Designation: D7677 – 16

Standard Test Method for the Continuous Measurement of Dissolved Ozone in Low Conductivity Water[1]

This standard is issued under the fixed designation D7677; 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 on-line and in-line determination of dissolved ozone (DO_3) in low conductivity water in the range from 0.001 mg/L to 5.0 mg/L DO_3 and conductivity <100 µS/cm, typical of pharmaceutical and microelectronics pure waters. DO_3 is detected by correlating the response of a membrane-covered electrochemical sensor to the dissolved ozone concentration.

1.2 This test method provides a more convenient means for continuous measurement than the colorimetric methods typically used for grab sample measurements.

1.3 This test method has the advantage of high sensitivity as well as durability in the process environment and has few interferences.

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]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
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

3. Terminology

3.1 *Definitions*—For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *dissolved ozone (DO_3), n*—Ozone is the tri-atomic form of oxygen and, when dissolved in water, is uniformly dispersed and remains in molecular form.

4. Summary of Test Method

4.1 Dissolved ozone measurements are made on a flowing water sample containing dissolved ozone gas.

4.2 The sensor flow housing is connected to a process-water sample line or the sensor probe is inserted into a pipe or vessel with flowing water.

4.3 The ozone gas permeates the sensor membrane and is reduced to oxygen and hydroxide ion at the sensor's cathode at a controlled potential, producing a current flow in direct proportion to the partial pressure of ozone in the sample outside the membrane.

4.4 The current is correlated with a calibration curve in the measuring instrument, accounting for temperature effects on membrane permeation rate and on the solubility of ozone in water. This correlation provides the conversion from ozone partial pressure to concentration.

4.5 The instrument readout is provided in units of mg/L (ppm) or µg/L (ppb). For the purposes of this standard, the paired units are considered equivalent.

5. Significance and Use

5.1 Dissolved Ozone is useful in many industries for water sanitization, TOC reduction, food preservation, cleaning-in-place of food and beverage systems, and pyrogen destruction. It is often necessary to know how much ozone has entered the water, how much remains, and the degree to which it has been removed before process use.

5.2 Some applications require that contact time, DO_3 concentration integrated over time, be calculated, to assure disinfection.

5.3 Continuous observation of trends in these measurements are needed for continuous quality monitoring and the measurement may be used for closed loop control of ozonation.

---

[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.

Current edition approved July 15, 2016. Published July 2016. Originally approved in 2011. Last previous edition approved in 2011 as D7677 – 11. DOI: 10.1520/D7677-16.

[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.

5.4 In many pure water applications and especially where water quality is regulated by the FDA or similar enforcement agencies, ozone removal must be complete before the water is used. This test method is useful for detecting and determining dissolved ozone levels in water at the trace level as well as at process concentrations where sanitization and chemical reactions occur.

6. Interferences

6.1 This technology is only effective with a flowing sample. Turbulent flow past the membrane is necessary to continuously replenish the ozone that diffuses through the membrane and is consumed in the probe. The replenishment of fresh liquid at the surface of the membrane ensures representative sampling. The required minimum linear velocity is dependent on membrane material and thickness and is manufacturer specific. A flow housing designed for the sensor provides the best control of flow velocity. Follow the manufacturer's flow rate specifications for the flow housing and membrane used.

6.2 Interferences are limited to gases which can permeate the membrane and react at the cathode or anode. Although many gases can pass through the membrane, only chlorine gas has been found to react at the applied potential. However, chlorine in high purity water is typically in ionic form which cannot pass through the membrane and so is not usually an interference. The exception is that under acidic conditions (pH <6), chlorinated water can produce dissolved chlorine gas and its presence must be minimized to avoid interference.

6.3 Polarographic ozone sensors must typically be polarized in the presence of ozone before they can measure reliably and be calibrated. The sensor must be connected to the powered measuring instrument to apply the polarization voltage across the electrodes while the sensor is in an ozonated sample. Length of time and ozone concentrations needed to achieve full polarization are manufacturer specific.

6.4 Sample temperature range is dependent on manufacturer design and specifications but is generally limited to between 0°C and 50°C. Temperatures below the freezing point of water can result in a disturbance of the electrolyte and an inability of the sensor to function. Ozone is seldom used in hot water because the rate of decay to oxygen is too fast to make it effective.

