



Designation: ~~D7677~~—~~11~~ D7677 – 16

Standard Test Method for the Continuous Measurement of Dissolved Ozone in Low Conductivity Water¹

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~~ <100 $\mu\text{S}/\text{cm}$, 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 test method, 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 of approximately +350 mV, potential, producing a current flow in direct proportion to the partial pressure of ozone in the sample outside the membrane.

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.

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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.

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.

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 $0^{\circ}C$ and $50^{\circ}C$. 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 $25^{\circ}C$.

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*—*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*—*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 DO₃. 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

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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. [Reference 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 DO₃. Preparation of an appropriate blank can be done by using preozonated feed water, degassing a water sample, destructing the water sample DO₃ through UV, or permitting a water sample to sit long enough for ozone to decay.

8.3.3 *Spectrophotometer or colorimeter*—*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*—*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*—*Reagent*—This reagent is used with other spectrophotometer or colorimeter systems and is supplied in manufacturer-specific formulations.