DQM Information Paper 3.1.1
Dissolved Oxygen Measurement Principles and Methods

By Revital Katznelson, Ph.D.

1.0 About this Information Paper

(This section is essentially common to all DQM Information Papers. If you have seen it already, please skip to Section 2 below). This Information Paper is a new type of guidance. It has been created for our new integrated system of guidance and tools for water quality monitoring called "the Data Quality Management (DQM) System". DQM is implemented by the Clean Water Team (CWT) where needed to support collection of **reliable** data of **known quality** in a fully documented, **scientifically defensible** manner. Most DQM materials are delivered in Parameter-Specific Folders, which provide both the traditional "protocol" materials and new, expanded guidance in three types of inter-related documents: Fact Sheet, Information Paper, and Standard Operation Procedures. Background information on the ecological significance of each parameter and the regulatory benchmarks that have been developed for it is summarized in the FACT SHEET. The technical information on measurement methodology provided in this IP with its method-menu. Then there are several detailed standard operating procedures (SOPs) that provide step-by-step instructions for each instrument or kit, as well as instrument-specific Quality Assurance/Quality Control and CCRR directions and data validation checklists.

This Information Paper (IP), a part of the Parameter-Specific Folder for dissolved oxygen (DO), provides "big picture" technical information on DO measurement methodology. If you are a Trainer or a Technical Leader of any monitoring project, this may help you select a good method to measure dissolved oxygen in your water body.

Section 2 of this IP introduces a "method menu" table with a list of kits and instruments commonly used by citizen monitoring groups, agency staff, or laboratory technicians, with information on the limitations, approximate cost, measurement range and resolution, and associated labor of each device. Next (Section 3), a description of the different physical or chemical principles underlying the commonly used methods to measure DO is provided. Section 4 provides practical tips and advice on DO measurement based on our cumulative experience (The Clean Water Team and others). This section is meant to be updated as we learn more. Finally, the "Sources & Resources" section (Section 5) provides a list of available SOPs as well as contact and website leads into further information.

2.0 Selecting a Method to Measure Dissolved Oxygen

The concentration of oxygen dissolved in water can be evaluated in different ways. Table 3.1.1-1 provides a "method menu" that includes the commonly used methods for measuring dissolved oxygen in water samples. It is intended for use as a selection tool in response to the specific needs, level of operator skill, data quality objectives, and safety concerns of each individual project.

Table 3.1.1-1: Selected Methods and Devices for Measurement of Dissolved Oxygen

Code *(Note a)*	Principle	Device	Resolution (@range)	Cost *(Note b)*	Labor	Limitations	Extent of Error *(Note c)*
DOC	Colorimetric	Reagent ampoules *(Note c)* and comparator (e.g., "CHEMets" by Chemetrics)	1 mg/l (1-6) 2 mg/l (6-12)	$36/20 tests	measure 3 min.		±1 mg/l (1-4) ±2 mg/l (4-8) ±4 mg/l (8-12)
DOC	Colorimetric	Reagent ampoules *(Note d)* and comparator (e.g., "AccuVac" by Hach)	0.2 mg/l (0-15)	$78/25 tests	measure 3 min.	Leaky seal leads to continuous color development	±1 mg/l
DOW	Titrimetric	Modified Winkler Method kit: DO bottle, reagents, vial and syringe for titration	0.2 mg/l (0-15)	$50 /100 tests	measure 8 min.	"Sliding" endpoint.	±0.5 mg/l
DOE	Polarographic	D.O. meter+electrode	0.05-0.2 mg/l (0-20)	$800	prep/calib. 1 h measure 0.5-3 min.	Requires expertise and experience	±5%
DOP	Polarographic	Rapid-Pulse probe, for Sonde (e.g., YSI or Hydrolab)	0.1 mg/l (0-20)	~$4,000 for entire Sonde	prep/calib. 2 h Download 1 hr	Requires expertise and experience	±5%

Notes: (a) The Codes on the left are consistent with the Instrument codes used in all other DQM materials
(b) Approximate Costs are updated for 2002.
(c) See Section 4.2 below and Table 3.1.1-2 for information on the sources of error
(d) Used ampoules from colorimetric kit present a hazard (sharp glass and unpleasant reagents combined) and need to be packed in a crush-proof container for transport and disposal.
(Table source: Katznelson 1998)

The codes in the table are descriptors of the measurement method: DOC stands for colorimetric methods, DOW is a code for the Winkler titration method, and DOE represents an oxygen electrode.

