SEAWATER CHEMISTRY

Introductory Oceanography Laboratory

Ray Rector - Instructor

Seawater Chemistry Lab

Three Parts

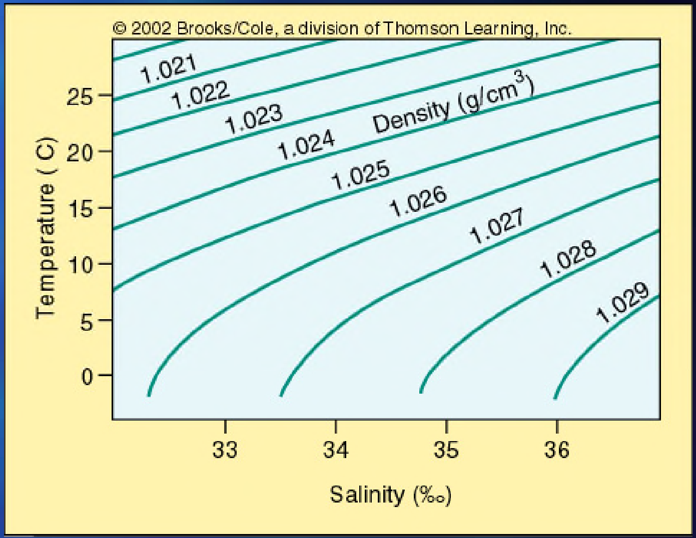
Part I: Explore the relationship between temperature, salinity & density of water masses and how it affects seawater mass movement

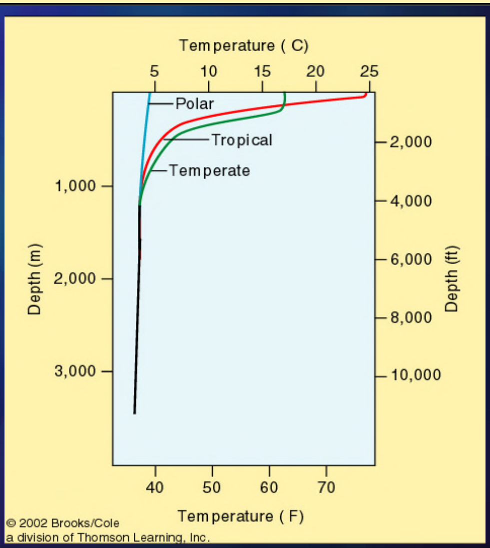
Part II: Measure and analyze how temperature and salinity affect conductivity of water samples and how to use conductivity to measure salinity

Part II: Measure and analyze dissolved oxygen content in fixed seawater samples using titration

Seawater Temperature-Salinity-Density Relationships

- **Density** of seawater is mainly a function of temperature and salinity
  - Pressure is also a factor
- Two samples of seawater can have the same density at different combinations of temperature and salinity
- Seawater tends to form stable density layers
  - Coldest saltiest at the bottom
  - Warmest, least saltiest at the surface
- Changes in the temperature and salinity of seawater are primarily controlled by surface processes



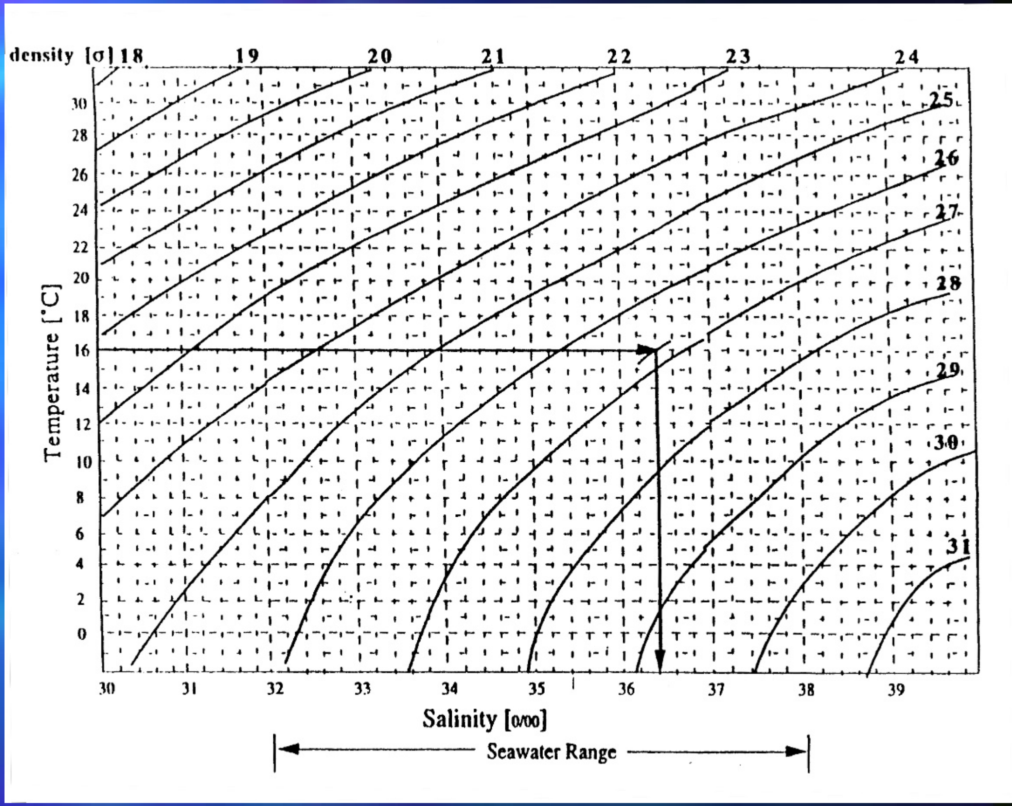


Salinity – Temperature - Density Chart

1) Find the measured temperature along the left side of graph

2) Find the measured density along the right side of the graph. Note: density lines are diagonal across graph

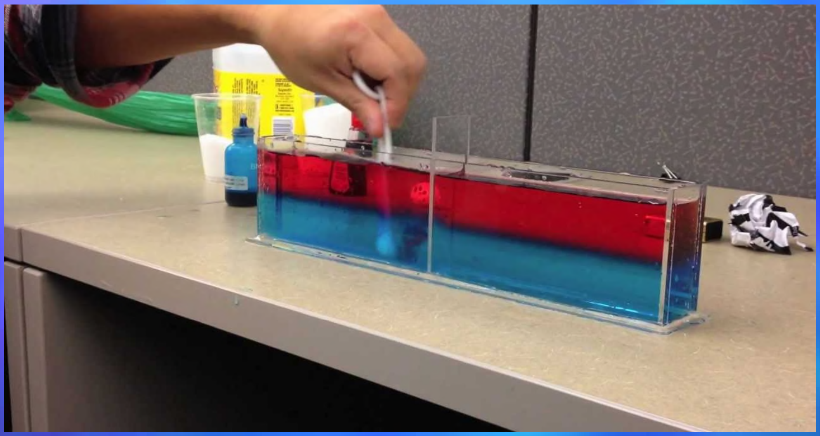
3) Follow the temperature line horizontally and the density line diagonally until they intersect

