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INSTRUMENTATION: VWR Scientific Dissolved Oxygen Meter
Model 4000

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1. Scope and Application

- 1.1 The membrane probe method for dissolved oxygen is recommended for those samples containing materials which interfere with the modified Winkler, iodometric procedure (*EPA Method 360.2*) such as sulfite, thiosulfate, polythionate, mercaptans, free chlorine or hypochlorite, organic substances readily hydrolyzed in alkaline solutions, free iodine, intense color or turbidity and biological flocs.
- 1.2 Membrane electrodes provide an excellent method for DO analysis in polluted waters, highly colored waters, and strong waste effluents.
 - 1.2.1. They are recommended for use especially under conditions that are unfavorable for use of the iodometric method, or when that test and its modifications are subject to serious errors caused by interferences.
 - 1.2.2. The membrane probe method is recommended as a substitute for the modified Winkler procedure in monitoring of streams, lakes, outfalls, etc., where it is desired to obtain a continuous record of the dissolved oxygen content of the water under observation.
- 1.3 The membrane probe method may be used as a substitute for the modified Winkler procedure in BOD determinations.

2. Summary of Method

- 2.1 The instrumental probe for determination of dissolved oxygen in water is dependent upon electrochemical reactions.
- 2.2 Oxygen-sensitive membrane electrodes of the polarographic or galvanic type are composed of two solid metal electrodes in contact with supporting electrolyte separated from the test solution by a selective membrane.
- 2.3 Under steady-state conditions, the current or potential can be correlated with DO concentrations.
 - 2.3.1. The "diffusion current" is linearly proportional to the concentration of molecular oxygen.
 - 2.3.2. The current can be converted easily to concentration units (e.g., milligrams per liter) by a number of calibration procedures.
- 2.4 Interfacial dynamics at the probe-sample interface are a factor in probe response and a significant degree of interfacial turbulence is necessary. For precision performance, turbulence should be constant.

3. Sample Handling and Preservation

- 3.1 Because membrane electrodes offer the advantage of analysis *in situ* they eliminate errors caused by sample handling and storage.
- 3.2 If sampling is required, collect the sample in a 300 mL BOD incubation bottle.
 - 3.2.1 Special precautions are required to avoid entrainment or solution of atmospheric oxygen or loss of dissolved oxygen.
 - 3.2.2 Where surface water samples are collected from shallow depths (less than 5 feet), use of an APHA-type sampler is recommended.
 - 3.2.3 Use of a Kemmerer type sampler is recommended for surface water samples collected from depths of greater than 5 feet.
 - 3.2.3.1 When a Kemmerer sampler is used, the BOD sample bottle should be filled to overflowing (overflow for approximately 10 seconds).



3.2.3.2 Outlet tube of Kemmerer should be inserted to bottom of BOD bottle.

3.2.3.3 Care must be taken to prevent turbulence and the formation of bubbles when filling bottle.

3.3 At time of sampling, the sample temperature should be recorded as precisely as required.

3.4 Do not delay the determination of dissolved oxygen in the samples.

4. Interferences

4.1 Dissolved organic materials are not known to interfere in the output from dissolved oxygen probes.

4.2 Dissolved inorganic salts are a factor in the performance of dissolved oxygen probe.

4.2.1 Probes with membranes respond to partial pressure of oxygen, which in turn is a function of dissolved inorganic salts.

4.2.2 Conversion factors for seawater and brackish waters may be calculated from dissolved oxygen saturation versus salinity data (Table I).

4.2.3 Conversion factors for specific inorganic salts may be developed experimentally.

4.2.4 Broad variations in the kinds and concentrations of salts in samples can make the use of a membrane probe difficult.

4.3 Reactive compounds can interfere with the output or the performance of dissolved oxygen probes.

4.4 Reactive gases, which pass through the membrane probes, may interfere.

4.4.1 For example, chlorine will depolarize the cathode and cause a high probe-output. Long-term exposures to chlorine will coat the anode with the chloride of the anode metal and eventually desensitize the probe.

4.4.2 Alkaline samples in which free chlorine does not exist will not interfere.

4.4.3 Hydrogen sulfide will interfere with membrane probes if the applied potential is greater than the half-wave potential of the sulfide ion.

4.4.3.1 If the applied potential is less than the half-wave potential, an interfering reaction will not occur, but coating of the anode with the sulfide of the anode metal can take place.

4.4.3.2 Prolonged use of membrane electrodes in waters containing gases such as hydrogen sulfide (H₂S) tends to lower cell sensitivity.

4.4.3.3 Eliminate this interference by frequently changing and calibrating the membrane electrode.

4.5 Dissolved oxygen probes are temperature sensitive, and the DO meter provides temperature compensation.

4.6 Plastic films used with membrane electrode systems are permeable to a variety of gases besides oxygen, although none is depolarized easily at the indicator electrode.

5. Apparatus

5.1 VWR Scientific Dissolve Oxygen Meter, Model No. 4000

5.2 Sample bottles-300 mL ±3 mL capacity BOD incubation bottles with tapered ground glass pointed stoppers and flared mouths.



