Application Note

No. 1.06

Practical tips for trace-level oxygen monitoring

FEATURES AND BENEFITS

- Simple troubleshooting procedures net higher accuracy and faster response
- Improved sensor performance yields longer intervals between service for consistent on-line monitoring
- Verification of on-line measurements allows greater confidence in oxygen analyzer readings

TECHNIQUES FOR SAMPLE VERIFICATION AND OPTIMIZATION

When measuring trace levels of oxygen in liquid samples, it is important that your oxygen analyzer system be maintained and operating properly. Erratic, inconsistent, or out-of-spec O_2 concentration readings may indicate either problems in the sample being measured or analyzer instrumentation inaccuracies.

Thus, it is essential to confirm that your analyzer is operating correctly before you look into problems with the sample or the sample processing. This is accomplished by the following steps:

1. Calibrate your sensor in air,
2. Verify your sensor's zero reading,
3. Check your sample lines for leaks.

Having completed all three steps as described in the following paragraphs, you will quickly ensure the highest quality oxygen measurements possible.

1. Calibrate The Sensor To The Instrument

Calibration of the oxygen sensor is the first step to verifying that your oxygen analyzer system is giving a linear response to the oxygen concentration in your sample.

To calibrate your oxygen sensor, first allow the sensor and membrane to equilibrate to the temperature of the room, so the measurement is being properly compensated by the thermistor in the sensor.

Next, follow the calibration instructions in the operator's manual for your oxygen sensor and instrument. If the sensor will not calibrate, it's time for a sensor service, as described in the manual.

2. Verify Sensor Residual

Checking the residual signal of your sensor is the second step in verifying proper oxygen readings.

Orbisphere oxygen sensors are unique in that they should generate a negligible current when in completely anaerobic conditions (that is, no oxygen). Nevertheless it is possible that a damaged or improperly maintained sensor may generate a positive or negative current (and subsequently a positive or negative oxygen display) in anaerobic conditions. It is good practice, therefore, to occasionally check the "zero" point of a sensor.

You can do this by placing the sensor in water that has been deaerated by supersaturating with sodium sulfite crystals. (Or you may choose to expose the sensor to nitrogen or argon gas in a flow chamber.) Note: Take care not to place the membrane surface of the sensor on any undissolved sulfite crystals, to prevent scratching and damaging the membrane. Refer to the "Residual Performance Check" table on the following page for sensor response to this procedure.

RESIDUAL PERFORMANCE CHECK

Your sensor should achieve these minimum performance times when placed in a deaerated sample (response reflects integrity of sensor — properly maintained sensors should be significantly faster than the time listed).

Concentration Span		Expected Response Time (for specific membranes)		
Starting from	Down to	2956A	2958A	2952A
20 ppm	100 ppb	2 minutes	5 minutes	10 minutes
100 ppb	10 ppb	15 minutes	30 minutes	1 hour
10 ppb	under 2 ppb	30 minutes	1 hour	2 hour

3. Check Sample Lines For Leaks

The final step in verifying your oxygen analyzer performance is checking for air leaks in the sample lines, fittings, and valves used to bring the sample to the oxygen sensor.

All Orbisphere dissolved oxygen sensors have a flow insensitive range when used in an Orbisphere flow chamber. Thus you can leak-check your sample lines for air leaks, by varying the flow rate via this flow chamber.

First set the flow rate to 100 ml/min and achieve a stable reading, then slowly increase the flow rate to 200 ml/min. (This flow rate is applicable for leak testing with any membrane, regardless of the recommended flow rate of that membrane.) If you have airtight sample lines, the displayed oxygen value should either increase or remain constant. If you see a significant decrease in the displayed value, it is probably due to an air leak in your sampling system. Decreasing the flow should cause the opposite effect.

The explanation of this phenomenon is that a small leak (such as a pin hole in the sample line around a fitting or valve that is too small to leak water) in a flowing line causes a venturi effect that sucks in air. A two-fold increase in the flow rate will not increase the venturi effect by double and therefore the concentration of DO_2 will decrease. Indeed it is normally observed that the leak rate remains constant and the DO_2 decreases in inverse proportion to the flow. Please note that if water is leaking out of a sample line, air *is* probably getting into your sample.

A leak can be located by resetting the flow rate to 100 ml/min, then systematically covering fittings, valves, or pump seals with water from a lab squirt bottle or nitrogen gas while watching the oxygen display. When the leak point is momentarily blocked, the oxygen display will decrease noticeably. Tighten or replace the leaking fitting or valve (following the manufacturer's recommendations).

Note: Plastic tubing (even those made with low permeability materials) can also contribute to the oxygen displayed, causing the same effect. Therefore, replace all sample plastic tubing with stainless steel tubing if possible. (Refer to the table on the next page for typical oxygen leakage effects using various types of plastic tubing.)

