



Designation: D5391 – 23

Standard Test Method for Electrical Conductivity and Resistivity of a Flowing High Purity Water Sample¹

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

1. Scope

1.1 This test method covers the determination of electrical conductivity and resistivity of high purity water samples below $10 \mu\text{S}/\text{cm}$ (above $0.1 \text{ Mohm}\cdot\text{cm}$). 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D1125 Test Methods for Electrical Conductivity and Resistivity of Water (Withdrawn 2023)³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D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)³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D2186 Test Methods for Deposit-Forming Impurities in Steam (Withdrawn 2014)³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

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

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.

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 $\mu\text{S}/\text{cm}$ 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 $\mu\text{S}/\text{cm}$ 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 $\mu\text{g}/\text{L}$ 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 $\mu\text{S}/\text{cm}$ 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.

effective and cells must be accessible for cleaning. Cell designs with electrode spacing greater than 1.5 mm have been found to be less likely to trap such particles.

6.9 Conductivity cells, if subjected to demineralizer regeneration reagents, would require excessive rinse time to obtain satisfactory results. Therefore, locate cells where they will be isolated during regeneration cycles.

7. Apparatus

7.1 Measuring Instrument:

7.1.1 The instrument shall be continuously reading in either conductivity or resistivity units. It shall be specifically designed to measure in high purity ranges, measuring with alternating current (ac) of appropriate voltage, frequency, wave shape, phase correction, and wave sampling technique to minimize errors due to parallel and series capacitance of cell and leadwire as well as minimizing electrode polarization errors and effects of small direct current (dc) potentials. A cell simulation technique to verify the performance of an unproven measuring circuit design under high purity conditions is provided in Annex A1.

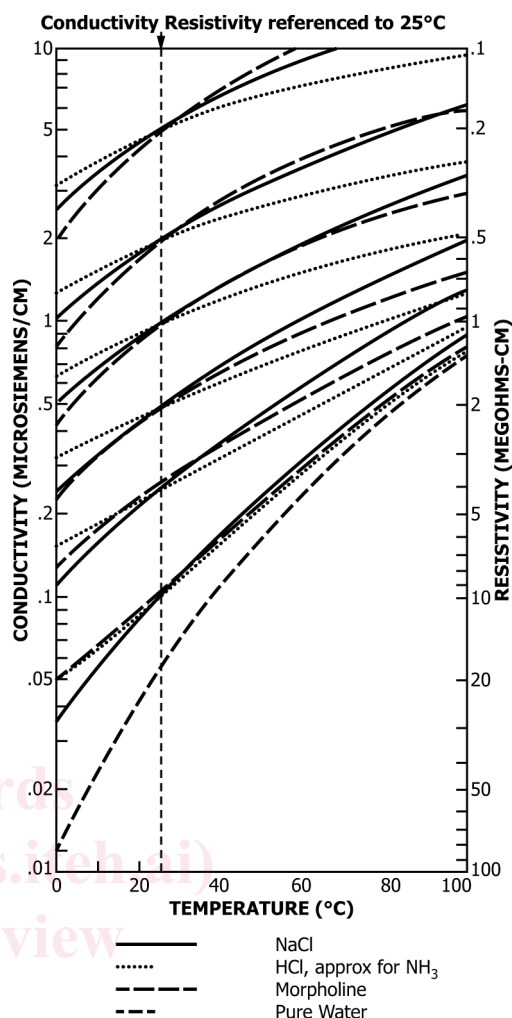
7.1.2 The measurement shall include algorithms to temperature compensate conductivity or resistivity values to 25.0 °C. The algorithm shall compensate for changes in water ionization as well as for solute ion mobility for neutral salt contaminants. The conductivity of pure water has been documented with high accuracy (3-5).