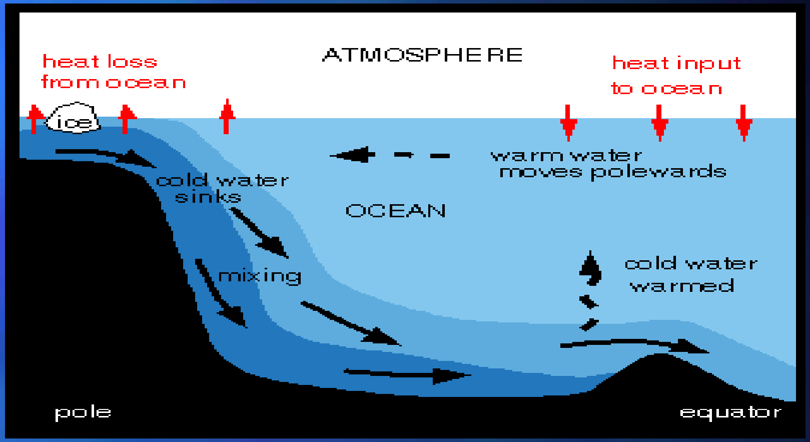


4) Drop a vertical line from intersection down to bottom of graph – read corrected salinity to nearest tenth of part per thousand

PART I: Density Flow Experiments:

Observing How *Temperature* and *Salinty* Affect Seawater Density and Movement



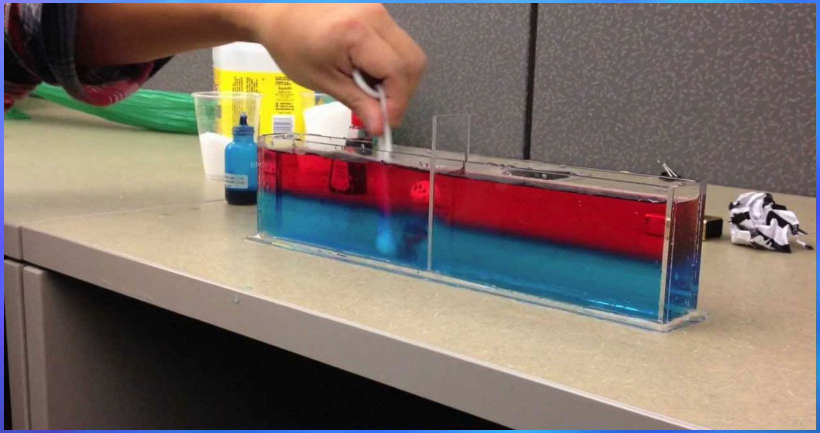


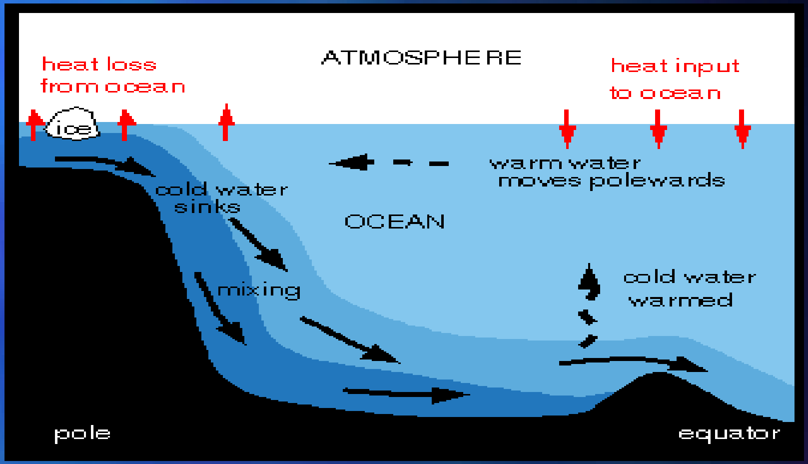
PART IA: Testing the *Temperature* Factor

1) Load two different temperature water masses – side-by-side
2) Color each water mass with different colored dye
3) Lift divider gate and observe: which flows over which? Why?
4) Put divider back in and mix one side. Repeat 3) Observe

PART I: Density Flow Experiments:

Observing How *Temperature* and *Salinity* Affect Seawater Density and Movement



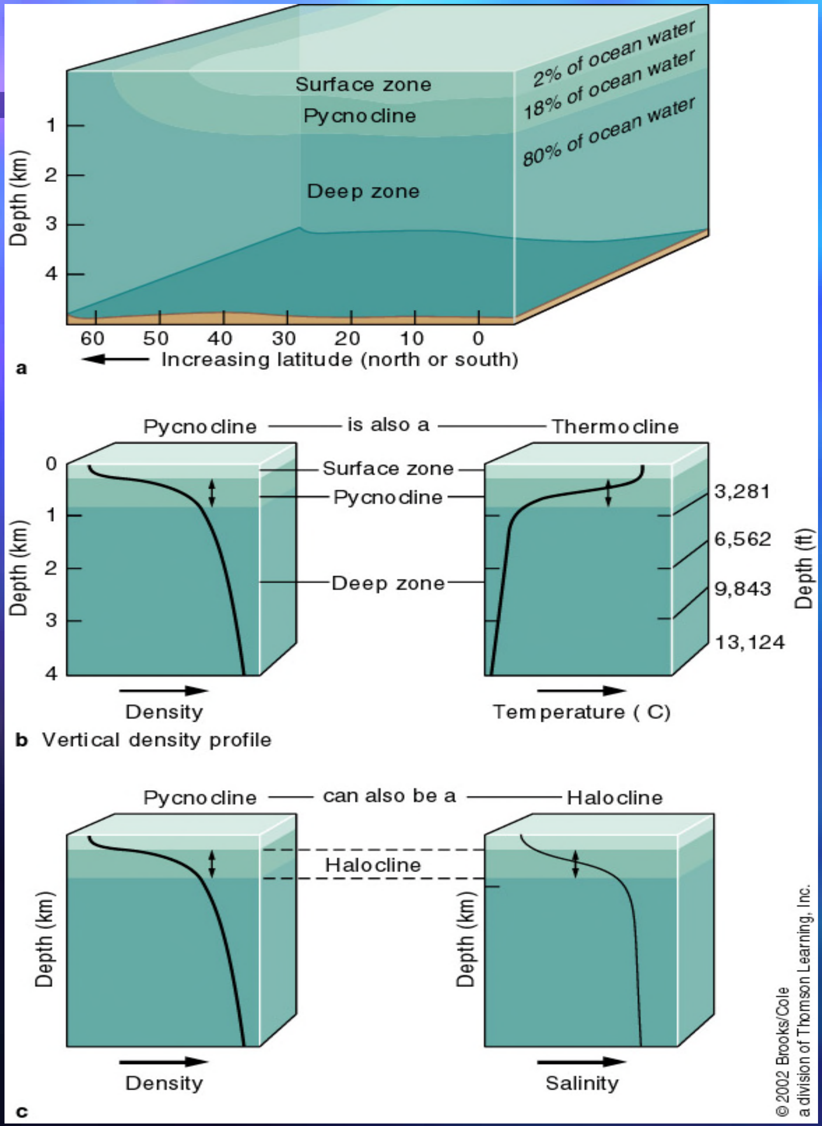


PART IB: Testing the *Salinity* Factor

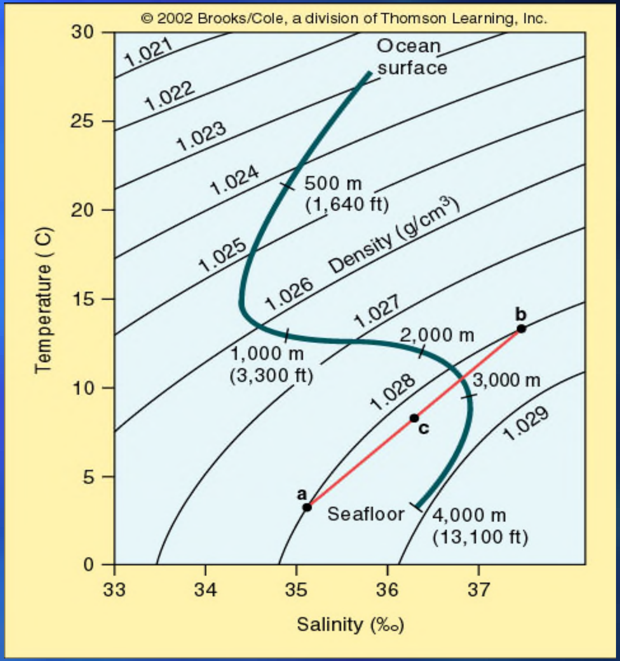
1) Load two different salinity water masses – side-by-side
2) Color each water mass with different colored dye
3) Lift divider gate and observe: which flows over which? Why?
4) Put divider back in and mix one side. Repeat 3) Observe

Thermohaline Circulation

Ocean Density-Stratification



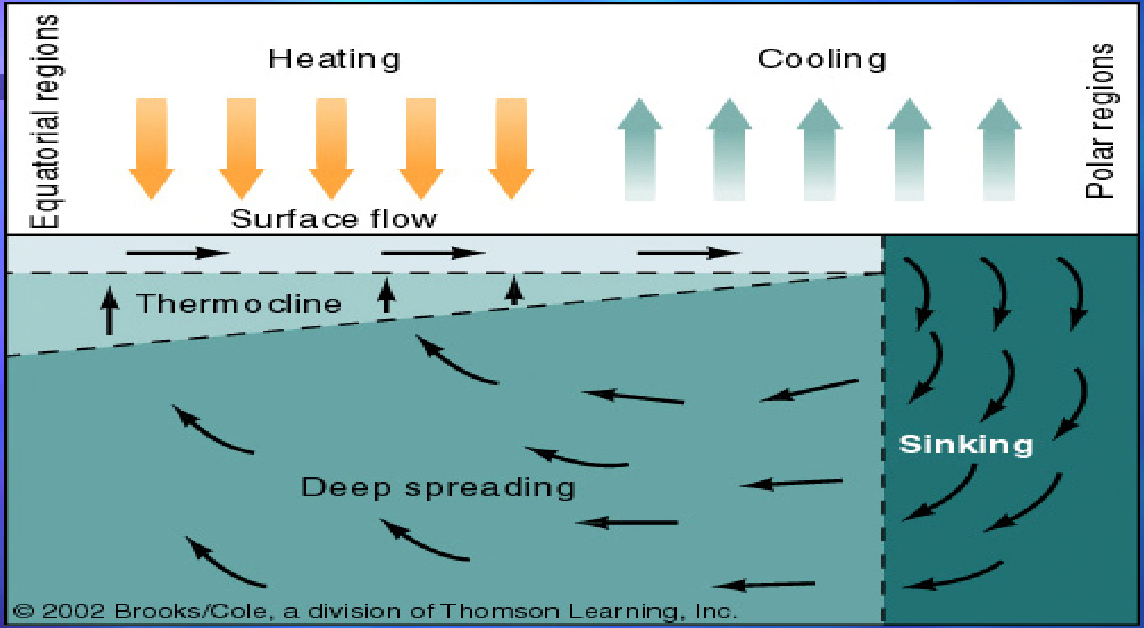
Temperature-Salinity (T-S) Diagram

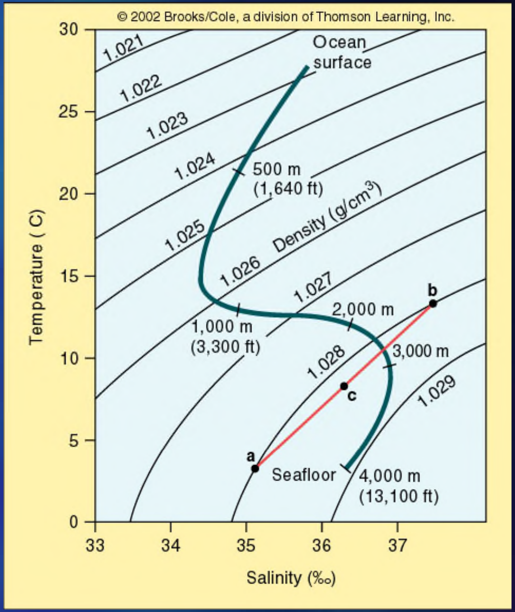


- ✓ Ocean column is density-stratified
- ✓ Ocean water masses are defined by their temperature and salinity
- ✓ Two water masses of different T and S can have identical densities
- ✓ Mixing two water masses of same density can produce a hybrid mass of lower density termed "caballing"

