Understanding dissolved oxygen

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Workshop goals:

My goal for this workshop is to provide participants with a full understanding of what goes into the measurement of dissolved oxygen in natural waters. Because of the rapid development of technology and the production of advanced meters that are capable of generating much information, the basics on which the technology is based are often 'forgotten', meaning that operators may not be able to distinguish 'good' and 'bad' data. By having a thorough understanding of what is involved with the measurement of DO, meaningful data will be collected.

At the end, participants should leave with an understanding of how temperature and pressure influence the amount of dissolved oxygen in water; the basics of operation of different sensors used to measure dissolved oxygen in water and their pros and cons; and be comfortable using a spreadsheet to automate and calculate the saturation concentrations of oxygen for calibrations at different elevations and atmospheric pressures.

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Background:

- oxygen discovered in 1773-1774 by Carl Wilhelm Scheele, in Uppsala, and Joseph Priestley in Wiltshire
- named by Antoine Lavoisier in 1777

Highly non-metalic reactive element - typically forms oxides
Present in all major classes of structural molecules in living organisms, such as proteins, carbohydrates, and fats.
Also present in major inorganic compounds such as animal shells, teeth, and bone.
Oxygen is the third most abundant chemical element in the universe, after hydrogen and helium
Ozone O_3- in stratosphere - pollutant at low level = smog

At standard temperature and pressure, oxygen is a colorless, odorless gas O_2, in which the two oxygen atoms are chemically bonded to each - double bond.

Industrially produced by fractional distillation of liquefied air (79% N_2, 20.9% O_2 + others)

Importance of oxygen

Necessary to all life that has aerobic metabolism

Biological oxygen demand - respiration of biota including bacteria

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{heat}$

oxygen is the final electron acceptor in cellular respiration

Chemical REDOX reactions

Chemical oxygen demand (COD - in water column SOD in sediment)

E.g., nitrification
In the presence of nitrifying bacteria, ammonia is oxidized first to nitrite, then to nitrate

$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H_+ + H_2O$

The stoichiometric requirement for oxygen in the above reaction is 4.57 mg of O_2 per mg of NH_4^+-N oxidized.

E.g., oxidation of iron

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$$Fe^{3+}PO_4 \text{ (insoluble)} \xrightarrow{-O_2} Fe_3^{2+}(PO4) \text{ (soluble)} \xleftrightarrow{} 3Fe^{2+} + 2PO_4^{3-} \text{ (free)}$$
$$\xleftarrow{+O_2}$$

Because the well-being of aquatic organisms is dependent on the availability of oxygen, many regulating agencies have adopted some form of an oxygen standard - a minimum. Regulatory action is taken if concentrations fall below this minimum.

Determine what the minimum is for your jurisdiction/regulating authority

Thus we need a reliable method(s) with which to measure the oxygen content of water bodies.

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Standards

- In physical sciences have standard conditions for temperature and pressure for experimental measurements

- allows comparison between different sets of data - should make effort to record - get temperature of water anyway - pressure is a bit more difficult

- whole variety of different sets

- most common is that of International Union of Pure and applied chemistry (IUPAC) and the National Institute of Standards and Technology (NIST)

- far from being universal standards.

Multiple standards within an organization - e.g. the International Organization for Standardization (ISO), the United States Environmental Protection Agency (EPA) and National Institute of Standards and Technology (NIST) each have **more than one definition of standard reference conditions** in their various standards and regulations.

Some standard reference conditions in current use

Temp	**Absolute pressure**	**Relative humidity**	**Publishing or establishing entity**
°C	**kPa**	**% RH**	
0	100.000		IUPAC (present definition)
0	101.325	IUPAC	(former definition), NIST, ISO 10780
15	101.325	0	ICAO's ISA, ISO 13443,
20	101.325		EPA, NIST
25	101.325		EPA
°F	**psi**	**% RH**	
60	14.696		U.S. OSHA, OPEC,
59	14.503	78	U.S. Army Standard Metro
59	14.696	60	ISO 2314, ISO 3977-2

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Ideal gas laws

Developed for an ideal gas - states that for any gas, a given number of its 'particles' occupy the same volume. Change in volume is inverse to changes in pressure and direct to temperature

PV = nRT

Boyle's Law - $P_1V_1 = P_2V_2$ or PV = constant
Where P = pressure and V = volume

From combined gas laws $P_1V_1/T_1 = P_2V_2/T_2$ or PV/T = constant
T = temperature

where (in SI metric units):
P = the absolute pressure of the gas, in Pa
n = amount of substance, in mol
V = the volume of the gas, in m^3
T = the absolute temperature of the gas, in K
R = the universal gas law constant of 8.3145 $m^3 \cdot Pa/(mol \cdot K)$

or where (in customary USA units):
P = the absolute pressure of the gas, in psi
n = number of moles, in lbmol
V = the volume of the gas, in $ft^3/lbmol$
T = the absolute temperature of the gas absolute, in °R
R = the universal gas law constant of 10.7316 $ft^3 \cdot psi/(lbmol \cdot °R)$

The value of the ideal gas constant, R, is found to be as follows.

R =	8.314472	$J \cdot mol^{-1} \cdot K^{-1}$	
=	8.314472	$m^3 \cdot Pa \cdot K^{-1} \cdot mol^{-1}$	
=	8.314472	$kPa \cdot L \cdot mol^{-1} \cdot K^{-1}$	
=	0.08205746	$L \cdot atm \cdot K^{-1} \cdot mol^{-1}$	
=	62.36367	$L \cdot mmHg \cdot K^{-1} \cdot mol^{-1}$	
=	10.73159	$ft^3 \cdot psi \cdot °R^{-1} \cdot lb\text{-}mol^{-1}$	(degrees Rankine)
=	53.34	$ft \cdot lbf \cdot °R - 1 \cdot lbm^{-1}$	(for air)

- Technical literature is confusing because authors fail to indicate if they are using the universal gas law constant R, which applies to any ideal gas, or whether they are using the gas law constant Rs, which only applies to a specific individual gas. The relationship between the two constants is

Rs = R / M, where M is the molecular weight of the gas.

