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

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 sample, which can also include an estimation of the amine

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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	...

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.

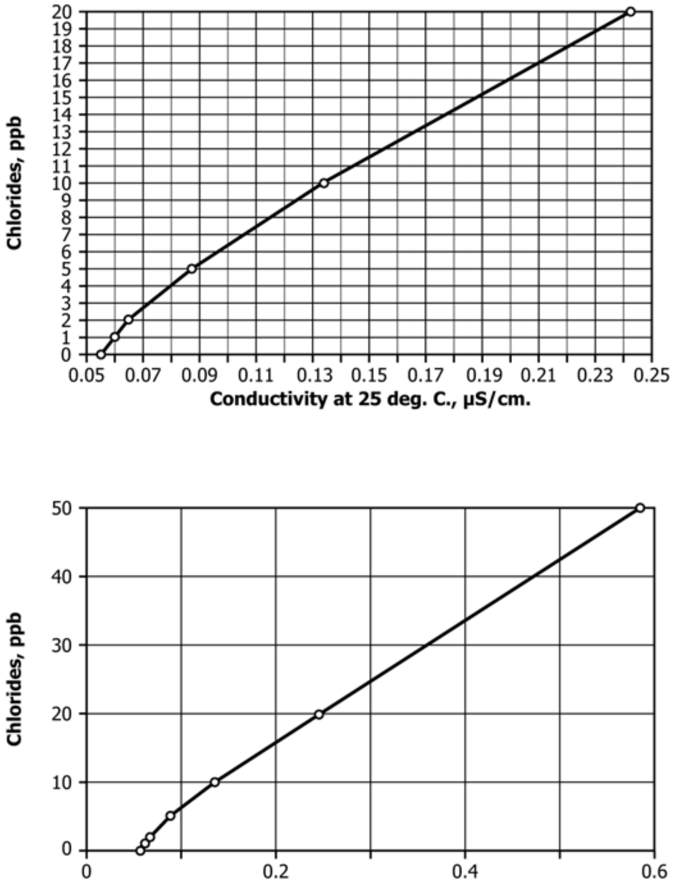

FIG. 1 Chloride Ion vs. Conductivity

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

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

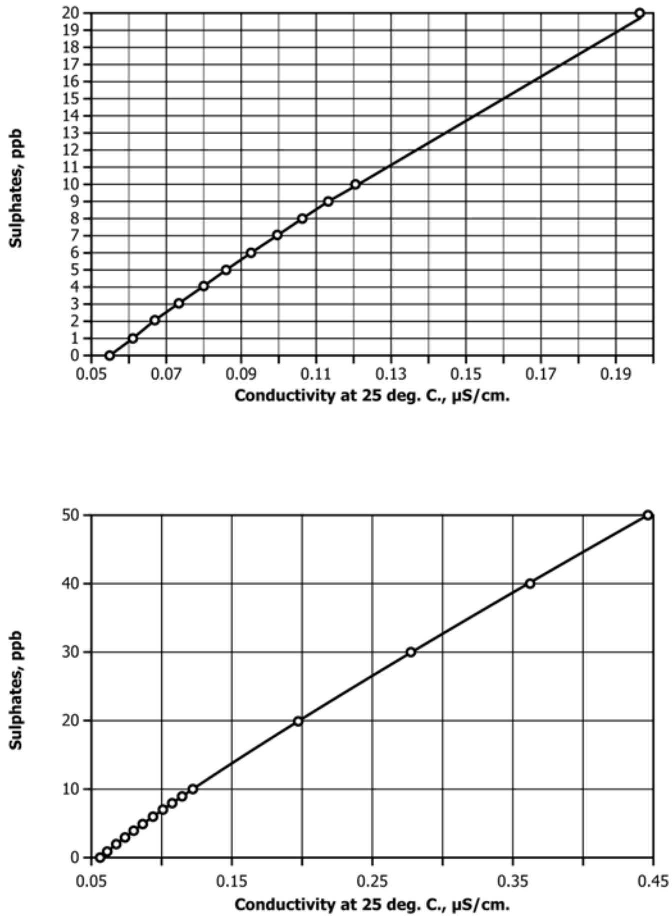

FIG. 2 Sulfate Ion vs. Conductivity

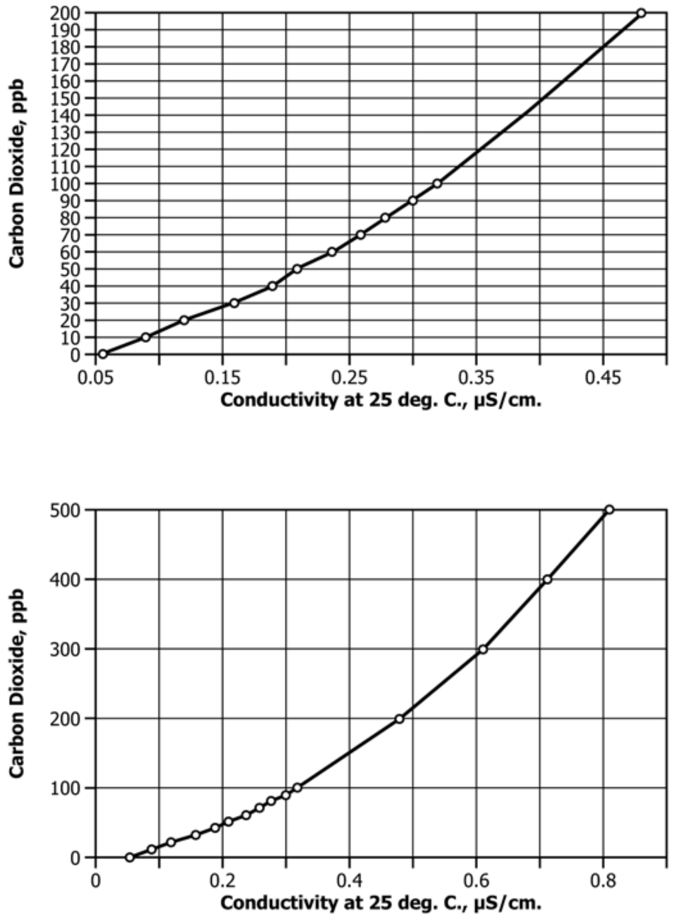

FIG. 3 Carbon Dioxide vs. Conductivity

plant operating conditions than the more accurate laboratory methods, such as ion chromatography and atomic absorption.

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

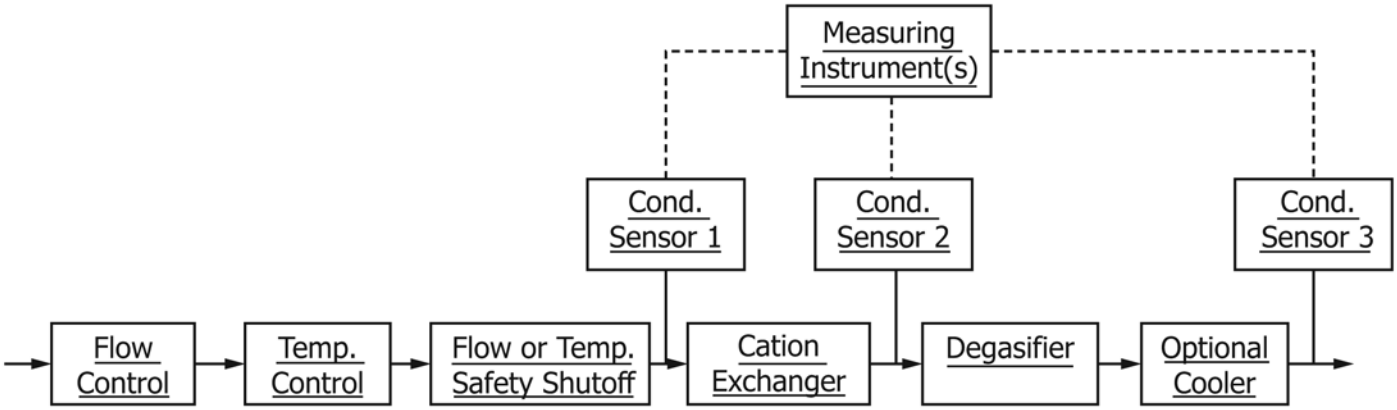

FIG. 4 Block Diagram of Measurement Apparatus

Chemical Society, where such specifications are available.[4] 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.

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 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 Establish sampling conditions in accordance with the applicable ASTM standards: Practice D1066 and Practices D3370.

10. Calibration

10.1 The instrument may be calibrated by pumping solutions of known concentrations of Cl^- (in NaCl form) or SO_4^- (in Na_2SO_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 (**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 sample line to be tested to the instrument influent connection. This water should preferably be at a temperature of 25 ± 0.5°C. The flow shall first pass through the flow control device, then into the instrument through the hydrogen ion exchanger and degasifier (Fig. 4).

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 or other means to maintain a stable flow rate, otherwise changes in cation resin exchange 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 µS/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.

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[4] *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.

11.7 In order to obtain the volatiles expressed as carbon dioxide in Table 2, subtract the conductivity of pure water (0.055 µS/cm) from the conductivity of the final effluent cell. Then deduct this value from the cation conductivity obtained from the cell immediately after the cation exchange resin. Use this adjusted conductivity value to look up the concentration of volatiles expressed as a concentration of carbon dioxide in Table 2, or Fig. 3, or both. Alternatively, use instrumentation containing software to make these conversions automatically and providing continuous real time readout.