Formation and Movement of Deep Waters

ThermoHaline Circulation Model



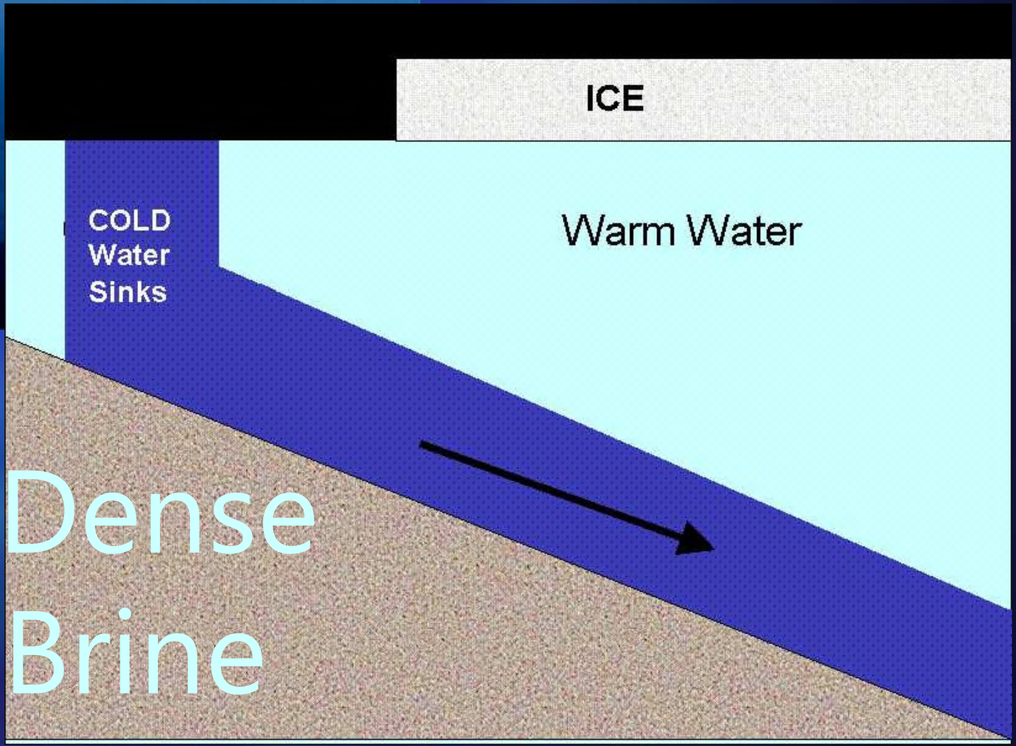


Temperature-Salinity Diagram

Density-driven Deep Ocean Currents

- ✓ Sinking of super-cooled, salty polar surface waters
- ✓ Very slow lateral deep water current flow
- ✓ Rising of mixed intermediate and deep waters
- ✓ Incorporation into mid- and low-latitude surface currents

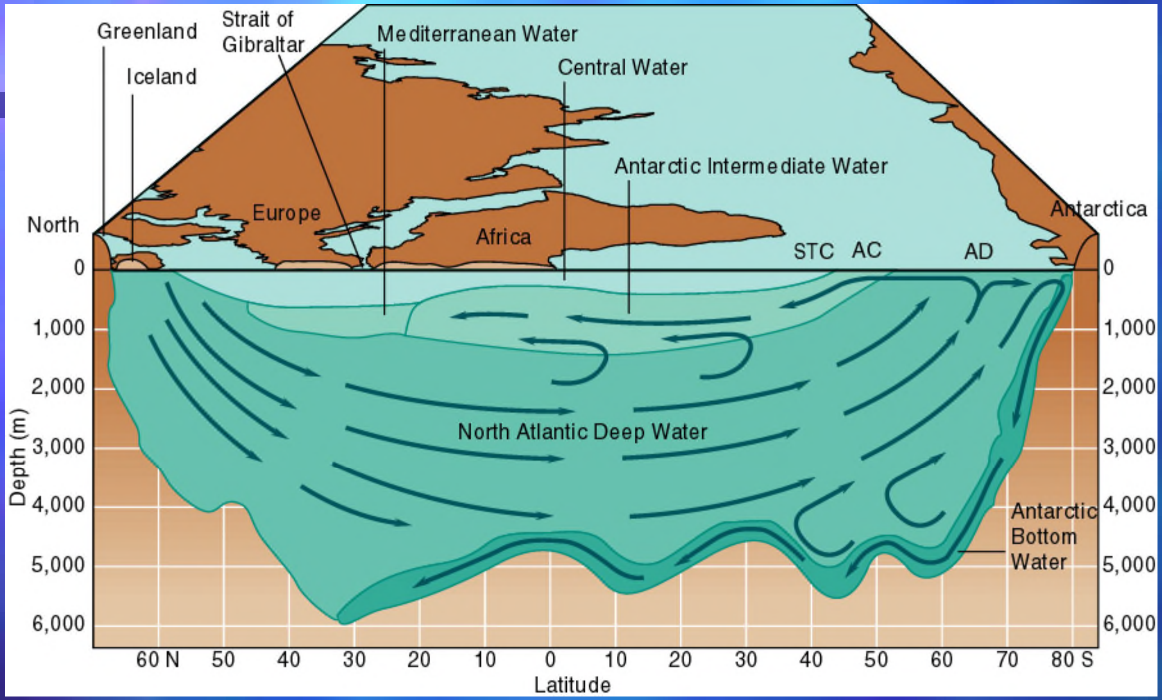
Formation of Polar Sea Ice & Brine

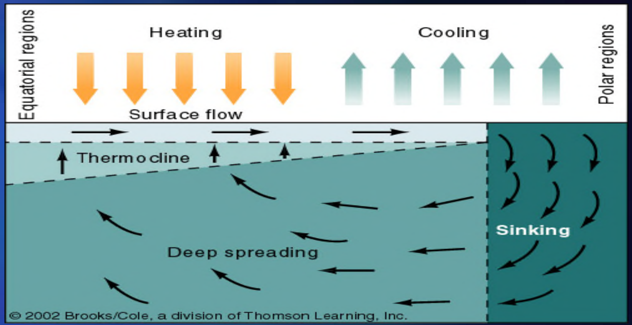


Sinking of Dense Seawater Brine

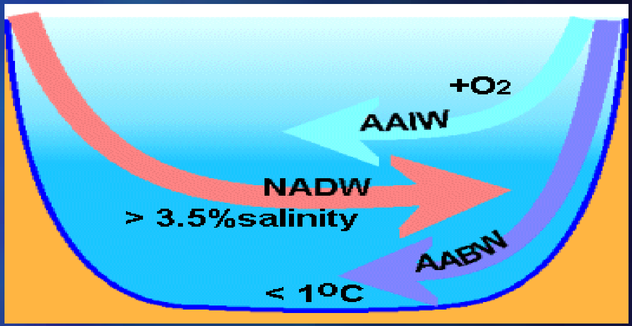
Deep Ocean Water Masses

Deep Circulation in the Atlantic Ocean





Density Circulation Model



Deep Ocean Water Masses

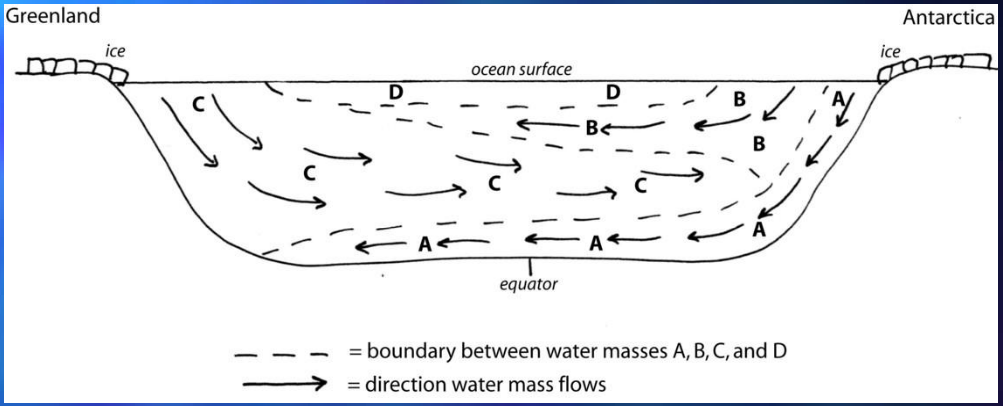
- ✓ Formation and sinking of polar Antarctic Bottom Water (AABW) and North Atlantic Deep Water (NADW) due to super-cooling of surface waters
- ✓ Formation and sinking of Antarctic (due to current convergence) and Mediterranean (due to hyper-evaporation) Intermediate Waters (AAIW and MIW)
- ✓ Very slow lateral deep water current flow and overlapping of water masses