6.5 Sample pressure must be within manufacturer specifications. In some cases varying process pressure can cause instability.

6.6 Response time can vary from as little as a few seconds to a few minutes depending on membrane and sensor design and materials. Time for full response must be allowed, especially when calibrating.

6.7 Although not a true interference in the measurement itself, the rapid decay of ozone to oxygen makes sampling and calibration especially time dependent. The decay rate is increased greatly at higher temperatures and to some degree at higher pH. The half-life of ozone in neutral water is approximately 20 minutes at 25°C.

6.7.1 Sample lines must be short and run at high flow velocity to bring a representative sample to the sensor that has not had a significant decrease in ozone concentration.

6.7.2 Where grab samples are taken to establish concentration values for calibration, they must be processed quickly to minimize ozone decay.

7. Apparatus

7.1 *Apparatus for Dissolved Ozone Determination*—A typical installation consists of a sampling connection to a process line, a sensor with flow housing, a cable connecting the sensor and electronics, and analyzer electronics.

7.1.1 *Sampling*—The sample can be delivered via a sensor flow housing or cell, or accessed through direct insertion into the process vessel or pipe. Flow through the flow housing must be continuous during measurements and is typically controlled by a flow control valve located after the flow housing. A weir set up is also acceptable in cases where out-gassing does not occur. The weir design requires that the flow control valve be located before the flow housing. Direct insertion probes can be mounted through a standard T-fitting connection or via an extraction valve. The valve set up permits the extraction of the probe without interrupting the process flow.

7.1.2 *Sensor*—The sensor has a body, a membrane, a cathode, an anode, a guard ring electrode (optional), a temperature sensor, and a cable connection to the electronics.

7.1.2.1 *Body*—The sensor body should be made of materials compatible with the process. Common materials of construction include PEEK, type 316L stainless steel, and titanium.

7.1.2.2 *Membrane*—Membranes are composed of a gas permeable material that is resistant to process conditions, sometimes reinforced with a fine internal mesh. Common membrane materials are PFA (PerFluoroAlkoxy), PTFE (PolyTetraFluoroEthylene), and Silicone rubber.

7.1.2.3 *Cathode*—The cathode is the reaction center for ozone analysis and is exposed to dissolved ozone gas and hydroxyl radicals continuously. The cathode is constructed of high purity noble metal such as gold or platinum which resists ozone degradation.

7.1.2.4 *Anode*—The anode is sacrificial in this method and requires a metal whose oxidation products will not interfere with the analysis such as silver which precipitates out of solution in the presence of halides in the electrolyte.

7.1.2.5 *Guard Ring Electrode*—The optional guard ring electrode surrounding the cathode is charged at the same potential as the cathode and prevents the migration of silver ions back over to the cathode. As the silver passes over the cathode it has a tendency to plate out, causing an increase in maintenance frequency as well as a background interference. The guard ring electrode can improve stability and response time but does not serve a direct measurement function. Platinum is typically used since it is resistant to ozone degradation.

7.1.2.6 *Temperature Sensor*—Changes in water temperature affect permeation rates through the membrane and require temperature compensation. Temperature is also used to compensate for changing ozone solubility with temperature in the conversion of the partial pressure signal to concentration. An accurate temperature sensor, typically embedded in the head of the sensor, is required for proper compensation.

7.1.3 *Cable*—The sensor cable must withstand the environmental conditions of the installation and provide continuous high impedance insulation and shielding to carry the low, nanoampere level signal. Installation in dedicated dc signal conduit is recommended, with proper shielding from electrical interference. Refer to the manufacturer's requirements.

7.1.4 *Analyzer Electronics*—The measuring circuit applies a controlled polarization voltage between the anode and cathode (and optional guard ring electrode) to promote the ozone reduction reaction. The sensor's ozone and temperature signals are combined with stored calibration data to compute and display concentration, as mg/L (ppm) or µg/L (ppb) of DO_3. Data may be accumulated in internal nonvolatile memory, or exported via analog or digital signals to printer, data acquisition or control systems.

8. Reagents and Materials

8.1 *Purity of Water*—Reference to water that is used for reagent preparation, rinsing or dilution shall be understood to mean water that conforms to the quantitative specifications of Type II reagent water of Specification D1193.