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Units and conversion between them

The international SI unit for pressure is the pascal (Pa), equal to one newton per square meter ($N \cdot m^{-2}$ or $kg \cdot m^{-1} \cdot s^{-2}$). The conversions to other pressure units are:

Pressure Units

	pascal (Pa)	bar (bar)	technical atmosphere (at)	atmosphere (atm)	torr (Torr)	pound-force per square inch (psi)
1 Pa	= 1 N/m^2	10^{-5}	1.0197×10^{-5}	9.8692×10^{-6}	7.5006×10^{-3}	145.04×10^{-6}
1 bar	100,000	= 10^6dyn/cm^2	1.0197	0.98692	750.06	14.5037744
1 at	98,066.5	0.980665	= 1 kgf/cm^2	0.96784	735.56	14.223
1 atm	101,325	1.01325	1.0332	= 1 atm	760	14.696
1 torr	133.322	1.3332×10^{-3}	1.3595×10^{-3}	1.3158×10^{3}	= 1 Torr; = 1 mmHg	19.337×10^{3}
1 psi	6,894.76	68.948×10^{-3}	70.307×10^{-3}	68.046×10^{-3}	51.715	= 1 lbf/in

Example reading: 1 Pa = 1 N/m^2 = 10^{-5} bar = 10.197×10^{-6} at = 9.8692×10^{-6} atm, etc.
kgf - kilogram force

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Solubility

The solubility of oxygen in water is temperature and pressure dependent

About twice as much (14.6 $mg \cdot L^{-1}$) dissolves at 0 °C than at 20 °C (7.6 $mg \cdot L^{-1}$)

Less oxygen dissolves at high elevations (Mount Everest)compared to low elevations (sea level) because the atmospheric pressure is less and thus the partial pressure is lower.

$$\% \text{ saturation} = \frac{\text{Oxygen conc} * 100}{\text{Oxygen solubility at saturation}}$$

- important to know for animal health - e.g., Total Dissolved Gas (TDG) limits (EPA limit is 110% currently

- in this case % saturation is needed rather than a concentration (mg/L)

Partial pressure

The pressure exerted by a particular component of a mixture of gases as if only that gas were present

Partial pressure of Oxygen = $DO/ß_{O2} * 0.5318$

where: DO measured concentration in mg/L
$ß_{O2}$ = Bunsen coefficient for Oxygen (standard methods table 2810:I)
The factor 0.5318 = 760/(1000K), where K is the ratio of molecular weight to molecular volume of oxygen gas

Effects of changing pressure (barometric or altitude)

Typically any barometric pressure reported as part of a TV broadcast has been converted to a value **relative to sea level**. This is to standardize data - and over large geographic areas pressures are typically similar, unless a storm is approaching. However, there are differences with altitude that can occur over a small distance. All avitation uses pressure altimeters to determine where the ground is.

To determine true - uncorrected barometric pressure:

1) obtain from calibrated mercury barometer - if you have another barometer close by - make sure it has been correctly set for your altitude (see reference on how to calibrate barometer)
2) call local airport or radio station
   ask if data are corrected to sea level, if yes - need to UNcorrect it
3) use known O_2 saturation tables / nomograms
4) use tables / formulae in standard methods (we'll get to this in a minute)

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To Uncorrect an airport or local weather station barometric pressure ex. 29.89 inches Hg

a) - determine altitude (in feet) of your lab (Oklahoma City = 1295' or 395 m)
Moscow, ID / Gritman Helipad = 2035 ft or 620.3m above sea leavel
Pullman Airport = 2556' or 779.1m above sea level.
b) - determine the correction factor (CF):
CF = [760 - (Altitude *0.026)]÷760
= (760- (1295*0.026)]÷760 (Highlight = altitude for your location in feet)
= [760-33.67]÷760
= 626.33 ÷760
= 0.9556
c) therefore the true uncorrected barometric pressure = 29.89*0.9556 = 28.56in Hg

Note: - pressure drops about 26 mm (about 1 in) for every 1000 feet above sea level; hence the multiplication by 0.026 (26/1000)

To convert inches Hg to mm Hg - multiply by 25.4 = 28.56*25.4 = 725.49 mm Hg

Determining DO Saturation

a) the temperature of the calibration sample is 21 °C
b) from standard tables we can determine that the maximum O_2 solubility at sea level and standard pressure is 8.915 mg/L
c) we know that the uncorrected barometric pressure is 725.49 mm Hg
d) to determine the correction factor to adjust maximum O_2 saturation to the actual pressure:
Pressure correction factor = [True barometric pressure ÷760]
= (725.49 ÷760)
= 0.954
e) multiply the sea level saturation by the pressure correction factor
= 8.915 * 0.954
= 8.51 mg/L

Using the standard method equations for determining the concentration at non-standard temperatures and pressures

$$Cp = C^*P((1-Pwv/P)(1-\theta P))/((1-Pwv)(1-\theta))$$

Where: Cp = equilibrium oxygen concentration at nonstandard pressure, mg/L
C* = equilibrium oxygen concentration at standard pressure of 1 atm, mg/L
P = non standard pressure, atm
Pwv = partial pressure of water vapor, atm, computed from:
$\ln Pwv = 11.8571-(3840.70/T)-(216961/T^2)$
T = temperature in °K (°K = °C+271.150)
$\theta = 0.00975-(1.426 \times 10^{-5}t) + (6.436 \times 10^{-8}t^2)$
t = temperature, °C

