



Designation: D 4190 – 99

## Standard Test Method for Elements in Water by Direct-Current Plasma Atomic Emission Spectroscopy<sup>1</sup>

This standard is issued under the fixed designation D 4190; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

### 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 *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.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 1066 Practice for Sampling Steam<sup>2</sup>
- D 1129 Terminology Relating to Water<sup>3</sup>
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits<sup>3</sup>
- D 1193 Specification for Reagent Water<sup>2</sup>
- D 3370 Practices for Sampling Water from Closed Conduits<sup>2</sup>
- D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents<sup>2</sup>
- E 1097 Guide for Direct Current Plasma Emission Spectrometry Analysis<sup>3</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol. 3.06.

**TABLE 1 Solutions for Analysis**

Element P	Solutions for Analysis, $\mu\text{g/L}$		
	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

### 3. Terminology

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

#### 3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *total recoverable element, n*—a term relating to forms of each element that are determinable by the digestion method that is included in this test method.

3.2.2 *LCS, n*—laboratory control standard.

### 4. Summary of Test Method

4.1 Elements are determined, either sequentially or simultaneously, by d-c plasma atomic emission spectroscopy.

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.

NOTE 1—The volatility of mercury<sup>4,5</sup> 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 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 E 1097 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<sup>6</sup> 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 D 1193. 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 *High Purity Hydrochloric Acid, (HCl)*, (sp gr 1.19), concentrated hydrochloric acid.

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

8.6 *Lithium Carbonate*, ultrapure.

8.7 *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.

8.8 *Concentrated Nitric Acid, (HNO<sub>3</sub>)*, (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.

8.9 *Dilute Nitric Acid, (1+1)*—Add one volume of HNO<sub>3</sub> (sp. gr. 1.42) to one volume of water.

8.10 *Dilute Nitric Acid, (1 + 499)*—Add one volume of HNO<sub>3</sub>(sp gr 1.42) to 499 volumes of water.

NOTE 3—If a high reagent blank is obtained on either HNO<sub>3</sub> or HCl, distill the acid or use high purity acid. **Caution**—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, 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 D 1066, Specification D 1192, or Practices D 3370.

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<sub>3</sub> is required per liter of sample. If only dissolved elements are to be determined, (Note 4) 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 D 4841.

NOTE 4—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.

## 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

<sup>4</sup> Standard Methods of Chemical Analysis, Editor, N. H. Furman, Vol 1, Sixth Edition, pp. 107 and 657.

<sup>5</sup> Smith, G. F., *The Wet Chemical Oxidation of Organic Compositions*, The G. Frederick Smith Chemical Co., 1965.

<sup>6</sup> 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.

(see 8.7) and an appropriate volume of stock solution with  $\text{HNO}_3(1 + 499)$ . Prepare the blank and standards each time the test is to be run.

11.2 Atomize the blank and standards and record the emission intensity or concentration. Atomize  $\text{HNO}_3(1 + 499)$  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 8.7) 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  $\text{HNO}_3$  (sp. gr. 1.42) and 5.0 mL of lithium solution to a 100.0-mL sample.

NOTE 5—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) 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 or 20 mL. Take care to see that the samples do not boil. Loss of sample could result from bumping or spattering.

NOTE 6—For samples with high levels of dissolved solids, the amount of reduction in volume is left to the discretion of the analyst.

12.5 Cool and filter 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  $\text{HNO}_3(1 + 499)$  between samples.

## 13. Calculation

13.1 Calculate the concentration of elements in each sample, in mg/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).

## 14. Precision and Bias <sup>7</sup>

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 1. 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 1 may be expressed as given in Table 2.

**TABLE 2 Precision**

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

where:

$S_T$  = overall precision,  $\mu\text{g/L}$ ,

$S_O$  = single-operator precision,  $\mu\text{g/L}$ , and

$X$  = concentration of element determined,  $\mu\text{g/L}$ .

14.4 *Bias*—See Table 3.

## 15. Quality Control (QC)

15.1 The following quality control information is recommended for the determination of dissolved and total recoverable elements in water.

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

15.4 Two method blanks should be prepared ensuring that an adequate method blank volume is present for a minimum of seven repetitive analysis. 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 LCS should be analyzed with each batch of sample 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.

<sup>7</sup> Supporting data are available from ASTM Headquarters. Request RR: D 19-1079.

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**TABLE 3 Bias**

Element	Amount Added, (µg/L)	Reagent Water, Type II, (% Bias)	Statistical Significance (95 % Confidence Level)	Water of Choice (% Bias)	Statistical Significance (95 % Confidence Level)
Al	50 100 190	+ 0.4 -5.3 -5.0	no yes yes	-9.2 -6.4 -6.7	yes yes yes
Be	50 500 1000	-0.2 -6.2 -7.2	no yes yes	-1.4 -5.8 -5.7	no yes yes
B	50 500 1000	-14.6 -6.6 -7.2	yes yes yes	-7.0 -5.3 -7.0	yes yes yes
Cd	50 500 1000	-0.6 -3.6 -3.5	no no no	0.0 -3.1 -3.3	no no yes
Cr	50 500 1000	-1.2 -4.2 -5.8	no yes yes	-4.5 -3.0 -3.8	yes yes yes
Co	50 500 1000	+ 2.6 -7.4 -9.9	no yes yes	+ 5.8 -8.1 -8.0	no yes yes
Cu	50 500 1000	+ 9.6 -0.6 -0.9	yes no no	+ 1.4 -1.4 -1.2	no no no
Fe	50 500 1000	+ 11.4 -4.0 -6.6	yes yes yes	+ 10.4 -5.8 -6.1	no yes yes
Pb	200 500 1000	-0.9 + 1.6 -0.9	no no no	-1.0 + 1.5 -1.0	no no no
Mn	50 300 800	+ 1.8 -5.3 -3.9	no yes yes	+ 1.6 -2.2 -2.5	no yes yes
Hg	200 500 1000	-9.8 -3.8 -2.7	yes yes no	+ 12.5 -1.6 -3.1	yes no yes
Ni	50 300 800	+ 1.0 -4.6 -6.4	no yes yes	+ 5.6 -3.5 -5.9	yes yes yes
Sr	50 300 600	+ 7.2 -5.4 -2.7	yes yes yes	+ 0.2 -4.1 -2.9	no yes yes
V	50 400 1000	-2.5 -6.4 -7.7	no yes yes	-8.8 -6.8 -6.8	yes yes yes
Zn	50 500	+ 2.6 -1.4	no no	+ 2.2 -0.1	no no