Processes that Change Seawater Density

Processes that make water less salty: 1) _______and 2) _____
Processes that make water more salty:1) ______and 2) _____

Ocean's Major Seawater Masses

D. _________ ?
C. _________ ?
B. _________ ?
A. _________ ?



1) Each major seawater mass has a unique temperature and salinity
2) The seawater mass's temp/salinity profile controls its density
3) Seawater mass's density controls its vertical position in water column
4) Each major seawater mass has a name and position in ocean column
   - Name based on location of surface water origin

Seawater's Salinity

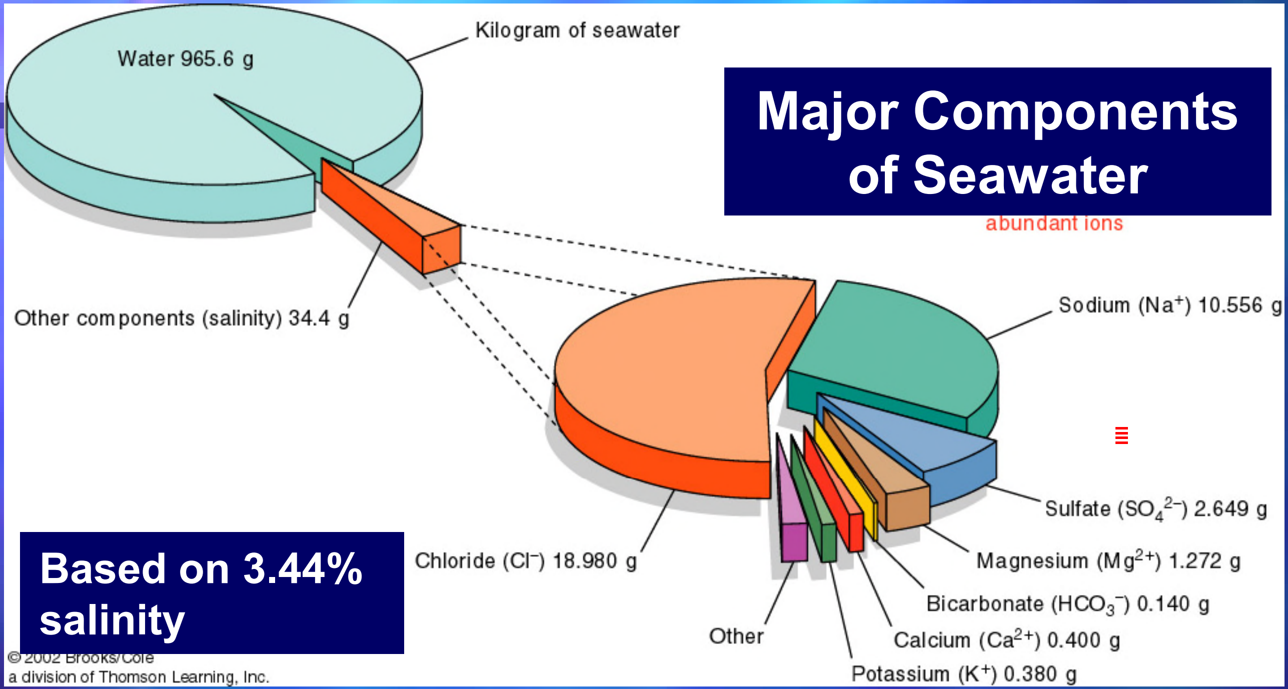
Key Concepts

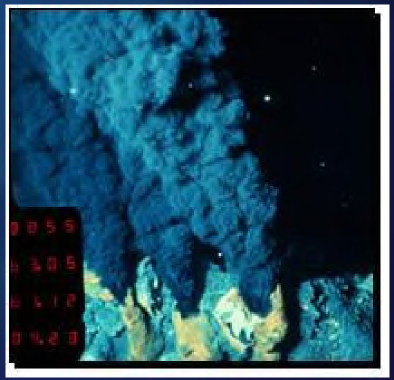
- Seawater is a complex solution of water, dissolved solids and gases, plus organics
- Salinity is the total quantity of dissolved inorganic solids and gases in water
- Salinity is expressed in parts per thousand ($^{0}/_{00}$)
- Salinity is determined by several methods

    1) Density 2) Refractometry 3) Conductivity 4) Chemically

    --- We will use the first two methods in this lab

Seawater: "Earth Soup"





Major Constituents

- Chloride
- Sodium
- Sulfate
- Magnesium
- Bicarbonate
- Calcium
- Potassium

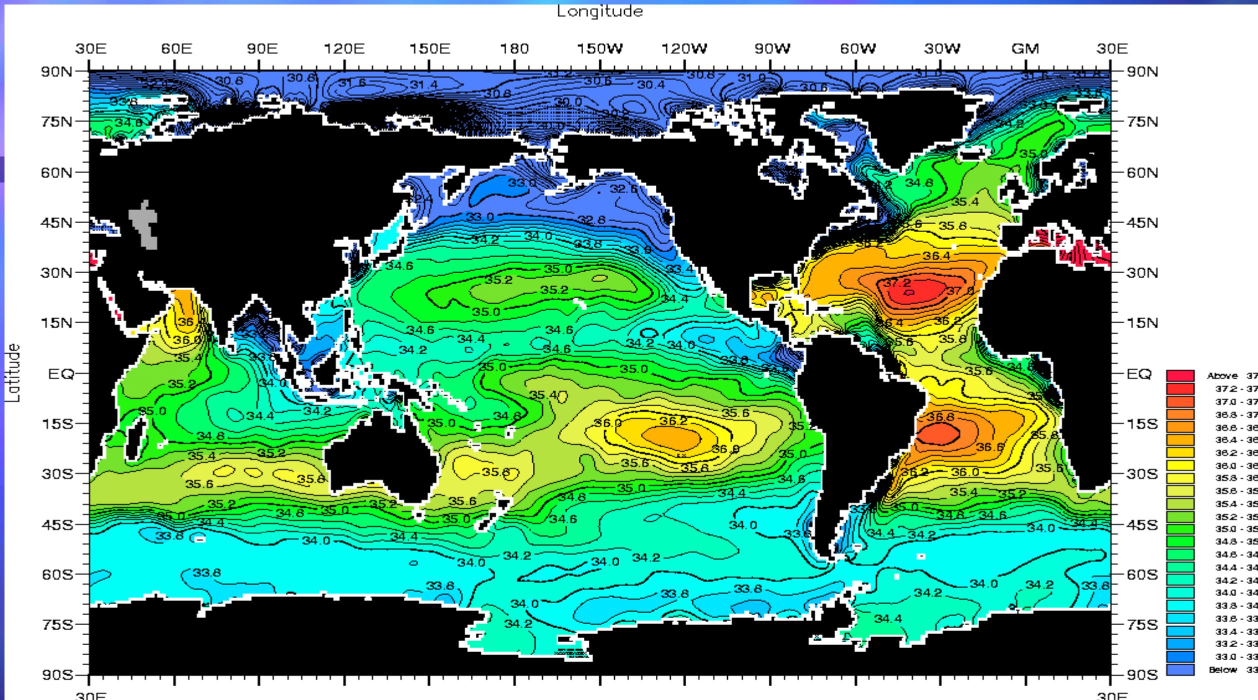
Minor Constituents

8. Bromine
9. Strontium
10. Boron
11. Fluorine

Trace Elements

Fe, Al, Mn, Cu, Ni, P, Zn

Ocean Surface Salinity



(Annual mean salinity (PSS) at the surface)

