LAB 6: EXPERIMENTS ON LAB 5
NAME OF THE GROUP MEMBERS

1
2
3
4
5

Things that are needed for the experiments
- Salt
- Beakers
- Pipette
- Petri dish
- Graduated cylinder
- Deionized water
- Thermometer
- Dropper
- Burette
- Stirrer
- AgNO3 solution (50 gm of AgNO3 dissolved in 1000mL of deionized water)
- K2CrO4 solution (3.5gm of K2CrO4 dissolved in1000mL of deionized water)

MEASUREMENT OF SALINITY BY VARIOUS EXPERIMENTAL METHODS

Introduction
Salinity is a measure of the total dissolved salts in seawater. This sounds simple enough, but measuring salinity becomes a problem when we realize that some of the salts do not simply dissociate into ions but chemically react with water to form complex ions, and some of the ions include dissolved gases such as CO_2 (which converts to carbonic acid, H_2CO_3, bicarbonate, HCO_3^-, and carbonate, CO_3^{2-}).

        Duxbury (1971) defines salinity as:
"The total amount in grams of solid material dissolved in 1 kilogram of seawater when all the carbonate has been converted to oxide, all of the iodine and bromine have been replaced by chlorine, and all the organic matter has been completely oxidized."

For this laboratory we will use a simpler definition: *The total amount in grams of solid material dissolved in 1 kg of seawater.*

Normally, salinity is expressed in parts per thousand (ppt), often written as $^o/_{oo}$. It is also sometimes abbreviated as per mil, much the same as parts per hundred is abbreviated as percent (%). For example, if you had 1000 g of seawater that contained 35 grams of dissolved salt, you would have a 3.5% salt solution or a salinity of 35 parts per 1000 ($35^o/_{oo}$).

lab 6 Experiments:

$$percent\ solution: \quad \frac{35\ grams\ salt}{1000\ grams\ H_2O} \times 100\% = 3.5\%$$

$$per\ mil\ solution: \quad \frac{35\ grams\ salt}{1000\ grams\ H_2O} \times 1000‰ = 35‰$$

In this laboratory our salt water is not seawater, it is a solution of table salt (NaCI) dissolved in de-ionized water. We only have two elements of the 11 commonly found in seawater (and the dozens that are present in trace amounts); however, the methodologies we use here will work for natural seawater as well as for our artificial seawater.

Why is the sea salty? Why do we care?
The salt in the ocean comes primarily from the weathering of rocks on land. When rocks are exposed at the surface of the Earth, minerals are weathered chemically to produce various solid compounds as well as free ions such as calcium (Ca_{2+}), potassium (K_+), and sodium (Na_+). Volcanic eruptions produce CO_2, hydrochloric acid (HCl), and sulfur dioxide (SO_2), all of which are soluble in water. These solutes are brought to the ocean by precipitation and by river transport. Evaporation of water concentrates these materials, bringing the salinity of the oceans well above the salinity found in rivers and lakes. Some materials (such as calcium and potassium) are gradually removed from the ocean by organisms that use them as nutrients. Other materials are lost through sediment interactions: the sediments at the ocean's bottom behave much like a water filter, adsorbing various ions associated with salinity and locking them away. These processes of adding salt to the oceans, concentrating it through evaporation, and removing it through various chemical and biochemical processes, have been active on Earth for billions of years; the average salinity of the ocean is therefore a function of the rates of these various processes, and has changed little through Earth's history. The water's salt content is one of the primary reasons that study of the ocean is different from the study of fresh water lakes (known as limnology).

Water circulation is also affected by salinity. In estuaries, fresh water can "float" on saltier, denser ocean water and even set up a current pattern which is based on the difference in density between the two water types. In the deep ocean, high salinity water is often the densest and will sink and flow along the ocean floor under the influence of gravity. Physical oceanographers, by knowing the salinity and temperature fields of the ocean, can make predictions about the velocity and direction of these density-driven currents.

Measuring Salinity
In this laboratory we will investigate five analytical methods for determining salinity. Some methods are straightforward and some are complicated, some are simple but imprecise and some are difficult but precise. As you perform these tests, pay particular attention to the results – the different methods produce different levels of precision and accuracy, since the components of salinity vary in their effects on the different measurement

techniques. Care in your technique should produce repeatable results, but do not expect that each technique will produce exactly the same numbers.