8.2 *Sensor Electrolyte*—A manufacturer-specific electrolyte bathes the anode and cathode to enable the electrochemical reaction reducing the ozone.

8.3 *Calibration and Verification Using a Colorimetric Method*—Materials or reagents are required for verification or calibration using a colorimetric method. This method uses a spectrophotometer or colorimeter and either indigo trisulfonate or N,N-diethyl-p-phenylenediamine (DPD) reagent. Indigo color is bleached by ozone; DPD develops a pink color in the presence of ozone.

8.3.1 *Containers*—Containers used for blanks and samples must be clean and free of contaminants. The typical container is a beaker or flask with large opening at the top for access to the water sample. Practices D3370 for proper container preparation. After the container has been cleaned and before being used, it should be rinsed thoroughly with the water sample.

8.3.2 *Blank*—Choose a blank water sample which is representative of the water to be sampled and known to have no DO_3. Preparation of an appropriate blank can be done by using preozonated feed water, degassing a water sample, destructing the water sample DO_3 through UV, or permitting a water sample to sit long enough for ozone to decay.

8.3.3 *Spectrophotometer or Colorimeter*—An instrument detecting at the appropriate wavelength is required for detecting the reagent color change related to ozone concentration. The ampoules or sample holders must be matched to the instrument and its selected range.

8.3.4 *Indigo Trisulfonate Reagent*—Commercially packaged kits are available using vacuum ampoules containing reagents for single sample analyses. The ampoule consists of both the volumetric container and the appropriate quantity of reagent and buffer. In use, the glass ampoule tip is broken off under water in the sample container. The vacuum sucks a controlled amount of sample into the ampoule where the indigo and ozone react, producing a color inversely proportional to the ozone concentration. Store these ampoules in accordance with manufacturer's instructions, as they are light, time and heat sensitive.

8.3.5 *N,N-diethyl-p-phenylenediamine (DPD) Reagent*—This reagent is used with other spectrophotometer or colorimeter systems and is supplied in manufacturer-specific formulations.

8.4 *Calibration and Verification Using Air as a Reference*—A certified thermometer and a certified barometer are used to perform a traceable air calibration.

9. Hazards

9.1 Ozone gas at high enough concentration is a health hazard. Areas where dissolved ozone is measured are typically near ozone generators and holding tanks that could potentially leak ozone gas into the ambient atmosphere. Ozone is generally detectable by its characteristic odor at 0.02 to 0.05 ppm by weight in air although prolonged exposure may cause some desensitization. The OSHA (U.S. Occupational Safety and Health Administration) limit is 0.1 ppm averaged over 8 hours. At least one ambient ozone gas alarm must be on site for safety of personnel working in the area.

9.2 Hazardous materials may be used in manufacturer-recommended sensor maintenance procedures. Sensor and material supplier safety precautions should be observed.

10. Sampling

10.1 Connect the sensor to the sample source in accordance with Practices D3370 and the instrument manufacturer's instructions. If any conflict exists in these instructions, give priority to the manufacturer's requirements, as they may be specific to a particular sensor.

10.2 When sampling with dissolved gases present, take special care to use a connection or insertion location that will result in representative sampling. DO_3, or dissolved oxygen from its decay, in a circulating system, can easily out-gas and form bubbles in the water which can affect stability of measurement. Often these bubbles are temporary in pressurized water. Choose locations for sampling that avoid degassing opportunities such as immediately after valves, immediately after pipe bends of $>90°$, before pumps, the tops of horizontal pipes, vertical pipes that have liquid flowing downward, immediately after increases in pipe diameter, after a depressurization or any turbulence creating point.

11. Calibration

11.1 *Calibration of Zero*—With the sensor removed from the line and still reading DO_3 values, place it in a location in the air known to be free of ozone gas. Dry the sensor membrane to remove all sample water which may contain DO_3. Allow the sensor to equilibrate with the air temperature to $\pm 2°C$. If there is a large temperature difference between the air and the process, for example, $>5°C$; this may take over an hour. Perform a zero calibration according to the manufacturer's instructions. Equivalence of zero is considered to be ≤ 0.005

mg/L (ppm) in most commercial instruments. Some polarographic sensors have an intrinsic zero and do not require a zero calibration. Follow the sensor manufacturer's recommendations.

11.2 Two methods are used for span calibration of polarographic ozone sensors: in-line calibration using a colorimetric reference and air calibration.

11.2.1 *Colorimetric Calibration of Span*—Either of the reagent systems noted in 8.3 can be used as the reference for span calibration. The IOA has approved the indigo method.[3] With the sensor inline and reading stable DO_3 values, collect a sample of water representative of the water the sensor is measuring. This can be from a port near an inserted sensor or on the outlet of the sensor flow housing drain. In either case, the sample must flow gently, without spray or turbulence that could de-gas the sample. Sample the water using three aliquots or ampoules, simultaneously noting the reading on the on-line instrument. Measure all three grab samples. Discard an outlier if it differs by ≥0.015 mg/L (0.02 mg/L for displays not reading to the third decimal place) from the mean of the other two. If no two of the three agree, redo all three. Calculate the average and input the value as the on-line instrument span calibration according to manufacturer's instructions.

11.2.2 *Air Calibration of Span (suitable for instruments so equipped)*—Since oxygen and ozone are similar in their permeation rates through the sensor membrane, the rate of permeation of a known oxygen quantity can be equated to an ozone calibration value. Single point air calibration can be a means to calibrate span in a DO_3 instrument with this capability. Remove the sensor from the line and place it in a location known to be free of ozone gas. Be sure the outer surface of the sensor membrane is dry and free of sample water, which may contain DO_3. Allow the sensor to equilibrate with the air temperature within ±2°C. If there is a large temperature difference between the air and the sensor, for example, >5°C, this may take over an hour. Enter the air calibration mode in the analyzer electronics which temporarily changes the polarization potential applied to the cathode and changes the response to oxygen (O_2) partial pressure. Determination of the O_2 partial pressure of air is determined from the barometric pressure and temperature of the air. Allow at least 10 minutes for the sensor to stabilize and then perform the calibration function according to the manufacturer's instructions. Return to the ozone measurement mode of the instrument and allow the extended period of time required for the sensor to repolarize and stabilize on ozone measurement per manufacturer's recommendations.

11.3 *Calibration Verification*—Span and zero verification are normally required.

11.3.1 *Colorimetric Verification of Span*—With the sensor inline and reading DO_3 values under stable conditions, collect a sample of water representative of the water the sensor is measuring, this can be from a spigot near an inserted sensor or on the outlet of the flow housing drain. The DO_3 value for verifying the span should be ≥70 % of the target process control limit DO_3 value. System DO_3 values for verification may be higher than the target control limit. Sample and measure the ozone concentration of the water the same as for calibration in 11.1. Compare the average of the three values to the reading of the instrument. If they differ by ≤0.015 mg/L (≤0.02 mg/L if either the spectrophotometer or ozone instrument displays do not read to the third decimal place) then a span calibration is required.

11.3.2 *Air Verification of Span (for instruments so equipped)*—With the sensor removed from the line and still reading DO_3 values, place it in a location known to be free of ozone gas. Dry the sensor membrane to remove sample water which may contain DO_3. Allow the sensor to equilibrate with the air temperature within ±2°C. If there is a large temperature difference between the air and the process, for example, >5°C, this may take over an hour. To check the air calibration value, enter into the air calibration mode (which changes the cathode polarization voltage to make it respond to O_2). Allow at least 10 minutes for equilibration and record the % last calibration value. If % last calibration value is not available then record % ideal value or absolute air value. Compare to % ideal or absolute air value when calibrated. If the two agree within the quality limits set (typically ±5 to 15 %), the sensor span has been verified. Restore the instrument to the ozone measurement mode and allow the manufacturer's extended repolarization time before ozone measurements are used.

11.3.3 *Air Verification of Zero*—With the sensor removed from the line and still reading DO_3 values, place it in a location in the air known to be free of ozone gas. Dry the sensor membrane to remove all sample water, which may contain DO_3. Allow the sensor to equilibrate with the air temperature within ±2°C. If there is a large temperature difference between the air and the process, for example, >5°C, this may take over an hour. The sensor must read zero or the equivalence of zero (≤0.005 mg/L, in most commercial instruments). Otherwise a zero calibration is required.

12. Procedure

12.1 The normal operation of the analyzer is automatic after configuration by the user and does not require user intervention for routine analysis.