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Example: at 20°C and 0.7 atm, Cp = C*P(0.990092) = 6.3 mg/L

To calculate C* the equilibrium concentration at standard pressure and atmospheres

$\ln C^* = -139.34411 + (1.575701 \times 10^5/T) - (6.642308 \times 10^7/T^2) + (1.243800 \times 10^{10}/T^3) - (8.621949 \times 10^{11}/T^4) - Chl[(3.1929) \times 10^{-2}) - (1.9428 \times 10^1/T) + (3.8673 \times 10^3/T^2)]$

where C* = equilibrium oxygen concentration a 101.325 kPa, mg/L
T = temperature (°K) = °C + 273.150 (for 0-40°C)
Chl - chlorinity

Example 1 - at 20°C and 0.000 Chlorinity, lnC* = 2.207442 = 9.092 mg/L

Migrate to spreadsheet to set this up to calculate automatically for any pressure unit and temperature or elevation.

Putting calibrations in perspective

- pressure drops about 1 inch per 1000 ft (26 mm/1000ft)
- Maximum DO saturation drops about 0.3 mg/L for each 1000 ft
- outside of storm systems, daily pressures fluctuate about 10 mm (0.4 inches)
- at 20°C the oxygen saturation decreases about 0.1 mg/L for each 0.5 degree rise in temperature

Instrument based barometers are making this sort of issue a thing of the past - however, you need to know that your on-board barometer is set correctly - many can be set to user defined points - and come factory set to correct to sea level!

You must realize how important pressure changes are to obtain accurate calibrations - this is especially true if you take your oxygen meter for hikes up mountains and re-calibrate when you get to the lake.

Important if you are analyzing samples - at high and low pressure systems - need to be able to accurately correct for pressure changes.

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Methods to determine dissolved oxygen

Method must meet two important criteria:

i) it must be accurate given low concentration (mg/L)
ii) apparatus must be suitable to field conditions

1) Bunsen method

- boil oxygen out of water and measure in absorbent materials
- too cumbersome for field and insufficient accuracy for lab

2) nomograms - be sure you get a correct one, and not one that has been photocopied to death - as you are typically required to line up points and read off a scale

3) Winkler method one of the best colorimetric methods (EPA Standard Methods approved)

4) Oxygen sensitive electrode

i) Clark-style membrane and galvanic (EPA, Standard Methods approved)
ii) Luminescence LDO (Chemical quenching of luminescence)

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2) Nomograms

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3) Chemical determination of oxygen in water (Winkler method)

Principle behind the method:

The Winkler titration method for the determination is based on the method developed by Winkler in 1888 (Winkler 1888). The method has seen several modifications to encompass interferences - (see APHA Standard methods for the examination of water and wastewater). It is an iodometric titration, in which the amount of oxygen in the sample is determined indirectly via iodine. It is the most precise and reliable titrimetric procedure for DO analysis.

Briefly: A divalent manganese solution is added followed by strong alkali to a water sample in a glass stoppered bottle. Any DO present in the sample rapidly oxidizes an equivalent amount of the dispersed divalent manganous hydroxide precipitate to hydroxides. The sample is then acidified with H_2SO_4. In the presence of iodide ions in an acidic solution, the oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent to the original DO content. The iodine is then titrated with sodium thiosulfate and starch as an indicator.

The method is a typical standardization and calibration check for other equipment such as membrane sensors and LDO probes. For the analysis of field samples, DO analysis is best done in the field, as there is less chance for the sample to be altered by atmospheric equilibration, changes in temperature and chance of escape of floc or gasses. The method has also been adapted for very small samples (ml), including oxygen samples extracted from animal burrows by divers. See the end of this for adjusting volumes of original sample and strength of titrant used.

Winkler, L. W. 1888. Die Bestimmung des im Waser gelösten Sauerstoffes. Chem. Ber. **21**: 2843-2855.

The equations are as follows:

i) Manganous sulfate reacts with hydroxide (potassium or sodium) to give a white precipitate of manganous hydroxide. In the presence of oxygen, brown manganic basic oxide is formed.

$Mn^{+2}SO_4 + 2KOH \rightarrow Mn^{2+}(OH)_2 + K_2SO_4$

$2Mn^{2+}(OH)_2 + O_2 \rightarrow 2\ Mn^{+4}O(OH)_2$

ii) Addition of sulfuric acid dissolves the brown manganic sulfate which reacts instantly with iodide to yield iodine.

$2Mn^{+4}O(OH)_2 + 4\ H_2SO_4 \rightarrow 2Mn^{+4}(SO_4)_2 + 6H_2O$

$2Mn^{+4}(SO_4)_2 + 4\ KI \rightarrow 2Mn^{+2}SO_4 + 2K_2SO_4 + 2I_2$

iii) In effect, oxygen oxidizes Mn^{2+} to Mn^{4+} and the Mn^{4+} oxidizes I^- to I_2. Iodine is then determined titrimetrically via titration with Sodium thiosulfate ($Na_2S_2O_3$) with starch as an end point indicator (deep blue).

iv) Thiosulfate solution (made up as $Na_2S_2O_3$) is used, with a starch indicator, to titrate the iodine.

$4Na_2S_2O_3 + 2I_2 \rightarrow 2Na_2S_4O_6 + 4NaI$

From the above stoichiometric equations it is apparent that four moles of thiosulfate are titrated for each mole of molecular oxygen (O_2).

Thus 1 ml of 0.025 M sodium thiosulfate is equivalent to 0.025 meq of oxygen. This value is commonly multiplied by 8 mg/meq to convert to mg O_2.