7.1.3 In the case of samples containing acidic or basic solutes (such as power plant treatment using ammonia, morpholine, etc., or acidic cation conductivity samples or microelectronics acid etch rinse monitoring), special algorithms shall be employed that account for the interaction of acids and bases with the ionization of water (6-8). The user is cautioned that accuracy of temperature compensation algorithms for these solutes may vary significantly. The user must determine the applicability and accuracy for a particular sample in the anticipated temperature range. Fig. 1 illustrates the variation in temperature effects on conductivity representative of neutral salts, ammonia, morpholine, and acids. Where specialized high purity temperature compensation algorithms are not provided to accurately compensate for these effects, sample temperature shall be controlled to 25.0 ± 0.2 °C. (Note that conductivity temperature coefficients exceed 7 % of reading per degree Celsius in the temperature range of 0 to 10 °C.)

7.1.4 Output signal(s) from the instrument, if provided, shall be electrically isolated from the cell and from the earth ground to prevent ground loop problems when the instrument is connected to grounded external devices.

7.2 Cell:

7.2.1 Flow-through or in-line conductivity/resistivity cells shall be used to prevent contamination from the atmosphere and wetted surfaces as described in 6.1 and 6.3. Flowrates shall be maintained within the manufacturer’s recommendations. The cell shall retain its constant calibration under the conditions of flowrate, temperature, and pressure of the installation. The cell shall incorporate an integral precision temperature sensor to ensure that it accurately senses the sample tempera-



NOTE 1—Curves represent concentrations of impurities given in Table 1.

FIG. 1 Temperature Effects on the Conductivity of High Purity Water

TABLE 1 Concentrations of Trace Contaminants Plotted in Fig. 1

Conductivity μS/cm at 25 °C	Concentration (μg/L)			
	NaCl	HCl	NH ₃	Morpholine
5.00	2295	430	638	13 755
2.00	903	172	177	2632
1.00	439	86	76	837
0.500	207	42.6	34.4	298
0.250	91	20.7	16.1	117
0.100	21.0	6.5	5.4	34.6
0.055	0.0	0.0	0.0	0.0

ture where the conductivity/resistivity is being detected to ensure accurate temperature compensation.

7.2.2 The cell for high purity water measurements shall not be used for measuring higher ionic content samples (greater than 20 μS/cm, less than 0.05 Mohm-cm) since it would retain ionic contaminants and require excessive rinse-down time for valid measurements in high purity ranges. A high purity cell in a demineralizer system shall not be located where it can be exposed to regeneration reagents.

7.2.3 Electrodes of the cell shall not be platinized for pure water measurements since the microscopically rough, porous surface would retain ionic contaminants and produce excessive downscale response times. Only a trace or flash of platinum black is permissible on electrode surfaces. Electrodes of titanium, nickel, monel, stainless steel, or platinum are suitable for high purity measurement. However, extra care must be taken using platinum cells not to exceed manufacturers' recommended flowrate and not to permit rough handling that could bend the electrodes and change the cell constant.

7.2.4 If the cell constant as checked does not fall within acceptable limits of its nominal value, it is necessary to clean or replace the cell. Even in pure water samples, coatings such as iron oxide crud in power plant installations, resin fines, and other solids and films can develop. Insulating coatings over electrode surfaces can cause negative conductivity errors. Conductive accumulations between electrodes can short them and cause positive errors. Mechanical cleaning must not be attempted with platinum electrodes since this would change the cell constant. Cleaning must either follow manufacturer's recommendations or that given in Test Methods D1125. Ultrasonic cleaners have also been found effective in some cases.

7.3 Extension leadwire type, size, and length shall be according to manufacturers' recommendations, primarily to prevent parallel leadwire capacitance errors with this high resistance ac measurement. In particular, the length shall not exceed the measuring instrument's ability to minimize capacitance errors.

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 Committee on Analytical Reagents of the American Chemical Society.⁵ 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 shall be understood to mean reagent water conforming to Type I of Specification D1193. In making up the potassium chloride comparison solution for cell constant determinations, use water of conductivity not greater than 1 $\mu\text{S}/\text{cm}$. If necessary, stabilize to the laboratory atmosphere by aspirating air through the water from a fritted glass or stainless steel gas dispersion tube. The equilibrium point is reached when the conductivity remains constant but not greater than 1.5 $\mu\text{S}/\text{cm}$.

