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Standard Test Method for Oxidation-Reduction Potential of Water[1]

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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method 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 test method described has been designed for the routine and process measurement of oxidation-reduction potential.

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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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 1129 Terminology Relating to Water
D 1193 Specification for Reagent Water
D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D 3370 Practices for Sampling Water from Closed Conduits

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:

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

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_{ox} and A_{red} = activities of the reactants in the process.

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

4. Summary of Test Method

4.1 This is a test method 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 test method describes the equipment available to make the measurement, the standardization of the equipment and the procedure to measure ORP. The ORP electrodes are inert and measure the ratio of the activities of the oxidized to the reduced species present.

[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.~~ 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.

5. Significance and Use

5.1 Various applications include monitoring the chlordination/dechlorination process of water, recgonition of oxidants/ reductants present in wastewater, monitoring the cycle chemistry in power plants, and controlling the processing of cyanide and chrome waste in metal plating baths.

5.2 The measurement of ORP has been found to be useful in the evaluation of soils, for evaluating treatment design data at sites contaminated with certain chemicals, and in evaluating solid wastes.

6. Interferences

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

6.2 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.

6.3 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.

6.4 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.

6.5 If the metallic portion of the ORP electrode is sponge-like, 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 concentrated solution. A brightly polished metal electrode surface is required for accurate measurements.

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

7. Apparatus

7.1 *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.

7.1.1 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.

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

7.2 *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, a slow outward flow of the reference-electrode solution is desired. To achieve this, 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 11.2.

7.3 *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^2.

7.4 *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.

8. Reagents and Materials

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.[3] 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, reference to water shall be understood to mean reagent water conforming to Specification D1193, Type I or II.~~ — References to water shall be understood to mean water that meets or exceeds the quantitative specifications for type I or II reagent water conforming to Specification D 1193, Section 1.1.

8.3 *Aqua Regia*—Mix 1 volume of concentrated nitric acid (HNO_3, 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.

8.4 *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.

8.4.1 *Phthalate Reference Buffer Solution (pH_s = 4.00 at 25°C)* —Dissolve 10.12 g of potassium hydrogen phthalate ($KHC_8H_4O_4$) in water and dilute to 1 L.

8.4.2 *Phosphate Reference Buffer Solution (pH_s = 6.86 at 25°C)* —Dissolve 3.39 g of potassium dihydrogen phosphate (KH_2PO_4) and 3.53 g of anhydrous disodium hydrogen phosphate (Na_2HPO_4) in water and dilute to 1 L.

8.5 *Chromic Acid Cleaning Solution* —Dissolve about 5 g of potassium dichromate ($K_2Cr_2O_7$) in 500 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84).

8.6 *Detergent*—Use any commercially available "low-suds" liquid or solid detergent.

8.7 *Nitric Acid (1 + 1)*—Mix equal volumes of concentrated nitric acid (HNO_3, sp gr 1.42) and water.

8.8 *Redox Standard Solution; Ferrous-Ferric Reference Solution*[4]—Dissolve 39.21 g of ferrous ammonium sulfate ($Fe(NH_4)_2$-$(SO_4)_2 \cdot 6H_2O$), 48.22 g of ferric ammonium sulfate ($FeNH_4(SO_4)_2 \cdot 12H_2O$) and 56.2 mL of sulfuric acid (H_2SO_4, sp gr 1.84) in water and dilute to 1 L. It is necessary to prepare the solution using reagent grade chemicals that have an assay confirming them to be within 1% of the nominal composition. The solution should be stored in a closed glass or plastic container.

8.8.1 The ferrous-ferric reference solution is a reasonably stable solution with a measurable oxidation-reduction potential. Table 2 presents the potential of the platinum electrode for various reference electrodes at 25°C in the standard ferrous-ferric solution.

8.9 *Redox Reference Quinhydrone Solutions*—Mix 1 L of pH 4 buffer solution, (see 8.4.1), with 10 g of quinhydrone. Mix 1 L of pH 7 buffer solution, (see 8.4.2), with 10 g of quinhydrone. Be sure that excess quinhydrone is used in each solution so that solid crystals are always present. These reference solutions are stable for only 8 h. Table 3 lists the nominal millivolt redox readings for the quinhydrone reference solutions at temperatures of 20°C, 25°C, and 30°C.

8.10 *Redox Standard Solution; Iodide/Triiodide*—Dissolve 664.04 g of potassium iodide (KI), 1.751 g of resublimed I_2, 12.616 g of boric acid (H_3BO_3), and 20 ml of 1 M potassium hydroxide (KOH) in water and dilut to 1 L. Mix solution. This solution is stable at least one year. Solution can be stored in a closed glass or plastic container. Table 4 provides the potential of the platinum electrode for various reference electrodes at various temperatures in the standard Iodide/Triiodide solution.

9. Sampling

9.1 Collect the samples in accordance with Practices D 3370.

10. Preparation

10.1 *Electrode Treatment*—Condition and maintain ORP electrodes as recommended by the manufacturer. If the assembly is in intermittent use, the immersible ends of the electrode should be kept in water between measurements. Cover the junctions and fill-holes of reference electrodes to reduce evaporation during prolonged storage.

10.2 *ORP Electrode Cleaning*—It is desirable to clean the electrode daily. Remove foreign matter by a preliminary treatment with a detergent or mild abrasive, such as toothpaste. If this is insufficient, use 1 + 1 nitric acid. Rinse the electrode in water several times. An alternative cleaning procedure is to immerse the electrode in chromic acid cleaning mixture at room temperature for

[3] *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.

[4] "Standard Solution for Redox Potential Measurements," *Analytical Chemistry*, Vol 44, 1972, p. 1038.

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

NIST Standard Sample Designation [A]	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

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