3.0 Principles and Applications of Dissolved Oxygen Measurement Methods

The methods that are most commonly used to measure dissolved oxygen (DO) can be sorted into three major groups: colorimetric, titrimetric, and polarographic (see below). Because oxygen can easily diffuse into a water sample during handling (and alter the concentration of dissolved oxygen), samples have to be collected and processed without contact with air. This section also introduces information regarding measurements of biochemical oxygen demand (BOD, see 3.2 below).

3.1 Methods

Colorimetric: (code: DOC) The sample fluid is sucked into an ampoule under vacuum (an ampoule is a sealed glass tube with an easy-to-break tip. Use of the ampoule involves breaking of the tip). Chemical reagents that are present in the ampoule in excess interact with oxygen to form a colored product (that absorbs light at a visible wavelength). The intensity of the color, which is proportional to the oxygen concentration in that sample, is compared to a series of tubes with color intensities that reflect known concentrations of dissolved oxygen and are expressed in units of mg/l. Colorimetric kits provide for rough and rapid measurement: they are often used for screening for low-oxygen conditions and can be easily used by non-professional operators.

Titrimetric: (code: DOW) A water sample is trapped in a “dissolved oxygen” bottle, which is a bottle with specially-designed cap (or specially-designed mouth and glass stopper, often sold as “BOD bottle”), that allow for enclosure of liquids without contact with air. Chemical reagents added in excess interact with oxygen to form a product, and another chemical (the “titrant”) is used quantitatively to “neutralize” that product. The amount of titrant needed is proportional to oxygen concentration and is translated to mg/l. The best known titrimetric method for dissolved oxygen is the Winkler method; this method and its modifications are widely applied, both in the field (using a syringe to dispense the titrant) and in the lab (using high-precision burettes). Field kits are useful for routine monitoring of D.O. in creeks. Samples can be collected and fixed in the field, and titrated later at home or in the lab. Laboratory applications include D.O. electrode calibration, BOD (see below), etc. .

Polarographic: (code: DOE) Electrodes measure the flux of oxygen across a membrane. Oxygen is consumed in the process, and the traditional electrodes require flushing of measured liquid at the membrane surface to constantly replace the oxygen consumed. A new technology provides Rapid-Pulse probes with intermittent operation period that are so short they consume only a negligible amount of oxygen; these probes are used in automatic/remote sensors with data loggers. The output of DO electrodes is expressed in mg/l. Electrodes are useful for measurements of D.O. along gradients or transects where many samples are needed in a short time, measurements of kinetics of change in D.O. concentrations, continuous monitoring of D.O. with data-logging, and micro-scale D.O. gradients on sediment surface (microelectrodes).

3.2 Biochemical oxygen demand (BOD)

Biochemical oxygen demand (BOD) evaluations are a very important application of DO measurements, and can be performed using titrimetric methods or electrodes. Essentially, biochemical oxygen demand (BOD) is a measure of how much oxygen can be consumed within a given length of time and it reflects the potential for oxygen depletion. To determine the BOD, a water sample is thoroughly aerated and split into two portions: one portion is analyzed immediately, and the other portion – in a bottle without air - is "incubated for 24 hours or 5 days in the dark at 20 C. The remaining oxygen as measured after incubations is used to calculate how much was lost from the original sample. BOD measurements can be easily performed using an extra "dissolved oxygen" bottle from the Winkler method kit, or with electrodes specially equipped for sealing the specially-designed mouths of "BOD bottles".

4.0 General DO Measurement Tips

4.1 What to expect out there

Cool, fast flowing turbulent water is expected to contain DO at saturation levels (9-10 mg/l, depending on the temperature). Algae and aquatic plants will add DO to the water in the light, as a result of photosynthesis. Pools may have super saturation (levels above saturation) of oxygen if there are algae or plants in them or immediately upstream, even if the water is turbid. Turbid, smelly water in stagnant pools may be depleted of oxygen.

4.2 What we know about the sources of error in DO measurements can help!

Table 3.1.1-2 lists the sources of error and uncertainty associated with the different methods. Some of the error can be easily reduced (or even eliminated) by proper and careful operations, while other sources of error are inherent to the methods and cannot be eliminated or diminished.