When 200 ml of the original sample is titrated, then 1 ml of 0.025M $Na_2S_2O_3$ = 1 mg dissolved oxygen/L. (200ml /1000ml = 0.2 mg O_2 and 8 mg/meq*0.025 = 0.2 mg O_2)

Interferences:

Some oxidizing agents liberate iodine from iodide (+ interference) while some reducing agents reduce iodine to iodide (-interference). Organic matter is partially oxidized when the manganese precipitate is acidified, causing negative errors. The azide modification removes interference caused by nitrate, common in biologically treated effluents. The permanganate modification is used to remove iron interference of >5 mg ferric iron salts/L. Ferrous interference can be removed by adding H_3PO_4 for acidification (only if Fe^{3+} is < 20 mg/L). With suspended solids the alum flocculation modification works well, while for activated-sludge mixed liquor the copper sulfate-sulfamic acid flocculation modification can be used. In many cases, these interferences can be overcome by using the dissolved oxygen probe method.

General methods:

A sample bottle (typical 300 ml glass BOD bottle with pointed ground glass stopper) is filled completely with water. Special precautions are required to prevent the entrainment of or solution of atmospheric oxygen or loss of DO. This is particularly important for samples at either end of the spectrum - anoxic samples tend to be highly sensitive to oxygen dissolution into the sample during handling, while those supersaturated may degas. To fill the bottle, lower it into the water at the surface, ensuring that sample water enters the bottle without splashing, to avoid oxygen entrainment. Samples from depth should be collected with a remote sample such as a Kemmerer sampler, which has a tube on the outlet. The tube should be placed at the bottom of the BOD while it is filled, and the bottle allowed to overflow for a period of time (10s or 2-3 bottle volumes) to ensure that a representative sample is obtained. For running water, two to three times bottle volume replacement is suggested to get a representative sample. Samples from turbulent streams may be collected via a funnel connected to a rubber tube which is placed in the bottom of the BOD bottle. This will ensure non-turbulent sample collection and avoid splashing in the bottle that could entrain oxygen. Temperature of the sample should be measured as accurately as possible.

Specific procedures: (Culled from standard methods, and various other sources - note that standard methods assume a solid chemistry background in terms of determining solution

standardization etc - these are not always apparent to the biologist/limnologist. Nor is it always readily apparent where constants come from - I've tried to summarize and explain these below).

Reagents:

1) Manganese sulfate

Dissolve 480 g of $MnSO_4 \cdot 4H_2O$; 400 g of $MnSO_4 \cdot 2H_2O$; or 364 g $MNSO_4 \cdot H_2O$ in distilled water. Filter and dilute to 1 liter. The $MnSO_4$ solution should not give a color with starch when added to an acidified potassium iodide (KI) solution.

2) Alkali-iodide-azide (Azide is a poison - thus this may require hazardous waste disposal. However the quantities used, are typically low and if not all the azide is spilled down the sink at once, generally does not pose a risk.)

for saturated or less-than-saturated samples
Dissolve 500 g NaOH (or 700 g KOH), and 135 g NaI (or 150 g KI), in distilled water and dilute to 1 liter. To this add 10 g sodium azide NaN_3 dissolved in 40 ml of distilled water.
Potassium and sodium salts may be used interchangeably. This reagent should not give a color with starch solution when diluted and acidified. (Test it to verify!)

3) Sulfuric acid

Concentrated H_2SO_4 (S.G. 1.84): one milliliter is equivalent to about 3 ml alkali-iodide-azide reagent.

4) Starch indicator

Bring 100 ml of distilled water to boil. Prepare a paste of 1 g potato starch in a few ml of distilled water. Add boiling water to the paste. Cool and store at 5°C. When a violet or grey tinge is noted, discard. Test this by adding it to a solution with iodine - not all starch is created equal.

Alternatively

Use either an aqueous solution or soluble starch powder mixtures. To prepare an aqueous solution, dissolve 2 g laboratory-grade soluble starch and 0.2 g salicylic acid, as preservative, in 100 ml hot distilled water.

5) Standard sodium thiosulfate (Stock 0.1 M - 0.1N)

Dissolve 24.82 g $Na_2S_2O_3 \cdot 5H_2O$ per liter, preserved with ammonium carbonate and chloroform 5 ml per liter after making up to mark. Deteriorates about 1% in 6 months.

Standard 0.025M (0.025 N) made by diluting 250 ml of stock to one liter. Add 5 ml chloroform after making up to mark. Deteriorates rapidly and should be made up fresh

every month.

Alternatively: Dissolve 6.205 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water. Add 1.5 ml 6N NaOH or 0.4 g solid NaOH and dilute to 1000 ml. Standardize with potassium bi-iodate or potassium dichromate before use. (Makes 0.025N $Na_2S_2O_3 \cdot 5H_2O$)

6) Potassium dichromate

Dissolve 4.903 g $K_2Cr_2O_7$ in distilled water and bring up to 1 liter. This will make a 0.10 N solution. Use this to standardize the 0.1 N sodium thiosulfate (see standardization below).

Alternatively: To make a 0.025 N $K_2Cr_2O_7$ solution, dissolve 1.225 g $K_2Cr_2O_7$ in distilled water and make up to 1 liter.

7) Dilute acid for standardization

3.6 N H_2SO_4 - 1 part concentrated H_2SO_4 to 9 parts water

Cautions:

A variety of manuals are available that describe the method. Be sure you read and understand what is being done before launching in! As occurs often, to save space, or because of things that are obvious to analytical chemists, not all methods offer all of the details you may want, or leave things out leading to questions between methods. I've tried to cobble all of the reasoning together here for a complete package.

