Designation: D 5391 – 99 (Reapproved 2005)

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

This standard is issued under the fixed designation D 5391; 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 the 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]
D 1066 Practice for Sampling Steam
D 1125 Test Methods for Electrical Conductivity and Resistivity of Water
D 1129 Terminology Relating to Water
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[3]
D 1193 Specification for Reagent Water
D 2186 Test Methods for Deposit-Forming Impurities in Steam
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water
D 3370 Practices for Sampling Water from Closed Conduits
D 3864 Guide for Continual On-Line Monitoring Systems for Water Analysis
D 4519 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:*
3.1.1 *electrical conductivity*—refer to Test Methods D 1125.
3.1.2 *electrical resistivity*—refer to Test Methods D 1125.
3.1.3 For definitions of other terms used in these test methods, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*
3.2.1 *cell constant*—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}. 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

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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 of Water and Water-Formed Deposits, Surveillance of Water, and Flow Measurement 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] Withdrawn.

to prevent trace contamination from wetted surfaces and from 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 D 1125 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 D 1125. 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 D 1125, D 2186, and D 4519.

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. (13,14)[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 effective and cells must be accessible for cleaning. Cell designs with electrode spacing greater than 0.06 in. (1.5 mm) have been found to be less likely to trap such particles.

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

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 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 (15,1).

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 (2, 3, 4). 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 temperature 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
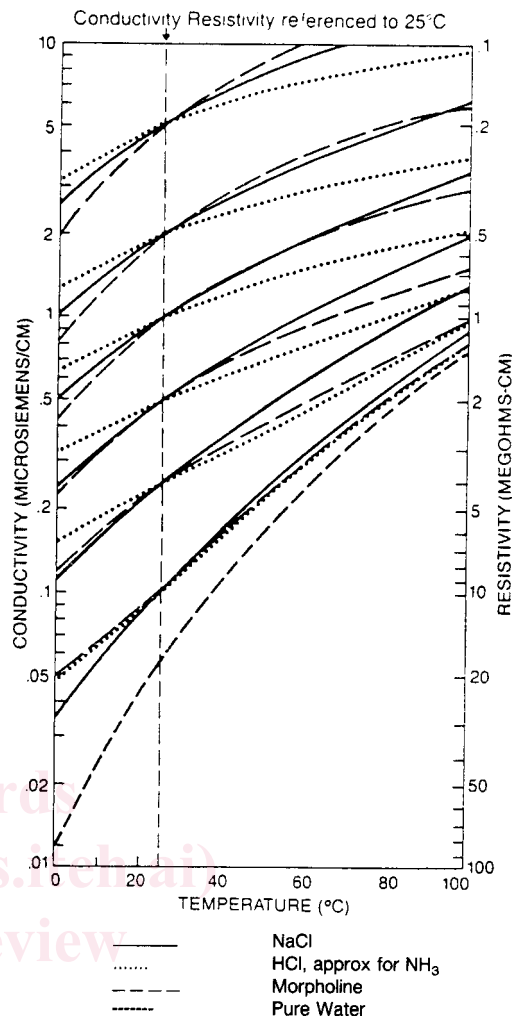
NOTE—Curves represent concentrations of impurities given in Table 1.
FIG. 1 Temperature Effects on the Conductivity of High Purity Water

TABLE 1 Concentrations of Trace Contaminants Plotted in Fig. 1

Conductivity µS/cm at 25°C	Concentration (µg/L)			
	NaCl	HCl	NH₃	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

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