



Designation: ~~D4519~~ – ~~10~~ D4519 – 16

# Standard Test Method for On-Line Determination of Anions and Carbon Dioxide in High Purity Water by Cation Exchange and Degassed Cation Conductivity<sup>1</sup>

This standard is issued under the fixed designation D4519; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 1. Scope

1.1 This on-line test method includes hydrogen exchange and degassing by ~~boiling-heating or gas stripping~~ and provides means for determining anions (such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{F}^-$ ) at levels as low as 2  $\mu\text{g/L}$  (2 ppb) and carbon dioxide at the level of 0.01 to 10 mg/L (ppm) at 25°C in high purity water and ~~steam condensate in steam and water samples in power plants~~ by measuring electrical conductivity.

1.2 The conductivity of all anions (except  $\text{OH}^-$ ) is determined and not the conductivity of an individual anion if more than one is present. If only one anion is present (such as  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ ), reference to Section 4, Table 1 and Table 2 or Figs. 1-3 provides the chloride or sulfate and  $\text{CO}_2$  concentration.

1.3 This test method has been improved in accuracy by using a modern microprocessor instrument for conductivity and temperature measurement and appropriate temperature compensation algorithms for ~~compensation to 25°C compensation, by using final sample cooling to 25°C, or both.~~

1.4 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the standard.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

Current edition approved Dec. 1, 2010; June 1, 2016. Published March 2011; June 2016. Originally approved in 1985. Last previous edition approved in 2005 as D4519-94 (2005); D4519-10. DOI: 10.1520/D4519-10.1520/D4519-16.

TABLE 1 Increase in Conductivity of Pure Water Expressed as Chloride Ion or Sulfate Ion

Conductivity due to Chlorides	Concentration Chlorides (PPB)	Conductivity due to Sulfates	Concentration Sulfates (PPB)
0.0548	0.0	0.0548	0.0
0.0595	1	0.0608	1
0.0651	2	0.0669	2
0.0717	3	0.0732	3
0.0791	4	0.0797	4
0.0872	5	0.0862	5
0.0958	6	0.0929	6
0.1049	7	0.0997	7
0.1145	8	0.1066	8
0.1243	9	0.1137	9
0.1344	10	0.1208	10
0.2427	20	0.1969	20
0.3560	30	0.2780	30
0.4709	40	0.3616	40
0.5865	50	0.4455	50
0.7023	60	0.5320	60
0.8183	70	0.6181	70
0.9345	80	0.7044	80
1.0507	90	0.7909	90
1.1669	100	0.8775	100
2.2209	200	1.7470	200
5.8252	500	4.362	500

**TABLE 2 25°C Conductivity of the Sample Immediately After the Cation Column, Relating to the CO<sub>2</sub> Concentration with the Anion Component Subtracted Out (See 11.7)**

Conductivity µs/cm	Carbon Dioxide	
	ppm	ppb
0.0548	0	0
0.09	0.01	10
0.12	0.02	20
0.16	0.03	30
0.19	0.04	40
0.21	0.05	50
0.24	0.06	60
0.26	0.07	70
0.28	0.08	80
0.3	0.09	90
0.32	0.1	100
0.48	0.2	200
0.61	0.3	300
0.71	0.4	400
0.81	0.5	500
0.89	0.6	600
0.97	0.7	700
1.04	0.8	800
1.11	0.9	900
1.17	1.0	...
1.69	2.0	...
2.09	3.0	...
2.42	4.0	...
2.72	5.0	...
2.98	6.0	...
3.23	7.0	...
3.46	8.0	...
3.67	9.0	...
3.88	10	...
5.46	20	...

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*:<sup>2</sup> <https://standards.iteh.ai/catalog/standards/sist/1ea63ba9-02e3-4971-9dc3-01ee0288d63f/astm-d4519-16>
- D1066 Practice for Sampling Steam
- D1125 Test Methods for Electrical Conductivity and Resistivity of Water
- D1129 Terminology Relating to Water
- ~~D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)~~<sup>3</sup>
- 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 Closed Conduits

**3. Terminology**

3.1 *Definitions*—For definitions of terms used in this test method, refer to Test Methods [D1125](#) and Terminology [D1129](#).