Methods of salinity determination:

- Evaporation of seawater
- Conductivity of seawater
- Measurement of water density by hydrometer
- Refraction of light through seawater
- Titration of the chloride ion (Cl-)

For each method you will be measuring the salinity of two samples: one known sample, whose salinity is $35^o/^{oo}$; and a sample A whose salinities are to be determined by you.

Fill two beaker with water having salinity (35⁰/∞) _and unknown A_

A. Determination of salinity by evaporation

As we have defined salinity as the total mass of dissolved salts (measured in grams) in one kilogram of seawater, the most straightforward way to measure salinity is to measure exactly one kilogram of seawater, evaporate the water, and weight the salt that precipitates out. Evaporating a full kilogram of water would take more time than we have today however, so we will shorten the process by evaporating a small fraction of a kilogram.

- Label two beakers for the two samples: 35o/∞, and unknowns A.

- Label two Petri dishes (with the same labels as the sample beakers) and weigh each to the   nearest 0.01 gram. Record the masses of the dishes in Table A on the answer   sheet.

- Using a pipette, transfer about 10 mL of each of the two salt solutions to the corresponding labeled Petri dishes. Weigh each Petri dish with the water to the nearest 0.01 gram and record the masses on the answer sheet. Determine the mass of the water samples by subtracting the weight of the dish only, and record the masses.

- Carefully bring the Petri dishes to the back of the room, where your instructor will place them in the drying oven. Leave them in the oven until dry – this will take the majority of the lab period. You will be doing exercises B through E while waiting for the samples dry.

- Once the samples are dry allow them to cool for a few minutes, then weigh each Petri dish and record the results on the answer sheet (dish + salt). Subtract the masses of the dishes to determine the mass of each of the salt samples and record the results on the answer sheet.

- Determine the salinity of each sample using equation 1 (below). Record your answers on the answer sheet.

$$Salinity = \frac{weight\ of\ salt}{weight\ of\ water} \times 1000\text{‰} = \frac{0.39\ grams}{10.60\ grams} \times 1000\text{‰} = 37\text{‰}$$

B. Determination of salinity by electrical conductivity

Take a conductivity meter reading of each sample to compare the relative salinity of each sample. Conductivity is a measure of the ability of water to pass an electrical current and is affected by the presence of dissolved solids. As the level of the total dissolved solids (TDS) rises, the conductivity (electrolytic activity) will also increase.

If you drink seawater you will become dehydrated. The sodium concentration in sea water is several times higher than the concentration in blood. The body has to excrete the extra salt in the urine and more water is required to get rid of the salt than was in the sea water in the first place. Therefore, you will literally "dry up" drinking sea water as your neuron-muscular reactions become erratic. Some sea birds, like penguins, sea gulls and albatross, can drink sea water but they have special glands in their heads to excrete the excess salt. Think about your salty tears.
In Miami saltwater has intruded into the water supply of some coastal communities. Coconut Grove is an example of a community where the groundwater is unfit for human consumption due to elevated levels of dissolved solids from seawater intruding into the aquifer.

NOTE: It is important to dilute the sample using only deionized water, as tap water contains ions such as sodium and calcium that will alter the salinity of your sample and skew the results of the experiment.

Conductivity meters can be made to measure a variety of salinity conditions. Unfortunately devices that can handle the high salt concentrations found in the world's oceans (and in today's lab) are quite costly. The device we will be using today is only accurate at much lower salinities so we must dilute our samples by a known amount in order to make our measurements.

lab 6 Experiments:

- Measure the water's temperature (allow 30-60 seconds for the thermometer to equilibrate) and record the temperature in Table B on the answer sheet.

- Measure the electrical conductance of the water (the units of conductance are Siemens/cm – the reciprocal of electrical resistance). Place the meter into the beaker (be sure that the probe sensors are completely submerged) and allow at least 30 seconds for the readout to equilibrate. Record the conductance on your answer sheet.

Multiple	Name	Symbol	Multiple	Name	Symbol
10^0	**siemens**	S			
10^1	decasiemens	daS	10^{-1}	decisiemens	dS
10^2	hectosiemens	hS	10^{-2}	centisiemens	cS
10^3	kilosiemens	kS	10^{-3}	millisiemens	mS
10^6	megasiemens	MS	10^{-6}	microsiemens	µS
10^9	gigasiemens	GS	10^{-9}	nanosiemens	nS
10^{12}	terasiemens	TS	10^{-12}	picosiemens	pS

NOTE: The conductivity meter is a valuable instrument – handle it carefully. Have a small beaker of deionized water at your station and use it to rinse the probe sensors between measurements.