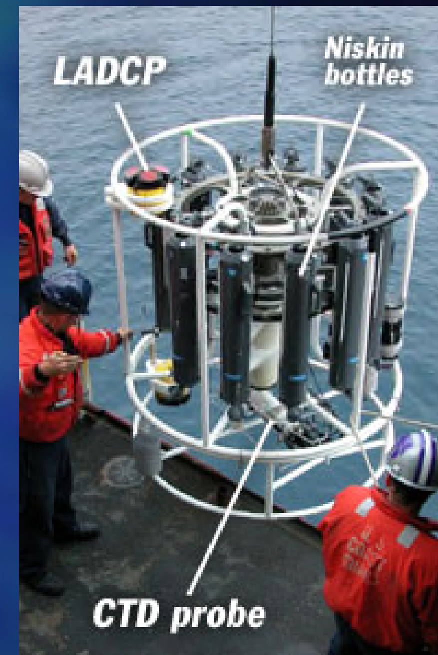
Sea Surface Salinity

- Saltiest in mid-latitude Atlantic, Pacific and Mediterranean
- Freshest in high latitudes

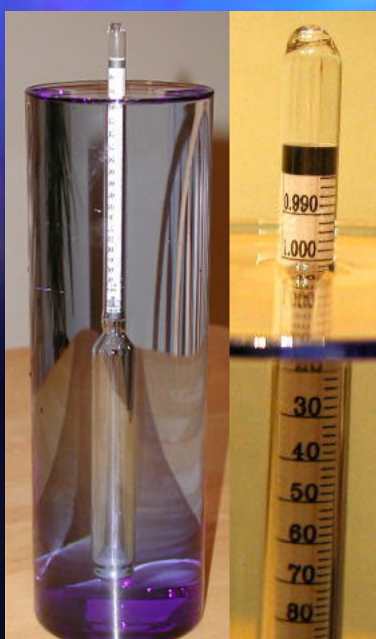
Salinity-Modifying Processes

- Freezing, Evaporation, Precipitation, Melting, Runoff
- Processes are Climate/Latitude-dependent

Measuring Ocean Salinity



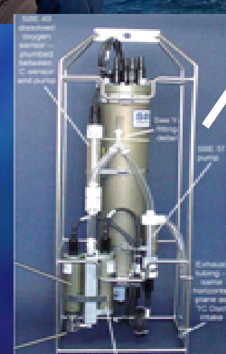
Various Means Available



PART II: Measuring Seawater Salinity

Methods Used to Measure Salinity

1) Seawater Density and Temperature
2) **Conductivity**
3) **Refractometry**
4) Chlorinity
5) Distillation



Conductivity-
Temperature-
Depth Probe

Measuring Salinity with a Conductivity Meter

Using a Conductivity Meter

1) Conductivity of a seawater sample is a function of the samples temperature and salinity

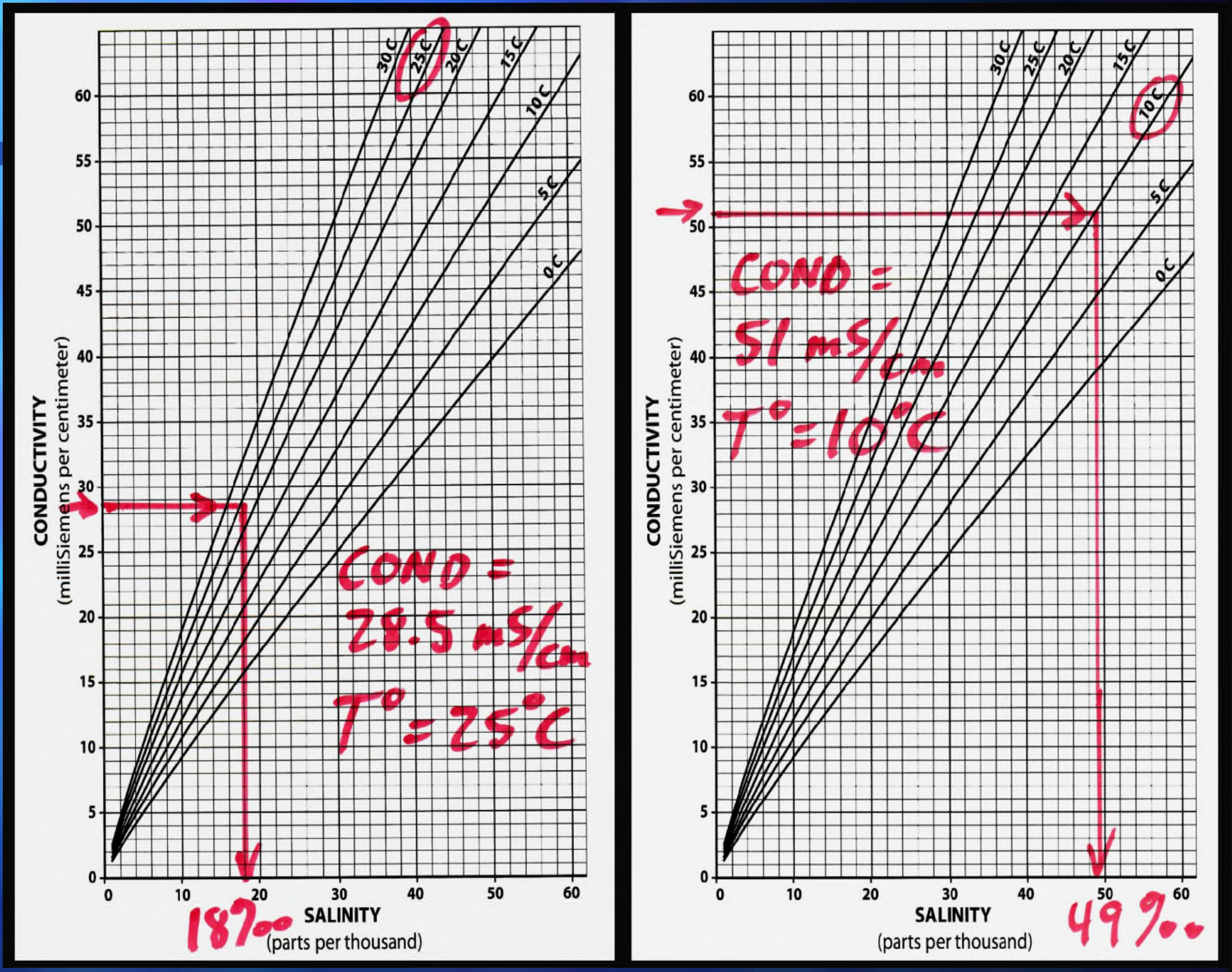
2) Measure conductivity and temperature using a hand-held conductivity meter.

