



## Standard Practice for Oxidation-Reduction Potential of Water <sup>1</sup>

This standard is issued under the fixed designation D 1498; 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.

### 1. Scope

1.1 This practice covers the apparatus and procedure for the electrometric measurement of oxidation-reduction potential (ORP) in water. It does not deal with the manner in which the solutions are prepared, the theoretical interpretation of the oxidation-reduction potential, or the establishment of a standard oxidation-reduction potential for any given system. The practice described has been designed for the routine and process measurement of oxidation-reduction potential.

1.2 *This standard does not purport to address all of the safety problems, 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 1129 Terminology Relating to Water <sup>2</sup>

D 1193 Specification for Reagent Water <sup>2</sup>

D 3370 Practices for Sampling Water from Closed Conduits <sup>2</sup>

### 3. Terminology

#### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 *oxidation-reduction potential*—the electromotive force,  $E_m$ , developed between a noble metal electrode and a standard reference electrode. This oxidation-reduction potential (ORP) is related to the solution composition by:

$$E_m = E^o + 2.3 \frac{RT}{nF} \log A_{\text{ox}}/A_{\text{red}}$$

where:

$E_m$	= ORP,
$E^o$	= constant that depends on the choice of reference electrodes.
$F$	= Faraday constant,
$R$	= gas constant,
$T$	= absolute temperature, °C + 273.15,

$n$  = number of electrons involved in process reaction, and

$A_{\text{ox}}$  and  $A_{\text{red}}$  = activities of the reactants in the process.

3.2 For definitions of other items used in this practice, refer to Terminology D 1129.

### 4. Summary of Practices

4.1 This is a practice designed to measure the ORP which is defined as the electromotive force between a noble metal electrode and a reference electrode when immersed in a solution. The practice describes the electronic equipment available to make the measurement and describes how to determine the sensitivity of the electrodes as well as the calibration of equipment to solutions having a known potential. The ORP electrodes are inert and measure the ratio of the activities of the oxidized to the reduced species in the process reactions.

### 5. Interferences

5.1 The ORP electrodes reliably measured ORP in nearly all aqueous solutions and in general are not subject to solution interference from color, turbidity, colloidal matter, and suspended matter.

5.2 The ORP of an aqueous solution is sensitive to change in temperature of the solution, but temperature correction is rarely done due to its minimal effect and complex reactions. Temperature corrections are usually applied only when it is desired to relate the ORP to the activity of an ion in the solutions.

5.3 The ORP of an aqueous solution is almost always sensitive to pH variations even to reactions that do not appear to involve hydrogen or hydroxyl ions. The ORP generally tends to increase with an increase in hydrogen ions and to decrease with an increase in hydroxyl ions during such reactions.

5.4 Reproducible oxidation-reduction potentials cannot be obtained for chemical systems that are not reversible. Most natural and ground waters do not contain reversible systems, or may contain systems that are shifted by the presence of air. The measurement of end point potential in oxidation-reduction titration is sometimes of this type.

5.5 If the metallic portion of the ORP electrode is spongelike, materials absorbed from solutions may not be washed away, even by repeated rinsings. In such cases, the electrode may exhibit a memory effect, particularly if it is desired to detect a relatively low concentration of a particular species immediately after a measurement has been made in a relatively

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

concentrated solution. A brightly polished metal electrode surface is required for accurate measurements.

5.6 The ORP resulting from interactions among several chemical systems present in mixed solutions may not be assignable to any single chemical.

## 6. Apparatus

6.1 *Meter*—Most laboratory pH meters can be used for measurements of ORP by substitution of an appropriate set of electrodes and meter scale. Readability to 1 mV is adequate. The choice will depend on the accuracy desired in the determination.

6.1.1 Most process pH meters can be used for measurement of ORP by substitution of an appropriate set of electrodes and meter scale. These instruments are generally much more rugged than those which are used for very accurate measurements in the laboratory. Usually, these more rugged instruments produce results that are somewhat less accurate and precise than those obtained from laboratory instruments. The choice of process ORP analyzer is generally based on how closely the characteristics of the analyzer match the requirements of the application. Typical factors which may be considered include, for example, the types of signals which the analyzer can produce to drive external devices, and the span ranges available.