- Repeat steps for the unknown samples A, recording the temperatures and conductivities in Table B on the answer sheet.

NOTE: Since we have only included lines for temperatures at 5 degree increments, you will be expected to interpolate your results. For example: if your water temperature was 17.5°C, use your measured conductivity and the graph to determine the salinity if the water were 20°C and if the water were 15°C. As 17.5°C is halfway between 15°C and 20°C, the salinity value is halfway between the two values you determined for these temperatures
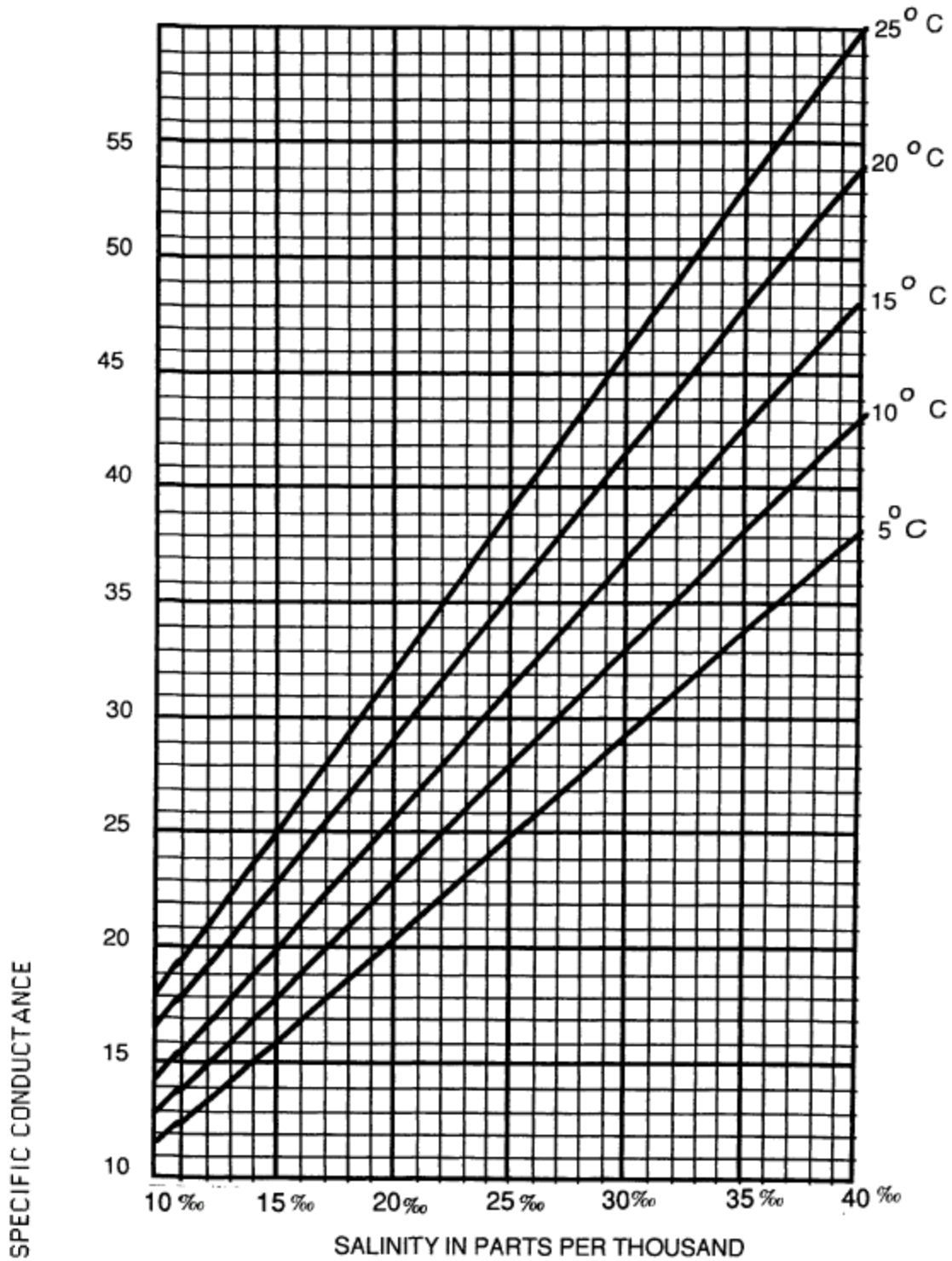
Figure Three: Conductivity as a function of salinity and of temperature. Lines show the relationship between conductivity and salinity at 5 degree increments between 15°C and 25°C.

