

Standard Test Methods for Electrical Conductivity and Resistivity of Water¹

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This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These test methods cover the determination of the electrical conductivity and resistivity of water. The following test methods are included:

	Range	Sections
Test Method A—Field and Routine Laboratory	10 to 200 000	12 to 18
Measurement of Static (Non-Flowing)	μS/cm	
Samples		
Test Method B—Continuous In-Line Measure	5 to 200 000	19 to 23
ment	µS/cm	

1.2 These test methods have been tested in reagent water. It is the user's responsibility to ensure the validity of these test methods for waters of untested matrices.

1.3 For measurements below the range of these test methods, refer to Test Method D5391.

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

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D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)³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
- 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
- D4519 Test Method for On-Line Determination of Anions and Carbon Dioxide in High Purity Water by Cation Exchange and Degassed Cation Conductivity
- D5391 Test Method for Electrical Conductivity and Resistivity of a Flowing High Purity Water Sample

E2251 Specification for Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids

3. Terminology

3.1 Definitions:

3.1.1 *electrical conductivity,* n—the reciprocal of the a-c resistance in ohms measured between opposite faces of a centimetre cube of an aqueous solution at a specified temperature.

3.1.1.1 *Discussion*—The unit of electrical conductivity is siemens per centimetre. (The previously used units of mhos/cm are numerically equivalent to S/cm.) The actual resistance of the cell, R_x , is measured in ohms. The conductance, $1/R_x$, is directly proportional to the cross-sectional area, A (in cm²), and inversely proportional to the length of the path, L (in cm):

$1/R_x = K \cdot A/L$

The conductance measured between opposite faces of a centimetre cube, K, is called conductivity. Conductivity values are usually expressed in microsiemens/centimetre or in siemens/centimetre at a specified temperature, normally 25°C.

3.1.2 *electrical resistivity,* n—the a-c resistance in ohms measured between opposite faces of a centimetre cube of an aqueous solution at a specified temperature.

3.1.2.1 *Discussion*—The unit of electrical resistivity is ohmcentimetre. The actual resistance of the cell, R_x , is measured in ohms, and is directly proportional to the length of the path, *L* (in cm), and inversely proportional to the cross-sectional area, *A* (in cm²):

$R_x = R \cdot L/A$

The resistance measured between opposite faces of a centimetre cube, R, is called resistivity. Resistivity values are

¹ These test methods are under the jurisdiction of Committee D19 on Water and are 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.

 $^{^{3}\,\}text{The}$ last approved version of this historical standard is referenced on www.astm.org.

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Reference Solution	Approximate Normality of Solution	Method of Preparation	Temperature, °C	Electrical Conductivity, µS/cm
A 1 74.2460 g of KCI weighed in air per 1 L of	0	65 176		
	solution at 20°C	18	97 838	
			25	111 342
В	B 0.1 7.4365 g of KCl weighed in air per 1 L of solution at 20°C	0	7 138	
		18	11 167	
			25	12 856
С	0.01	0.01 0.7440 g of KCl weighed in air per 1 L of solution at 20°C	0	773.6
			18	1 220.5
		25	1 408.8	
D 0.001 Dilute 100 mL of Solution C to 1 L at 20°C	0	77.69 ^{<i>B</i>}		
	18	127.54 ^{<i>B</i>}		
		25	146.93	

^A Excluding the conductivity of the water used to prepare the solutions. (See 7.2 and Section 14.) These tabulated conductivity values are in international units. When using measuring instruments calibrated in absolute units, multiply the tabular values by 0.999505.

^B From Glasstone (1).^C

^c The boldface numbers in parentheses refer to a list of references at the end of this standard.

usually expressed in ohm centimetre, or in megohm centimetre, at a specified temperature, normally 25°C.

3.1.3 For definitions of other terms used in these methods, refer to Terminology D1129.

3.2 Symbols:

3.2.1 Symbols used in the equations in Sections 14 and 16 are defined as follows:

 $J = \text{cell constant, cm}^{-1},$

K = conductivity at 25°C, μ S/cm,

 $K_{\rm x}$ = measured conductance, S,

 K_1 = conductivity of the KCl in the reference solution at the temperature of measurement (Table 1), µS/cm,

 K_2 = conductivity of the water used to prepare the reference solution, at the same temperature of measurement, μ S/cm,

Q = temperature correction factor (see Section 11),

 $R = \text{resistivity at } 25^{\circ}\text{C}, \text{ ohm } \cdot \text{ cm},$

 $R_{\rm x}$ = measured resistance, ohm.