Sources consulted included:

APHA standard methods for the examination of water and wastewater.
EPA standard method 360.2, a variety of books and appendices explaining Winkler titrations.
Carpenter, J. H. 1965. The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. Limnol. Oceanogr. 10:141-143.
Stainton, M.P., M.J. Capel and F.A. Armstrong. 1977. The chemical analysis of freshwater. 2nd ed. Fish. Envir. Can. Miscellaneous Special Publ. 25 (available from the Freshwater Inst., Winnipeg, Manitoba)
ASTM E200-86 Standard practice for preparation, standardization, and storage of standard solutions for chemical analysis (59-63).

Most methods use a titration standard of 0.025 N sodium thiosulfate ($Na_2N_2O_3$) with an adjusted sample volume of between 200-203 ml depending if 1 or 2 ml of each reagent were added (see below) because at those proportions 1 ml of sodium thiosulfate is equal to 1 mg of DO which makes things simple. However, 200 ml out of a 300 ml bottle only gives you one shot at getting it right. You can do any number of titrations between 50 and 200 ml (using an adjusting formula - see below) so you can get replicates out of a single bottle.

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Standardize the 0.10 N sodium thiosulfate solution.

1) Potassium dichromate ($K_2Cr_2O_7$) primary standard solution (used to standardize the sodium thiosulfate - see below for details on primary standard solutions)

For our purposes - we will make a 0.1 N $K_2Cr_2O_7$ solution. Take 4.903 g of $K_2Cr_2O_7$ and dissolve in distilled water, make up to 1L.

$$\text{Normality of } K_2Cr_2O_7 = \frac{\text{(g dissolved in 1 L)}}{49.03}$$

2) Dissolve approximately 2 g of KI, free of iodate, in a 500-ml Erlenmeyer flask with 100-150 ml of distilled water;

add 10 ml of 10% H_2SO_4 solution, followed by exactly 20.00 ml of standard dichromate solution (0.10 N $K_2Cr_2O_7$)

Place in the dark for 5 min.

Dilute to 300 ml with distilled water, and titrate the liberated iodine with the 0.10 N thiosulfate titrant to pale straw color;

Add starch 1-2 ml and continue until blue is discharged

Calculate the volume of the 0.10 N stock sodium thiosulfate that must be diluted to 1 L to get exactly 0.025 N standard sodium thiosulfate solution:

$$\text{Vol of stock } Na_2S_2O_3 \text{ solution required} = \frac{\text{Vol. of titrant (ml)}}{20.0 \text{ (ml)}} * 250.$$

A couple of things about the above - typically you determine the Normality of your standard by the following calculation:

$$1 - \text{Normality of reagent} = \frac{\text{(normality of standard * volume of Standard used (ml))}}{\text{Volume of reagent used in titration (ml)}}$$

thus if your 0.1 N Sodium thiosulfate is exactly 0.1 N, then it should have taken 20.0 ml of reagent to dissipate the blue of the 20 ml of potassium dichromate standard.

If it is not 0.1 N - then you need to re-calculate how much you will need to make 0.025 N

2 - remember that normality of sodium thiosulfate = normality of Potassium dichromate
3 - remember that in this case then N1*V1 = N2*V2 (N - normality, V - volume)

if your standard is 0.1 N, then to make a 0.025N solution you need:

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$$V1 = \frac{N2*V2}{N1}$$ N1 - 0.10, N2 - 0.025, V2 - 1.0L

= 0.25 L or 250 ml of 0.1 N $Na_2S_2O_3$ (this is where the 250 multiplication comes from in the above equation)

If the stock is not 0.1 N - then the above equation uses a ratio by which to adjust the typically required 250 ml. (Just make sure you use the same units - if you use L, then re-adjust the 250 by dividing by 1000ml/L to 0.25).

Potassium dichromate is an ideal primary standard solution because it can be made by direct weighing of a chemical.

Standard solutions are the ones whose exact concentration/normality/molarity is known and if it has to be made by direct weighing. Some of the desirable properties for making a primary solution are:

1. It must be solid. It is difficult to weigh an exact quantity of gases/liquids.
2. Must be available in high purity (100 % +/- 0.02%) and available commercially.
3. Must be very stable and not change its composition on storage/keeping or exposure to air/atmosphere.
4. Must have uniform composition.
5. Non-hygroscopic
6. Must readily dissolve and must be stable in solution form as well.
7. High equivalent weight (to minimize balance errors)
7. Preferably nontoxic

Barwick, V., Burke, S., Lawn, R., Roper, P., and Walker, R. 2001. Applications of Reference Materials in Analytical Chemistry, Royal Society of Chemistry, London, UK.

Potassium dichromate: Chemical Formula $K_2Cr_2O_7$ (CAS No. 7778-50-9)
Formula Weight 294.18
Equivalent Weight 49.03 (Molar = 6 Normal)

Equivalent Weight

In chemistry, the quantity of a substance that exactly reacts with, or is equal to the combining value of, an arbitrarily fixed quantity of another substance in a particular reaction.

Substances react with each other in stoichiometric, or chemically equivalent, proportions, and a common standard has been adopted. For an element the equivalent weight is the quantity that combines with or replaces 1.00797 grams (g) of hydrogen or 7.9997 g of oxygen; or, the weight of an element that is liberated in an electrolysis (chemical reaction caused by an electric current) by the passage of 96,500 coulombs of electricity.

The equivalent weight of an element is its gram atomic weight divided by its valence (combining power). Some equivalent weights are: silver (Ag), 107.868 g; magnesium (Mg), 24.312/2 g; aluminum (Al), 26.9815/3 g; sulfur (S, in forming a sulfide), 32.064/2 g.