## C. Determination of salinity by density using a hydrometer

.Hydrometer are devices designed to measure fluid density. The hydrometer's mass is precisely fixed and it is concentrated at the bottom of the tube (like a buoy) so that the hydrometer will always float upright. The narrow stem is precisely graduated so that as the device sinks and displaces its own mass, the level to which it sinks is equal to the seawater density (Figure Four). As density of the seawater increases, the volume of the displaced seawater decreases (the hydrometer sinks less in the higher density fluid).

FRESH WATER   LOW   MEDIUM   HIGH
                     SALINITY   SALINITY   SALINITY
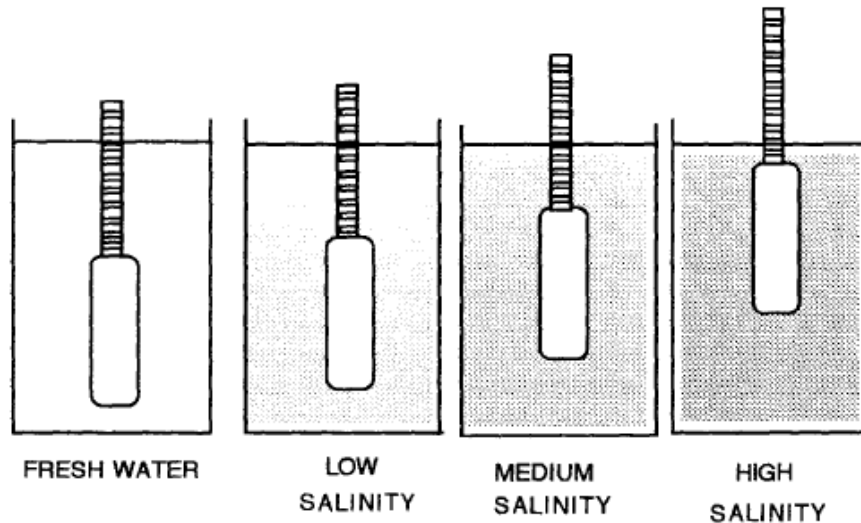
Figure Four: Hydrometer function. As the density of the fluid increases, the hydrometer displaces less water. Since the upper tube is very narrow this difference in volume corresponds to a significant change in depth. The density of the fluid can be read from the graduations on the stem.

Figure Five below shows a close-up view of the hydrometer stem: there are labeled divisions representing 5/1000 gram/mL (1.010, 1.015, and so on); these are divided into five parts (1/1000 g/mL) by secondary unlabeled divisions; these are divided into halves (0.5 g/mL) by tertiary unlabeled divisions. If you are careful using this device you can determine density to a precision of 5 parts in 10,000 (1/2 milligram/mL).

lab 6 Experiments:
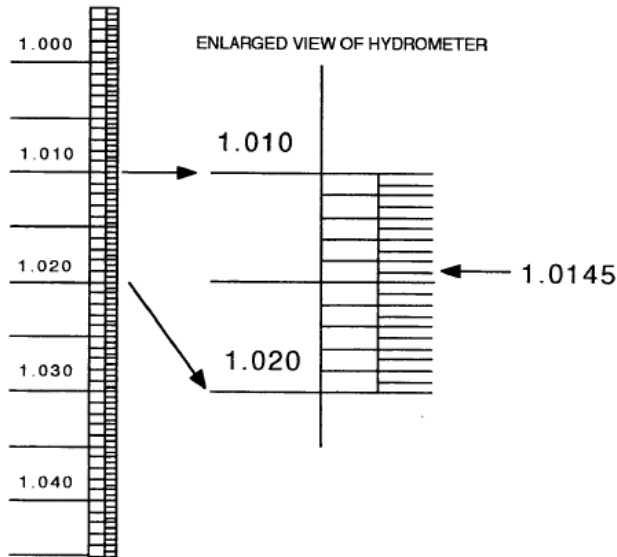
Figure Five: Reading density from the hydrometer. The major lines are labeled to 5 parts in 1000, the secondary unlabeled lines to 1 part in 1000, and the tertiary unlabeled lines to 5 parts in 10,000. This device can be read to the fourth decimal place.

- . Pour approximately 220-240 mL of water from the known (35o/oo) salinity sample
- into a 250 mL graduated cylinder.

- . Measure and record the water temperature in Table C on the answer sheet.