12.2 Based on calibration verification results showing an increasing drift rate, it is necessary to replace the electrolyte or membrane or both. With some sensors a cleaning process is also required. If using manufacturer-recommended materials for sensor cleaning, observe all safety precautions when handling those materials.

13. Quality Control

13.1 Instrument and sensor verification and calibration must be performed according to the manufacturer's instructions for both the continuous measuring equipment and the colorimetric standard, if used.

13.2 *Verification Frequency*—Calibration verification should be checked on a periodic basis. Verification frequency is determined based on risk of sensor drift or failure. Factors that contribute to sensor drift and failure are (*1*) continuous high levels of ozone exposure (in accordance with manufacturer

---

[3] International Ozone Association Revised guideline document, "Colorimetric Method for Manual Determination of Ozone Concentration in Water," *Ozone Science and Engineering*, Vol 20.6, 1998, p. 443.

specifications), (*2*) membrane wear due to excessive flow rates, pressure fluctuations, or abrasive water action, and (*3*) electrolyte depletion. Verification should be performed at least every two months or according to manufacturer's recommendations.

13.3 *Calibration Frequency*—Calibration must be performed at least as frequently as the manufacturer's schedule and instructions and whenever a sensor is returned to service after maintenance. Sensors must be allowed to fully polarize and reach stability before calibration after maintenance. Minimally, calibration should be performed semi-annually.

13.4 Where the verification and calibration of ozone sensors depend on a colorimetric method as the standard, at least three colorimetric samples and measurements must always be made as outlined in 11.2.1 and 11.3.1.

14. Precision and Bias

14.1 Neither precision nor bias data can be obtained for this test method from a collaborative study designed in accordance with the requirements of Practice D2777 since this test method is a continuous determination. This inability to obtain precision and bias data for continuous determinations is recognized and stated in the scope of Practice D2777.

14.2 The ephemeral nature of ozone makes it impossible to provide stable ozone standards for comparisons.

14.3 Accuracy of ozone measurements by this method are primarily limited by the reference method to which they are calibrated.

14.3.1 Some colorimetric methods to measure ozone using good technique have been found to give repeatability on the order of ±0.02 mg/L in the range of 0.05 to 0.50 mg/L.[4]

14.3.2 Air span calibration, in instruments so equipped, has been found to give repeatability of ±5 %, that is, 0.0025 mg/L at an ozone concentration of 0.05 mg/L.

15. Keywords

15.1 dissolved gas; high purity water; ozone; pharmaceutical water; sanitization

---

[4] St. Germain, M., and Gray, D, "Ozone Measurement Technology in Pure Water Systems," Semiconductor Pure Water and Chemicals Conference, Santa Clara, CA 2006, and related work.

APPENDIX

(Nonmandatory Information)

X1. POLAROGRAPHIC OZONE SENSOR OPERATION

X1.1 The typical polarographic ozone sensor consists of at least two electrodes. Minimally there is an anode and cathode and sometimes a third electrode known as a guard ring electrode. The sensor also includes a temperature sensor for compensation of the ozone measurement. The electrodes are covered by a gas permeable membrane and submersed in electrolyte typically containing a bromide salt dissolved in water. The cathode is set to a potential suitable for the reduction of molecular ozone to hydroxide ion and oxygen. The change in chemical species results in an amperometric draw at the cathode and this draw is directly related to the partial pressure of ozone contacting the cathode. The partial pressure at the cathode is, in turn, proportional to the ozone partial pressure in the sample. The relationship between chemistry and electrical current can be described by the following pair of redox reactions.

Cathode Reduction:	$H_2O + O_3 + 2\,e^- \rightarrow O_2 + 2\,OH^-$
Anode Oxidation:	$Ag + 2\,Br^- \rightarrow 2\,AgBr + 2\,e^-$
Overall Reaction:	$H_2O + 2\,Ag + 2\,Br^- + O_3 \rightarrow 2\,AgBr + O_2 + 2\,OH^-$

The permeation rate of ozone through the membrane is the limiting factor for how much ozone from the liquid makes its way to the cathode. Variation in membrane permeation rate results in the need for calibration. Once the membrane permeation rate is normalized by calibration, the partial pressure value can be converted to dissolved ozone concentration. The measuring system compensates for the temperature dependence of the permeation rate and the solubility of ozone in water.