



Standard Practice for Oxidation-Reduction Potential of Water ¹

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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 ²

D 1193 Specification for Reagent Water ²

D 3370 Practices for Sampling Water from Closed Conduits ²

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 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 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

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² *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 cm².

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.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.

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 (HNO₃, 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 ^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

^AThe 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_s = 4.00 at 25°C)—Dissolve 10.12 g of potassium hydrogen phthalate (KHC₈H₄O₄) in water and dilute to 1 L.

7.4.2 *Phosphate Reference Buffer Solution* (pH_s = 6.86 at 25°C)—Dissolve 3.39 g of potassium dihydrogen phosphate (KH₂PO₄) and 3.53 g of anhydrous disodium hydrogen phosphate (Na₂HPO₄) in water and dilute to 1 L.

7.5 *Chromic Acid Cleaning Solution*—Dissolve about 5 g of potassium dichromate (K₂Cr₂O₇) in 500 mL of concentrated sulfuric acid (H₂SO₄, 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 (HNO₃, sp gr 1.42) and water.

7.8 *Redox Standard Solution; Ferrous-Ferric Reference*

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 Pharmacopoeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

Solution⁴—Dissolve 39.21 g of ferrous ammonium sulfate ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), 48.22 g of ferric ammonium sulfate ($\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) 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.

7.8.1 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.

7.9 *Redox Reference Quinhydrone Solutions*—Mix 1 L of pH 4 buffer solution, (see 7.4.1), with 10 g of quinhydrone. Mix 1 L of pH 7 buffer solution, (see 7.4.2), 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.

TABLE 2 Potential of the Platinum Electrode for Several Reference Electrodes at 25°C in Ferrous-Ferric Reference Solution

Reference Electrode	Potential EMF, mV
Hg, Hg ₂ Cl ₂ , satd KCl	+ 430
Ag, AgCl, 1.00 M KCl	+ 439
Ag, AgCl, 4.00 M KCl	+ 475
Ag, AgCl, satd KCl	+ 476
Pt, H ₂ (p = 1), H (a = 1)	+ 675

TABLE 3 Nominal ORP of Reference Quinhydrone Solutions

Buffer solution, nominal pH	ORP, mV					
	4			7		
Temperature, °C	20	25	30	20	25	30
Reference Electrode						
Silver/silver chloride	268	263	258	92	86	79
Calomel	223	218	213	47	41	34
Hydrogen	470	462	454	295	285	275

8. Sampling

8.1 Collect the samples in accordance with Practices D 3370.

9. Preparation

9.1 *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.

9.2 *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. Gradually, warm the solution and electrode to boiling. Maintain it just below the boiling point for about 5 min and then allow the solution and electrode to cool. 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 several minutes, then rinse with dilute hydrochloric acid, and then thoroughly rinse with water. If these steps are insufficient, immerse the ORP electrode in warm (70°C) aqua regia and allow to stand for 1 min. This solution dissolves noble metal and should not be used longer than the time specified. In these cleaning operations, particular care must be exercised to protect glass-metal seals from sudden changes of temperature, which might crack them.

10. Calibration and Standardization

10.1 Before using electronic type meters, turn them on and allow them to warm up thoroughly. Bring them to electrical balance by carefully following the manufacturer's instructions. Set the scale or range to the desired millivolt level expected in the test solution.

10.2 Verify the sensitivity of the electrodes by noting the change in millivolt reading when the pH of the test solution is altered. The ORP will increase when the pH of the test solution decreases and the ORP will decrease if the test solution pH is increased. Place the sample in a clean glass beaker and agitate the sample. Insert the electrodes and note the ORP or millivolt reading. Add a small amount of a dilute NaOH solution and note the value of the ORP. If the ORP drops sharply when the caustic is added, the electrodes are sensitive and operating properly. If the ORP increases sharply when the caustic is added, the polarity is reversed and must be corrected in accordance with the manufacturer's instructions. If the ORP does not respond as above when the caustic is added, the electrodes should be cleaned as described in 9.2 and the above procedure repeated.