- Carefully lower *(do not drop)* the hydrometer in the graduated cylinder until it floats. If there is not enough water to allow the hydrometer to float, more water can be added until the hydrometer rises from the bottom.

- . Read the density of the water from the graduated lines on the hydrometer and
- record this value in Table C.

- Rinse and dry the hydrometer and the graduated cylinder with deionized water.

- . Repeat steps 1-5 for the unknown samples A and B, recording the temperatures and the density values in Table C.

Figure Six (below) is a graph relating water density (vertical axis) to salinity (horizontal axis). It can be read like Figure Three, as it has lines representing the density-salinity relationship at several fixed temperatures. Determine the salinity of your sample by finding the salinity that crosses the lines representing your measured density and temperature. As before you may need to interpolate between the temperature lines. Record your salinity values in the appropriate space on Table C.
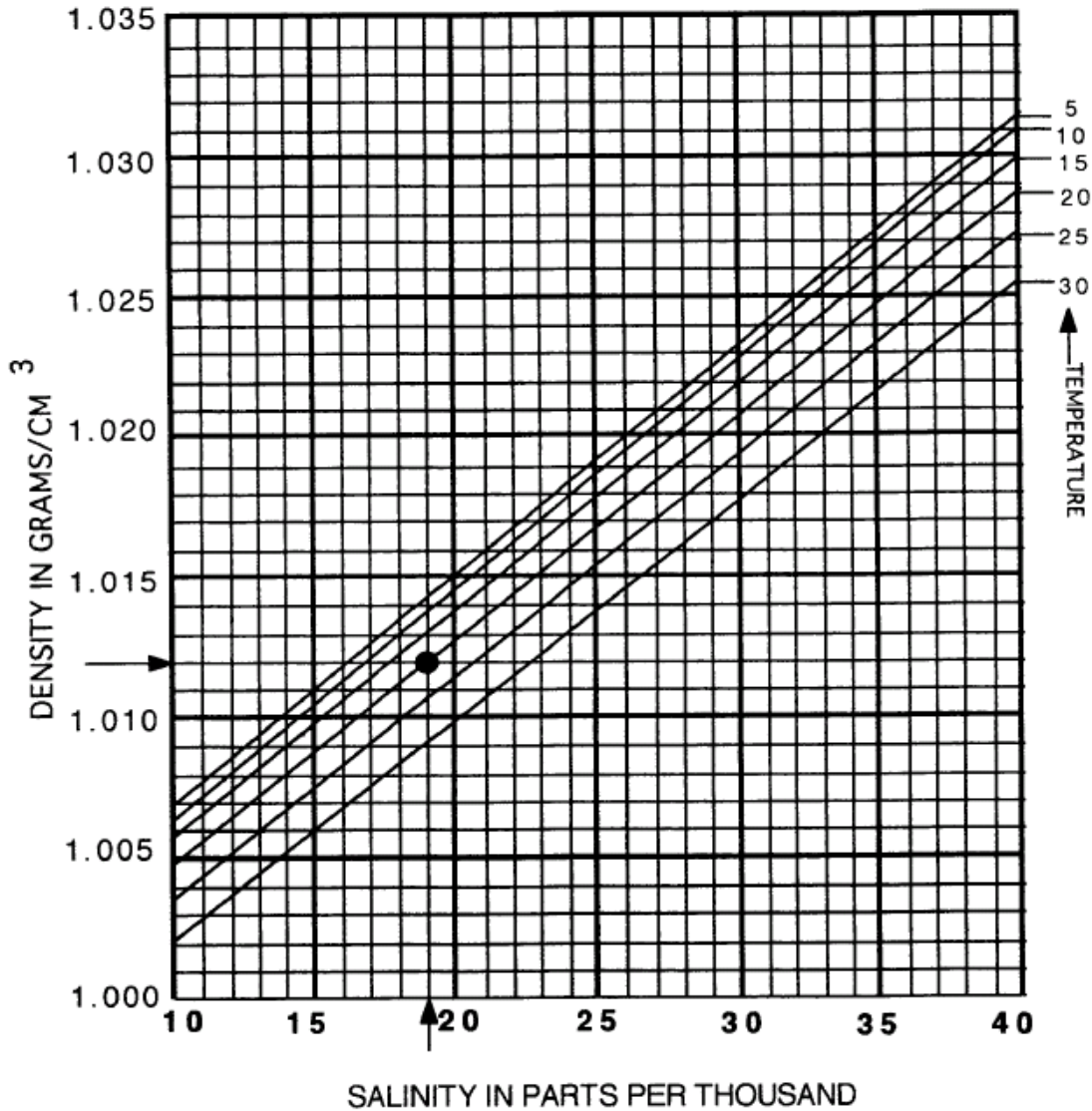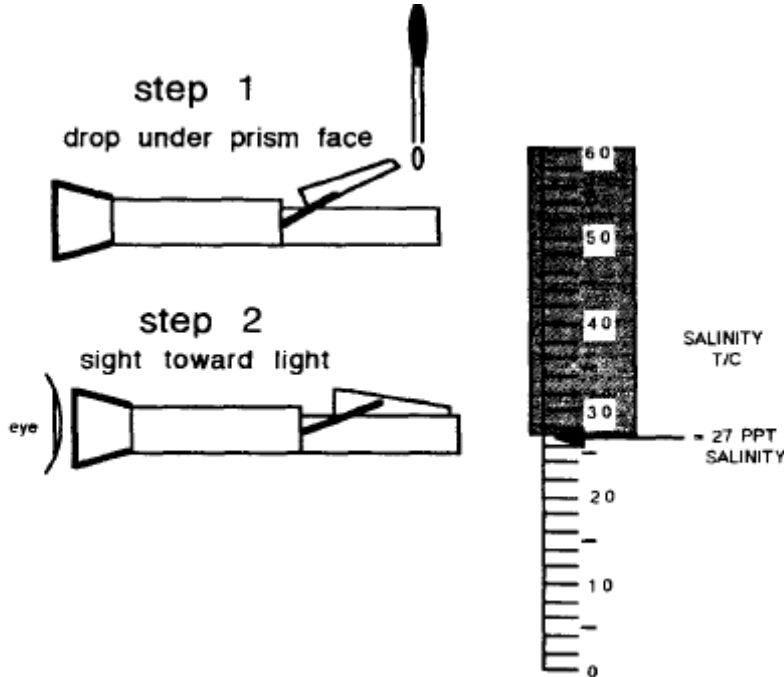
Figure Six: Density as a function of salinity and of temperature. Lines show the relationship between density and salinity at 5 degree increments between 15°C and 30°C.