8.3 *Conductivity Standard Reference Solutions*—See Test Methods D1125.

9. Sampling

9.1 Direct measurements in the process shall have the cell located in an active flowing part of the piping. Stagnant areas

or *dead legs* must be avoided to ensure a representative sample and prevent any bubbles from adhering to cell surfaces.

9.2 Design and operate side stream sample lines to maintain sample integrity.

9.2.1 Do not expose the sample to the atmosphere to prevent absorption or loss of gases, particularly carbon dioxide, that affect conductivity.

9.2.2 The sample line shall not have pH electrodes upstream of the conductivity cell as noted in 6.7.

9.2.3 In power plant installations where iron oxide and other solids occur in pure water samples, flowrates must be controlled to minimize accumulation of deposits that could greatly delay transport of ionic materials. A sample flow velocity of 2 m/s in horizontal sample lines has been found optimum. Additional sample line design criteria have been documented (9-11).

9.2.4 The sample shall be continuously flowing at a stable flowrate to enable sample line wetted surfaces to reach equilibrium with sample conditions. Do not make measurements following changes to the sample flowrate for the period of time required to recover from transient effects on the particular sampling system.

9.2.5 Control the sample temperature within the capabilities of the temperature compensation algorithms used in the measuring instrument. The sample temperature shall be sufficiently stable to maintain reasonable equilibrium with the sample line wetted surfaces.

9.2.6 Do not locate the cell where it would be exposed to demineralizer reagents as noted in 6.9.

9.2.7 Additional sampling precautions are provided in Practices D1066 and D3370 and Guides D1192 and D3864.

10. Calibration

10.1 *Measuring Instrument*—Evaluate instrumentation of unproven performance in high purity samples using the procedure in Annex A1. Thereafter, use calibrating resistors with $\pm 0.1\%$ tolerance in place of the measuring cell and temperature compensator. The conductivity check resistance in ohms equals the cell constant (cm^{-1}) divided by the conductivity to be indicated (S/cm). Resistivity check resistance equals the cell constant (cm^{-1}) times the resistivity to be indicated ($\text{ohm}\cdot\text{cm}$). The temperature compensator resistance as defined by the manufacturer must simulate a sample temperature of 25.0 $^{\circ}\text{C}$, the reference temperature, that eliminates any compensation in order to follow the relationships given above.

NOTE 1—It should be understood that the use of a precision resistor in place of the cell checks only the ability of the instrument to measure a pure resistance, whereas the cell and leadwire characteristics include parallel and series capacitance. The manufacturer's circuit design must have the capability to measure with installed cell and leadwire characteristics, verified by the test in Annex A1.

10.2 *Leadwire Effects*—When leadwire length between the instrument and cell is greater than 7 m, check calibration of the instrument a second time by connecting the calibrating resistors at the far end of the leadwire and noting the difference, if any, in readings with the long leadwire in the circuit. Check both temperature and conductivity/resistivity readings. Leadwire-induced errors in high purity measurements are

⁵ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

typically caused by parallel capacitance of the cell leads and resistance of the temperature compensator leads. Leadwire capacitance is minimized on some instruments by isolating one cell lead within a driven shield. With other instruments, the use of fluorocarbon insulated or shortened leadwire, or both, may be necessary. (Fluorocarbon provides the best available dielectric properties and can reduce capacitance to about half that of cable using other insulating material.) Do not use long shielded leadwire unless the instrument is specifically designed for it since the shield can increase capacitance and associated errors with conventional measuring circuits. Follow manufacturer's wiring recommendations closely.

10.3 Temperature Measurement Circuit—Some temperature measurement circuits require precise temperature calibration after installation to compensate for leadwire resistance and ensure accurate temperature compensation. Where necessary, perform this according to manufacturer's recommendations.

10.4 Conductivity Cells—The cell constant calibration of conductivity/resistivity cells is ultimately referenced to standard solutions of potassium chloride of known conductivity from Test Methods D1125 or NIST standards (12). However, due to the high uncertainties of atmospheric and container surface contamination, direct cell calibration with standard solutions below 100 $\mu\text{S}/\text{cm}$ is not recommended. Although these solutions are available, their successful use for calibration is beyond the scope of this test method. See Note 2 and Note 3.