10.3 *Checking Response Electrodes to the Standard Redox Solutions* (see 7.8 and 7.9)—Wash the metal and reference electrode and the sample cup or container with three changes of water or by means of a flowing stream from a wash bottle. Fill the sample container with fresh redox standard solution and immerse the electrodes. Turn the range switch to the proper range and engage the operating button. The reading should be within 30 mV of the value expected for the standard solution. Adjust the asymmetry control to the millivolt potential of the standard redox solution. Without changing the setting of the asymmetry potential knob, repeat the above procedure until two successive instrument readings are constant and the readings do not differ from the millivolt value of the standard redox solution by more than 10 mV.

10.3.1 It usually suffices to check the sensitivity of the electrodes since the important feature is the change of potential as related to the concentration of the oxidant or reductant present. The actual numerical value of the potential will vary depending on the constituents present in the water.

10.4 Indirect Calibration and Standardization:

10.4.1 Employ this procedure when it is not convenient or practical to remove the electrodes from the flowing stream or container in which the ORP is being determined. Use of a

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

laboratory ORP meter or an additional analyzer is required.

10.4.2 Verify the sensitivity of the laboratory ORP meter or additional process analyzer in accordance with 10.2.

10.4.3 Collect a grab sample that is representative of the material that is in contact with the electrodes of the analyzer that is to be standardized. If a submersion-style electrode chamber is in use, collect the sample from the discharge of the chamber. Immediately transport the sample to the laboratory ORP meter or additional process analyzer and measure the ORP. It is absolutely essential that the sample be representative of the solution in contact with the electrodes of the analyzer being adjusted and that the integrity of the sample be maintained until its ORP has been measured. In particular, the temperature of the sample must remain constant. Then adjust the standardization control on the process analyzer being calibrated until the reading corresponds to the ORP of the sample. Repeat the procedure described above until two successive readings are obtained that differ by no more than 10 mV. This procedure cannot be employed if the ORP of the solution being tested is fluctuating by more than 10 mV at the time of standardization.

10.4.4 The sensitivity of the electrodes can also be verified by a determination of the concentration of the oxidants or reductants in a grab sample collected in accordance with 10.4.3. It is necessary to determine the conditions required in each individual system to use this method of verifying electrode sensitivity. For example, the chlorine residual determination can be used to verify the sensitivity of an ORP electrode system used to control an alkaline chlorination-cyanide destruction system.

11. Procedure

11.1 After the assembly has been checked for sensitivity (10.2) or standardized as described in 10.4, wash the electrodes with three changes of water or by means of a flowing stream from a wash bottle. Place the sample in a clean glass beaker or sample cup and insert the electrodes. Provide adequate agitation throughout the measurement period. Read the millivolt potential of the solution allowing sufficient time for the system to stabilize. Measure successive portions of the sample until readings on two successive portions differ by no more than 10 mV. A system that is very slow to stabilize probably will not yield a meaningful ORP.

11.2 *Continuous Determination of the ORP of Flowing Streams or Batch Systems*—Process ORP analyzers with their rugged electrodes and electrode chambers provide continuous measurements which are the basis for fully automatic control. Make selection of the electrodes and electrode chamber to suit

the physical and chemical characteristics of the process material. Locate the submersion-style electrode chamber so that fresh solution representative of the process stream or batch continuously passes across the electrodes. Agitation may be employed in order to make the stream or batch more nearly homogeneous. The ORP value is usually displayed continuously and can be noted at any specific time. Frequently, the pH value is continuously recorded, yielding a permanent record.

12. Calculation

12.1 Report the oxidation-reduction potential in millivolts directly from the meter. The electrode system employed must also be reported.

12.2 If it is desired to report the oxidation-reduction potential referred to the hydrogen electrode, calculate as follows:

$$E_h = E_{obs} + E_{ref}$$

where:

E_h = oxidation-reduction potential referred to the hydrogen scale, mV,

E_{obs} = observed oxidation-reduction potential of the noble metal-reference electrode employed, mV, and

E_{ref} = oxidation-reduction potential of the reference electrode as related to the hydrogen electrode, mV.