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For compounds that function as oxidizing or reducing agents (compounds that act as acceptors or donors of electrons), the equivalent weight is the gram molecular weight divided by the number of electrons lost or gained by each molecule;

e.g., potassium permanganate ($KMnO_4$) in acid solution, 158.038/5 g;

potassium dichromate ($K_2Cr_2O_7$), 294.192/6 g = (49.032) - constant used in thiosulfate standardization

sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), 248.1828/1 g.

For all oxidizing and reducing agents (elements or compounds) the equivalent weight is the weight of the substance that is associated with the loss or gain of 6.023 × 1023 electrons.

The equivalent weight of an acid or base for neutralization reactions or of any other compound that acts by double decomposition is the quantity of the compound that will furnish or react with or be equivalent to 1.00797 g of hydrogen ion or 17.0074 g of hydroxide ion;

e.g., hydrochloric acid (HCl), 36.461 g;
sulfuric acid (H_2SO_4), 98.078/2 g;
sodium hydroxide (NaOH), 74.09/2 g;
sodium carbonate (Na_2CO_3), 105.9892/ 2 g.

Equivalent weight. 2009. In Encyclopædia Britannica. Retrieved February 17, 2009, from Encyclopædia Britannica Online:
http://www.britannica.com/EBchecked/topic/190933/equivalent-weight

Understanding dissolved oxygen

Procedure:

1. Carefully fill a 300-mL glass Biological Oxygen Demand (BOD) stoppered bottle brim-full with sample water.

2. Immediately add 2 mL of manganese sulfate to the collection bottle by inserting the calibrated pipette just below the surface of the liquid. (If the reagent is added above the sample surface, you will introduce oxygen into the sample.) Squeeze the pipette slowly so no bubbles are introduced via the pipette.

3. Add 2 mL of alkali-iodide-azide reagent in the same manner.

4. Stopper the bottle with care to be sure no air is introduced. Mix the sample by inverting several times. Check for air bubbles; discard the sample and start over if any are seen. If oxygen is present, a brownish-orange cloud of precipitate or floc will appear. When this floc has settle to the bottom, mix the sample by turning it upside down several times and let it settle again.

5. Add 2 mL of concentrated sulfuric acid via a pipette held just above the surface of the sample. Carefully stopper and invert several times to dissolve the floc. At this point, the sample is "fixed" and can be stored for up to 8 hours if kept in a cool, dark place. As an added precaution, squirt distilled water along the stopper, and cap the bottle with aluminum foil and a rubber band during the storage period.

6. In a glass flask, titrate between 201 ml and 203 mL of the sample with sodium thiosulfate to a pale straw color. Titrate by slowly dropping titrant solution from a calibrated pipette into the flask and continually stirring or swirling the sample water.

   Standard methods - suggests calculating a titration volume before you start titrating by calculating (200*300/(300-4) = 203 ml.

   Alternatively - you can use any volume between 50 and 200 ml - see calculations below for adjusting.

7. Add 2 mL of starch solution so a blue color forms.

8. Continue slowly titrating until the sample turns clear. As this experiment reaches the endpoint, it will take only one drop of the titrant to eliminate the blue color. Be especially careful that each drop is fully mixed into the sample before adding the next. It is sometimes helpful to hold the flask up to a white sheet of paper to check for absence of the blue color.

9. The concentration of dissolved oxygen in the sample is equivalent to the number of milliliters of titrant used. Each ml of sodium thiosulfate added in steps 6 and 8 equals 1 mg/L dissolved oxygen.

10. Calculations

Understanding dissolved oxygen

$$O_2 \text{ in ppm (mg/L)} = K * 200 * \frac{\text{Volume of 0.025 N thiosulfate used in titration}}{\text{Volume of sample titrated}}$$

K is a constant to correct for displacement of oxygen in the sample when manganous sulfate and alkaline iodide azide were added. (No correction needed for acid unless floc is displaced)

$$\text{For a 300 ml bottle } K = \frac{\text{Volume of bottle}}{\text{Vol. Of bottle - Vol. of reagents}} = \frac{300}{(300\text{-}4)}$$

Note 1 You should check to make sure you know the volume of each BOD bottle before you start. Determine this volumetrically or gravimetrically and write on bottle - or next to notes and number of bottle.

Note 2 1.0 ml of 0.025 N thiosulfate is equivalent to $25*10^{-6}$ equivalents of iodine which is in turn equivalent to $25*10^{-6}$ equivalents of oxygen

$$25*10^{-6} \text{ equivalents of } O_2 = 200 * 10^{-6} \text{ g } O_2$$

If volume titrated is 200 ml then 1.0 ml of 0.025 N thiosulfate is equivalent to 1.0 mg O_2/liter in the original sample. (This is where the 200 factor in the above calculation comes from)

If oxygen concentrations to 0.1 mg/L are acceptable, the above equality is sufficient to determine dissolved oxygen.

If greater accuracy is required, one must take into account the dilution effect of the first 3 reagent additions. This dilution effect is (V-4)/V where V is the volume in ml of the oxygen bottle used. Oxygen values obtained by assuming 1.00 ml of 0.025 N thiosulfate equivalent to 1.00mg/L dissolved oxygen should then be multiplied by V/(V-4) to correct for dilution.

Note 3 If neither 0.025 N titrant is used, other volumes are used and bottles are not 300 ml, then a convenient method to figure out mg O_2/L is:

$$mgO_2/L = \frac{(\text{ml of titrant})\,(\text{Molarity of Thiosulfate})(8000)}{(\text{ml of sample})\,\frac{(\text{ml of Bottle-2})}{(\text{titrated})\qquad(\text{ml of bottle})}}$$

Adjust 2 in this equation to however many ml of reagents were added. 8000 is factor related to $8mgO_2$/meq (see above).

