

Region 4
U.S. Environmental Protection Agency
Science and Ecosystem Support Division
Athens, Georgia

OPERATING PROCEDURE

Title: Field Measurement of Dissolved Oxygen

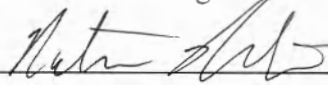
Effective Date: April 12, 2017

Number: SESDPROC-106-R4

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Revision History

The top row of this table shows the most recent changes to this controlled document. For previous revision history information, archived versions of this document are maintained by the SESD Document Control Coordinator on the SESD local area network (LAN).

History	Effective Date
<p>SESDPROC-106-R4, <i>Field Measurement of Dissolved Oxygen</i>, replaces SESDPROC-106-R3</p> <p>General: Corrected any typographical, grammatical, and/or editorial errors. In addition, any references to former Division organizational structure was updated to reflect current structure.</p> <p>Title Page: Changed the Author from Hunter Johnson to Nathan Barlet. Changed the Field Quality Manager from Bobby Lewis to Hunter Johnson. Updated cover page to represent SESD reorganization.</p> <p>Table of Contents: Added Sections 3.2.1 Water-Saturated Air Method, 3.2.2 Air-Saturated Water Method, and 3.2.3 Zero-DO Verification & 2-Point Calibration. Changed Section 3.5 from “Operational Check” to “Operational Verification.” Updated page numbers.</p> <p>Section 1.4: Added the citations for Benson and Krause (1980), Benson and Krause (1984), USGS (2013a), and USGS (2013b) as references,</p> <p>Section 3.1: Changed “volume of oxygen contained in a volume of water” to “mass of molecular oxygen contained in a volume of water.” Changed “pressure” in first paragraph and third bullet point to “atmospheric pressure.”</p> <p>Section 3.2: Added “However, some optical DO meters are capable of a two-point calibration at 0% and 100% saturation, refer to Section 3.2.3 for applicability.”</p> <p>Added Section 3.2.1 Water-Saturated Air Method, which includes information on the calibration procedure for the water-saturated air method. Added “Allow at least 10-15 minutes for the temperature and dissolved oxygen readings to equilibrate. Ensure that water droplets are removed from the luminescence cap or Clark cell membrane and thermistor before calibration. Refer to Section 3.5 for calibration verification procedure.”</p> <p>Added Section 3.2.2 Air-Saturated Water Method, which includes information on the calibration procedure for the air-saturated water</p>	<p>April 12, 2017</p>

<p>method. Added “Refer to Section 3.5 for calibration verification procedure.”</p> <p>Added Section 3.2.3 Zero-DO Verification & 2-Point Calibration. Added “It is recommended that a zero-DO verification is conducted periodically or when concentrations are expected to be below 1 mg/l (USGS, 2013a). A zero-DO solution can be prepared by dissolving 1 gram of sodium sulfite in 1 liter of deionized water. This should be made fresh weekly or as needed. If the unit is equipped with a wiper, it should be removed before immersing in zero-DO solution. The reading should not exceed a concentration of 0.2 mg/l dissolved oxygen in the zero-DO solution. For Clark cells that exceed this concentration, replace the electrolyte and membrane before repeating the zero-DO verification process. For optical probes that read above 0.2 mg/l in zero-DO solution, replace the sensor cap if it is expired or perform a 2-point calibration if applicable. Some optical DO probes are capable of 2-point calibrations using a zero-DO solution and the air-saturated water method discussed in Section 3.2.2. Refer to the manufacturer’s instruction manual for the appropriate 2-point calibration procedure. Ensure that the probe is thoroughly rinsed of zero-DO solution after verification or calibration to avoid measurement interferences caused by residual sodium sulfite.”</p> <p>Section 3.4: Changed the fifth bullet point to read “The DO meter should be capable of auto-correcting for specific conductivity/salinity or a separate instrument should be used to measure specific conductivity/salinity so that the final DO measurement(s) can be corrected.”</p> <p>Section 3.5: Changed the title from “Operational Check” to “Operational Verification.”</p> <p>Changed first paragraph to read “A post-calibration and post-operation instrument verification check should be performed using one of the techniques described in Sections 3.2.1 and 3.2.2 or 3.2.3 (for 2-point calibrations) to quantify potential instrument drift during use. A verification check will be performed after a calibration and at the end of all measurements”</p> <p>Changed second paragraph to read “It may be appropriate to verify the calibration of a DO meter periodically during the course of a day’s measurements when conducting individual measurements. A DO probe may be re-calibrated throughout the day if drift is occurring. The verification DO concentration should be measured and recorded in the field logbook prior to any instrument adjustment.” Also added the sentence “For long-term deployments a post-operation verification should be performed at the end of the deployment.”</p> <p>Added third paragraph which reads “Verification is done by comparing a post-calibration or post-operation reading at 100% saturation conditions to a DO solubility table value at the ambient air/water</p>	
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temperature and barometric pressure. Post-calibration and post-operation readings should not exceed a maximum of ± 0.2 mg/l from the DO solubility table value. DO solubility tables can be accessed via the U.S. Geological Survey's DOTABLES software (USGS, 2013b) which are based on equations from Benson and Krause (1980; 1984)."	
SESDPROC-106-R3, <i>Field Measurement of Dissolved Oxygen</i> , replaces SESDPROC-106-R2	January 8, 2014
SESDPROC-106-R2, <i>Field Measurement of Dissolved Oxygen</i> , replaces SESDPROC-106-R1	February 12, 2010
SESDPROC-106-R1, <i>Field Measurement of Dissolved Oxygen</i> , replaces SESDPROC-106-R0	November 1, 2007
SESDPROC-106-R0, <i>Field Measurement of Dissolved Oxygen</i> , Original Issue	February 05, 2007