6. Reagent

- 6.1 Reagent Water
- 6.2 Compressed Air
- 6.3 Sodium Sulfit, Na_2SO_3

7. Instrument Check Out Procedure

- 7.1 It is recommended that this procedure be performed when the meter is received and any time operation problems arise.
- 7.2 This procedure verifies the proper operation of the VWR Model 4000 Dissolved Oxygen Meter.
- 7.3 Attach the dissolved oxygen electrode to the DIN connector on top of the meter.
- 7.4 Press **POWER** key to turn meter on. If battery indicator remains on, replace battery or use line adapter.
- 7.5 Press the **POWER** key to turn meter off.
- 7.6 Press and hold the **YES** key while pressing the **POWER** key. The instrument automatically performs electronic and hardware diagnostic tests.
- 7.7 After code 7, a "0" will appear on the display. Press each key once in any order (the numeric digits will change). Note: All keys must be pressed within 10 seconds to complete test 7.
- 7.8 After the keypad test, the meter will display Test 8 and then the meter will turn off.
- 7.9 If any problems are found during self-test, the meter will display the operator assistance code until acknowledged (with the **YES** key).

8. Instrument Setup Mode Functions

- 8.1 SALINITY TOGGLE (1-1)
 - 8.1.1 The SALINITY TOGGLE function is used to activate and deactivate the salinity correction feature.
 - 8.1.2 If this function is enabled, the meter will proceed to the SALINITY FACTOR function (7.2).
 - 8.1.3 If this function is disabled, the meter will proceed to the BAROMETRIC PRESSURE function (7.3).
- 8.2 SALINITY FACTOR (1-2)
 - 8.2.1 The SALINITY FACTOR function is used to set the salinity correction factor.
 - 8.2.2 The SALINITY FACTOR range is 0 to 40 ppt (parts per thousands).
 - 8.2.3 The default value is 0 ppt.
 - 8.2.4 Use the SCROLL key to set the salinity correction factor accordingly (answer YES to accept a new value).
- 8.3 BAROMETRIC PRESSURE (1-3)
 - 8.3.1 The BAROMETRIC PRESSURE function is used to set the atmospheric pressure correction factor (in the units mm Hg).
 - 8.3.2 The BAROMETRIC PRESSURE range is 540-850 mmHg. The default value is 760.
 - 8.3.3 Use the SCROLL key to set the current barometric pressure which can be obtained locally, press YES key to accept value.



8.4 AUTOCALIBRATION TOGGLE (2 - 2)

8.4.1 The AUTOCALIBRATION TOGGLE function is used to activate and deactivate the autocalibration feature.

8.4.2 If this function is enabled, the meter will perform calibrations without the need for editing; upon reaching "ready", the meter automatically sets the standard value to 101.7%.

8.4.3 This feature is used only for calibrations performed using- water saturated air as the calibration standard (i.e. the Calibration sleeve or B.O.D. bottle with a small amount of distilled or deionized water and tightly closed around electrode).

8.4.4 If this function is disabled, the meter will require editing of the value corresponding to the calibration standard (in this case, air-saturated water).

8.5 ELECTRODE "ZEROING" (2 - 3)

8.5.1 The ELECTRODE ZERO function is used to perform a zeroing of the electrode.

8.5.2 If the electrode has been polarized such that it is in a steady state, it may be zeroed.

8.5.2.1 Place the electrode into an oxygen scavenging solution (such as 20% sodium sulfite) (see Sec. 8.1) for at least five minutes and then perform a zeroing.

8.5.2.2 When the ELECTRODE ZERO function is entered, "0" is displayed and is flashing.

8.5.2.3 To activate the zeroing of the electrode, press the SCROLL key.

8.5.2.4 After pressing SCROLL key, "I" will be displayed.

8.5.2.5 The meter will take measurements and perform stability checking.

8.5.2.5.1 When the input has stabilized, the "ready" annunciator will light and the main readout will display "000.0" for approximately 5 seconds. .

8.5.2.5.2 NOTE: Zeroing of the electrode is not necessary unless measuring 3 mg/L or less.

8.6 PRINT MODES (3 - 1)

8.6.1 This function determines when the printer will be sent data.

8.6.2 When the code for the PRINT MODES is displayed, the current setting (1 or 2) will flash in the rightmost position of the main readout.

8.6.2.1 If "1" (Manual PRINT) is displayed, no automatic output to the printer will occur. Press the PRINT key at any time while in the measure mode to initiate a printout.

8.6.2.2 If "2" (Print on ready) is displayed, the meter will print when the "ready" display is flashing.

8.7 To exit out of the SETUP mode, simply press the "mode" key to access either Concentration (ppm or mg/L) or % Saturation (% SAT) measure mode.

9. Calibration

9.1 The following calibration procedure should be performed at the beginning of each day for maximum performance.

9.2 Prior to operation, connect electrode to the meter and power up. Allow the electrode to polarize before attempting a calibration of the electrode.