D. Determination of salinity by refractometer

. A refractometer can precisely measure the amount of refraction that is caused by the density. The instrument that you will be using is temperature compensated. This means that the temperature effects on refraction can be ignored for these measurements, and you will be able to read the salinity directly from the refractometer. The refractometer consists of a blue-tinted glass prism and a beveled, clear plastic cover lens, each with a known refractive index. When a thin layer of water is placed between these two lenses it will refract light through an angle that depends upon the salinity of the water sample. When you look through the eyepiece you will see a calibrated scale with an upper blue-shaded region and a lower white region. The boundary between these two regions will cross the scale at a value representing the sample's salinity (Figure Seven).

lab 6 Experiments:

step 1

drop under prism face

step 2

sight toward light

eye

60

50

40   SALINITY
         T/C

30   — 27 PPT
         SALINITY

20

10

0

Figure Seven: The refractometer. Place a drop of the water sample between the two lenses and lower the upper lens into place. Look through the eyepiece and aim the refractometer toward a light source. The boundary between the upper blue-shaded region of the scale and the lower white region crosses the calibration scale at a value that represents the salinity of the sample.

Before you begin, carefully rinse the face of the prism and the cover lens of the refractometer with deionized water, and dry with a cloth towel. Place a drop of deionized water on the lens and close the cover. Look through the eyepiece. The boundary of the shaded region should cross the scale at the zero line. If it does not, inform your instructor so that she/he can adjust it or assign you a different refractometer. If you have a problem reading the scale you can sharpen it using the focus ring.

- Using an eyedropper, place one or two drops of your known (35o/oo) sample onto the prism face as shown in Figure Seven. Close the prism cover being careful not to trap any air bubbles in the water on the prism face.

- Holding the prism toward the light, look though the refractometer and note where the intersection lies between the upper shaded portion and lower clear portions of the scale. This boundary represents the salinity. Record to the nearest part per thousand ($^0/^{00}$) and enter in Table D on the answer sheet.

- . Rinse the prism and cover plate in deionized water and dry with a cloth towel.

- Repeat steps for the unknowns and record the salinities in Table D.