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1 General Information

1.1 Purpose

This document describes methods and considerations to be used and observed when conducting field measurements of dissolved oxygen in surface water, treated wastewater and in gas media for specific applications (e.g., reaeration measurement).

1.2 Scope/Application

On the occasion that SESD field investigators determine that any of the procedures described in this section are inappropriate, inadequate or impractical and that another method must be used to obtain a measurement of dissolved oxygen, the alternate procedure will be documented in the field log book, along with a description of the circumstances requiring its use. Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use.

1.3 Documentation/Verification

This procedure was prepared by persons deemed technically competent by SESD management, based on their knowledge, skills and abilities and has been tested in practice and reviewed in print by a subject matter expert. The official copy of this procedure resides on the SESD Local Area Network (LAN). The Document Control Coordinator (DCC) is responsible for ensuring the most recent version of the procedure is placed on the LAN and for maintaining records of review conducted prior to its issuance.

1.4 References

Benson, B.B., and Krause, D., Jr, 1980. The concentration and isotopic fractionation of gases dissolved in freshwater in equilibrium with the atmosphere—1. Oxygen: *Limnology and Oceanography*, v. 25, no. 4, p. 662–671.

Benson, B.B., and Krause, D., Jr, 1984. The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere: *Limnology and Oceanography*, v. 29, no. 3, p. 620–632.

SESD Operating Procedure for Equipment Inventory and Management, SESDPROC-108, Most Recent Version

SESD Operating Procedure for Logbooks, SESDPROC-010, Most Recent Version

SESD Field Branches Quality Management Plan, SESDPLAN-001, Most Recent Version

USEPA. Safety, Health and Environmental Management Program Procedures and Policy Manual. Region 4 SEDS, Athens, GA, Most Recent Version

USGS, 2013a. Dissolved Oxygen (ver. 3.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, sec. 6.2, http://water.usgs.gov/owq/FieldManual/Chapter6/6.2_v3.0.pdf.

USGS, 2013b. DOTABLES (ver. 3.5): Dissolved Oxygen Solubility Tables, <https://water.usgs.gov/software/DOTABLES/>.

1.5 General Precautions

1.5.1 Safety

Refer to the SEDS Safety, Health and Environmental Management Program Procedures and Policy Manual and any pertinent site-specific Health and Safety Plans (HASPs) for guidelines on safety precautions. These guidelines, however, should only be used to complement the judgment of an experienced professional. When using this procedure, minimize exposure to potential health hazards through the use of protective clothing, eye wear and gloves. Address chemicals that pose specific toxicity or safety concerns and follow any other relevant requirements, as appropriate.

Appropriate precautions should be observed when working in and around bodies of water and on boats. Be aware of fast flowing waters, waterway obstructions such as dams, and other vessels on the water.