4. Significance and Use

4.1 These test methods are applicable for such purposes as impurity detection and, in some cases, the quantitative measurement of ionic constituents dissolved in waters. These include dissolved electrolytes in natural and treated waters, such as boiler water, boiler feedwater, cooling water, and saline and brackish water.

4.1.1 Their concentration may range from trace levels in pure waters $(2)^4$ to significant levels in condensed steam (see Test Methods D2186 and D4519, and Ref (3)), or pure salt solutions.

4.1.2 Where the principal interest in the use of conductivity methods is to determine steam purity, see Ref (4). These test methods may also be used for checking the correctness of water analyses (5).

5. Interferences

5.1 Exposure of a sample to the atmosphere may cause changes in conductivity/resistivity, due to loss or gain of

dissolved gases. This is extremely important in the case of very pure waters with low concentrations of dissolved ionized materials. The carbon dioxide, normally present in the air, can drastically increase the conductivity of pure waters by approximately 1 μ S/cm. Contact with air should be avoided by using flow-through or in-line cell where feasible. Chemically pure inert gases, such as nitrogen or helium, may be used to blanket the surface of samples.

5.2 Undissolved or slowly precipitating materials in the sample can form a coating on the electrodes of the conductivity cell that may cause erroneous readings. For example, biofouling of the cell or a build-up of filming amines may cause poor cell response. In most cases these problems can be eliminated by washing the cells with appropriate solvents.

5.3 If an unshielded cell is used to measure the resistivity/ conductivity of high resistivity water there is a possibility of electrical pickup causing erroneous reading. For this reason it is recommended that conductivity cells for this application be of coaxial shielded type or equivalent, and that the cables and instrument also be shielded.

5.4 Formation of bubbles on the surfaces of conductivity cell electrodes will cause erroneously low conductivity readings and must be prevented during calibration and measurement. Bubble formation can occur with measurements of water containing dissolved gases when the water is warming up or dropping in pressure or both. For laboratory samples, swirling or tapping the sensor on the bottom of the sample container can dislodge bubbles. For continuous measurements, cell installation in a high flow velocity location (within manufacturers recommendations) can prevent bubble adherence.

6. Apparatus

6.1 *Measuring Circuit*—The instrument may be a manually operated wheatstone bridge or the equivalent, or a direct reading analog or digital meter. Instruments shall energize the conductivity cell with alternating current and, together with the cell and any extension leadwire, shall be designed to reduce errors from the following sources:

6.1.1 In Highly Conductive Solutions—Uncompensated electrode polarization due to excessive current density at the

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

TABLE 2 Recommended Cell Constants for Various Conductivity Ranges Using a Laboratory Bridge

Range of Conductivity, µS/cm	Cell Constant, cm ⁻¹
0.05 to 10	0.01 to 0.1
10 to 200	0.1 to 1
200 to 5000	1 to 10
5000 to 1 000 000	10 to 100

electrode surfaces can cause negative conductivity errors. Insufficient series capacitance at the electrode/solution interface can allow charging effects to distort the a-c measurement and cause errors if not compensated. Leadwire resistance can add significantly to the measured resistance. Four-electrode type conductivity cells can reduce the effects of polarization by energizing two or more electrodes to create an a-c field across the sensing area and measuring from another pair of electrodes within the field with minimal current flow.

6.1.2 In Low Conductivity Solutions—Excessive parallel capacitance in the cell and extension leadwire can shunt the measurement and cause positive conductivity errors. Temperature compensation errors can be significant below 5 μ S/cm if variable coefficient algorithms are not employed as described in Test Method D5391.

6.1.3 These sources of error are minimized by an appropriate combination of a-c drive voltage, wave shape, frequency, phase correction, wave sampling technique and temperature compensation designed in by the instrument manufacturer. The instrument manufacturer's recommendations shall be followed in selecting the proper cell constant, leadwire size, and length and maintenance of the electrode surface condition for the range of measurement. Calibration may be in either conductivity or resistivity units.

6.1.4 When an output signal is required from an on-line instrument, it shall be electrically isolated from the cell drive circuit to prevent interaction between a solution ground at the cell and an external circuit ground.

6.2 Cells:

6.2.1 Flow-through or in-line cells shall be used for measuring conductivities lower than 10 μ S/cm (resistivities higher than 100 000 ohm \cdot cm), to avoid contamination from the atmosphere. However, samples with conductivity greater than 10 μ S/cm may also be measured. In all other cases, pipet-type or dip cells can also be used. Pipet or dip cells may be used to measure samples in the range of 1 to 10 μ S/cm if the sample is protected by an inert gaseous layer of nitrogen or helium.