13. Report

13.1 Report the oxidation-reduction potential to the nearest 1 mV, interpolating the meter scale as required. When considered appropriate, the temperature at which the measurement was made and the pH at the time of measurement, may also be reported.

14. Precision and Bias

14.1 Precision and bias of the measurement depends largely on the condition of the electrode system and on the degree to which the chemical system being measured fits the qualifications given in Sections 3 and 5. In the absence of substances that coat or poison the electrode, the precision is ± 10 mV.

15. Keywords

15.1 electrodes; ferrous-ferric reference solutions; noble metal electrodes; ORP; oxidation-reduction potential; quinhydrone; redox; redox standards; reference electrodes; reference solutions

APPENDIX
(Nonmandatory Information)
X1. OXIDATION REDUCTION POTENTIAL

X1.1 *Meaning of the Term ORP*—The ORP measurement establishes the ratio of oxidants and reductants prevailing within a solution of water or waste water. The measurement is nonspecific in contrast, for example, to the pH measurement. The ORP electrode pair senses the prevailing net potential of a solution. By this measurement, the ability to oxidize or reduce species in the solution may be determined.

X1.2 Use of ORP Control of Waste Processes:

X1.2.1 ORP measurements are used in industrial process control to monitor the treatment of unwanted materials which are amenable to oxidation or reduction. Frequently, only one species in solution is to be treated, in which case the oxidation-reduction profile of the process can be predicted with some accuracy. Two examples in this category are found in the plating industry: Waste cyanide is oxidized to cyanate and then (if required) to carbon dioxide and nitrogen, and waste hexavalent-chromium is reduced to the trivalent state. ORP measurements are useful for process control in both instances if the pH is constant and controlled.

X1.2.2 In addition to control of processes in which a specific material is treated, ORP measurements can be used to control nonspecific processes if a correlation can be established between prevailing ORP and the reaction in the process. An example is the use of ORP measurements in odor control of municipal waste by chlorination. In some cases, the extent of odor production correlates with ORP. Also, sewage treatment plants may be protected from unwanted oxidizing or reducing agents which might harm treatment materials if the ORP of the influent is monitored.

X1.3 Temperature Effects on ORP Measurements:

X1.3.1 The effect of temperature on ORP measurements can be understood by considering the Nernst equation:

$$E = E^{\circ} + 2.3 \frac{RT}{nF} \log Q$$

where

E = measured potential,

E° = potential when all components involved in the reaction are at unit activity and 25° C,

R = gas constant,

T = absolute temperature, t °C + 273.15,

F = Faraday,

n = number of electrons involved in the reaction, and

Q = product of the activities of the oxidants divided by the product of the activities of the reductants, each activity raised to that power whose exponent is the coefficient of the substance in the applicable chemical reaction.

Changes in E° with temperature produce the same changes in E . Further, the slope of the curve that relates E and T depends directly on T . Finally, changes in activity with temperature will produce changes in E .

X1.3.2 Automatic temperature compensation is seldom attempted in ORP measurements, due to the appearance of n in the prelogarithmic factor of the Nernst equation. The slope of the plot of E versus T thus depends not only on T , but on n as well, so that different amounts of compensation are required, depending on the value of n . If the process under study is well characterized and the value of n known, automatic temperature compensation is possible. However, if the value of n is unknown or variable (see X1.2.1), then compensation is not possible.

X1.4 *Polarity Check*—The polarity of the input of the analyzer may also be determined by connecting a battery of known polarity and observing the deflection of the meter. A resistive voltage divider may be connected between the battery and analyzer, if necessary, to prevent the meter from being driven off-scale due to application of an excessively high potential.

X1.5 *Increase Precision of Measurement*—If the system is electrochemically reversible, and a precision of better than ± 5 mV is desired, control the temperature of the assembly to within $\pm 1^{\circ}$ C. Use silver/silver chloride reference electrodes with a flowing junction to avoid temperature hysteresis.

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