E. Determination of salinity by chemical titration

The final method of salinity determination that we will demonstrate is very precise (that is, it will replicate well) and accurate (it produces a result that is very close to the true salinity). It is a bit complicated; however, we introduce it here because for decades it was the standard technique in oceanography for determining salinity.

In this section we will use a silver nitrate solution to precipitate out all of the chloride in a known volume of artificial seawater. Although natural seawater contains a much wider array of ions than a mixture of NaCl and fresh water, the analytical technique is the same. When we add a solution containing silver nitrate (that is, Ag_+ ions and $NO3_-$ ions) to a solution containing sodium chloride (that is, Na_+ ions and Cl_- ions), the chloride ions in the solution will react with the silver ions to produce a solid precipitate, silver chloride (and leaving the sodium and nitrate ions in solution):

$$Na^+ + Cl^- + Ag^+ + NO_3^- \rightarrow Na^+ + NO_3^- + AgCl$$

sodium　　chloride　　silver　　nitrate　　　　sodium　　nitrate　　silver chloride
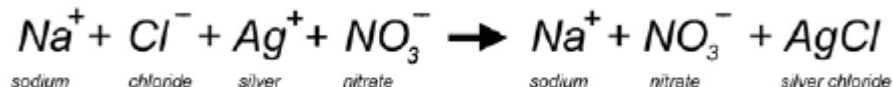
Hypothetically we could then dry and weigh the precipitate AgCl, and from the weight determine the amount of chloride in the sample. But first we have to calculate the mass percentage of chloride in silver chloride. This is done in the following manner:

$$\frac{atomic\ weight\ of\ Cl^-}{atomic\ weight\ of\ AgCl} \times 100\% = \%\ Cl^-\ in\ AgCl$$

$$\frac{35.4\ amu}{107.9\ amu + 35.4\ amu} \times 100\% = 24.7\%\ Cl^-\ in\ AgCl$$

From this we can see that AgCl contains 24.7% chloride ions. If we precipitate 100 grams of AgCl from 1000 grams of seawater that would represent 24.7 grams of Cl_-. Chloride represents a majority of the negative ions present in seawater, but not all. Fortunately the proportion of chloride is consistent. We know from chemical oceanography that chlorides make up about 55% of the total salts (salinity) in seawater. Therefore if we know the chlorinity (the mass of chloride present) we can determine the overall salinity:

Salinity = 100/55 x mass Cl- = 1.8 x mass Cl-

In the above example we measured 1000 grams of seawater and found 24.7 grams of chloride so the salinity can be determined:

*Salinity = 1.8 x mass Cl- = 1.8 x 24.7g Cl- = 44.5 $^0/_{00}$*

The problem with drying and weighing the AgCl precipitate is that it takes a lot of time, and the mass of the precipitate is a function of the oven temperature you use for drying,

since the AgCl can hold onto a significant amount of water even when it has seemingly dried out (similar problems occur when we determine salinity by evaporation). So rather than drying and weighing the silver chloride, we can use the same reaction to measure the salinity by knowing exactly how much $AgNO_3$ was used to precipitate all of the chloride. We can do this by adding another chemical reagent, potassium chromate (K_2CrO_4), which acts as an indicator to tell us exactly when all of the chloride in the seawater has reacted to form AgCl. The potassium chromate indicator remains colorless as long as there is Cl^- present, but the instant the last of the Cl^- is bound up as silver chloride, the solution turns orange. The orange color occurs when the extra chromate ion (CrO_4^{2-}) combines with the silver ion to form a complex ion called silver chromate.