Understanding dissolved oxygen

4) Oxygen sensitive electrodes

i) Polarographic Oxygen Sensors

A polarographic oxygen sensor (POS) is an electrochemical cell used to continuously measure the activity of oxygen in solutions, gases and semi-solids in a single-step operation. Voltammetry and polarography comprise electroanalytical methods in which information about an analyte is derived from the measurement of current as a function of applied potential during an electrolysis which is carried out under conditions that encourage polarization of the working electrode (Skoog *et al*. 1988). Since their inception, polarographic oxygen sensors have undergone improvements and refinements including: electrode metal selection and preparation (Baumgärtl and Lübbers 1983, Mickel *et al*. 1983, Fatt 1965, Lübbers *et al*. 1969), membrane types and application techniques (Carey and Teal 1965, Helder and Bakker 1985) and the inclusion of guard cathodes (Visscher *et al*. 1991, Revsbech 1989). All parts of the electrochemical cell including cathode, anode and electrolyte reservoir have been combined and recombined in various forms to produce a wide array of sensors, from those that can be inserted into blood vessels to those that are sturdy enough for industrial applications at high pressures and temperatures (Reed 1972, Graber 1983).

Theory of Operation

The general theory of operation of a typical polarographic oxygen sensor is covered below; (for exhaustive reviews see Fatt 1976, Hitchman 1978, Forstner and Gnaiger 1983). Typically the cell consists of two electrodes covered by a membrane separating them and the electrolyte solution from the test solution. The membrane is permeable to oxygen, but prevents other interfering ions from reaching the electrodes. Oxygen from the test solution diffuses through the membrane into the film of electrolyte solution over the cathode. The oxygen then diffuses across the electrolyte layer to the cathode where it is reduced:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

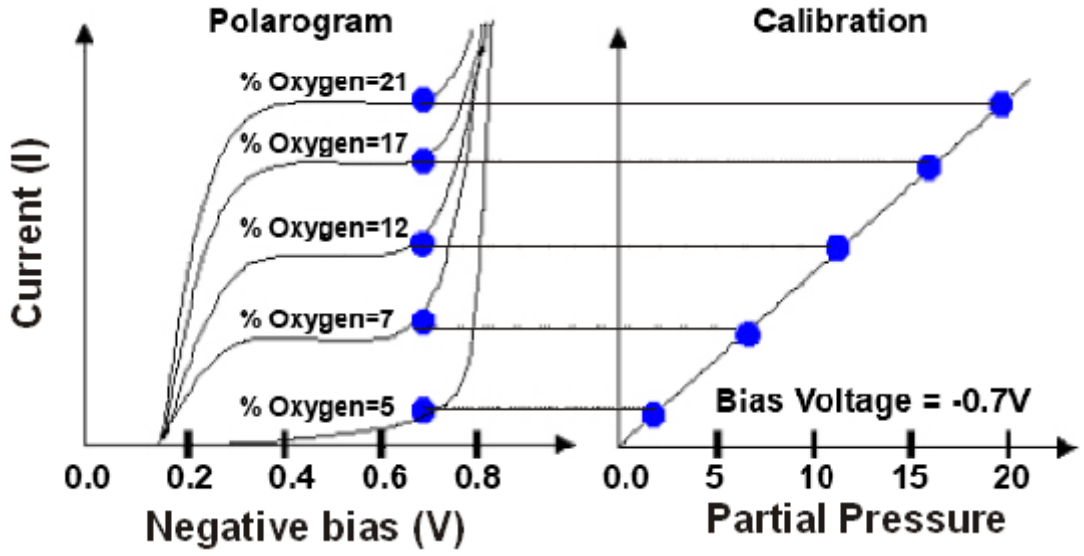
Reduction occurs because the cathode is sufficiently negative (i.e., greater than the reduction potential for the oxygen half-cell reaction) with respect to the to the other electrode, which serves both as an anode and reference electrode. The most common anode is the silver-silver chloride where the following reaction takes place:

$$4Ag + 4Cl^- \longrightarrow 4AgCl + 4e^-$$

The reduction of oxygen at the cathode causes current flow between the electrodes. Current flow increases with applied voltage, resulting in a characteristic polarogram (see below).

In the region below -0.2v there is little oxygen reduction. Between -0.2 and -0.5 to -0.60 the current increases proportionally to the applied voltage. In this region, oxygen supply to the cathode is adequate and reduction is only limited by the applied potential. This is called the overvoltage region where the applied voltage is greater than that of the equilibrium half-cell reaction, but low enough so that there is a surplus of oxygen at the cathode (Fatt 1976). Above -

Understanding dissolved oxygen



0.65, a small plateau region is encountered where increasing voltage does not cause much of a current increase. This is the polarized region because the voltage-current relationship is no longer linear (Skoog et al. 1988). It is in this region that all oxygen reaching the cathode is immediately reduced, leaving the cathode surface at zero oxygen. The current of the cell is independent of all external factors except the oxygen concentration in the bulk of the test solution. This is described as concentration polarization (Skoog et al. 1988); the current output of the cell is proportional to the partial pressure of oxygen in the bulk of the test solution. As the applied voltage increases above -1.0v the current again increases with voltage due to electrode reactions and the reduction of other elements.

As pointed out above, a polarographic oxygen sensor does not measure the concentration of oxygen in solution, rather the current output is proportional to the partial pressure of oxygen (activity) in the test solution (Fatt 1976, Forstner and Gnaiger 1983). If a measure of dissolved oxygen in terms of concentration is required, Henry's law proportionality constant relating activity and concentration at given temperatures and liquid composition must be known (Hitchman 1983). This is easily accomplished given the equations presented above, or by consulting the appropriate tables.

Factors influencing POS operation

Although the operation of a POS seems straight forward, operation is influenced by a variety of factors.