3.1 Definitions:

3.1.1 For definitions of terms used in this standard, refer to Test Methods [D1125](#) and Terminology [D1129](#).

**4. Summary of Test Method**

4.1 This test method measures the anion concentration (such as Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) by measuring the electrical conductivity of the anions after passing cooled condensate or high purity water—the sample through a cation exchanger in the hydrogen form, then through an electric reboiler, a degasifier. Passage through the cation resin replaces cations (including ammonia and other amines) in the water with hydrogen ions. This eliminates interference in the measurement of anions. Three conductivity cells located in the instrument provide measurements of the influent conductivity, cation conductivity at the incoming sample temperature, and the effluent conductivity at atmospheric boiling water temperature after acidic (volatile) gas removal.

<sup>2</sup> 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.

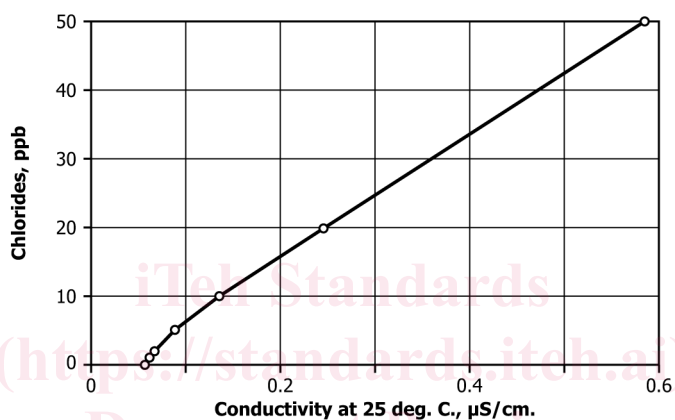
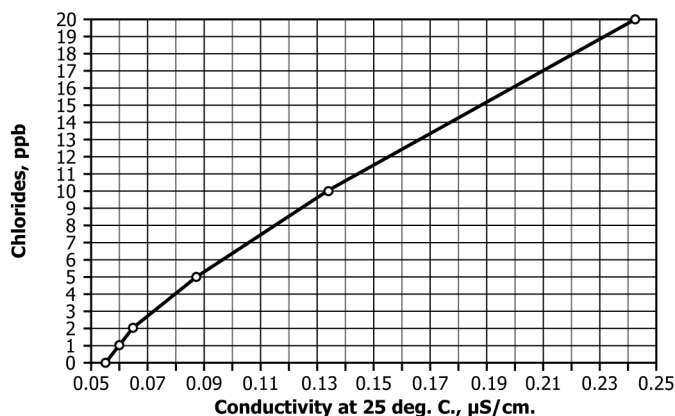


FIG. 1 Chloride Ion vs. Conductivity

ASTM D4519-16

Conductivity values are then corrected. The sample is then either cooled to 25°C or conductivity values are compensated to 25°C. While the influent conductivity measurement is not necessary in determining the total anion conductivity, its determination provides a more complete evaluation of the sample, which can also include an estimation of the amine content. Measurement of the cation and reboil effluent degassed sample conductivities are necessary in determining the composition of the influent (total anions and acidic gas content). Reference to Table 1 and Table 2 or Figs. 1-3, or both, are then necessary to complete the determinations.

4.2 In-depth studies provide additional background and updated experience with the degassed cation conductivity technique (1).<sup>3</sup>

5. Significance and Use

5.1 This test method can be a useful diagnostic tool in measuring the impurities and detecting their sources in high purity water, the boiler feed water and steam condensate of high pressure power plants, and in the process water of certain industries requiring water of the highest purity attainable. high purity water.

5.2 The measurement of such impurities is most important to these industries since plant outages or product contamination can result from events such as condenser leakage. Also, water quality deviations can occur from condensate polishing and makeup water equipment malfunctions.

5.3 The continuous measurement and trends provided by this test method are of particular interest and can indicate the need for corrections in water treating or operating procedures and equipment. The equipment for this test method can be considered more rugged and adaptable to installation under plant operating conditions than the more accurate laboratory methods, such as ion chromatography and atomic absorption.

<sup>3</sup> The last approved version of this historical standard is referenced on www.astm.org; boldface numbers in parentheses refer to a list of references at the end of this standard.

