Designation: 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[1]

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 reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This on-line test method includes hydrogen exchange and degassing by heating or gas stripping and provides means for determining anions (such as Cl^-, SO_4^-, NO_3^-, and F^-) at levels as low as 2 µg/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 in steam and water samples in power plants by measuring electrical conductivity.

1.2 The conductivity of all anions (except 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 Cl^- or SO_4^-), reference to Section 4, Table 1 and Table 2 or Figs. 1-3 provides the chloride or sulfate and 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, 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.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *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
D1125 Test Methods for Electrical Conductivity and Resistivity of Water
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 Closed Conduits

3. Terminology

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^- and SO_4^-) by measuring the electrical conductivity of the anions after passing the sample through a cation exchanger in the hydrogen form, then through 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 after acidic (volatile) gas removal. 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

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[1] 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.

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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 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_2 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	...

sample, which can also include an estimation of the amine content. Measurement of the cation and 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.

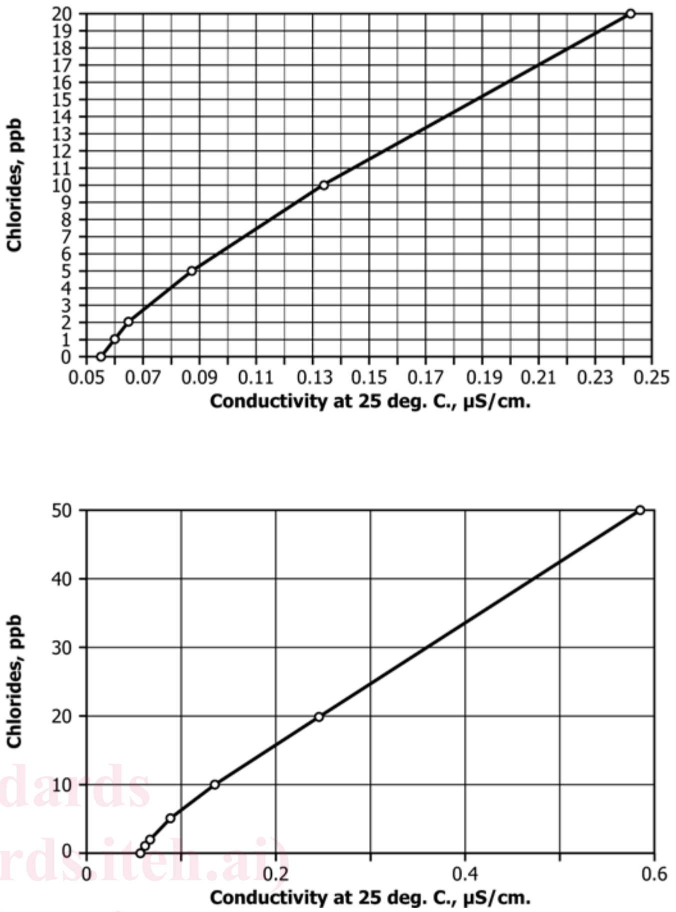

FIG. 1 Chloride Ion vs. Conductivity

4.2 In-depth studies provide additional background and updated experience with the degassed cation conductivity technique (**1**).[3]

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, boiler feed water and steam condensate of high pressure power plants, and in the process water of certain industries requiring 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.

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[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