- 9.2.1 Dissolved oxygen electrodes are continuously polarized when they are connected to the instrument.
- 9.2.2 Polarization when the electrode is new or has been unplugged for more than an hour will take 20-30 minutes.
- 9.2.3 Interrupted connections of less than one hour will take between 20-25 minutes to repolarize.
- 9.3 Calibration Procedure
 - 9.3.1 Enable the SALINITY TOGGLE (7.1) function on the DO meter.
 - 9.3.2 Determine specific conductance of the sample to be measured according to SOP #PP005.
 - 9.3.3 Set the SALINITY FACTOR (7.2) using the Table I.
 - 9.3.4 Determine the elevation of the sampling site using GPS SOP #SP003.
 - 9.3.5 Set the BAROMETRIC PRESSURE function (7.3) according to the elevation using Table II.
 - 9.3.6 Set the AUTOCALIBRATION TOGGLE function to ON (7.4).
 - 9.3.7 "Zeroing" the Electrode
 - 9.3.7.1 Add 20 g anhydrous sodium sulfite, Na_2SO_3 to 100 mL reagent water.
 - 9.3.7.2 Connect the electrode to the meter and turn the power on.
 - 9.3.7.3 Place the electrode in the sodium sulfite solution (8.3.1).
 - 9.3.7.4 Swirl a few times and proceed to the SETUP mode of the meter (Sec. 7.5).
 - 9.3.8 Calibration Procedure
 - 9.3.8.1 Prepare a calibration standard by bubbling compressed air into 50 mL reagent water for 5 minutes.
 - 9.3.8.2 Position the tip of the electrode one inch above the surface of the water.
 - 9.3.8.3 Press CAL key.
 - 9.3.8.3.1 Display will show four dashes (- - -) indicating the unit is in the CALIBRATION mode.
 - 9.3.8.3.2 In addition, "SP" indicating slope is displayed in the lower display field.
 - 9.3.8.4 When the electrode is calibrated, the READY light will come on and the calibration slope is displayed.
 - 9.3.8.5 Press YES key to accept calibration.
 - 9.3.8.6 Press MODE key to select mg/L (ppm).
 - 9.3.8.7 Place electrode in the calibration standard, and when "READY" light is displayed, record calibration value.
 - 9.3.8.8 Rinse the electrode thoroughly and blot dry. Additional measurements can now be made.

10. Procedure

- 10.1 Take care in changing membrane to avoid contamination of sensing element and also trapping of minute air bubbles under the membrane, which can lead to lowered response and high residual current.
- 10.2 Record the temperature and the specific conductivity of the sample solution.
- 10.3 Correct for salinity by converting specific conductivity to salinity using Table I and entering the salinity value into the SALINITY FACTOR function.



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- 10.4 For different elevations, refer to Table II to set the BAROMETRIC PRESSURE function (7.3).
- 10.5 Perform calibration of the DO meter.
- 10.6 Insert probe into the sample and provide sufficient sample flow across membrane surface to overcome erratic response by gently stirring the solution with the probe.
- 10.7 Meter will display DO reading in mg/L and temperature simultaneously.
- 10.8 When finished, store electrode in "calibration sleeve" or B.O.D. bottle with reagent water covering the bottom of the bottle and press **POWER** key to turn unit off.
- 10.9 Using proper measurement technique, an accuracy of ± 0.1 mg DO/1L and a precision of ± 0.05 mg DO/ L can be obtained.

11. Bibliography

- 11.1 Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 450, Method 422F (1975).
- 11.2 EPA Method 360.1
- 11.3 Operator's manual for VWR Dissolved Oxygen Meter, Model 4000.



Table I

Salinity/Conductivity Table

Estimate the salinity correction factor by using the following table:

(to the nearest whole number, input value into meter)

(20°C)	Salinity	(20°C)	Salinity	(20°C)	Salinity
<u>in mS/cm</u>	<u>in ppt</u>	<u>in mS/cm</u>	<u>in ppt</u>	<u>in mS/cm</u>	<u>in ppt</u>
5	3.0	23	15.5	42	30.2
6	3.6	24	16.2	44	31.8
7	4.3	25	17.0	46	33.5
8	4.9	26	17.8	48	35.1
9	5.6	27	18.5	50	36.7
10	6.3	28	19.3	52	38.4
11	6.9	29	20.0	54	40.1
12	7.6	30	20.8	56	41.8
13	8.3	31	21.6		
14	9.0	32	22.3		
15	9.7	33	23.1		
16	10.4	34	23.9		
17	11.2	35	24.7		
18	11.9	36	25.5		
19	12.6	37	26.2		
20	13.3	38	27.0		
21	14.1	39	27.8		
22	14.8	40	28.6		



Table II

Elevation barometric pressure table

This table is used to determine the barometric pressure at certain elevations. The correspondence is based on the assumption that at sea level the barometric pressure is 760. After determining the barometric pressure from the table or a local weather service, in put this reading into the instrument (see calibration instructions for VWR Model 4000).

Elevation in feet	Barometric pressure in mm
0	760
500	746
1000	733
1500	720
2000	708
2500	695
3000	683
3500	671
4000	659
4500	647
5000	635
5500	624
6000	613
6500	601
7000	590
7500	579
8000	568
8500	559
9000	548
9500	538
10000	527
10500	517
11000	506