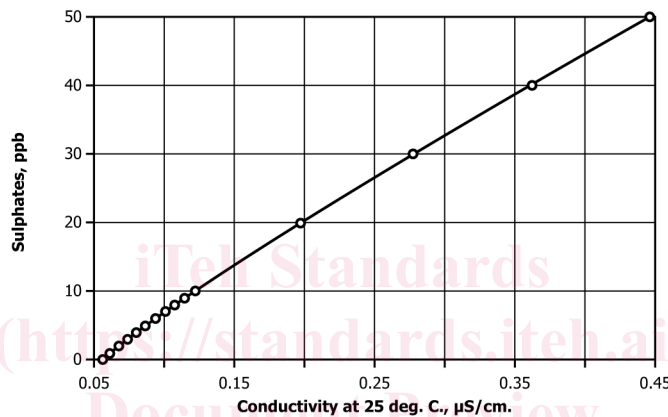
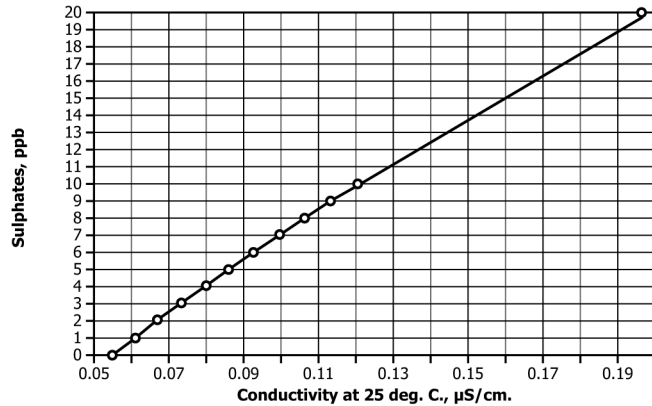


FIG. 2 Sulfate Ion vs. Conductivity

ASTM D4519-16

6. Interferences

6.1 It is important to devote particular attention to accurate flow and temperature control as variations can cause inaccuracies. See Annex A1, Annex A2, and Annex A3 for additional information on this subject.

7. Apparatus

7.1 Mechanical Ion Exchanger-Degasser Instrument.

7.2 Constant Head Device, for providing approximately 1.5 m (5 ft) head pressure for water entering the instrument.

7.3 Constant Temperature Equipment, for adjusting the influent temperature to  $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ .

7.4 Conductivity Instruments and Sensors, for measuring the conductivity of the sample to determine the concentration of anions and carbon dioxide. Use of instruments that have a specialized temperature compensation for high purity water (to  $25^{\circ}\text{C}$ ) based on an acid such as HCl or  $\text{H}_2\text{SO}_4$  is required for this test method.

7.1 Hydrogen Exchange Cartridge, Degassed Cation Conductivity System, 1 5/8 in. inside diameter, 12 in. height, containing 1 lb of 8 % cross-linked styrene-divinylbenzene, strong acid gel cation exchange resin in the  $\text{H}^+$  form; U.S. standard mesh 16 by 50 (1190 by 297  $\mu\text{m}$ ) may be used. Regenerate with 1500 mL of hydrochloric acid (1 + 6) at a flow rate of 40 to 50 mL/min; followed by rinsing with 300 mL of Type II water at the same flow rate. Then rinse with 3500 mL of Type II water at a flow rate of 100 to 150 mL/min. Rinse down when placing in service; may be provided as a complete panel or may be assembled from components.

NOTE 1—The column inside diameter, resin bed height, inlet sample temperature (11.3), and service flowrate (11.4) have been standardized to provide comparable results. They may not be the optimum values. The user should realize that those parameters affect the measurement.