2 Quality Control

All dissolved oxygen meters will be maintained and operated in accordance with the manufacturer's instructions and the SESD Operating Procedure for Equipment Inventory and Management (SESDPROC-108). Before a meter is utilized in the field, it will be calibrated and verified, according to Section 3.2 of this procedure, to ensure it is operating properly. These calibration and verification checks will be documented and maintained in a logbook.

For in-situ measurements, an instrument warm-up period appropriate for that instrument should be provided. Consult manufacturer's documentation for appropriate warm-up time.

The ambient temperature in the immediate vicinity of the meter should be measured and recorded in the field logbook to insure the instrument is operated within the manufacturer's specified range of operating temperatures. For instruments that are deployed for in-situ measurements, the temperature of the medium being monitored should be measured and recorded in the logbook prior to deployment. *In-situ monitoring equipment may be utilized in unattended deployments where autonomous logging may preclude temperature measurement prior to deployment. Because in situ instrumentation generally has a wide range of operating temperature, the field investigator may utilize professional judgment in determining if the operating environment is suitable for unattended deployment.*

Following instrument use, an end check should be performed using one of the techniques described in Section 3.2 to quantify potential instrument drift during use.

If at any time during a field investigation, it appears that the environmental conditions could jeopardize the quality of the measurement results, the measurements will be stopped. This will be documented in the field logbook.

3 Field Measurement of Dissolved Oxygen

3.1 General

Dissolved oxygen can be defined as the mass of molecular oxygen contained in a volume of water. The solubility of oxygen in water is dependent on the water temperature, salinity and atmospheric pressure.

- As the temperature of the water decreases, the solubility of oxygen increases.
- As salinity increases, the solubility of oxygen decreases.
- As atmospheric pressure decreases (altitude increases), the solubility of oxygen decreases.

Several methods for measurement of dissolved oxygen in water are available utilizing a variety of technologies. When measuring dissolved oxygen for compliance with the National Pollutant Discharge Elimination System (NPDES) Program, only approved methods will be used. Approved methods can be found in the Code of Federal Regulations (CFR) 40 CFR Part 136.

3.1.1 Clark Cell Probes

Clark cell probes utilize an oxygen permeable membrane that covers an electrolytic cell which consists of a cathode and an anode. The anode acts as a reference electrode. After passing through the permeable membrane, the oxygen is reduced by an applied potential voltage that is referenced to the anode. The reduction current at the cathode is directly proportional to the partial pressure of oxygen in liquid, expressed as %-air saturation. The concentration of oxygen, in mg/l, is calculated based on the %-air saturation reading and the solubility of oxygen in water at the sample temperature.

In general, sample collection using a DO probe requires only lowering the probe into the sample media and recording or logging the results. The probe should be lowered gently to prevent damage to the membrane and gently turned when initially lowered to remove any attached air bubbles. If the instrument requires the use of a stirrer, the stirrer should be turned on before recording any readings. Prior to use, the instrument should be calibrated and any manufacturer specified warm-up period should be observed.

3.1.2 Luminescent Probes

Luminescent dissolved oxygen probes employ a light emitting diode (LED) to provide incident light, which excites the oxygen-sensitive luminescent-dye

molecule substrate of the sensor. After dissipation of the excitation energy, longer-wavelength light is emitted (luminescence). The magnitude of steady-state luminescence (intensity) is measured by the sensor and is inversely proportional to the dissolved oxygen concentration.

Sample collection with this type of probe should follow the sample procedures described in the second paragraph of Section 3.1.2 for Clark Cell probes.

3.2 Calibration

Many brands of instruments are commercially available for *in-situ* measurement of dissolved oxygen using Clark cell probes and luminescent probes. The manufacturer's instruction manual should be consulted for specific procedures regarding their calibration, maintenance and use. Calibration of any measurement instrument must be conducted and/or verified prior to each use or on a daily basis, whichever is most appropriate.

In general, calibrations should be conducted at temperatures and pressures as close as possible to those of the sample media for the most accurate measurements. Due to the sensitivity of dissolved oxygen measurements to changes in temperature, the temperature probe or thermistor should be verified using a NIST traceable thermometer prior to each calibration. Most dissolved oxygen meters utilize a one-point calibration which is generally performed using either water-saturated air or air-saturated water. However, some optical DO meters are capable of a two-point calibration at 0% and 100% saturation, refer to Section 3.2.3 for applicability.