The following two reagents will be made available for the titration analysis: $AgNO_3$ solution (50 grams of $AgNO_3$ dissolved into a 1000 mL solution) and the K_2CrO_4 solution (3.5 grams of K_2CrO_4 dissolved into a 1000 mL solution).
The experimental setup is shown below in Figure Eight:
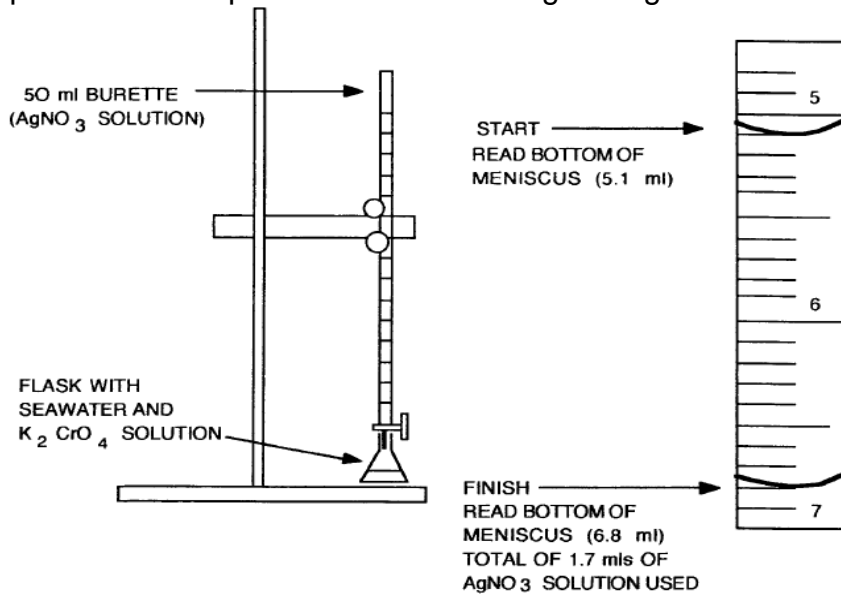
Figure Eight: Set up for chemical titration. Note that the burette reads from top to bottom.

- Pour approximately 20 mL of the 35o/oo sample into a 50 mL beaker.

- Using a graduated 5 mL pipette, transfer *exactly* 5 mL of this 35o/oo sample into a beaker

- Add 5 mL of the K_2CrO_4 solution to the same beaker. (Figure Eight).

- .Fill the 50 ml burette with the $AgNO_3$ solution, pouring it carefully down a funnel into the top of the burette. This can be done once for this entire set of four titrations. Record the starting point in Table E.

- .Add the AgN0₃ solution *slowly* from the burette and continuously stir it with the help of a stirrer until you detects an abrupt color change from milky yellow to orange.

- . Record the new burette reading (the end point) in Table E.

- Repeat the analysis for the known sample, again recording the starting and ending points on the burette in Table E (the starting point for the second analysis should be the same as the ending point for the first analysis).

- . Repeat steps to titrate the unknown sample, recording the data in Table E.

- . Calculate the salinity of unknown sample A using the *average* amount of AgNO₃ required to titrate the 35o/oo using the equation below:

$$\frac{milliliters\ of\ AgNO_3\ to\ titrate\ known}{S\ \%_{oo}\ in\ known} = \frac{milliliters\ of\ AgNO_3\ to\ titrate\ unknown}{S\ \%_{oo}\ in\ unknown}$$

Rearranging the above equation:

$$unknown\ salinity = \frac{\#\ mL\ AgNO_3\ (unknown)}{\#\ mL\ AgNO_3\ (known)} \times known\ salinity$$

A.   Determination of salinity by evaporation

TABLE A:

SAMPLE	MASS OF EMPTY DISH	MASS OF DISH + WATER	MASS OF WATER	MASS OF DISH + SALT	MASS OF SALT	SALINITY OF SAMPLE
35 %oo	_____	_____	_____	_____	_____	_____
A	_____	_____	_____	_____	_____	_____

B. Determination of salinity by electrical conductivity

TABLE B:

SAMPLE	TEMPERATURE (°C)	ELECTRICAL CONDUCTANCE (MMHOS/CM)	SALINITY ($^o/_{oo}$)
35 $^o/_{oo}$			
A			

Is warmer or colder water a better conductor of electricity? Why might this be true?

_____

_____

_____

_____

_____

_____

_____

_____

C. Determination of salinity by density using a hydrometer

TABLE C:

SAMPLE	TEMPERATURE (°C)	DENSITY (GRAMS/ML)	SALINITY ($^o/_{oo}$)
35 $^o/_{oo}$			
A			

lab 6 Experiments:

A fully loaded ship moving from a fresh water port heads over to the Persian Gulf, an area known for high salinities. Will the ship ride higher or lower in the Gulf compared with the port it left? Explain.

_____

_____

_____

_____

_____

_____

D. Determination of salinity by refractometer

TABLE D:

SAMPLE	SALINITY ($^0/_{00}$)
35 $^0/_{00}$	
A	

E. Determination of salinity by chemical titration

TABLE E:

SAMPLE	INITIAL READING	FINAL READING	ML OF $AgNO_3$	SALINITY OF SAMPLE
35 $^0/_{00}$				
A				

1. Record the given salinities for each exercise.

	(A) EVAPORATION	(B) CONDUCTIVITY	(C) HYDROMETER	(D) REFRACTION	(E) TITRATION
35 $^0/_{00}$					
A					