7.1.1 Constant Head Device or Other Means, for providing constant sample flow through the apparatus.

7.1.2 Constant Temperature Equipment, for adjusting the influent temperature to  $25 \pm 0.5^{\circ}\text{C}$ .

7.1.3 Flow or Temperature Safety Shutoff, as needed to protect the degasifier heater.

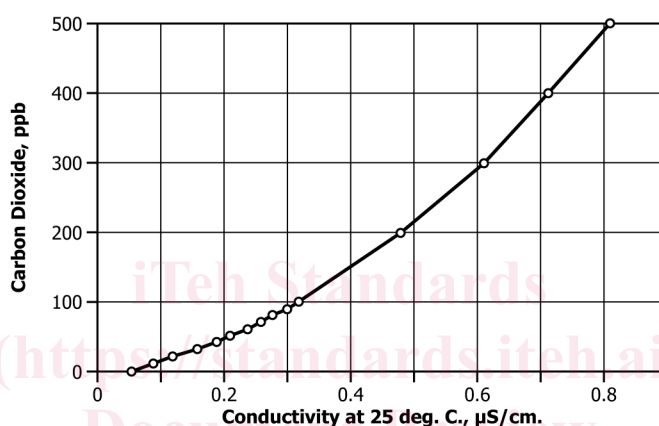
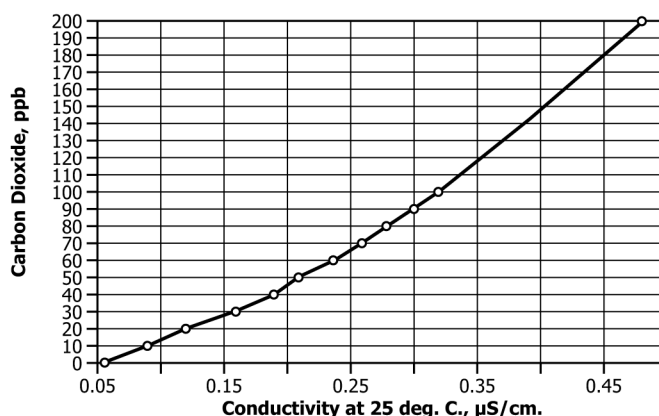


FIG. 3 Carbon Dioxide vs. Conductivity

7.1.4 *Conductivity Instrument(s) and Sensors*, for measuring the conductivity of the sample to determine the concentration of anions and carbon dioxide. Use of instruments that have a specialized temperature compensation for high purity water (to 25°C) based on a trace acid contaminant such as HCl or H<sub>2</sub>SO<sub>4</sub> is required for this test method. Instrumentation may also include software to automate the determination of anions and carbon dioxide based on Table 1 and Table 2.

7.1.5 *Hydrogen Ion Exchange Cartridge*, 1 5/8 in. inside diameter, 12 in. height, containing 1 lb of 8 % cross-linked styrene-divinylbenzene, strong acid gel cation exchange resin in the H<sup>+</sup> form; U.S. standard mesh 16 by 50 (1190 by 297 µm) may be used. Regenerate with 1500 mL of hydrochloric acid (1 + 6) at a flow rate of 40 to 50 mL/min, followed by rinsing with 300 mL of Type II water at the same flow rate. Then rinse with 3500 mL of Type II water at a flow rate of 100 to 150 mL/min. Rinse down when placing in service.

NOTE 1—The column inside diameter, resin bed height, inlet sample temperature (11.3), and service flowrate (11.4) have been standardized to provide comparable results. They may not be the optimum values. The user should realize that those parameters affect the measurement.

7.1.6 *Degasifier*, for removing carbon dioxide from the sample. The degasifier may operate by heating the sample to near boiling temperature with a reboiler or by sparging with a CO<sub>2</sub>-free gas such as nitrogen. Following a reboiler, a cooler may be used to reduce the sample temperature and potential errors in temperature compensation. (Membrane gas stripping has been used experimentally for degassing but this technique has not been standardized.) (2)

7.6 Software to automate the determination of anions and carbon dioxide is available.

## 8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the American Chemical Society, where such specifications are available.<sup>4</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

<sup>4</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.

