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

# OPERATING PROCEDURE

Title: **Field Measurement of Dissolved Oxygen**

| | |
|---|---|
| **Effective Date:** February 12, 2010 | **Number:** SESDPROC-106-R2 |

**Author**

Name: Hunter Johnson
Title: Environmental Engineer
Signature: [signature] Date: 2/12/10

**Approvals**

Name: Archie Lee
Title: Chief, Enforcement and Investigations Branch
Signature: [signature] Date: 2/12/10

Name: Bill Cosgrove
Title: Chief, Ecological Assessment Branch
Signature: [signature] Date: 2/12/10

Name: Liza Montalvo
Title: Field Quality Manager, Science and Ecosystem Support Division
Signature: [signature] Date: 2/11/10

## Revision History

This table shows changes to this controlled document over time. The most recent version is presented in the top row of the table. Previous versions of the document are maintained by the SESD Document Control Coordinator.

| History | Effective Date |
|---|---|
| SESDPROC-106-R2, *Field Measurement of Dissolved Oxygen*, replaces SESDPROC-106-R1<br><br>**General**<br>Corrected any typographical, grammatical, and/or editorial errors.<br><br>**Title Page**<br>Changed author from Laura Ackerman to Hunter Johnson. Changed Chief, Enforcement and Investigations Branch from Antonio Quinones to Archie Lee. Changed Field Quality Manager from Laura Ackerman to Liza Montalvo.<br><br>**History**<br>Changed Field Quality Manager to Document Control Coordinator.<br><br>**Section 1.1**<br>Added treated wastewater.<br><br>**Section 1.3**<br>Omitted reference to the H: drive. Changed the Field Quality Manager to the Document Control Coordinator.<br><br>**Section 2**<br>Omitted sentence in paragraph 1 regarding labeling meters to indicate time of next calibration. Omitted "shall" in paragraph one and added "will". Reworded paragraph 3. Added sentence in paragraph 4 to identify minimum requirements for calibration. Added sentences in paragraph 5 regarding in situ instrumentation range of operating temperature.<br><br>**Section 3.1**<br>Added the last sentence on NPDES compliance.<br><br>**Section 3.2**<br>Added sentence in paragraph 3 regarding | February 12, 2010 |

| | |
|---|---|
| verification of temperature probe or thermistor by using NIST traceable thermometer. Added sentence in last paragraph regarding recording of data.<br><br>**Section 3.4**<br>Clarified first bulleted guideline.<br><br>**Section 3.5**<br>Added Section 3.5. | |
| SESDPROC-106-R1, *Field Measurement of Dissolved Oxygen*, replaces SESDPROC-106-R0<br><br>**General**<br>Deleted all references to SOSA.<br><br>**Title Page**<br>Changed title for Antonio Quinones from Environmental Investigations Branch to Enforcement and Investigations Branch. Changed Bill Cosgrove's title from Acting Chief to Chief.<br><br>**Section 1.3**<br>Updated information to reflect that procedure is located on the H: drive of the LAN.<br><br>**Section 1.4**<br>Updated referenced procedures due to changes in title names. Alphabetized and revised the referencing style for consistency.<br><br>**Section 2**<br>Updated referenced procedures due to changes in title names. Added last paragraph regarding stopping measurements due to environmental conditions. | November 1, 2007 |
| SESDPROC-106-R0, *Field Measurement of Dissolved Oxygen*, Original Issue | February 05, 2007 |

## TABLE OF CONTENTS

**1 General Information** ........ 5

**1.1 Purpose** ........ 5
**1.2 Scope/Application** ........ 5
**1.3 Documentation/Verification** ........ 5
**1.4 References** ........ 5
**1.5 General Precautions** ........ 6

***1.5.1 Safety*** ........ 6

**2 Quality Control** ........ 7

**3 Field Measurement of Dissolved Oxygen** ........ 8

**3.1 General** ........ 8

***3.1.1 Iodometric Method (Winkler Titration)*** ........ 8
***3.1.2 Clark Cell Probes*** ........ 9
***3.1.3 Luminescent Probes*** ........ 9

**3.2 Calibration** ........ 9
**3.3 Maintenance** ........ 10
**3.4 Conducting Field Measurement of Dissolved Oxygen** ........ 11
**3.5 Operational Check** ........ 11

# 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., diffusion 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.

## 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


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

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

United States Environmental Protection Agency (US EPA). 2001. Environmental Investigations Standard Operating Procedures and Quality Assurance Manual. Region 4 Science and Ecosystem Support Division (SESD), Athens, GA

US EPA. Safety, Health and Environmental Management Program Procedures and Policy Manual. Region 4 SESD, Athens, GA, Most Recent Version

## 1.5 General Precautions

### *1.5.1 Safety*

Refer to the SESD 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 taken to 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.