3) Graduated units are in milli- and micro-seimens.

4) Use the C-T-S graph to estimate the corrected salinity of the sample

Conductivity – Temperature - Salinity

1) Measure sample's conductivity
2) Determine sample's temperature
3) Find the associated salinity for specific pair of conductivity & temperature along the bottom of graph

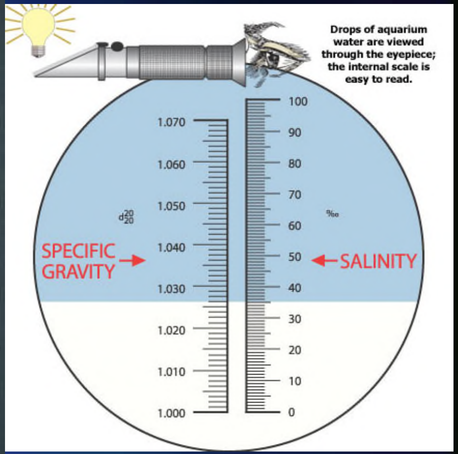


Two Examples of Determining Salinity

Measuring Salinity with a Refractometer

1) Refractometer needs a a bright light source

2) Add a few drops of sample onto the test surface of meter



3) Measure salinity at the line separating the blue from the white field

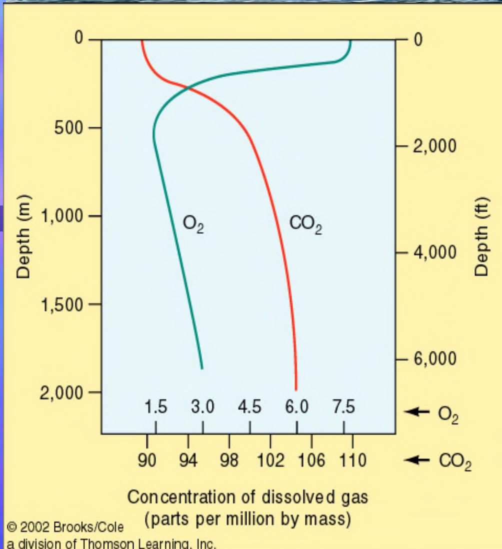
1) Graduated units are in either grams per milliliter or parts per thousand

Seawater's Dissolved Oxygen

Major Concepts

- Seawater has 3 major dissolved gases: nitrogen, oxygen, and carbon dioxide.
- Dissolved Gases measured in milliliters per liter (ml/l)
- **Origin** of Dissolved Oxygen in Seawater
  - Byproduct of *Photosynthesis by Phytoplankton*
- **Amount** of Dissolved Oxygen in Seawater Varies
  - **Biological factors:** *Photosynthesis (+) and Respiration (-)*
  - **Physical factors:** *Water Temperature and Pressure*
- Dissolved Oxygen can be measured chemically
- Use modified *Winkler Method* to quantify the amount of dissolved oxygen in unknown seawater samples

Seawater – Dissolved Oxygen



Major Gases in Seawater and Air

Gas	Percent of Gas in Atmosphere, by Volume	Percent of Dissolved Gas in Seawater, by Volume	Concentration in Seawater in Parts per Million, by Mass
Nitrogen (N_2)	78.08%	48%	10–18 ppm
Oxygen (O_2)	20.95%	36%	0–13 ppm
Carbon dioxide (CO_2)*	0.035%	15%	64–107 ppm

Enrichment of Oxygen in Seawater

1. Marine Plants (Photosynthesis)
2. Surface mixing with atmosphere
3. Temperature (Decrease)

Depletion of Oxygen in Seawater

1. Marine Animals (Respiration)
2. Temperature (Increase)
3) Pollutants

Factors Controlling Dissolved Oxygen Content

1. Biological Factors
   - ✓ Photosynthesis = increase
   - ✓ Respiration = decrease
2. Physical Factors
   - ✓ Water Temperature
   - ✓ Water Agitation (Mixing)
   - ✓ Water Pressure
   - ✓ Stagnation (Lack of mixing)

PART III: Seawater Titration – Dissolved Oxygen

Modified Winkler Method

1. “Fix” Seawater Samples

2. Prepare and Titrate a “Standard” Sample

3. Titrate “Standard” sample

4) Titrate “Unknown” samples

5) Use Titration formula to determine dissolved gas content for Unknown samples

The 3-Phase Winkler Method for Determining Amount of Dissolved Oxygen in Seawater

The procedure is composed of several phases:

Phase 1 -- "Fixing"

- ✓ Oxygen in the sample is "fixed" by reagents that we add to the sample bottle, to form a chemical complex between the free oxygen and some of the reagents

Phase 2 -- "Standardization"

- ✓ Determine theoretical saturation of oxygen of known "standard" sample from comparing its temperature to those found in the Oxygen Table.

Phase 3 -- "Titration"

- ✓ The amount of the complex (which reflects the original concentration of dissolved oxygen in the sample) is quantified by slowly adding a "neutralizing agent" until all the complex molecules disappear.
- ✓ This process is called "titration", the neutralizing agent is called "titrant", and the amount of titrant used reflects the original oxygen concentration in the sample.

The 3-Phase Winkler Method for Determining Amount of Dissolved Oxygen in Seawater

Phase 1 -- "Fixing" the Dissolved Oxygen in Seawater Sample

- Sensitivity to atmosphere requires us to "fix" oxygen concentration in water samples to prevent gain or loss of dissolved oxygen.
- Adding $MnSO_4$ and KI to sample will turn dissolved O_2 into stable compound along with the formation of an iodide precipitate.
- The amount of dissolved iodine ion released from dissolving of the solid iodine precipitate in the "fixed sample by reaction of adding HCl acid solution equals the amount of dissolved oxygen in sample.

Phase 2 -- "Standardization"

- Determine theoretical saturation of oxygen of a known sample. .
- The known sample must be titrated to establish a "standard". .