11.7.1 Example: Based on a final cell conductivity reading of 0.087 µS/cm (equivalent to 5 ppb of Cl^- in a system predominant in chloride ion), 0.055 µS/cm is deducted for the conductivity of pure water to obtain a value of 0.087 − 0.055 = 0.032 µS/cm. Then deduct this number (0.032) from the cation conductivity (0.242 − 0.032) = 0.21 µS⁄cm due to volatiles, which corresponds to 50 µg/L (ppb) of carbon dioxide, as read from Table 2. This deduction is necessary to account for the anion conductivity (other than carbon dioxide) obtained in the cation conductivity measurement.

11.8 The service life of the cation cartridge may vary from one month to several months depending on the amine concentration in the influent and the sample flow rate.

12. Report

12.1 Report the results as g/L (ppb) Cl^-, or SO_4^{--}, or both, and CO_2 as obtained from Table 1 and Table 2, or Figs. 1-3, or both with resolution of 1 µg/L (ppb).

13. Quality Control

13.1 In order to be certain that analytical values obtained using this test method are valid and accurate, the following QC procedures must be followed:

13.1.1 *Periodic Verification of Calibration of the Measurement System:*

13.1.1.1 Verify calibration of the conductivity cell constant in accordance with Test Methods D1125 on at least a yearly basis. If results are outside the acceptable tolerance, clean the sensor and repeat the verification. If results are still outside acceptable limits, re-determine the sensor cell constant. If the cell constant changes by more than ±5 % of its initial value, replace the sensor.

13.1.2 *Initial Demonstration of Capability:*

13.1.2.1 Verify the conductivity measuring circuit (and temperature measuring circuit if used for temperature compensation) by installing precision resistor(s) in place of the conductivity cell and temperature sensor as described in Test Methods D1125.

13.1.2.2 Alternatively for 13.1.2.1, use instrument manufacturer-certified resistance calibrators and procedures.

13.1.3 *General Precautions:*

13.1.3.1 Confirm that temperature compensation algorithms are accurate and that settings for each measurement are appropriate, that is, ammonia/amine compensation for specific conductivity; cation compensation (accounting for trace acid effect on dissociation of pure water) for cation and degassed cation conductivity measurements. Where accurate and appropriate compensation is not available, control the temperature of the sample to 25 ± 1°C ahead of each sensor.

13.1.3.2 Where color indicating cation exchange resin is used, confirm that at least 20 % of the resin column remains in the hydrogen form. Replace when <20 % of the resin remains in the hydrogen form. Where applicable, establish resin replacement practice that includes consideration of operating experience with the pH levels being measured, any exceptional contamination spikes that may have occurred and whether there is significant iron fouling.

13.1.3.3 When resin is replaced or when the sample flow has been stopped for other reasons, allow sufficient time for rinsing to achieve a stable, low, cation conductivity reading and do not use measurement results until stable readings are obtained.

13.1.3.4 Confirm that the sample flow and resin column diameter provide the required sample flow velocity cited in Annex A2. For heat degassing, confirm that the degasser temperature is set and controlling according to the manufacturer's instructions. For degassing by gas stripping, confirm that the gas flowrate is set according the manufacturer's instructions.

13.1.3.5 Where flow in the resin column is upwards, confirm that the resin is not being fluidized, allowing channeling and poor ion exchange. Where flow in the resin is downward, at startup remove all air bubbles by venting to prevent slow dissolution of CO_2 from delaying a stable response.

14. Precision and Bias

14.1 Since this test method involves continuous sampling and measurement and requires extensive rinsing with the sample before usable results can be obtained, Practice D2777 is not applicable. Refs. **(3-6)** show excellent agreement between the theoretical and measured conductivity values of Cl^- and SO_4^{--} ions in the 0 to 50 g/L (ppb) range.

15. Keywords

15.1 anion electrical conductivity; carbon dioxide; cation conductivity; degassed cation conductivity; electrical conductivity; high purity water; reboiled conductivity degasification

ANNEXES

(Mandatory Information)

A1. EFFECTS OF THE INFLUENT WATER TEMPERATURE

A1.1 The cation resin loses its ability to maintain its holding power with increases in temperature. Therefore, it is important to maintain a constant temperature so as to avoid any changes in the baseline of the measurement. Fig. A1.1 shows the effects of temperature of the influent water versus the conductivity (at 25°C) of the effluent water of a cation column when supplied with 0.055 µS/cm water.