A 24 hour burn-in period is recommended for Clark Cell probes after changing the membrane to allow the membrane to stabilize.

Winkler titrations should be performed in pairs. If the resulting DO measurements are not within 0.2 mg/l, the samples should be discarded and a new pair run. When the water-saturated air calibration method is utilized the DO measurement should be within 4% of the air's known calculated saturated value.

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 volume of oxygen contained in a volume of water. The solubility of oxygen in water is dependant on the water temperature, salinity, and pressure. As the temperature of the water decreases, the solubility of oxygen increases. As salinity increases, the solubility of oxygen decreases. And finally, as the pressure decreases (altitude increases), the solubility of oxygen decreases. Several methods for measurement of dissolved oxygen in water are available, including iodometric methods (Winkler Titration), Clark cell probes and luminescent probes. 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 Iodometric Method (Winkler Titration)*

The iodometric method (Winkler Titration) for measuring dissolved oxygen in water is the most precise and reliable titrimetric procedure for dissolved oxygen analysis. It is based on the addition of divalent manganese solution, followed by strong alkali, to the sample in a glass stoppered bottle. The dissolved oxygen rapidly oxidizes an equivalent amount of the dispersed divalent manganous hydroxide precipitate to hydroxides of higher valency states. In the presence of iodide ions in an acidic solution, the oxidized manganous reverts to the divalent state and releases an amount of iodine equivalent to the dissolved oxygen content. The iodine is then titrated with a standard solution of thiosulfate. Oxidizing and reducing materials may be present in the sample and can cause interferences with the iodometric method. The most common interference is from nitrite. The azide modification effectively removes interferences caused by nitrite. Consult Standard Methods for the Examination of Water and Wastewater, Part 4500-O for additional information regarding measurement of dissolved oxygen in water using the Azide Modified Winkler Titration method.

Using this method, careful collection of the sample is paramount to prevent aeration of the sample during collection. The sample should be collected into a 300 ml glass bottle with a ground glass air-tight cap. The sample may be transferred from the collection site to the bottle using a submersible pump or a submerged horizontal sampler (e.g., Van Dorn) fitted with tubing at the outlet. The tubing is inserted to the bottom of the sample bottle and the bottle is allowed to overfill to purge any entrained air. After allowing the bottle to overfill, slowly remove the tubing and gently cap the bottle. The sample is then ready for iodometric analysis.

### *3.1.2 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.

### *3.1.3 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

The iodometric method of dissolved oxygen measurement is an analytical technique used to quantify the amount of oxygen in water and certain wastewaters and therefore, does not require calibration. The iodometric method can be used to assist with calibration of instruments designed to measure dissolved oxygen *in-situ*.

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 performed using either water saturated air, air-saturated water or the iodometric method. When using the water-saturated air method, the probes should be placed in a 100% relative humidity environment and the temperature and dissolved oxygen readings should be allowed to equilibrate. After equilibration, the meter should be set to read the appropriate dissolved oxygen concentration based on the temperature and barometric pressure.

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. Once the water is saturated, the temperature of the water and the barometric pressure can be used to determine the dissolved oxygen value. The meter can then be set to read that value.

The iodometric method for calibration requires filling a vessel with de-ionized water or tap water which has been dechlorinated by sitting exposed to the air for 24 hours then performing an Azide Modified Winkler Titration to determine the dissolved oxygen concentration of the water. The temperature of the water should remain constant throughout the calibration process. Once the dissolved oxygen concentration has been determined, the probe should be placed in the water and allowed to equilibrate. Following equilibration, the meter should be set to read the concentration of dissolved oxygen determined using the Winkler titration. During calibration, the dissolved oxygen concentration, temperature, and barometric pressure should be recorded.

### 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 fore 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.
- If DO measurements are conducted in saline water, the DO meter should either be capable of correcting for salinity or a separate instrument should be used to measure salinity so that the final DO measurements can be corrected.

### 3.5 Operational Check

A post-operation instrument verification check will be performed using one of the techniques described in Section 3.2 to quantify potential instrument drift during use. A verification check will be performed at the end of all measurements for a day or at the end of a deployment. The verification DO concentration will be measured and recorded in the field logbook prior to any instrument adjustment.

It may be appropriate to check the calibration of a DO meter periodically during the course of a day's measurements when conducting individual measurements rather than deploying an instrument. When this is done, it should be noted in the field logbook. The calibration of meters checked throughout the day maybe adjusted if drift is occurring.