Membranes

The membrane type and thickness influence the amount of oxygen and the speed with which it can diffuse into the electrolyte layer. Common membrane materials include polyethylene, Teflon, Mylar, natural rubber, silicone rubber, and PVC, D.P.X., and PTFE (Fatt 1976, Hitchman 1978, Forstner and Gnaiger 1983, Helder and Bakker 1985). Membrane thickness ranges from less than 1 µm to 1000 µm depending on the application and membrane material. Very thin membranes are used for micro-needle sensors which give very fast response times, while thicker membranes are sturdier and are used on larger field sensors subject to rough conditions. Clogging of the membrane by bacteria, or algae causes a decrease in POS response. The application of membranes to sensors can also change the operating characteristics. Small

micro-sensors are generally not affected by this because they usually have permanent cast membranes. A membrane is usually stressed during the application procedure and must be given 0.5-1 hours to relax before measurements can be made. Also, in sensors with the electrolyte reservoir directly behind the membrane, orientation of the sensor may cause pressure from the electrolyte to distort the membrane leading to erroneous readings. Generally, the application for which the sensor is to be used dictates the type and thickness of the membrane to be used.

Electrolyte

To function properly, the electrolyte of a POS must be compatible with the oxidation and reduction mechanisms at the electrodes. It must also provide a conductive path for the transport of ionic species between the electrodes (Hitchman 1978, Bucher 1983). The operation of a POS depends on a stable electrolyte, yet it is the nature of an electrochemical cell to alter the composition of the electrolyte as a result of electrode reactions. Changes in the electrolyte are influenced by the size of the reservoir, the thickness of the electrolyte between the cathode and membrane, and the path between electrodes (Bucher 1983). If a silver-silver chloride anode is used, the electrolyte generally contains a chloride species. The thickness of the electrolyte film between the membrane and the cathode determines the diffusion rate of oxygen to the cathode, where a thin film allows oxygen to reach the cathode faster than a thick film. As a POS operates the Cl^- ions are depleted. Therefore, the useful time of operation for a POS is proportional to the size of the electrolyte reservoir. A POS with electrolyte just between the membrane and the cathode will only last for several hours before the membrane must be removed and the electrolyte replaced. Another problem associated with the electrolyte solution is the loss of solvent through evaporation either while the POS is not in use or during operation in a gas phase (Hitchman 1978). Loss of solvent can be minimized by storing the POS in a moist chamber while not in use. Sensitivity of POS users to the complexity of the POS-electrolyte interactions may be the best solution to avoid serious electrolyte related problems. Bucher (1983) stated that "the electrochemistry of the electrolyte makes every POS a rather complex system and no general formula exists for its optimization".

Cathode

The cathode, made of either gold or platinum, is central in the operation of a POS because it is the surface at which oxygen is reduced. Cathode diameter is one of the major factors contributing to the operational characteristics of a POS. As the oxygen reduction area is increased, more oxygen can be reduced, leading to a higher current flow. In large field probes such as a YSI probe, the current from the cathode can be measured without amplification, whereas the current from a micro-electrode is in the picoampere range and must be amplified. However, several problems are associated with a large cathode area. As cathode area increases, both electrolyte and the anode deterioration also increase. Large cathodes also have a significant stirring artefact. Oxygen is reduced at such a rate that diffusion is unable to supply the reaction and a boundary layer starts to form outward from the cathode into the bulk of the test solution. To avoid this problem the sample must be stirred, or a thick membrane which limits the diffusion of oxygen can be installed on the POS. With a thick membrane however, the response time of the sensor is slowed significantly. Cathode diameters of < 25 μm can be entirely supplied by diffusion (Fatt 1965, Revsbech and Ward 1983). This permits the use of thin, fast response membranes (Fatt 1965, Fatt 1976).

Advantages

- study design, with long proven record, field and laboratory

- simple and inexpensive to change membranes
- allows continuous sampling of oxygen
- approved methods
- electrodes for wide range of applications (micro to high pressure)

disadvantages

- consumptive use of sample
- stirring artefact
- fouling issues during long deployment
- drift of signal as electrolyte and electrodes are consumed
- frequent calibrations required (daily)
- sometimes difficult to avoid trapping air bubble when changing membranes
- requires time to achieve 'polarization'

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ii) Luminescence dissolved oxygen sensors (LOD)

A probe used to determine the concentration of oxygen in situ. The sensor cap contains a coated membrane coated with a luminescent material. Light from a blue LED is transmitted to the surface where it excites the luminescent material causing it to luminesce. A red light is emitted as the material relaxes to it's pre-excitation state. A red sensor measures this emitted light as well as the time over which it occurs from when the blue light excited the coating. In the presence of oxygen, the luminescence is reduced as oxygen quenches the excitation. A relationship exists between time of excitation, quenching and the amount of oxygen present. A red light is typically also employed and flashed alternately between the blue light as an internal reference. Output is converted to typical % saturation or mg/L.

Each sensor is unique in its response to oxygen and the time to quenching, so they are calibrated at the factory and each is supplied with specific calibration values that must be entered - or read in for each particular 'cap'. Because there is a non-linear relationship at high oxygen pressures, constants in the relationships vary for each individual cap.

Advantages - little if any maintenance / easy to use
- no consumptive use of oxygen from the sample, and therefore no stirring artefact
- can be deployed for long time
- use of LED reduces power consumption
- no electrolyte to replace

Disadvantages - currently not approved via Standard Methods (see letters)
- sensors are very temperature sensitive during calibration
- caps are throw away and last approximately 1 year, necessitating replacement
- need to ensure correct calibration values are entered for cap that is in use
- need to take care of cap end

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http://www.ysi.com/parametersdetail.php?Dissolved-Oxygen-1 - need login (free) to get the 'We know DO' handbook. Very nicely summarized reading.

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