10.4.1 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 $\mu\text{S}/\text{cm}$ with a single cell constant, use Test Methods D1125, Solution D, 146.93 $\mu\text{S}/\text{cm}$ or NIST Standard Reference Material 3191, nominal value 100 $\mu\text{S}/\text{cm}$ directly. This calibration with documented certification can be provided by some cell manufacturers.

10.4.2 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 $\mu\text{S}/\text{cm}$ with a single cell constant, accomplish calibration using an intermediate higher constant cell as a secondary standard. Calibrate in a higher conductivity standard solution from Test Methods D1125, Reference Solution C, 1408.8 $\mu\text{S}/\text{cm}$, or Reference Solution D, 146.93 $\mu\text{S}/\text{cm}$ or NIST Standard Reference Materials 3192, nominal value 500.0 $\mu\text{S}/\text{cm}$ or 3193, nominal value 1000.0 $\mu\text{S}/\text{cm}$ (12). This cell then becomes the secondary standard for comparison with low constant cells in lower conductivity solutions that need not be standards (13 and 14). This calibration with documented certification can be provided by cell manufacturers. Refer to Annex A2 for details of cell constant calibration.

NOTE 2—Direct cell calibration in a low conductivity standard near 15 $\mu\text{S}/\text{cm}$ has been proposed under highly controlled conditions. However, determination of the contribution of the background water conductivity, which represents about 7 % of the total measurement if performed in open air, was not addressed (15).

NOTE 3—The lowest conductivity NIST Standard Reference Material has a nominal conductivity of 5 $\mu\text{S}/\text{cm}$ at 25.0 °C. However, the typical uncertainty is greater than that expected by other methods.

11. Procedure

11.1 Set up the flow type conductivity/resistivity cell, leadwire and instrument with calibration verified as in Section 10. Where severe fouling is anticipated at startup, divert the sample initially to prevent an accumulation of contaminants in the cell. If using a sample line, establish a flowrate through the cell of 200 cc/min or according to manufacturer's recommendations and allow several hours of rinse time if using new sample components, flow chamber, or cell to ensure complete removal of air and trace contaminants.

11.2 If specialized temperature compensation is not available, verify that the sample temperature is stabilized at 25.0 ± 0.2 °C.

11.3 Read the conductivity or resistivity.

12. Precision and Bias

12.1 Neither precision nor bias data can be obtained for this test method from a collaborative study designed in accordance with the requirements of Practice D2777 since this test method is a continuous determination. This inability of Practice D2777 procedures to obtain precision and bias data for continuous determinations is recognized and stated in the scope of Practice D2777. (Some experience approximating single-operator precision on high purity specific and cation conductivity measurements in power plants has been reported as a part of EPRI project RP2712-3 (16).)

13. Quality Control

13.1 Follow sensor manufacturer recommendations for storage, preparation, use and periodic cleaning of the sensor.

13.2 Verify that the conductivity temperature compensation in the instrument provides a close match to the temperature characteristics of the sample in accordance with 7.1.2.

13.3 Depending on accuracy requirements of the measurement, verify that conductivity readings are within acceptable tolerance periodically, using a standard reference solution or comparing with a standard reference measuring system.

13.3.1 When a reference solution is used, it should have a conductivity value high enough that it will have negligible influence from variable exposure to the carbon dioxide in air, in accordance with 6.1. Follow the standard solution manufacturer's instructions regarding air exposure and other precautions carefully. The reference solution value must also be within the accurate measuring range of the sensor/instrument combination.

13.3.2 When a standard reference measuring system is used on the flowing high purity water sample for comparison, take precautions to keep the sample enclosed without exposure to air, in accordance with 6.1, all the way through the flow path.

13.4 Because measurement is performed continuously on a pure water sample, normal quality control (QC) batch testing of blanks, matrix spikes, and control standards are not applicable.