4.3 Quality Control, Check, Record, and Report (CCRR) guidance for DO

(This paragraph is essentially common to all DQM-IPs. If you have seen it already, please skip to Section 4.4 below) The DQM guidance and tools provide ways to Control, Check, Record, and Report (CCRR) the quality of numerous water quality measurements. Essentially, **"Control"** is about things we can do to affect and improve data quality. **"Check"** is about testing how good a measurement actually is. **"Record"** is about the language we use to express the results of our quality checks and about entering our findings into the "placeholders" on DQM forms or spreadsheets. **"Report"** is about the way we calculate the measures of quality, i.e., the data quality indicators, so they can be shared with others. Specific CCRR procedures are added on top of the generic quality assurance procedures such as keeping everything clean, waiting for stabilization of the reading, and keeping good records. Because each type of instrument or kit requires its unique CCRR actions (that cannot be generalized for all measurement devices), the step-by-step instructions for these actions are provided in the instrument-specific standard operating procedures (SOP). Specific issues for DO measurements include the need to find a natural point as a Standard (e.g., the concentration of dissolved oxygen in a 100%-- saturated solution) and the fact that detection limit per se is not really meaningful for DO.

Table 3.1.1-2: Sources of Error and Uncertainty in Dissolved Oxygen Measurements

Sources of Error and Uncertainty	(DOC) Colorimetric Visual Comparison	(DOW) Titrimetric	(DOE) Polaro-graphic
Sample has been in contact with atmospheric air during collection	X	X	
Constituents in the sample interfere with chemical reagents	XX	XX	
Pigments in sample interfere with color absorbency measurements	XX		
Particles in sample interfere with color absorbency measurements	XX		
Color intensity keeps changing as a function of time and temperature	X		
Human eye cannot distinguish small color increments; human eyes are not objective	XX		
Dispensing of volumes is not accurate		X	
Titration endpoint is not clear-cut, blue color of indicator reappears after a while.		XX	
Titration is performed too fast or too slow		X	
Sample bottle and/or other kit utensils are contaminated with titrant, reagents, and/or other interfering substances	X	X	
Reagents and/or titrant are not reacting as specified	X	X	
Electrode not assembled properly (e.g., air bubble trapped under membrane)			X
Electrolyte too weak			X
Instrument not calibrated correctly			X
Membrane not under equilibrium at recording time			X

X - error/uncertainty can be diminished or controlled by operator (better training, more attention, more patience, fresh reagents)
XX - error/uncertainty due to nature of sample or operator and cannot be reduced.

(Table source: Katznelson 1998)

4.4 Calibration and Accuracy checks

Instrument calibration is adjustment of the output to reflect reality, as defined by a "Standard". Accuracy checks – done for devices for which you cannot tweak the output – provide for "correction" of the output based on comparison with reality, as defined by a "Standard". In both and all other cases, the accuracy of any measurement depends on the Standard that is used to assess how close the measurement was to the absolute truth. However you cannot really obtain an oxygen "Standard", so you need to use a natural physical condition as your Standard. One of the checks you can do is to measure DO in clean water (e.g., deionized water, DI) at dissolved oxygen saturation at a given temperature. To assure saturation, use clean water that has been at ambient temperature, not in the refrigerator. Prepare a saturated DI sample by transferring about a glass of water, from cup to cup back and forth, about 20 times, creating turbulence and ample contact with air. With this sample, you can:

- Fill a small container, measure temperature, break a reagent ampoule (CHEMets or Vacu-Vial) and dip in container.
- Fill D.O. bottle, measure temperature, and fix sample for titrimetric method.
- Measure temperature and D.O. with an electrode (this could also be used for calibration of the electrode).

There are several other Accuracy Checks you can do, such as getting a "standard" solution for the Winkler titration, to test the strength of the titrant. If you want to use water with no D.O. for calibration, or to "zero" a D.O. electrode, you can use sodium dithionite or sodium sulfite (CAUTION! Read MSDS sheet!) to consume all D.O. (from any water sample). After you have added a few grains (about 10 mg) per cup, the oxygen should drop very rapidly; you can check it immediately and wait till the electrode reads zero. Once the reading has stabilized, you can calibrate the electrode to zero if it showed something different. Note that the "zero oxygen" solution prepared with these chemicals is not stable, and should be made fresh every time.