3.2.1 Water-Saturated Air Method

When using the water-saturated air method, the probes should be placed in a 100% relative humidity environment open to ambient air temperature and barometric pressure. Allow at least 10-15 minutes for the temperature and dissolved oxygen readings to equilibrate. Ensure that water droplets are removed from the luminescence cap or Clark cell membrane and thermistor before calibration. Refer to Section 3.5 for calibration verification procedure.

3.2.2 Air-Saturated Water Method

When using air-saturated water for calibration, an aeration device such as an aquarium pump with a diffusion stone should be placed in a vessel containing tap water. The water in the vessel should be aerated for a minimum of one hour at a

constant temperature. Saturation should be verified by placing the dissolved oxygen probe in the vessel and monitoring the temperature and dissolved oxygen readings for stabilization. Avoid placing the probe in the direct stream of air bubbles. Bubbles can accumulate on the probe surface and cause erroneous readings. Refer to Section 3.5 for calibration verification procedure.

3.2.3 Zero-DO Verification and 2-Point Calibration

It is recommended that a zero-DO verification is conducted periodically or when concentrations are expected to be below 1 mg/l (USGS, 2013a). A zero-DO solution can be prepared by dissolving 1 gram of sodium sulfite in 1 liter of deionized water. This should be made fresh weekly or as needed. If the unit is equipped with a wiper, it should be removed before immersing in zero-DO solution. The reading should not exceed a concentration of 0.2 mg/l dissolved oxygen in the zero-DO solution. For Clark cells that exceed this concentration, replace the electrolyte and membrane before repeating the zero-DO verification process. For optical probes that read above 0.2 mg/l in zero-DO solution, replace the sensor cap if it is expired or perform a 2-point calibration if applicable. Some optical DO probes are capable of 2-point calibrations using a zero-DO solution and the air-saturated water method discussed in Section 3.2.2. Refer to the manufacturer's instruction manual for the appropriate 2-point calibration procedure. Ensure that the probe is thoroughly rinsed of zero-DO solution after verification or calibration to avoid measurement interferences caused by residual sodium sulfite.

3.3 Maintenance

Maintenance procedures vary depending on the technology utilized by each instrument and the manufacturer. The manufacturer's instruction manual should be consulted for instrument specific procedures. Following are some general guidelines for maintaining dissolved oxygen meters:

- Inspect probes for damage prior to use.
- For Clark cell probes, membranes and electrolyte solution should be changed prior to each study, when feasible.
- Battery voltages should be checked. For meters that will be deployed unattended, new or fully charged batteries should be used for each study.
- All calibration and maintenance procedures performed should be thoroughly documented.

3.4 Conducting Field Measurement of Dissolved Oxygen

Following are guidelines for conducting field measurements of dissolved oxygen:

- Except as described in specific operating procedures, dissolved oxygen measurements should if possible be conducted *in-situ*.
- When measuring DO at distinct points in the water column, the probe should be allowed to equilibrate at each location prior to recording the measurement.
- In water bodies with a great deal of flow, a weight may be attached to the probe guard or support cable to insure the probe is maintained at the proper depth.
- Insure that the measurement location is representative of conditions within the water body or reach. Avoid measurements directly below turbulent sections or still water unless these conditions represent most of the water body or reach.
- The DO meter should be capable of auto-correcting for specific conductivity/salinity or a separate instrument should be used to measure specific conductivity/salinity so that the final DO measurement(s) can be corrected.

3.5 Operational Verification

A post-calibration and post-operation instrument verification check should be performed using one of the techniques described in Sections 3.2.1 and 3.2.2 or 3.2.3 (for 2-point calibrations) to quantify potential instrument drift during use. A verification check will be performed after a calibration and at the end of all measurements.

It may be appropriate to verify the calibration of a DO meter periodically during the course of a day's measurements when conducting individual measurements. A DO probe may be re-calibrated throughout the day if drift is occurring. The verification DO concentration should be measured and recorded in the field logbook prior to any instrument adjustment. For long-term deployments a post-operation verification should be performed at the end of the deployment.

Verification is done by comparing a post-calibration or post-operation reading at 100% saturation conditions to a DO solubility table value at the ambient air/water temperature and barometric pressure. Post-calibration and post-operation readings should not exceed a maximum of ± 0.2 mg/l from the DO solubility table value. DO solubility tables can be accessed via the U.S. Geological Survey's DOTABLES software (USGS, 2013b) which are based on equations from Benson and Krause (1980; 1984).