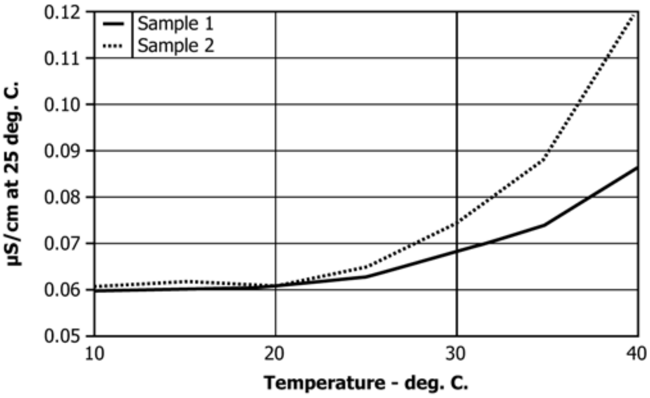

FIG. A1.1 Cation Resin Performance, Amount of Ionic Leaching Versus the Temperature for IWT Type TCD1 Resin in a 2-in. Diameter Tube

A2. EFFECTS OF SAMPLE VELOCITY

A2.1 The cation resin has an optimum dynamic efficiency at a given sample flow rate. Fig. A2.1 depicts the change in conductivity of the effluent of a 2 in. insider diameter column with 1 lb of cation resin versus flow rate. As indicated by this chart, it is important to provide a flow of 200 mL/min through the resin in order to maximize the efficiency of the resin and to minimize resin bleed-off. While this is a larger-sized diameter cartridge than that described in the present test method (1⅝ in. (41 mm) inside diameter), the same conclusions and need for accurate flow control are to be expected. Any deviations in the flow rate will cause variations in the baseline of the measurement and therefore should be held to a minimum in order to reduce any errors in measurement. More accurate cation conductivity results have been reported with this lesser diameter column (**6**).

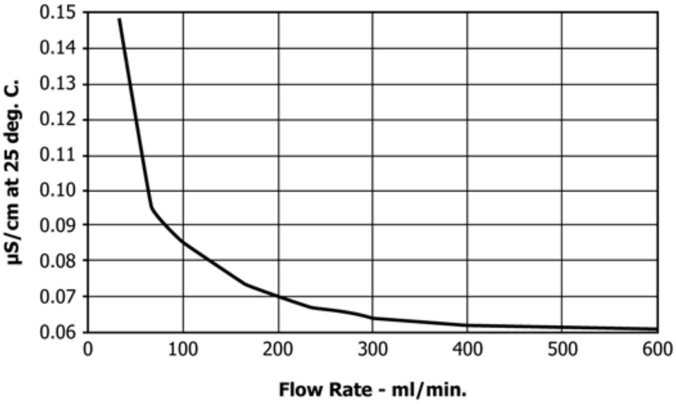

FIG. A2.1 Cation Resin Performance, Amount of Ionic Leaching Versus the Flow Rate for IWT Type TCD1 Resin in a 2-in. Diameter Tube

A3. TEMPERATURE COMPENSATION OF THE INSTRUMENT

A3.1 In the past, conductivity instruments without temperature compensation were used for this test method. This led to large errors due to fluctuations in temperature at the reboil chamber effluent and difficulty in accounting accurately for conductivity changes resulting from changes in atmospheric boiling water temperature. Due to the steep slope of pure water samples (5 %/°C) and the large temperature variations (often more than 5°C), large errors were introduced and not accounted for. With a modern microprocessor instrument that measures the temperature very accurately and by using appropriate temperature compensation algorithms to correct the conductivity to the equivalent conductivity at 25°C, one can minimize the errors associated with the effluent temperature and the atmospheric pressure over the previous test method described in Test Method D4519 – 85.

A4. ORGANIC ACIDS

A4.1 It has been theorized that the final effluent results (degassed cation conductivity) for Cl^- and SO_4^{--} may be inaccurate if there are appreciable organic acids present (as acetic and formic). Evaluation of the effects of organic acids confirms that they remain in the liquid phase and contribute to the degassed conductivity which would be interpreted as additional Cl^- and SO_4^{--} (**1**).

REFERENCES

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(2) Drew, N., “Evaluation of Degassed After-Cation-Exchange Conductivity Techniques,” *PowerPlant Chemistry*, Vol 6, No. 6, June 2004, pp. 343–349.

(3) Lane, R. W., Sollo, F. W., Neff, C. H., “Continuous Monitoring of Anions in Feedwater by Electrical Conductivity,” Illinois State Water Survey Reprint 473, Reprinted from *Water and Steam, Their Properties and Current Industrial Applications*, Pergammon Press, Oxford and New York, 1980.

(4) Electric Power Research Institute, “Monitoring Cycle Water Chemistry in Fossil Plants,” EPRI GS-7556, Vol 1: Monitoring Results.

(5) “Continuous Conductivity Monitoring of Anions in High-Purity Water,” *ASTM STP 742*, ASTM, 1981, p. 195.

(6) Internal report from Carl C. Scheerer, C.I.P.S., Springfield, IL, April 18, 1989.