4.5 Ways to Collect Samples without contact with air, or Rig Electrodes to keep the water moving

As mentioned above (Section 3), sampling for DO should be conducted without contact with air, and electrodes need constant movement of water past the membrane because they consume oxygen. To diminish the error generated from these sources, the following procedures can be applied:

Colorimetric and titrimetric methods - Objective/principle: Collect sample after flushing D.O. bottle with several volumes of sample water without contact with air.

1. Use water sampling apparatus (e.g., Kemmerer Bottle, a.k.a. LaMotte Water Sampler) with intake tube inserted into D.O. bottle (see SOP-3.1.1.1 in this folder)
2. Use water-trapping sampler (e.g. Van Dorn Bottle, Nansen Bottle) with tap and tube, insert tube into bottom of D.O. bottle and flush several times (see SOP-2.1.1.1 in the Water Sampling Folder).
3. Use the Syringe Pump Apparatus with three-way stopcock (see SOP-2.1.1.2 in the Water Sampling Folder).

Electrodes (Polarographic methods) - Objective: Keep water moving past electrode membrane, i.e., keep flushing sample liquid at the membrane surface to constantly replace the oxygen consumed by the electrode. (Rapid-Pulse and microelectrodes exempted)

1. Use stirrer (buy with electrode. Note: turning the "stirrer" button ON is not going to do it if there is no stirrer!)
2. Enclose electrode in vented tube, pump water through tube so water is sucked fast alongside membrane
3. Stir manually, or attach electrode to rigid pole and stir manually
4. Attach asymmetric weight to bottom of electrode cable, so that up-and-down tugging movement will be transformed to lateral movement of electrode tip

How far away can we be from the "true" value if we cannot apply these procedures? In other words, what happens if the sample is collected in a way that allows for contact with air, such as when the D.O. bottle is dipped directly into a creek? It depends on the D.O. concentration in the creek: the closer it is to saturation, the smaller the error introduced by "air contamination" will be. Thus, if we collect a sample in the bottle directly and measure D.O. of 8 mg/l, chances are that the true concentration in our creek is no less than 7.5 mg/l. But if we take a sample by dipping the D.O. bottle directly in a stagnant pool, and measure 2 mg/l, it could be as low as 1 mg/l in the pool.

However, because we know that anything above 7 mg/l is acceptable and anything below 5 mg/l indicates a potential problem, for most of our purposes we could tolerate the error caused by this "air contamination" and use data generated by the Winkler titration or the colorimetric methods even if samples were not collected with a special apparatus.

Using D.O. electrodes, we will underestimate D.O. concentrations if the measured liquid is not flushed past the membrane adequately and this can introduce a severe error. On the other hand, in a pool or a sample container we cannot shake the electrode very rigorously without introducing D.O. that wasn't there before, so we need to strike a balance. The best we can do is constantly monitor the reading while gently moving the electrode, and recording what appears to be the maximum when the reading is stable for a while.

5.0 Sources and Resources

This IP is an integral part of the Data Quality Management (DQM) System implemented by the Clean Water Team, the Citizen Monitoring Program of the California State Water Resources Control Board.

For an electronic copy, to find many more CWT guidance documents, or to find the contact information for your Regional CWT Coordinator, visit our website at
www.swrcb.ca.gov/nps/volunteer.html

If you wish to cite this IP in other texts you can use "CWT 2004" and reference it as follows:

"Clean Water Team (CWT) 2004. Dissolved Oxygen Measurement Principles and Methods, DQM IP-3.1.1. in: The Clean Water Team Guidance Compendium for Watershed Monitoring and Assessment, Version 2.0. Division of Water Quality, California State Water Resources Control Board (SWRCB), Sacramento, CA."

Available SOPs (2004 Compendium)

- SOP-3.1.1.1 Dissolved oxygen measurements with colorimetric ampoules
- SOP-3.1.1.2(DOW)V2: DO measurements with the Winkler titration (LaMotte or Hach)
- SOP-3.1.1.3(DOE) Dissolved oxygen measurements with an oxygen electrode

Please recall that sampling techniques for collecting a water sample without contact with air are also available in this Compendium (SOP-2.1.1.2 - Water sampling using the Kemmerer bottle ("Sampling Bottle") and SOP-2.1.1.3-Water sampling using the syringe apparatus.

References

Katznelson, R. Tailoring of Data Quality Objectives to Specific Monitoring Questions. in: Proceedings of the First National Monitoring Conference of the National Water Quality Monitoring Council, "Monitoring: Critical Foundations to Protecting Our Waters", July 7-9, 1998, Reno, NV., 1998