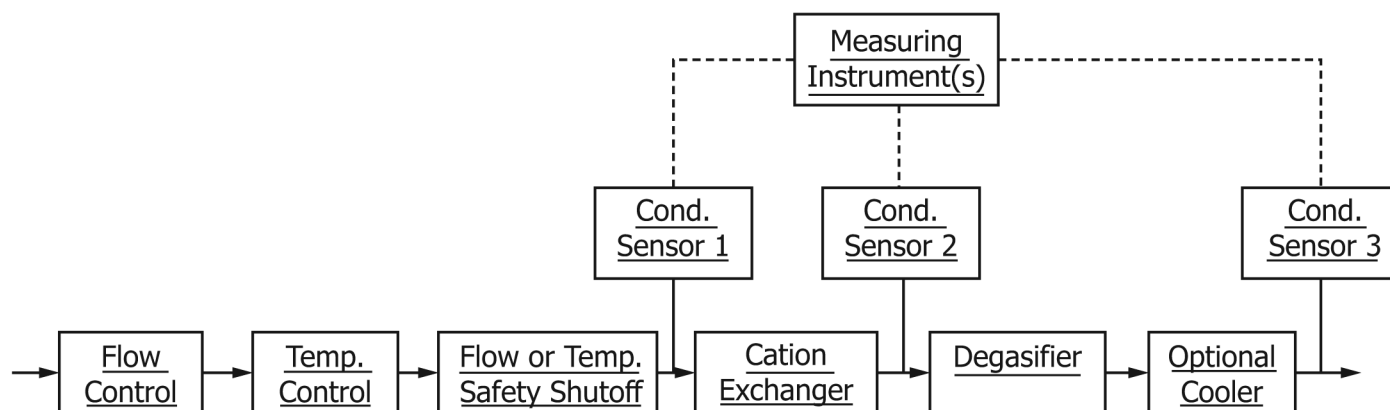


FIG. 4 Flow Diagram for Mechanical Ion-Exchanger-Degasser Instrument Block Diagram of Measurement Apparatus

8.2 *Purity of Water*—Unless otherwise indicated, references to water that is used for reagent preparation, rinsing or dilution shall be understood to mean water that conforms to the quantitative specifications of Type II reagent water of Specification D1193.

8.3 *Chloride Solution, Stock* (1 mL = 0.1 mg  $\text{Cl}^-$ )—Dissolve in water 0.1649 g of sodium chloride (NaCl) dried to constant weight at 105°C, and dilute to 1 L in a thoroughly cleaned polyethylene flask.

8.4 *Chloride Solution, Standard* (1.00 mL = 0.001 mg)—Dilute 10.00 mL of chloride stock solution (8.3) to 1 L with water.

8.4.1 This standard chloride solution is to be used in the calibration of the instrument if desired, or reference can be made to the instruction booklet furnished with the instrument.

8.5 *Hydrochloric Acid* (1 + 6)—Add 100 mL concentrated HCl (sp. gr. 1.19) to 600 mL water.

## 9. Sampling

9.1 ~~Collect the sample~~ Establish sampling conditions in accordance with the applicable ASTM standards: Practice D1066; Specification D1192, and Practices D3370.

## 10. Calibration

10.1 The instrument may be calibrated by pumping solutions of known concentrations of  $\text{Cl}^-$  (in NaCl form) or  $\text{SO}_4^{2-}$  (in  $\text{Na}_2\text{SO}_4$  form) through the instrument and observing the conductivity increases. It may be preferred to use the calibration charts shown in the instruction book accompanying the instrument or in referenced articles-articles (3-6)."

10.2 If it is desired to calibrate the instrument using known chloride solutions, the range of 0.001 to 0.010 mg/L (1 to 10 ppb) of chloride may be covered by application of 0.2 to 2.0 mL/min of the standard chloride solution (8.4.1) to the 200 mL/min flow by injecting the flow from a small peristaltic pump to a hypodermic needle inserted in a plastic tubing connection.

## 11. Procedure

11.1 Flush out the piping thoroughly by flow of high purity water through the instrument before starting the flow of water to be tested.

11.2 Refer to the manufacturer's instruction booklet before starting the instrument. Because of the nature of this measuring technique, it is very important to follow the manufacturer's instructions very carefully in order to achieve accurate results. See Annex A1 – Annex A4 for a discussion on the effects caused by variations in operating conditions and interfering substances.

11.3 Connect the ~~high purity water or condensate sample line~~ to be tested to the instrument influent connection. This water should preferably be at a temperature of  $25 \pm 0.5^\circ\text{C}$ . The flow shall first pass through the ~~constant head flow control~~ device, then into the instrument through the hydrogen ion exchanger and ~~electric reboiler and out the reboil chamber effluent~~ degasifier (Fig. 4 and Fig. 5).

11.4 Adjust the flow through the instrument to the proper flow rate (200 mL/min), or as specified by the instrument manufacturer. It is important to use a constant head device ~~in order or other means~~ to maintain a stable flow rate, otherwise changes in cation resin exchange ~~efficiency and degassing efficiencies~~ may occur with changes in the flow rate.

11.5 Clean up the system by maintaining the recommended flow rate through the instrument for 24 h or longer to approach a minimum value of 0.055  $\mu\text{S}/\text{cm}$  reading for pure water at the final effluent conductivity. On restart, several hours of operation may be required before this minimum conductivity value is obtained.

11.6 Refer to Table 1, or Fig. 1 and Fig. 2, or both, to determine the equivalent concentration of chloride ion or sulfate ion based on the conductivity reading of the final conductivity cell.