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An American National Standard

# Standard Test Methods for Electrical Conductivity and Resistivity of Water<sup>1</sup>

This standard is issued under the fixed designation D 1125; 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  $(\epsilon)$  indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the 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                                       | μ S/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 D 5391.
- 1.4 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:
- D 1066 Practice for Sampling Steam<sup>2</sup> dards/sist/18c5a8
- D 1129 Terminology Relating to Water<sup>2</sup>
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits<sup>3</sup>
- D 1193 Specification for Reagent Water<sup>2</sup>
- D 2186 Test Method for Deposit-Forming Impurities in Steam<sup>3</sup>
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water<sup>2</sup>
- D 3370 Practices for Sampling Water from Closed Conduits<sup>2</sup>
- D 4519 Test Method for On-Line Determination of Anions and Carbon Dioxide in High Purity Water by Cation

Exchange and Degassed Cation Conductivity<sup>2</sup> D 5391 Test Method for Electrical Conductivity and Resistivity of a Flowing High Purity Water Sample<sup>2</sup> E 1 Specification for ASTM Thermometers<sup>4</sup>

# 3. Terminology

- 3.1 Definitions:
- 3.1.1 *electrical conductivity*—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.

Note 1—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 cm.  $^2$ ), and inversely proportional to the length of the path, L (in cm):

$$1/R_{\rm v} = K \cdot A/L$$

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  $25^{\circ}$ C.

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

Note 2—The unit of electrical resistivity is ohm-centimetre. 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 cm $^2$ ):

$$R_x = R \cdot L/A$$

The resistance measured between opposite faces of a centimetre cube, R, is called resistivity. Resistivity values are 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 D 1129.
  - 3.2 Symbols: Symbols:
- 3.2.1 Symbols used in the equations in Sections 14 and 16 are defined as follows:
  - $J = \text{cell constant, cm}^{-1}$ ,

<sup>&</sup>lt;sup>1</sup> These test methods are under the jurisdiction of Committee D19 on Water and are the direct responsibility of Subcommittee D19.03 on Sampling of Water and Water-Formed Deposits, Surveillance of Water, and Flow Measurement of Water. Current edition approved Oct. 10, 1995. Published December 1995. Originally

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<sup>2</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>&</sup>lt;sup>3</sup> Annual Book of ASTM Standards, Vol 11.02.

<sup>&</sup>lt;sup>4</sup> Annual Book of ASTM Standards, Vol 14.03.

TABLE 1 Electrical Conductivity Values Assigned to the Potassium Chloride in the Reference Solution A

| Reference<br>Solution | Approximate<br>Normality of<br>Solution          | Method of Preparation                            | Tempera-<br>ture, °C | Electrical<br>Conductivity,<br>μS/cm |
|-----------------------|--|--|----------------------|--------------------------------------|
| A 1 74                | 1  | 74.2460 g of KCl weighed in air per 1 L of       | 0                    | 65 176                               |
|                       | solution at 20°C                                 | 18   | 97 838               |                                      |
|                       |  |  | 25                   | 111 342                              |
| B 0.1 7.4365 g of     | 7.4365 g of KCl weighed in air per 1 L of        | 0  | 7 138                |                                      |
|                       | solution at 20°C                                 | 18   | 11 167               |                                      |
|                       |  |  | 25                   | 12 856                               |
| С                     | C 0.01 0.7440 g of KCI weighed in air per 1 L of | 0.7440 g of KCI weighed in air per 1 L of        | 0                    | 773.6                                |
| solution at 20°C      | solution at 20°C                                 | 18   | 1 220.5              |                                      |
|                       |  | 25   | 1 408.8              |                                      |
| D 0.001               | 0.001  | 0.001 Dilute 100 mL of Solution C to 1 L at 20°C | 0                    | 77.69 <sup><i>B</i></sup>            |
|                       |  |  | 18                   | 127.54 <sup><i>B</i></sup>           |
|                       |  |  | 25                   | 146.93                               |

<sup>&</sup>lt;sup>A</sup>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.

<sup>B</sup>From Glasstone (13).

 $K = \text{conductivity at } 25^{\circ}\text{C}, \, \mu\text{S/cm},$ 

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

 $K_1$  = conductivity of the KCl in the reference solution at the temperature of measurement (Table 1),  $\mu$ S/cm,

 $K_2$  = conductivity of the water used to prepare the reference solution, at the same temperature of measurement,  $\mu$ 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 (1)<sup>5</sup> to significant levels in condensed steam (see Test Methods D 2186 and D 4519, and Ref (2)), or pure salt solutions
- 4.1.2 Where the principal interest in the use of conductivity methods is to determine steam purity, see Ref (3). These test methods may also be used for checking the correctness of water analyses (4).

#### 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  $\mu\text{S/cm}$ . 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.

#### 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 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.
- 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  $\mu$ S/cm if variable coefficient algorithms are not employed as described in Test Method D 5391.
- 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

<sup>&</sup>lt;sup>5</sup> The boldface numbers in parentheses refer to the list of references at the end of

TABLE 2 Recommended Cell Constants for Various Conductivity
Ranges

| Range of Conductivity, µS/cm | Cell Constant, cm <sup>-1</sup> |  |
|------------------------------|---------------------------------|--|
| 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                       |  |

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  $\mu S/cm$  (resistivities higher than 100 000 ohm  $\cdot$  cm), to avoid contamination from the atmosphere. However, samples with conductivity greater than 10  $\mu S/cm$  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  $\mu S/cm$  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  $\mu$ 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  $\mu$ 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  $\mu$ S/cm (see 9.4). Because of the cost and fragility of platinum cells, it is common practice to use titanium, monel, 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 (1).

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  $\pm 0.1^{\circ}\text{C}$  or

better are acceptable for this application. An ASTM precision thermometer, Number 63C, as defined in Specification E 1, is recommended. The calibration of temperature probes should be checked periodically by comparison to a reference temperature probe whose calibration is traceable to the U.S. National Institute of Science and Technology (formerly NBS) 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 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. 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 Specification D 1193, Type I. In making up the potassium chloride solutions for cell constant determinations, use water of conductivity not greater than 1.5  $\mu$ S/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 $\mu$ 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 (HNO<sub>3</sub>, 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 ( $H_2$ PtCl<sub>6</sub>·  $6H_2$ O) 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  $100.0\pm0.1$  %. This standardization grade of KCl is available from NIST and from commercial sources. Dry at  $150^{\circ}$ 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.

<sup>&</sup>lt;sup>6</sup> 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.