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

OPERATING PROCEDURE

Title: **Field Measurement of Total Residual Chlorine**

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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-112-R2, *Field Measurement of Total Residual Chlorine,* Replaces SESDPROC-112-R1 **Cover Page:** The Author was changed from Ron Phelps to John Williams. The EIB Branch Chief was changed from Antonio Quinones to Archie Lee. The FQM was changed from Laura Ackerman to Liza Montalvo. **Section 1.2:** Added the following statement: Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use. **Section 1.3:** Omitted the reference to the H: drive of the LAN. **Throughout the document:** Replaced "mls" with "ml," and "insure" with "ensure." Corrected typographical errors.	April 20, 2011
SESDPROC-112-R1, *Field Measurement of Total Residual Chlorine,* Replaces SESDPROC-112-R0 **Cover Page:** Author was changed from John Williams to Ron Phelps. **Revision History** Changed Field Quality Manager to Document Control Coordinator. **Section 1.3** Changed Field Quality Manager to Document Control Coordinator. **Section 1.5** Added second paragraph. **Section 2** Removed last sentence in paragraph 3. **Section 3.1 General** Added chemical name for DPD. **Section 3.2** Deleted MDL Study.	June 13, 2008
SESDPROC-112-R0, *Field Measurement of Total Residual Chlorine,* Original Issue	October 19, 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 total residual chlorine in surface water and wastewater effluent.

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 total residual chlorine, the alternate procedure will be documented in the field logbook, 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 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

USEPA Region 4 Environmental Assessment Standard Operating Procedures and Quality Assurance Manual (EISOPQAM), November 2001

SESD Safety, Health and Environmental Management Program (SHEMP) Manual, Most Recent Version

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

Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998

Hach Company Pocket Colorimeter Chlorine Manual, Hach, 1994

Code of Federal Regulations, 40 CFR Part 136, Appendix B

1.5 Safety Precautions

Refer to the SESD Safety, Health and Environmental Management Program 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, safety glasses, and gloves. Address chemicals that pose specific toxicity or safety concerns and follow any other relevant requirements, as appropriate.

2 Quality Control

All total residual chlorine meters will be maintained and operated in accordance with the manufacturer's instructions and SESD Operating Procedure for Equipment Inventory and Management, SESDPROC-108. The following are general guidelines for maintaining total residual chlorine meters:

- Each meter should be visually inspected before and after each use.
- Check the battery strength.
- Ensure that the reagents are fresh before field trips.

Before a meter is taken to the field, it shall be properly calibrated and verified, according to Section 3.2.2 of this procedure, to ensure it is operating properly. These calibration verifications and maintenance procedures shall be documented and maintained in a logbook.

The ambient temperature in the immediate vicinity of the meter should be measured and recorded in the field logbook to ensure the instrument is operated within the manufacturer's specified range of operating temperatures.

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 Total Residual Chlorine

3.1 General

The chlorination of water supplies and polluted water serves primarily to destroy or deactivate disease-producing microorganisms. Chlorine applied to water in its molecular or hypochlorite form initially undergoes hydrolysis to form free chlorine consisting of aqueous molecular chlorine, hypochlorous acid, and hypochlorous ion. Free chlorine reacts with ammonia and certain nitrogenous compounds to form combined chlorine. With ammonia, chlorine reacts to form the chloramines: monochloramine, di-chloramine, and nitrogen tri-chloride. Total residual chlorine is the sum of the combined available residual chlorine and the free available residual chlorine remaining after a given contact time.

Chlorination may produce adverse effects. Potentially carcinogenic chloroorganic compounds such as chloroform may be formed. To fulfill the primary purpose of chlorination and to minimize any adverse effects, it is essential that proper testing procedures be used. Several methods for measurement of total residual chlorine are available including iodometric methods, amperometric titration methods, and *N*,*N*-diethyl-*p*-phenylenediamine (DPD) methods. This operating procedure will discuss the DPD Colorimetric Method.

3.2 Initial Laboratory Verification

See Standard Methods for the Examination of Water and Wastewater, Method 4500 Cl for directions in preparing the ASTM Standard D1193 "Consumption of Potassium Permanganate."

- Potassium permanganate stock – Prepare a stock solution containing 891 mg/1000 ml. Keep stock cool and store in the dark.