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

**16. Keywords**

16.1 direct-current plasma; DCP; elements; water

**ANNEXES**

**(Mandatory Information)**

**A1. ANALYTICAL WAVELENGTHS**

A1.1 Table A1.1 shows analytical wavelengths (see 1.3).

**TABLE A1.1 Analytical Wavelengths**

Element	Wavelength, nm <sup>A</sup>	Range, µg/L
Al	396.15	The range for the elements determined in this study is given in Table 1. <sup>B</sup>
Be	234.86	
B	249.68	
Cd	214.44	
Cr	425.43	
Co	345.35	
Cu	324.75	
Fe	371.99	
Pb	405.78	
Mn	279.48	
Hg	253.65	
Ni	305.08	
Sr	407.77	
V	437.92	
Zn	213.86	

<sup>A</sup>Wavelengths other than those specified may be used if determined that they have adequate sensitivity and are linear over the working range. Alternative wavelengths should be checked for significant interferences.

<sup>B</sup>It is possible to go lower by concentration of the sample or higher by dilution of the sample.

## A2. POSSIBLE INTERFERENCES

A2.1 Table A2.1 additional possible interferences (see 6.2).

**TABLE A2.1 Some Possible Spectral Interferences**

Element	Wavelengths, nm	Relative Intensity	Possible Interferences <sup>A</sup>
Al	236.76	...	Cu, Rb, Yb, Pd, ... Hf, V, Os, W, Er, Ir, Re
	396.15 <sup>B</sup>	...	Mo, U, ... Yb, Zr
Be	234.86	...	Re, Nb, Te, Ni, Os, ... Lu, Ta, Zr, Mo, W, Pt, Co, Nd
B	208.96	137	Zr, Pd, ... Nd
	249.68	456	Pd, Re, Sn, ... Hg, Ru
	249.77 <sup>B</sup>	1000	V, Ca, Ru, Fe, Sn, ... Hg, Mn, Ni, Fe
Zn	202.55	1000	In, Cu, Ir, ... U
	206.19	634	Zr, Ir, Ga, Pd, ... Sb, Ta, V
	213.86 <sup>B</sup>	131	Cu, As, Nb, ... Ir, Ni, Fe, Os
	334.50	186	U, ... Mo

<sup>A</sup>L & R—When using the echelle grating spectrograph, some wavelengths may appear in two adjacent orders of reflection. “L” denotes the left side of the grating, “R” denotes the right side of the grating. It should be noted that the large majority of elements listed here as possible interferences have not been observed to cause problems in the solutions so far analyzed.

<sup>B</sup>Wavelengths used by the manufacturer and reported by users of DCP.

## A3. STOCK SOLUTIONS

A3.1 Table A3.1 lists stock solutions (see 8.3).

**TABLE A3.1 Preparation of Metal Stock Solutions<sup>A,B</sup>**

Element (Compound)	Weight, g	Solvent
Al	1.000	HCl (1 + 1)
Be	1.0000	HCl (sp gr 1.19)
H <sub>3</sub> BO <sub>3</sub>	5.720	Water <sup>B</sup>
CdO	1.142	HNO <sub>3</sub> (sp gr 1.42)
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	3.762	Water <sup>B</sup>
Co	1.000	HCl (sp gr 1.19)
CuO	1.252	HCl (sp gr 1.19)
Fe	1.000	HCl (sp gr 1.19)
Pb(NO <sub>3</sub> ) <sub>2</sub>	1.599	Water <sup>B</sup>
MnSO <sub>4</sub> ·H <sub>2</sub> O	3.076	Water <sup>B</sup>
HgCl <sub>2</sub>	1.354	Water <sup>B</sup>
Ni	1.000	HNO <sub>3</sub> (1 + 1)
SrCO <sub>3</sub>	1.6849	HCl (sp gr 1.19)
V <sub>2</sub> O <sub>5</sub>	1.785	HCl (sp gr 1.19)
ZnO	1.245	HCl (sp gr 1.19)

<sup>A</sup>Metal stock solutions, 1.00 mL = 1.00 mg of metal. Dissolve the listed weights of each compound or metal in 20 mL of the specified solvent and dilute to 1 L. The metals and oxides require heat to increase rate of dissolution.

<sup>B</sup>Where water is used as the solvent, acidify with 20 mL of HNO<sub>3</sub> (sp. gr. 1.42) and dilute to volume. See Section 8 for concentration of acids. Commercially available standards may also be used.

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