$S_O = 0.034X + 12.2$
Pb	$S_T = 0.038X + 9.69$	$S_T = 0.037X + 18.3$
	$S_O = 0.027X + 5.36$	$S_O = 0.016X + 20.7$
Mn	$S_T = 0.058X + 2.35$	$S_T = 0.034X + 1.98$
	$S_O = 0.023X + 3.30$	$S_O = 0.018X + 3.79$
Hg	$S_T = 0.008X + 22.3$	$S_T = 0.009X + 28.0$
	$S_O = 0.003X + 14.7$	$S_O = 0.009X + 23.7$
Ni	$S_T = 0.078X + 5.47$	$S_T = 0.088X + 3.38$
	$S_O = 0.029X + 7.17$	$S_O = 0.039X\ 5.54$
Sr	$S_T = 0.073X + 1.47$	$S_T = 0.024X + 3.56$
	$S_O = 0.034X + 1.72$	$S_O = 0.021X + 1.27$
V	$S_T = 0.053X + 1.74$	$S_T = 0.050X + 3.97$
	$S_O = 0.038X + 0.794$	$S_O = 0.048X - 0.156$
Zn	$S_T = 0.025X + 8.38$	$S_T = 0.022X + 10.9$
	$S_O = 0.011X + 6.67$	$S_O = 0.014X + 9.47$

where:
S_r = overall prevision, µg/L,
S_O = single-operator precision, µg/L, and
X = concentration of element determined, µg/L.

15. Quality Control (QC)

15.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing each element.

15.2 *Calibration and Calibration Verification:*

15.2.1 Analyze at least four working standards containing concentrations of each element that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument (11.2). 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.

15.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

15.2.3 If calibration cannot be verified, recalibrate the instrument.

15.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

15.3 *Initial Demonstration of Laboratory Capability:*

15.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

15.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of each element. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

15.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 4. This study should be repeated until the recoveries are within the limits given in Table 3. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

15.4 *Laboratory Control Sample (LCS):*

15.4.1 To ensure that the test method is in control, analyze a LCS containing a known concentration of each element with each batch (laboratory-defined or twenty samples). The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within ±15 % of the known concentration

15.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

15.5 *Method Blank:*

15.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of each element found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of each element is found above this level, analysis of samples is halted until the