- Potassium permanganate intermediate stock 10 ppm – Prepare intermediate stock solution containing 10 mg/l $KMnO_4$ by diluting 10 ml of stock solution to 1 liter.

  Note: The intermediate stock should be stable for approximately 5 days if kept cool and away from light.

- Potassium permanganate calibration standards – Prepare calibration standards from the intermediate stock solution and/or KMnO4 calibration standard solutions for each day of use. The calibration standards are good for about 2 hours and will fade rapidly (within 15 minutes) if chlorine demand-free water is not used.

Calibration Standard (mg/l)	ml of Intermediate Stock/100 ml
0.05	10.0 of 0.5 mg/l std.
0.10	10.0 of 1.0 mg/l
0.5	5.0 of 10 mg/l
1.0	10.0 of 10 mg/l
2.0	20.0 of 10 mg/l

When checking the instrument verification with the five standards, a linear regression should be performed and the result should correlate to 0.995 or better. Records of this verification will be maintained by ASB staff.

3.2.1 Field Calibration Verification *for Regulatory Monitoring*

For regulatory monitoring, the calibration curve must be verified onsite with a minimum of three points: a blank and two known standards that bracket the expected sample concentrations. The meter's internal calibration scale must be verified daily using a blank, one **high,** and one **low** standard representative of the meter's linear working range. These standard checks must agree to within ±10% of the original curve or a new curve must be prepared. Verification data should be recorded and maintained on file. Use either 1-cm or 2.5-cm cells depending upon concentration range of the sample.

DPD total residual chlorine powder packets – The packets deteriorate in the presence of moisture or high temperature. The packets should be discarded if they have caked or have turned brown, or the expiration date has expired.

Note: Always wear gloves when handling the DPD oxalate, and do not ingest. If accidentally spilled on skin, rinse off immediately. Additionally, EPA might elect to use the facility's equipment to verify chlorine residual values that may be outside of the permit limits. The procedure and equipment used to document the findings should be written in the field logbook.

3.3 Sample Measurement Procedure *for EPA Field Screening*

Total or free residual chlorine measurements should always be conducted within 15 minutes of sample collection. The pH of the source should be checked and documented in the field logbook. When using the DPD colorimetric method for total residual chlorine, gel standards can be used for meter verification. The gel standards should be verified by the SESD laboratory personnel (ASB) to ensure accuracy prior to use. The tolerance ranges for the gel standards used for verification are as follows: 0.2 ± 0.09; 0.81 ± 0.10; 1.53 ± 0.14. If other gel standards are used, the tolerance ranges must also be verified by the SESD laboratory personnel.

For sample screening purposes, the following steps should be followed using a 2.5 cm sample cell for total residual chlorine concentrations ranging between 0 - 2 mg/l.

1. Fill a clean sample cell to the 10-ml mark with a sample blank. Cap the sample cell.

2. Press the **Power** key to turn the meter on.

3. Remove the meter's cover. Wipe off any excess liquid and fingerprints from the sample cell. Place the blank in the cell holder with the diamond mark facing the keypad. Fit the meter cover over the cell compartment to completely cover the cell.

4. Press the **ZERO** button**.** The display will show "- - - -" then go to "0.00". Record the blank's value in the logbook. Remove the blank from the cell holder.

5. Fill a second 10-mL cell to the 10-mL line with the sample.

6. Open a DPD total chlorine powder packet and add the contents to the sample cell.

7. Replace the cap on the sample cell and swirl or mix for approximately 20 seconds. **Note**: Wipe off any excess liquid and fingerprints from the sample cell.

8. Wait three to six minutes (3-6) after adding the DPD.

9. Press **READ/ENTER**. The instrument will show "- - - -" followed by the actual results in mg/L chlorine. Record the sample's value in the logbook.

Also for screening purposes, all of the above steps should be followed using a 1.0 cm sample cell for total residual chlorine concentrations ranging between 0 - 3.5 mg/l.

3.4 Units

Measurements for total residual chlorine are reported in mg/l.

3.5 Limitations

Do not use with or in the presence of any oxidizing agents including bromine, chlorine dioxide, iodine, permanganate, hydrogen peroxide, and ozone. Sample color and turbidity may also interfere.