6.1.2 For remote ORP measurements the potential generated can be transmitted to an external indicating meter. Special shielded cable is required to transmit the signal.

6.2 *Reference Electrode*—A calomel, silver-silver chloride, or other reference electrode of constant potential shall be used. If a saturated calomel electrode is used, some potassium chloride crystals shall be contained in the saturated potassium chloride solution. If the reference electrode is of the flowing junction type, the design of the electrode shall allow for each measurement a fresh liquid junction to be formed between the solution of potassium chloride and the standard or the test solution. The electrode design shall also allow traces of solution to be washed from the outer surfaces of the electrodes. To ensure the desired slow outward flow of the reference-electrode solution, the solution pressure inside the liquid junction should be somewhat in excess of that outside the junction. In nonpressurized applications this requirement can be met by maintaining the inside solution level higher than the outside solution level. If the reference electrode is of the nonflowing junction type, these outward flow and pressurization considerations shall not apply. The reference electrode and junction shall perform satisfactorily as required in the procedure for checking sensitivity described in 10.2.

6.3 *Oxidation-Reduction Electrode*—A noble metal is used in the construction of oxidation-reduction electrodes. The most common metals employed are platinum and gold; silver is rarely used. It is important to select a metal that is not attacked by the test solution. The construction of the electrode shall be such that only the noble metal comes in contact with the test solution. The area of the noble metal in contact with the test solution should be approximately 1 cm<sup>2</sup>.

6.4 *Electrode Assembly*—A conventional electrode holder or support can be employed for laboratory measurements. Many different styles of electrode holders are suitable for

various process applications such as measurements in an open tank, process pipe line, pressure vessel, or a high pressure sample line.

## 7. Reagents and Materials

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.<sup>3</sup> 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, reference to water shall be understood to mean reagent water conforming to Specification D 1193, Type I or II.

7.3 *Aqua Regia*—Mix 1 volume of concentrated nitric acid (HNO<sub>3</sub>, sp gr 1.42) with 3 volumes of concentrated hydrochloric acid (HCl, sp gr 1.18). It is recommended that only enough solution be prepared for immediate requirements.

7.4 *Buffer Standard Salts*—Table 1 lists the buffer salts available from the National Institute of Standards and Technology specifically for the preparation of standard buffer solutions. The NIST includes numbers and drying procedures.

**TABLE 1 National Institute of Standards and Technology (NIST) Materials for Reference Buffer Solutions**

NIST Standard Sample Designation <sup>A</sup>	Buffer Salt	Drying Procedure
186-II-e	disodium hydrogen phosphate	2 h in oven at 130°C
186-I-e	potassium dihydrogen phosphate	2 h in oven at 130°C
185-g	potassium hydrogen phthalate	drying not necessary

<sup>A</sup>The buffer salts listed can be purchased from the Office of Standard Reference Materials, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899.

7.4.1 *Phthalate Reference Buffer Solution* (pH<sub>s</sub> = 4.00 at 25°C)—Dissolve 10.12 g of potassium hydrogen phthalate (KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>) in water and dilute to 1 L.

7.4.2 *Phosphate Reference Buffer Solution* (pH<sub>s</sub> = 6.86 at 25°C)—Dissolve 3.39 g of potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>) and 3.53 g of anhydrous disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) in water and dilute to 1 L.

7.5 *Chromic Acid Cleaning Solution*—Dissolve about 5 g of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) in 500 mL of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, sp gr 1.84).

7.6 *Detergent*—Use any commercially available “low-suds” liquid or solid detergent.

7.7 *Nitric Acid* (1 + 1)—Mix equal volumes of concentrated nitric acid (HNO<sub>3</sub>, sp gr 1.42) and water.

7.8 *Redox Standard Solution; Ferrous-Ferric Reference*

<sup>3</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 Pharmacopoeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.