6.2.2 A cell constant shall be chosen which will give a moderate cell resistance, matching the instrument manufacturer's requirements for the range of measurement. For laboratory bridges, Table 2 provides conservative guidelines.

6.2.3 Flow-through and in-line cells shall be mounted so that continuous flow of the sample through or past it is possible. Flow rate should be maintained at a constant rate consistent with the manufacturer's recommendations for the cell being used, particularly at conductivities below 10 μ S/cm. The cell shall retain calibration under conditions of pressure, flow, and temperature change, and shall exclude the atmosphere and be constructed of corrosion resistant, chemically

inert materials. The chamber or cell shall be equipped with means for accurate measurement of the temperature.

6.2.4 Platinized cells shall not be used for measurement of conductivities below 10 μ S/cm, except that a trace or flash of platinum black may be used on cells for measurements in the range of 0.1 to 10 μ S/cm (see 9.4). Because of the cost and fragility of platinum cells, it is common practice to use titanium, monel, hastelloy, stainless steel and graphite electrodes for measurements with accuracies on the order of 1 %. Note that these electrodes may require special surface preparation. Titanium and monel electrodes are especially suitable for high resistance solutions such as ultrapure water, but may introduce a small surface resistance which limits their accuracy when the measured resistance is less than a few thousand ohms (2).

6.2.5 It is recommended that cells intended for the measurement of conductivities below 10 $\mu S/cm$ be reserved exclusively for such applications.

6.3 Temperature Probes:

6.3.1 For Temperature Control—The measurement of temperature is necessary for control of a temperature bath, manual temperature compensation, or automatic temperature compensation, or all of these. Thermometers, thermistors, and resistance temperature detectors with accuracies of ± 0.1 °C or better are acceptable for this application. An ASTM precision thermometer, Number S63C, as defined in Specification E2251, is recommended. The calibration of temperature probes should be checked periodically by comparison to a reference temperature probe whose calibration is traceable to NIST or equivalent.

6.3.2 For Temperature Correction—A thermometer accurate to 0.1°C is acceptable for this application, when the instrument is not provided with manual or automatic temperature compensation. (See Section 11).

7. Reagents

7.1 Purity of J

7.1 *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, where such specifications are available.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.

7.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to the quantitative specifications of D1193, Type I. In making up the potassium chloride solutions for cell constant determinations, use water of conductivity not greater than 1.5 μ S/cm. If necessary, stabilize to the laboratory atmosphere by aspirating air through the water from a fritted glass or stainless

⁵ 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.

steel gas dispersion tube. The equilibrium point is reached when the conductivity remains constant but not greater than 1.5 μ S/cm. The equilibrium conductivity must be added to Table 1.

7.3 *Alcohol*—95 % ethyl alcohol. Alternatively, use isopropyl alcohol or methyl alcohol.

7.4 Aqua Regia (3 + 1)—Mix 3 volumes of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of concentrated nitric acid (HNO₃, sp gr 1.42). This reagent should be used immediately after its preparation.

7.5 Ethyl Ether.

7.6 Hydrochloric Acid (sp gr 1.19)—Concentrated HCl.

7.7 *Hydrochloric Acid* (1 + 1)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 1 volume of water.

7.8 *Platinizing Solution*—Dissolve 1.5 g of chloroplatinic acid (H_2PtCl_6 · $6H_2O$) in 50 mL of water containing 0.0125 g of lead acetate ($Pb(C_2H_3O_2)_2$).

7.9 *Potassium Chloride* (KCl)—The assay of the potassium chloride must be 100.0 \pm 0.1 %. This standardization grade of KCl is available from NIST and from commercial sources. Dry at 150°C for 2 h or until weight loss is less than 0.02 %; store in desiccator.

7.10 Potassium Chloride Reference Solution A—Dissolve 74.2460 g of KCl (weighed in air) in water and dilute to 1 L at $20 \pm 2^{\circ}$ C in a Class A volumetric flask.

7.11 Potassium Chloride Reference Solution B—Dissolve 7.4365 g of KCl (weighed in air) in water and dilute to 1 L at $20 \pm 2^{\circ}$ C in a Class A volumetric flask.

7.12 Potassium Chloride Reference Solution C—Dissolve 0.7440 g of KCl (weighed in air) in water and to dilute 1 L at $20 \pm 2^{\circ}$ C in a Class A volumetric flask.