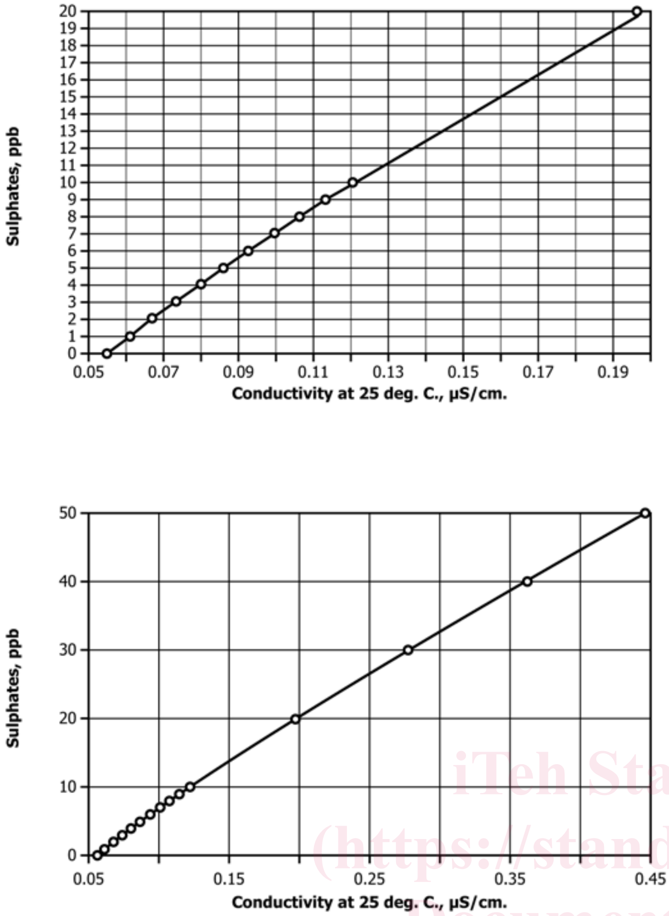

FIG. 2 Sulfate Ion vs. Conductivity

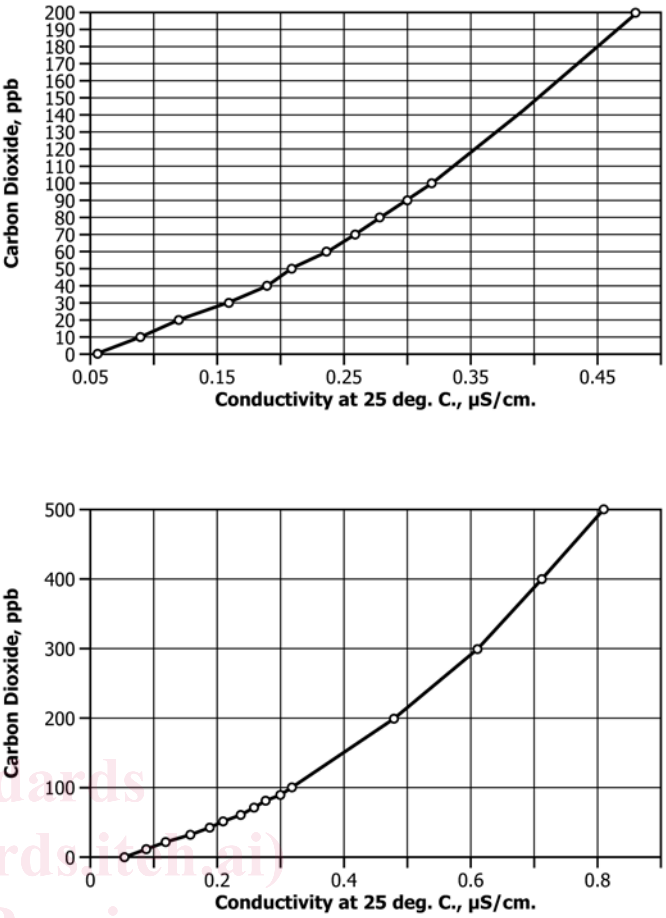

FIG. 3 Carbon Dioxide vs. Conductivity

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.

7. Apparatus

7.1 *Degassed Cation Conductivity System,* may be provided as a complete panel or may be assembled from components.

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 ± 0.5°C.

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

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_2SO_4 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,* 1⅝ in. inside diameter, 12 in. height, containing 1 lb of 8 % cross-linked styrene-divinylbenzene, strong acid gel cation exchange resin in the H^+ 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_2-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)**

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