Designation: D5391 – 23

Standard Test Method for Electrical Conductivity and Resistivity of a Flowing High Purity Water Sample[1]

This standard is issued under the fixed designation D5391; 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 electrical conductivity and resistivity of high purity water samples below 10 µS/cm (above 0.1 Mohm-cm). It is applicable to both continuous and periodic measurements but in all cases, the water must be flowing in order to provide representative sampling. Static *grab* sampling cannot be used for such high purity water. Continuous measurements are made directly in pure water process lines, or in side stream sample lines to enable measurements on high temperature or high pressure samples, or both.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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.*

1.4 *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D1125 Test Methods for Electrical Conductivity and Resistivity of Water (Withdrawn 2023)[3]

D1129 Terminology Relating to Water

D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[3]

D1193 Specification for Reagent Water

D2186 Test Methods for Deposit-Forming Impurities in Steam (Withdrawn 2014)[3]

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

D3864 Guide for On-Line Monitoring Systems for Water Analysis

D4519 Test Method for On-Line Determination of Anions and Carbon Dioxide in High Purity Water by Cation Exchange and Degassed Cation Conductivity

3. Terminology

3.1 *Definitions*—For definitions of other terms used in these test methods, refer to Terminology D1129.

3.1.1 *electrical conductivity*—refer to Test Methods D1125.

3.1.2 *electrical resistivity*—refer to Test Methods D1125.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *cell constant, n*—the ratio of the length of the path, *L* (cm), and the cross-sectional area of the solution, A (cm^2), between the electrodes of a conductivity/resistivity cell, with units of cm^{-1}.

3.2.1.1 *Discussion*—In high purity water measurements, the cell constant is normally between 0.001 and 0.1 cm^{-1} to prevent electrical interference. This is lower than the 1 cm^{-1} of the standard centimetre cube and is taken into account by direct reading instrument ranges that are matched with specific cell constants.

4. Summary of Test Method

4.1 Conductivity or resistivity is measured with a cell and temperature sensor or compensator in a flowing, closed system to prevent trace contamination from wetted surfaces and from

[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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

the atmosphere. Specialized temperature compensation corrects the measurement to 25 °C, taking into account the temperature effects on the ionization of water, the contaminants, and interactions between the two. In the absence of specialized temperature compensation, the sample temperature is controlled to 25 ± 0.2 °C.

4.2 To determine the cell constant of a high purity conductivity cell with an instrument capable of accurate measurement over the range of pure water to 150 µS/cm with a single cell constant, Test Methods D1125 are used directly. Manufacturers' certification of cell constant traceability by this means is an acceptable alternative.

4.3 To determine the cell constant of a high purity conductivity cell with an instrument which does not accurately cover the range from pure water to 150 µS/cm with a single cell constant, a secondary standard cell is used that has an intermediate cell constant with precise value determined by Test Methods D1125. That secondary standard cell is then used in low conductivity water (not a standard) and readings are compared with those of the low constant cell under test. In this manner, the cell constant of the latter is determined. Manufacturers' certification of cell constant traceability by this means is an acceptable alternative.

5. Significance and Use

5.1 Conductivity measurements are typically made on samples of moderate to high ionic strength where contamination of open samples in routine laboratory handling is negligible. Under those conditions, standard temperature compensation using coefficients of 1 to 3 % of reading per degree Celsius over wide concentration ranges is appropriate. In contrast, this test method requires special considerations to reduce trace contamination and accommodates the high and variable temperature coefficients of pure water samples that can range as high as 7 % of reading per degree Celsius. In addition, measuring instrument design performance must be proven under high purity conditions.

5.2 This test method is applicable for detecting trace amounts of ionic contaminants in water. It is the primary means of monitoring the performance of demineralization and other high purity water treatment operations. It is also used to detect ionic contamination in boiler waters, microelectronics rinse waters, pharmaceutical process waters, etc., as well as to monitor and control the level of boiler and power plant cycle chemistry treatment chemicals. This test method supplements the basic measurement requirements for Test Methods D1125, D2186, and D4519.

5.3 At very low levels of alkaline contamination, for example, 0–1 µg/L NaOH, conductivity is suppressed, and can actually be slightly below the theoretical value for pure water. **(1 and 2)**[4] Alkaline materials suppress the highly conductive hydrogen ion concentration while replacing it with less conductive sodium and hydroxide ions. This phenomenon is not an interference with conductivity or resistivity measurement itself but could give misleading indications of inferred water purity in this range if it is not recognized.

6. Interferences

6.1 Exposure of the sample to the atmosphere may cause changes in conductivity/resistivity due to loss or gain of dissolved ionizable gases. Carbon dioxide, normally present in the air, can reach an equilibrium concentration in water of about 1 mg/L and add approximately 1 µS/cm to the conductivity due to formation of carbonic acid. Closed flow-through or sealed in-line cell installation is required for this reason.

6.2 Power plant installations utilizing long sample lines can experience significant sampling problems. New sample lines normally require longterm conditioning. Iron oxides and other deposits accumulate in slow flowing horizontal sample lines and can develop chromatograph-like retention of ionic species, resulting in very long delay times. Precautions are described in Section 9.

6.3 Cell and flow chamber surfaces will slowly leach trace ionic contaminants, evidenced by increasing conductivity readings with very low or zero flowrate. There must be sufficient flow to keep these contaminants from accumulating to the point that they affect the measurement. The high and convoluted surface area of platinized cells precludes their use for high purity measurements for this reason.

6.4 Capacitance of the cell and extension leadwire, especially in high purity ranges can add significant positive error to conductance readings (negative error to resistance readings). The measuring instrument must be designed to accommodate cell and leadwire characteristics in high purity water as described in 7.1.1 and Annex A1. In addition, the instrument manufacturers' recommendations on cell leadwire must be carefully followed.

6.5 Conductivity and resistivity measurements are referenced to 25 °C. Either samples must be controlled to 25.0 ± 0.2 °C or specialized temperature compensation must be employed that accounts for the characteristics of high purity water with specific contaminants, as described in 7.1.2.

6.6 Samples containing dissolved gases must have sufficient flow through the cell that bubbles cannot accumulate and occupy sample volume within the cell, causing low conductivity (high resistivity) readings. This problem is typical in makeup water treatment systems where water warms up, drops in pressure, and is acidified by cation exchange operations. This releases dissolved air and converts carbonates to carbon dioxide gas.

6.7 High purity conductivity measurement must not be made on a sample downstream of pH sensors since they invariably contaminate the sample with traces of reference electrolyte salts. Use a dedicated sample line or place the conductivity cell upstream from the pH sensors.

6.8 Conductivity cells mounted downstream from ion exchangers are vulnerable to catching resin particles between the cell electrodes. Resin particles are sufficiently conductive to short the cell and cause high off-scale conductivity or extremely low resistivity readings. Resin retainers must be

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