NORTH CAROLINA WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION APPROVED PROCEDURE FOR THE ANALYSIS OF DISSOLVED OXYGEN (DO)

This document provides an approved procedure for the analysis of DO for compliance monitoring per 15A NCAC 2H .0805 (a) (6) (F) and (g) (3).

HOLDING TIME:

- Samples must be analyzed within 15 minutes of collection (40 CFR Part 136 Table II); however, *in situ* or immediate analysis is recommended due to the unstable nature of dissolved oxygen in samples.

GENERAL INFORMATION:

- Types of probes:

    a. Dissolved Oxygen Membrane Electrode
    b. Luminescence Dissolved Oxygen (LDO) Sensor

- Movement of water across the membrane (for membrane electrode technologies) is important for accurate readings. Some probes come with stirrers for this purpose. Measurements should be taken while the stirrer is in use or by swirling the DO probe in the sample flow. Preferably, insert the probe into flowing conditions. If analyzed in a container, stir gently with the probe or add a stir bar. Do not put the probe on the sides or the bottom of the container.

- Follow the manufacturer's instructions for probe storage.

- Sample duplicates are not a required quality control element for Field parameters.

METER CALIBRATION:

- Instruments are to be calibrated according to the manufacturer's calibration procedure prior to analysis of samples each day compliance monitoring is performed.

- The laboratory must use moist air for the air calibration. This is accomplished by calibrating the electrode in an environment with a high relative humidity. Using dry air for the calibration can result in errant readings.

- The laboratory must document each time that a calibration is performed. Calibration documentation must include the following, where applicable to the instrument used and the type of calibration performed: elevation, temperature, barometric pressure (in mmHg), salinity. After calibration, record the final DO reading in mg/L, the slope or % efficiency.

- For LDO sensors that cannot be calibrated, the calibration must be verified each day of use. This can be performed by back calculating the theoretical DO for the current air calibration conditions (e.g., temperature, elevation, barometric pressure, etc.). The calculated DO value must verify the meter reading within ±0.5 mg/L. Refer to the *Dissolved Oxygen Meter Calibration Verification* handout at the end of this document. If the meter verification does not read within ±0.5 mg/L of the theoretical DO, corrective action must be taken.

- When performing analyses at multiple sample sites, a post-analysis calibration verification must be performed at the end of the run, regardless of meter type. It is recommended that a mid-day calibration verification be performed when samples are analyzed over an extended period of time. The calculated DO value must verify the meter reading within ±0.5 mg/L. If the meter verification does not read within ±0.5 mg/L of the theoretical DO, corrective action must be taken. Alternatively, if the meter is calibrated at each sample site prior to analysis, a post-analysis calibration verification is not required.

DOCUMENTATION:

The following must be documented in indelible ink whenever sample analysis is performed.

1. Date and time of sample collection

2. Date and time of sample analysis to verify the 15-minute holding time is met. Alternatively, one time may be documented for collection and analysis with the notation that samples are measured *in situ* or immediately at the sample site
3. Facility name, sample site (ID or location), and permit number
4. Collector's/analyst's name or initials
5. Calibration variables (elevation, temperature, barometric pressure [in mmHg], salinity)
6. Meter calibration and/or verification time(s)
7. Final calibration information (final DO reading in mg/L, the slope or % efficiency)
8. Theoretical value and value obtained for the calibration verification(s), where applicable
9. Units of measure
10. Instrument identification (serial number preferred)
11. Parameter analyzed
12. Method reference
13. Data qualifier(s), when applicable
14. Equipment maintenance (recommended)

Refer to *Quality Assurance Policies for Field Laboratories* (at http://deq.nc.gov/about/divisions/water-resources/water-resources-data/water-sciences-home-page/laboratory-certification-branch/technical-assistance-policies) for additional quality assurance and quality control requirements.

Ref: Standard Methods 4500-O G - 2011
Hach Method 10360, Rev. 1.2, October 2011
In Situ Method 1002-8-2009
ASTM Method D888-09 (B)
ASTM Method D888-09 (C)

Dissolved Oxygen Meter Calibration Verification

DO meters/probes must be calibrated each day of use prior to sample analysis. If the meter cannot be calibrated, the calibration must be verified each day of use. Additionally, when performing DO analyses at multiple sample sites, a post analysis calibration verification must be analyzed at the end of the run for all types of DO probes, unless the meter is recalibrated at each sample site. Below is a procedure for verifying the calibration of a DO probe.

1) Follow the manufacturer's instructions for meter operation.
2) Place probe in a plastic bag, the probe storage cup, the storage well of the meter (each containing a wet sponge), or a BOD bottle partially filled with water. Allow appropriate instrument warm up time.
3) Read DO and temperature.
4) Check the reading vs. the solubility table below and apply appropriate atmospheric (barometric) pressure or altitude correction factor.
5) Calculated DO value must verify meter reading within ± 0.5 mg/L (do NOT calculate and apply a correction factor to calculated DO).

Temp. °C	DO mg/L		Temp. °C	DO mg/L
4.0	13.11		19.5	9.18
4.5	12.94		20.0	9.09
5.0	12.77		20.5	9.00
5.5	12.61		21.0	8.92
6.0	12.45		21.5	8.83
6.5	12.30		22.0	8.74
7.0	12.14		22.5	8.66
7.5	11.99		23.0	8.58
8.0	11.84		23.5	8.50
8.5	11.70		24.0	8.42
9.0	11.56		24.5	8.34
9.5	11.42		25.0	8.26
10.0	11.29		25.5	8.18
10.5	11.16		26.0	8.11
11.0	11.03		26.5	8.04
11.5	10.90		27.0	7.97
12.0	10.78		27.5	7.90
12.5	10.66		28.0	7.83
13.0	10.54		28.5	7.76
13.5	10.42		29.0	7.69
14.0	10.31		29.5	7.62
14.5	10.20		30.0	7.56
15.0	10.08		30.5	7.50
15.5	9.98		31.0	7.43
16.0	9.87		31.5	7.37
16.5	9.77		32.0	7.31
17.0	9.67		32.5	7.24
17.5	9.57		33.0	7.18
18.0	9.47		33.5	7.12
18.5	9.38		34.0	7.07
19.0	9.28		34.5	7.01

Atmospheric Pressure mm Hg	Equivalent Altitude Ft.	Correction Factor
760	0	1.00
752	278	.99
745	558	.98
737	841	.97
730	1126	.96
722	1413	.95
714	1703	.94
707	1995	.93
699	2290	.92
692	2587	.91
684	2887	.90
676	3190	.89
669	3496	.88
661	3804	.87
654	4115	.86
646	4430	.85
638	4747	.84
631	5067	.83
623	5391	.82
616	5717	.81
608	6047	.80
600	6381	.79
593	6717	.78

Ref: YSI Model 5000/5100 DO Meter Manual. Slight variations in DO, pressure, and/or altitude may be found in other manuals.

Example: If ambient temperature is 21°C and elevation is approximately 1126 ft, the theoretical DO would be:

8.92 X 0.96 = 8.56 mg/L

or, If ambient temperature is 21°C and the atmospheric (barometric) pressure is 745 mm Hg, the theoretical DO would be:

8.92 X 0.98 = 8.74 mg/L