7.13 Potassium Chloride Reference Solution D—Dilute 100 mL of reference solution C to 1 L with water at $20 \pm 2^{\circ}$ C in a Class A volumetric flask shortly before using. Store the solution in a glass-stoppered bottle of chemically resistant glass which has only been used for storage of this solution.

NOTE 1—The electrical conductivity of each of the referenced solutions is given in Table 1. The values for electrical conductivities for the solutions are those of G. Jones and B. C. Bradshaw (6), confirmed in 1987 (7) and 1989 (8) by the National Institute of Standards and Technology (NIST). The data of T. Shedlovsky (9) are used for Solution D. Solutions A, B, and C were prepared by Jones and Bradshaw using the molal or *demal* basis by dissolving 71.1352, 7.4191, and 0.7453 g, respectively, of KCl (in vacuum) per 1000 g of solution (in vacuum). The method of preparation given in Table 1 includes the corrections to weights of KCl (in air against brass weights) per litre of solutions at 20°C and assumes the density of KCl = 1.98, density of brass = 8.4, and the density of air = 0.00118. The densities of 1.0 N, 0.10 N, and 0.010 N KCl at 20°C, 1.04420, 1.00280, and 0.99871 g/mL, respectively, were interpolated from the data in the International Critical Tables (10).

8. Sampling

8.1 Samples shall be collected in accordance with Practice D1066, Specification D1192, and Practices D3370, as applicable.

8.2 Avoid exposure of the sample to atmospheres containing ammonia or acidic gases. Protect the sample to avoid gain or

loss of dissolved gases, particularly if there is some delay before the conductivity measurements are made. Preferably, use a flow-type cell for sampling and measuring condensed steam or water having a conductivity of less than 10 μ S/cm. For waters in the range of 5 to 10 μ S/cm, a dip-type cell may be used if a layer of chemically pure nitrogen or helium is maintained over the surface.

9. Preparation of Electrodes

9.1 If the cell constant as checked does not fall within reasonable limits of its nominal value, it is necessary to clean or replatinize the electrodes or replace the cell. In general, no mechanical cleaning should be attempted with platinum or graphite electrodes. In high purity water measurements, where the presence of finely divided platinum is undesirable due to its long retention of impurities, platinization of electrodes should be omitted, especially for testing of water having a conductivity below 10 μ S/cm (see 9.4). On the other hand, clean and well-platinized electrodes are increasingly important in testing water of higher conductivities, particularly above 1000 μ S/cm.

9.2 The cell manufacturer's instructions may be followed for cleaning the electrodes as well as other parts of the cell. A suitable cleaning solution consists of a mixture of 1 part by volume of isopropyl alcohol, 1 part of ethyl ether, (with polymer cells, check compatibility) and 1 part of HCl (1 + 1). After cleaning, thoroughly flush the cell with water. If the old platinum black coating is to be removed, judicious application of aqua regia to the electrodes, or electrolysis in HCl (sp gr 1.19) is frequently successful.

9.3 Platinize the electrodes of the cell with H₂PtCl₆ solution. A suitable plating apparatus consists of a 6 volt a-c supply, a variable resistor, milliammeter, and an electrode. The deposit should present a black, velvety appearance and should adhere well to the electrode surface. The procedure for platinizing is not critical. Follow the manufacturer's instructions or the following guidelines. Good platinized coatings are obtained using from 1.5 to 3 coulombs/cm² of electrode area. For example, for an electrode having a total area (both sides) of 10 cm^2 , the plating time at a current of 20 mA would be from $12\frac{1}{2}$ to 25 min. The current density may be from 1 to 4 mA/cm² of electrode area. Plate the electrodes one at a time with the aid of an extra electrode. During the plating, agitate the solution gently, or use ultrasonic bath. When not in use, platinized cells should be filled with water to prevent the drying out of electrodes while in storage.

9.4 For measurement of conductivities in the range of 0.1 to 10 μ S/cm, a trace or flash coating of platinum black may be used. For a flash coating, the cell is left in the platinic chloride solution for only 2 or 3 s at a current of about 20 mA. A flash coating will leave the electrodes with their metallic appearance, but with a faint blackish tint.

9.5 Generally, cells with titanium, monel, stainless steel, hastelloy or graphite electrodes do not require any special preparation other than soaking in water or sample for at least 5 min before measurement, if they have been stored dry. This ensures that electrodes are fully wetted. Follow the manufacturer's recommendations for startup, cleaning and maintenance.