Phase 3 -- "Titration"

- Measures the amount of dissolved iodine in sample, which is equivalent to the amount of dissolved oxygen in sample. This is done with a carefully measured addition of a thiosulfate solution (the titrant).
- Titration results gives you the proportion between the amount of thiosulfate used to the amount of dissolved oxygen in the "standard"

The 3-Phase Winkler Method

Phase 1: "Fixing" the dissolved oxygen in sample

Step 1 - Add 20 drops (1ml) of manganese sulfate solution (*labeled "**A**"*) to your fully-filled sample bottle

Step 2 - Add 20 drops (1ml) of potassium iodide solution (*labeled "**B**"*) to your fully-filled sample bottle

Step 3 - Cap sample bottle over a dish and shake well –

$MnSO_4 + 2\ KOH \longrightarrow Mn(OH)_2 + K_2SO_4$ (white)

If there is any ***DO*** in the water a second reaction between the Mn(OH)2 and ***DO*** occurs immediately to form a brownish manganese oxide solid:

$2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2$ (brown)

Step 5 - Add 20 drops (1ml) of sulfuric acid solution (*labeled "**Acid**"*) to your fully-filled sample bottle – **BE CAREFUL – It BURNS**

Step 6 - Cap sample bottle over a dish and shake well – wipe excess

$2MnO(OH)_2 + H_2SO4 \longrightarrow 2Mn(SO4)_2 + 6H_2O$

Amount of iodine exactly equivalent to the amount of dissolved oxygen present sample

$2Mn(SO_4)_2 + 4KI \longrightarrow 2MnSO_4 + 2K_2SO_4 + 2I_2$

Phase I: The 3-Phase Winkler Method

"Fixing" the dissolved oxygen in sample

Step 1 - Add 20 drops (1ml) of manganese sulfate solution (*labeled "**A**"*) to your fully-filled sample bottle

Step 2 - Add 20 drops (1ml) of potassium iodide solution (*labeled "**B**"*) to your fully-filled sample bottle

Step 3 - Cap sample bottle over a dish and shake well -

Step 4 - Add 20 drops (1ml) of sulfuric acid solution (*labeled "**Acid**"*) to your fully-filled sample bottle – **BE CAREFUL – It BURNS**

Step 5 - Cap sample bottle over a dish and shake well – wipe excess

The 3-Phase Winkler Method

Phase 2: Standardization Procedure:

"Standardization" defined: *Calibrating the amount of thiosulfate solution to a known amount of the dissolved oxygen in a "standardized" sample called the "Standard"*

Standardization Must Be Done Prior to Testing Unknowns

Step 1) Measure and Record Temperature of a fully aerated fresh water sample of known temperature.

Step 2) Determine theoretical saturation of oxygen of known "standard" sample from Oxygen Table

Step 3) "Fix" your known standard sample (See Phase 1 procedures)

Step 4) Titrate your "fixed" known sample (See Phase 3 procedures)

- Titration results of your "standard" gives you the *proportion* between the amount of thiosulfate used to neutralize the sample to the amount of dissolved oxygen in the "standard"

Calibration Using a Standard Sample

Step 1: Measure Temperature of Fresh Water Sample

-- Record This temperature in calibration table

Step 2: Determine the Theoretical Maximum Oxygen Content of Known Fresh Water Sample

- Use the Temp-Oxygen Chart for the known standard sample

Temperature (°C)	Oxygen (mL/L)	Temperature (°C)	Oxygen (mL/L)
0	10.22	13	7.37
1	9.44	14	7.21
2	9.66	15	7.05
3	9.39	16	6.90
4	9.14	17	6.75
5	8.90	18	6.61
6	8.68	19	6.48
7	8.47	20	6.36
8	8.27	21	6.23
9	8.07	22	6.11
10	7.88	23	6.00
11	7.71	24	5.89
12	7.54	25	5.77

Values extracted from Murray, C.N., and J.P. Riley (1969), The Solubility of Gases in Distilled Water and Seawater: II. Oxygen, Deep Sea Research, 16: 311-320.

Theoretical oxygen saturation values

CALIBRATION TABLE

Calibration	Water Temp	Theoretical Oxygen	Start Point	End Point	mLs of Thiosulfate
1	______	________	________	________	________
2	______	________	________	________	________
				Average =	________

Standard known sample titration data chart

Standardization Procedure for Comparing Known Oxygen Content Sample to an Unknown Sample

Before testing unknown samples we need to know how much thiosulfate titration solution it takes to indicate a given amount of dissolved oxygen in a known sample, called the "*Standard*"

Modified Winkler Method

Phase #1 – "Fixing"
Phase #2 – "Standardization"
Phase #3 – "Titration"

CALIBRATION TABLE

Calibration	Water Temp	Theoretical Oxygen	Start Point	End Point	mLs of Thiosulfate
1	______	________	_______	_______	________
2	______	________	_______	_______	________
				Average =	________

❖ **We must titrate our standard sample before titrating the unknowns**

Calibration Using a Standard Sample

✓ Use this table for calibrating your "Standard"

✓ Use this information in the Unknown formula

The 3-Phase Winkler Method

Phase 2: "Titration": *Measured amount of dissolved iodine equivalent to amount of dissolved oxygen in sample*

Step 1 - Measure 25 ml of sample into 50 ml plastic graduated cylinder

Step 2 - Transfer 25 ml sample into a 50 ml Erlenmeyer flask

Step 3 - Fill 50 ml burette with thiosulfate solution – No bubbles; Lower tip slightly into flask

Step 4 - Record initial level of thiosulfate (in ml) as "***START POINT***" in table

Step 5 - Begin titrating until the sample color begins to fade to pale yellow.

Step 6 - Add 5 drops of starch to sample – it will turn a dark blue color

Step 7 - Continue titrating SLOWLY (one drop at a time) until the sample solution becomes colorless. Stop: This is your "***END POINT***"

Step 8 - Record final level (end point) of thiosulfate solution in buret (in ml) in the calibration table

Step 9 - Note difference between the "start point" and the "end point", and record the number of milliliters require to turn your sample clear

Titration Data for Unknown Samples

DISSOLVED OXYGEN IN UNKNOWN SAMPLES

	Start Point	End Point	mls of thiosulfate	Oxygen Content (mL / L)
Unknown 1 (lagoon surface)				
Unknown 2 (lagoon deep)				
Unknown 3 (harbor)				
Unknown 4 (beach)				

Final Step: Use Equivalence Formula below to determine the dissolved oxygen content of your unknown sample

$$\text{Unknown } [O_2] \text{ mL/L} = \frac{[\text{ theoretical } O_2 \text{ of standard }] \times [\text{ ml thiosulfate in unknown }]}{[\text{ averaged ml thiosulfate used in aerated standard }]}$$

Next Week's Lab – Lab Midterm Practical Exam

Preparation

- The Study Guide is all your completed lab worksheets
- Study all the online lab PowerPoint's
- An example of the test will be posted online
- Bring a Scantron card, #2 pencil, and calculator
- You are allowed to use your lab worksheets during test
- A strictly individual effort while taking test
- You have the entire three hours to take the test

Next Regular Lab – Wave Fieldtrip

Oceanside Pier – Oceanside, CA

Preparation

- We meet at entrance to O-side Pier at @ 2:15 pm
- Wear Appropriate Beach Attire – you may get cold, sandy, and/or wet!
- Bring a calculator and a clipboard
- Study Textbook on Ocean Swell and Longshore Currents
- Study lab manual on waves and shoreline currents
- Do the Swell/Wave Pre-lab – due at start of lab

Next Week's Lab – Tidepools Fieldtrip

Tide Beach Park – Solana Beach CA

Preparation

- We meet at entrance to Tide Beach Park at @ 2:15 pm
- Wear Appropriate Beach Attire – you may get cold, sandy, and/or wet!
- Bring a calculator and a clipboard
- Study Textbook on Tidepool Marine Life
- Study lab manual on tide zones and tidepool marine life
- Do the Tidepool Pre-lab – due at start of lab