ADDITIONAL PRACTICAL TIPS

Several additional "good practice" measures can be taken to assure the best performance and response from your oxygen sensor and analyzer.

Cool The Sensor (If Possible)

Your Orbisphere oxygen sensor can be safely exposed to sample temperatures up to 100° C, but can only yield accurate temperature compensated results up to 50 to 60° C, depending on the membrane choice. However the sensor maintenance interval becomes significantly longer as the sample temperature decreases down to 25° C and below. The addition of another heat exchanger (or a sample chiller in warm climates) can significantly increase the service interval, and quickly pay for itself.

LEAKAGE OF OXYGEN THROUGH PLASTIC TUBING WALLS

Common plastic materials used for sample tubing, showing leakage of oxygen into water flowing through tubing due to the permeability of the material. Listed from least permeable to most.

Material	O_2 pickup in water, ppb/meter	O_2 reading at 10 minutes, ppb
Polyvinylidene chloride (Saran)	0.02	2.7
Nylon	0.03	3.8
Polychloro trifluoroethylene (Kel-F)	0.05	4.6
Polyvinyl fluoride (Tedlar)	0.05	4.7
Polyvinylidene fluoride (Kynar)	0.1	6.7
Polyethylene Terephthalate (Mylar)	0.12	6.9
Polyvinyl chloride (non-plasticized)	0.14	7.6
Polyacetal (Delrin)	0.2	7.8
Ethylene/Monochlorotrifluoroethylene co-polymer (Halar)	0.43	13.6
Ethylene/Tetrafluoroethylene copolymer (Tefzel)	1.70	27
High density polyethylene (opaque)	2.04	30
Polypropylene	3.2	38
High density polyethylene (clear)	3.9	42
Polycarbonate (Lexan)	5.1	46
Polystyrene	5.3	48
Low density polyethylene	8.5	60
Fluorinated ethylene/propylene (FEP)	13	77
Tetrafluoroethylene (PTFE)	19	94
Natural rubber (Latex)	60	150
Silicone rubber (Silastic)	1700	1700

Use Barrier Films If Measuring In Harsh Conditions

When measuring in harsh conditions, such as in higher than ideal temperatures, or in high levels of ammonia, ethanolamines, hydrocarbons, or hydrosulfites, you will lengthen your maintenance interval if you use a barrier film.

A barrier film is a donut-shaped piece of material that goes over your membrane. It allows oxygen to permeate through to the electrode, but not to all of the electrolyte.

Note: Be sure to use the correct model of membrane holding ring for your membrane and barrier film to assure a proper fit.

Turn Off The Instrument When Not Measuring

When an Orbisphere oxygen sensor is operated in relatively high DO_2 conditions for long periods of time, it will dramatically shorten the maintenance interval.

This is easily avoided. When your generating unit shuts down, and measurements are not required, simply switch off your analyzer. As long as the instrument is off, the sensor will not react electrochemically, thus lengthening your maintenance interval. If the unit will be down for months, it is advisable to remove the sensor, remove its membrane, rinse and store dry until needed.

Clean The Sensor Thoroughly

As Orbisphere sensors have improved over the years, cleaning techniques have also evolved. In addition to the standard chemical cleaning method described in the Sensor Service instructions supplied with the Orbisphere analyzer, Orbisphere strongly recommends the use of a Model 32301 Sensor Cleaning and Regeneration Center, which provides a thorough electrochemical sensor cleaning.

The 32301 Cleaning Center also can be used to perform sensor diagnostics when an electrical fault is suspected.

Utilize Orbisphere Support

When you purchase an Orbisphere analyzer you also purchase Orbisphere support.

Please do not hesitate to call your local sales office or national Orbisphere sales and service office if you have any problems, questions, comments, or, for that matter, compliments!

OPERATING CHECK LIST

The following check list is provided as a quick reference to the various tips and recommended practices provided in this Application Note. (You may wish to photocopy this page for review and notetaking.)

PRACTICAL TIPS	NOTES
❑ Calibrate your Sensor	
❑ Verify your sensor's residual (zero) reading	
❑ Check your sample lines for leaks	

OTHER RECOMMENDED PRACTICES	
❑ Cool the Sensor	
❑ Use Barrier Film in Harsh Conditions	
❑ Turn off Instrument when not measuring	
❑ Clean Sensor thoroughly	
❑ Utilize Orbisphere support	

orbisphere laboratories
INSTRUMENTS THAT TELL THE TRUTH™
20, rue du Puits-Godet, CH-2000 Neuchâtel, Switzerland
(032) 721 41 95 FAX (032) 725 34 33
70 Kinderkamack Road, Emerson, NJ 07630, U.S.A.
(201) 265-4900 FAX (201) 265-5899
E-mail: salesinfo@orbisphere.ch

Represented by: