

# Experiment 14

## NAVY BOILER WATER TESTS

FV 09/16/20

**MATERIALS:** Automatic zero burets, 100 and 10 mL graduated cylinders, evaporating dish, 0.050 M HNO<sub>3</sub>, indicator solutions of phenolphthalein, methyl purple, bromphenol blue and diphenylcarbazone (labeled 'chloride indicator'), 0.0050 M Hg(NO<sub>3</sub>)<sub>2</sub>, 250 mL flask, two 100 mL volumetric flasks, 0.0200 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 2 M MnSO<sub>4</sub>, 10 M KOH containing 100 g KI per liter (labeled KOH-KI solution), conc. H<sub>2</sub>SO<sub>4</sub>, starch solution, stirring rod, and boiler water sample.

**PURPOSE:** The purpose of this experiment is to familiarize the student with the chemical tests used for Navy boiler water systems. These tests are used aboard ships to monitor the quality of the feed water to prevent scale formation and corrosion.

**LEARNING OBJECTIVES:** By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Explain the use of buffers in boiler water treatment.
2. Determine the pH of boiler water from a nitric acid titration and the Emergency pH table.
3. Explain the process of an acid/base titration and the use of pH indicators.
4. Explain the process of a redox titration and the use of an indicator to determine the endpoint.
5. Convert concentration units of molarity to ppm (parts per million).

### DISCUSSION:

Aboard ship, fresh water is obtained by distilling sea water in evaporators. A typical arrangement of a tank freshwater system is shown in Figure 1. The portion of the distillate which is set aside for use in the boilers is known as *make-up feedwater*. The water that is actually in use within the boiler is called *boiler water*. Make-up feedwater should be pure distilled water, but in practice some contamination is always present, usually from evaporator carryover and leaks. Since make-up feedwater is the source of boiler water, it is important that the make-up feedwater be monitored frequently, as impurities in the boiler water must be carefully controlled to prevent boiler damage due to the formation of scale and corrosion. The tests that are run on the make-up feedwater and boiler water aboard ship are:

1. **pH (phosphate buffer check):** This test is run with a pH meter. Its purpose is to ensure that the water is about pH = 10.5.
2. **Conductivity (not tested in this lab):** This test is performed continuously with installed conductivity cells and is done to check for evaporator carry-over or for leaks in the salt water cooled condensers.
3. **Hardness (not tested in this lab):** This test monitors the concentration of calcium ions, Ca<sup>2+</sup>, and magnesium ions, Mg<sup>2+</sup>, that are the major cations present in scale formation.
4. **Chloride (Salinity):** This test is a check on the installed conductivity cells. Without this back-up test, a failure in the conductivity cells could lead to serious boiler damage if sea water enters the make-up feedwater.
5. **Dissolved Oxygen:** This test is essential to ensure that make-up feedwater is oxygen free to prevent corrosion of the boiler. At the high temperature at which the boiler operates, the presence of oxygen can quickly lead to corrosion *inside* the boiler where it cannot be readily detected.

These tests are run frequently, usually once each watch, because boiler water must be constantly replaced due to steam and condensate losses.

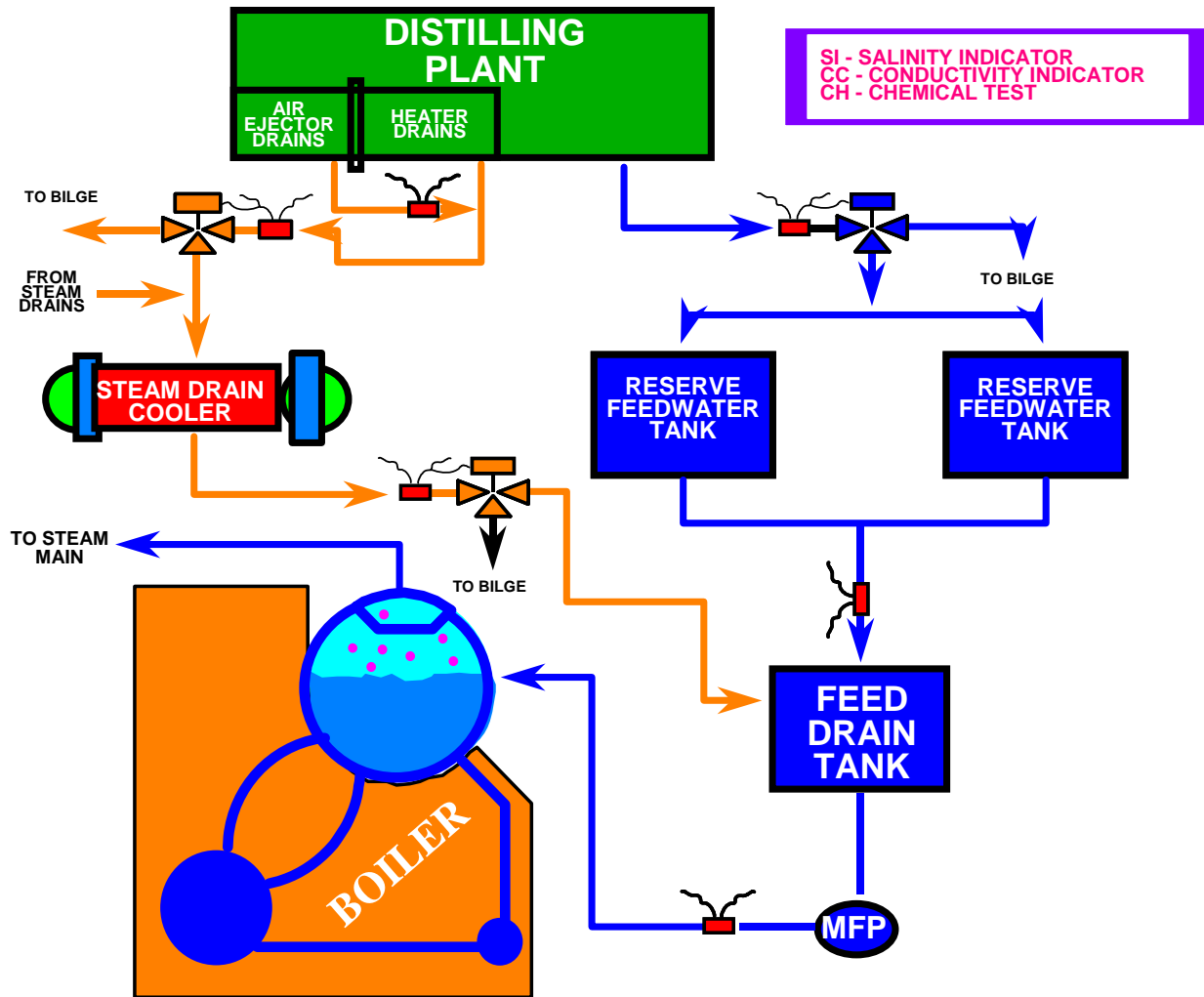


Figure 1: Typical boiler system as outlined by Naval school brief.

Boiler water is treated with a mixture of  $\text{Na}_2\text{HPO}_4$ , commonly called disodium phosphate or DSP, and  $\text{Na}_3\text{PO}_4$ , commonly called trisodium phosphate or TSP. This mixture serves as a buffer to maintain the pH of the boiler water in the region of 10.5. Also, the presence of phosphates causes the precipitation of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions as a soft sludge that prevents the formation of hard boiler scale.

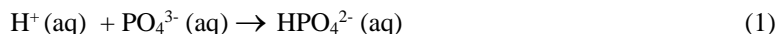
The tests run on boiler water samples are essentially the same as those run on the make-up feedwater, except total phosphate is determined in place of hardness (test 3 on page E14-1). In this experiment, we will run the three *chemical* tests as they are done aboard ship.

#### A. Total Phosphate and Emergency pH.

The objective here is to determine the total phosphate concentration in the sample of boiler water to investigate whether the buffer is still present and working or if it needs to be replenished. In order to understand the principle of this test, it is helpful to first refer to the titration curve for the titration of  $\text{PO}_4^{3-}$  with  $\text{HNO}_3$  (see Figure 2).

DSP and TSP are added to boiler water to buffer the system to pH 10.5. A buffer is a mixture of a weak acid, HA, and its conjugate base,  $\text{A}^-$ . As seen in the titration curve, the conjugate acid for this buffer system is hydrogen phosphate,  $\text{HPO}_4^{2-}$ , and the conjugate base is phosphate ion,  $\text{PO}_4^{3-}$ . The *total phosphate concentration* is the sum of the phosphate ion concentration and the hydrogen phosphate ion concentration. The presence of these two species complicates the analysis slightly when determining the total phosphate concentration. Converting one species to the other first would simplify the measurement.

To determine the total phosphate concentration, it is first necessary to convert all of the phosphate ions to hydrogen phosphate ions by adding  $H^+$ . Then, the concentration of hydrogen phosphate ions can be determined. Both processes are most easily done by performing a titration with nitric acid. The phosphate present is first titrated with  $H^+$  (from nitric acid), according to the equation:



Completion of this step is monitored by the color change of an indicator, phenolphthalein, from pink to colorless, as the pH of the solution drops to 9.5. At this point, all of the phosphate ions are converted to hydrogen phosphate ions and the total phosphate concentration can now be determined by further titration with nitric acid.

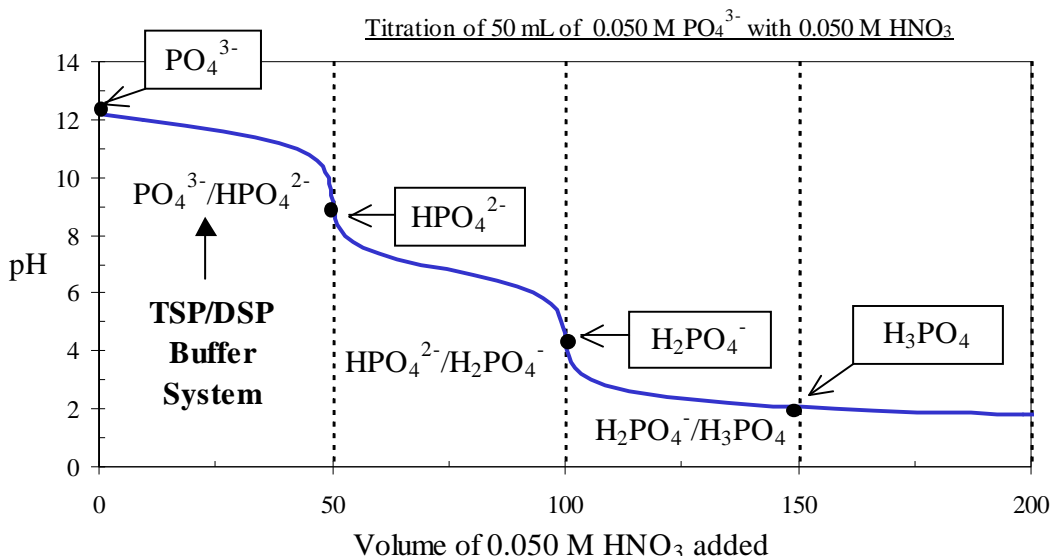
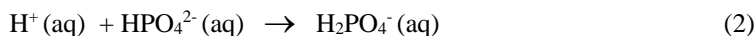


Figure 2: Titration of phosphate ion with nitric acid.

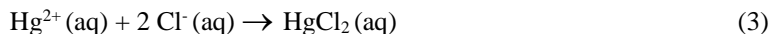
The hydrogen phosphate ion,  $HPO_4^{2-}$ , reacts with nitric acid in a second step according to the equation:



This conversion is monitored with a different indicator, methyl purple, which shows a green to purple color change at the end point. Thus **all** of the phosphate is titrated in the second step, both the original hydrogen phosphate ions as well as the converted hydrogen phosphate ions. **The “total phosphate concentration” will be calculated from data for this titration step only**, and the calculated molarity will be converted to parts per million (ppm) of phosphate.

## B. Chloride (Salinity).

The salinity of boiler water is determined by titrating the chloride ions present with a standard  $Hg(NO_3)_2$  solution. A mercury indicator that contains diphenylcarbazone and bromphenol blue is used for this process. In this method the sample is first acidified by addition of a standard  $HNO_3$  solution, making use of the color change of the bromphenol blue. This step is necessary because acidic conditions are required for a satisfactory end point in the subsequent chloride titration. Then, upon addition of  $Hg(NO_3)_2$  solution, the mercury(II) ions combine with the chloride ions to form  $HgCl_2$ .



After this reaction has reached the equivalence point, any additional mercury(II) ions added will combine with the diphenylcarbazone to form a blue-violet complex:



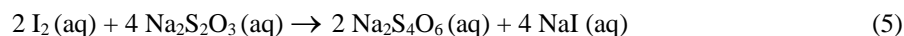
Thus, the end point of the titration is when the first blue-violet color appears in the solution. Chloride ion concentration is calculated from the titration data. The calculated molarity of chloride ions is then converted to parts per million of chloride.

### C. Dissolved Oxygen.

Iron rusts rapidly in the presence of oxygen and moisture and very rapidly when the partial pressure of oxygen is high or when the temperature is high. In boilers, corrosion causes pitting of the metal surface followed by debris buildup and capping over the pit. Within these pits, the solution conditions can remain corrosive, even after the boiler's overall bulk environment is back to normal. If the cap over the pit is lost and the bulk solution is non-corrosive, the pitting can be arrested. It is extremely important to guard against the presence of more than trace amounts of dissolved oxygen in boiler water.

The solubility of gases in water depends upon both temperature and pressure, and is different for each individual gas. Water in contact with air at 25°C contains about 1 liter of oxygen per 100 liters of water, but this solubility decreases with increased temperature and increases with increased pressure. Therefore, an accurate analytical method is necessary for the determination of oxygen dissolved in any particular water sample.

The method employed in the Navy is a modification of Winkler's method. Dissolved oxygen oxidizes iodide,  $\text{I}^-$ , to iodine,  $\text{I}_2$ , in the presence of manganese(II) salts. In basic solution, manganese(II) hydroxide,  $\text{Mn}(\text{OH})_2$ , is oxidized to hydrated manganese(IV) oxide,  $\text{MnO}_2$ . This compound in acidic solution oxidizes iodide ion to free iodine and the manganese(IV) oxide is reduced to the original  $\text{Mn}^{2+}$ . Since the manganese(II) ions are present at both the beginning and the end of the process in the same valence state,  $\text{Mn}^{2+}$ , they can be regarded as catalysts and are omitted when writing the overall equations. The iodine produced can be determined by titration with a standard sodium thiosulfate solution,  $\text{Na}_2\text{S}_2\text{O}_3$ , using starch as an indicator. Starch forms a dark blue/violet complex with iodine, and the end point of the titration is indicated by the disappearance of the blue color. From the volume of the thiosulfate solution used, the amount of iodine generated can be determined. This can be related to the amount of oxygen in the original sample. The chemical equations for the reactions are shown in equations (4) and (5).



On board ships, the amount of oxygen present in the boiler water is determined on a sample of water withdrawn through a cooler into a specially designed sample bottle. Special precautions are taken to prevent the sample from dissolving additional oxygen from the air while the analysis is being performed. However, in this experiment, tap water will be used since the sample of boiler water has been exposed to the air and thus contains much more dissolved oxygen than one would normally encounter aboard ship, whereas the tap water is closer to what would be expected from a closed distillation system.

## PROCEDURE:

### Part A. Total Phosphate and Emergency pH.

1. Using a graduated cylinder, add 100.0 mL of boiler water to an evaporating dish along with two drops of phenolphthalein indicator solution. Zero the automatic buret containing the standard solution of 0.050 M HNO<sub>3</sub>. Be sure that the buret tip is filled with liquid and does not contain air bubbles. Carefully titrate the boiler water while stirring gently until the pink color just disappears. This indicates the conversion of all the PO<sub>4</sub><sup>3-</sup> to HPO<sub>4</sub><sup>2-</sup>. Record the volume of acid used in the DATA SECTION. Save this solution for the next step.
2. Rezero the automatic buret. To the solution from Step 1, add 2 drops of methyl purple and continue titrating the sample to the end point of this indicator, signified by a color change from green to purple. Record the volume of acid used in this titration in the DATA SECTION.
3. Repeat Steps 1 and 2 with a fresh sample of boiler water.

### Part B. Chloride (Salinity).

*Note: Place all mercury containing waste solutions into the special waste container. Do not discard any mercury-containing material in the sink.*

1. Using a graduated cylinder, add 25.0 mL of boiler water to an evaporating dish and then add 5 drops of chloride indicator solution. This solution will become red or violet, depending on the acidity of the solution.
2. Zero the automatic buret containing 0.050 M HNO<sub>3</sub>. Be sure that the buret tip is filled with liquid and does not contain air bubbles. Add nitric acid from the buret dropwise with stirring until the sample passes through a violet color and becomes pale yellow. Then add exactly 1.00 mL more of the nitric acid solution. Save this solution for the next step. You don't need to record the volume of HNO<sub>3</sub>; this step is to ensure an acidic solution for the following titration.
3. Zero the automatic buret containing 0.0050 M Hg(NO<sub>3</sub>)<sub>2</sub>. Be sure that the buret tip is filled with liquid. To the solution from Step 2, add the 0.0050 M Hg(NO<sub>3</sub>)<sub>2</sub> solution with continuous stirring until the pale yellow color disappears and a pale purple color persists throughout the solution. The rate of addition of the Hg(NO<sub>3</sub>)<sub>2</sub> solution should be reasonably constant during the early part of the titration and then reduced to a dropwise rate as the end point is approached. Record the volume of Hg(NO<sub>3</sub>)<sub>2</sub> added in the DATA SECTION.
4. Repeat Steps 1 through 3 with a fresh sample of boiler water.
5. Place all solutions containing mercury in the waste container in the hood.

### Part C. Dissolved Oxygen.

*Remember to use regular tap water for this part.*

1. Using two 100 mL volumetric flasks, obtain from the same water tap, two consecutive 100 mL samples of regular tap water. To each sample, add 10 drops of KOH-KI solution and then 10 drops of MnSO<sub>4</sub> solution. Stopper the flasks and swirl gently to mix. Observe the initial formation of a light fluffy precipitate. Set the flasks aside for 5-10 minutes to allow the precipitate to react with the oxygen in the water and settle out of solution. Did the original precipitate change with time? Record your observations in the DATA SECTION.
2. CAREFULLY add 1 mL (20 drops) of concentrated H<sub>2</sub>SO<sub>4</sub> to each water sample. Invert each capped flask to mix the solution thoroughly. Describe any changes in appearance which indicate that a chemical reaction has taken place. Record your observations in the DATA SECTION.
3. Each solution now contains free iodine in an amount determined by the original oxygen content. The oxygen is said to be "fixed", since oxygen from the air will not readily liberate more iodine. Pour the solution from one of the volumetric flasks into a 250 mL Erlenmeyer flask.

4. Zero the automatic buret containing the 0.0200 M standard sodium thiosulfate solution. Be sure that the buret tip is filled with liquid and does not contain air bubbles. Stir the iodine sample (from Step 3 above) and slowly titrate with the 0.0200 M  $\text{Na}_2\text{S}_2\text{O}_3$  until the solution is pale yellow (original orange color should be gone); *then add 1 dropperful of starch solution*. The solution will become blue, indicating the presence of iodine. Add more starch if your solution is not blue. Continue the titration until addition of one drop causes the disappearance of the blue color. Read and record the level of the sodium thiosulfate solution in the buret. Note that this is the total volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution added, not just the volume after the addition of starch.
5. Empty the Erlenmeyer flask and rinse it with distilled water. Titrate the second sample as described in Steps 3 and 4.

**Clean up:**

1. Dispose of all solutions except those containing mercury in the sink.
2. Dispose of all mercury-containing solutions in the proper waste container.
3. Wash all glassware and return them to their proper locations.

Name \_\_\_\_\_

Section \_\_\_\_\_

Partner \_\_\_\_\_

Date \_\_\_\_\_

**DATA SECTION**  
**Experiment 14**

**Part A. Total Phosphate and Emergency pH.**

Volume of the boiler water sample tested \_\_\_\_\_

|                                                                                                                        | <u>Trial 1</u> | <u>Trial 2</u> | <u>Average Volume</u> |
|------------------------------------------------------------------------------------------------------------------------|----------------|----------------|-----------------------|
| <b>1. PO<sub>4</sub><sup>3-</sup> Titration</b><br><b>(to phenolphthalein end point)</b>                               |                |                |                       |
| Volume of 0.050 M HNO <sub>3</sub> added                                                                               | _____          | _____          | _____ *               |
| <b>2. HPO<sub>4</sub><sup>2-</sup> Titration</b><br><b>(from phenolphthalein</b><br><b>to methyl purple end point)</b> |                |                |                       |
| Volume of 0.050 M HNO <sub>3</sub> added                                                                               | _____          | _____          | _____                 |

**Part B. Chloride (Salinity).**

Volume of the boiler water sample tested \_\_\_\_\_

|                                                            | <u>Trial 1</u> | <u>Trial 2</u> |
|------------------------------------------------------------|----------------|----------------|
| Volume of 0.0050 M Hg(NO <sub>3</sub> ) <sub>2</sub> added | _____          | _____          |
| Average volume used                                        | _____          | _____          |

**Part C. Dissolved Oxygen.**

Volume of the tap water sample tested \_\_\_\_\_

Observations:

Initial precipitate: \_\_\_\_\_

Precipitate after 10 minutes: \_\_\_\_\_

Upon addition of concentrated sulfuric acid: \_\_\_\_\_

|                                                                        | <u>Trial I</u> | <u>Trial 2</u> |
|------------------------------------------------------------------------|----------------|----------------|
| Volume of 0.0200 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> added | _____          | _____          |
| Average volume used                                                    | _____          | _____          |

**DATA TREATMENT**  
**Experiment 14**

**Part A. Total Phosphate and Emergency pH.**

- (A.1) Using the average volume of 0.050 M HNO<sub>3</sub> added in the PO<sub>4</sub><sup>3-</sup> titration (marked with an \* in the data table) and Table 1 on page E14-13, an emergency pH test can be done aboard ship in the event of a pH meter failure. Determine this emergency pH value from your data.

Average Emergency pH = \_\_\_\_\_

- (A.2) Using the stoichiometry for the second step of the phosphate titration (reaction (2)), the volume of nitric acid used in **Part A.2 only**, the molarity of the nitric acid titrant, and the volume of the boiler water sample, calculate the molarity of the phosphate ions (as HPO<sub>4</sub><sup>2-</sup>) in the boiler water sample.

Total phosphate, molarity = \_\_\_\_\_

- (A.3) Using the definition of parts per million (ppm), convert the units of molarity to ppm phosphate (as HPO<sub>4</sub><sup>2-</sup>).

Total phosphate, ppm = \_\_\_\_\_

**Part B. Chloride (Salinity).**

- (B.1) From the molarity and the average volume of the Hg(NO<sub>3</sub>)<sub>2</sub> solution used in the titration, the stoichiometry of the reaction, and the volume of the boiler water sample, calculate the molarity of chloride ions in the boiler water sample.

Chloride ions, molarity = \_\_\_\_\_

- (B.2) Convert the molarity of the chloride ions to parts per million (ppm).

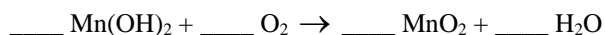
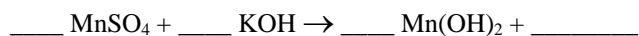
Chloride ions, ppm = \_\_\_\_\_



### Part C. Dissolved Oxygen.

Using the discussion on page E14-4 and your observations, answer the following questions.

(C.1) Complete and balance the following equations for the reactions occurring in solution:



(C.2) What is the precipitate which first appears in the flask when the  $\text{MnSO}_4$  solution is added? Give its chemical formula and its proper chemical name.

\_\_\_\_\_

(C.3) Why does the precipitate become darker in a short time? What is the new precipitate that forms? Give its chemical formula and its proper chemical name.

\_\_\_\_\_

\_\_\_\_\_

(C.4) Write the overall balanced redox reaction that results from these two half-reactions.



→

What did you do in lab to dissolve the precipitate (in C.3)? \_\_\_\_\_

(C.5) From the molarity and the average volume of sodium thiosulfate used in the titration, calculate the number of moles of iodine consumed in reaction (5) for your sample.

Moles of iodine consumed = \_\_\_\_\_

(C.6) From the moles of iodine calculated in (C.5), calculate the moles of oxygen present in the original water sample.

Moles of oxygen present = \_\_\_\_\_

(C.7) Calculate the molarity of the dissolved oxygen in the sample.

Dissolved oxygen, molarity = \_\_\_\_\_

(C.8) Convert the molarity of oxygen to units of parts per million (ppm).

Dissolved oxygen, ppm = \_\_\_\_\_

**POSTLAB QUESTIONS**  
**Experiment 14**

A.1) What is boiler scale?

A.2) Why does it adversely impact boiler performance?

A.3) How does the presence of phosphate help to minimize boiler scale?

B.1) Salinity of feedwater is assessed by conductivity meter or, as a backup, by titration of chloride ions (Chloride Test). The expected limit of  $\text{Cl}^-$  concentration in a properly operated boiler is 1.00 meq/L (milliequivalents per L). Determine whether or not your observed  $\text{Cl}^-$  concentration is under this limit. 1 equivalent unit is defined as the amount of negative ion that can donate 1 mole of electrons. (For monovalent ions such as chlorine one mole = one equivalent, so molarity = equivalents per liter).

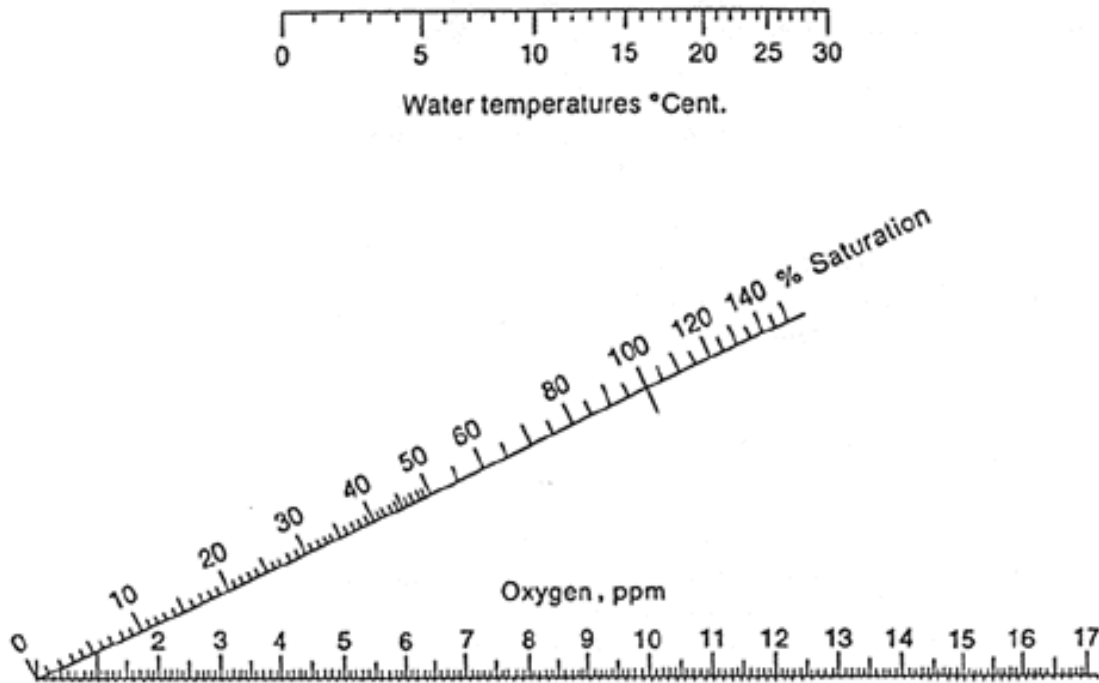
B.2) The concentration of  $\text{Cl}^-$  is often measured and listed in epm (equivalents per million), which is easily confused with ppm. Remember, however, that ppm is an extension of the concentration units of mass fraction, while epm is equivalents per million grams (or milliequivalents per kilogram). Thus, 1.00 epm is equal to 1.00 meq/L, but NOT equal to 1.00 ppm.

If a sample of feedwater is assessed by Chloride Test to contain 5.32 ppm of  $\text{Cl}^-$ , is this boiler water within the maximum limit of 1.00 epm  $\text{Cl}^-$ ?

B.3) What problem does a significant concentration of  $\text{Cl}^-$  ion boiler water indicate? What negative impact does this have on boiler performance?

C.1) Feedwater should contain no more than 15 ppb (parts per billion) of oxygen (NAVSEA 9255/4). Assess whether your observed concentration of dissolved oxygen is under this limit.

C.2) Using your observed concentration of oxygen and the nomogram shown below, determine the % saturation of the feedwater you tested. The room temperature on lab day was \_\_\_\_\_.



(To use a nomogram, use a ruler to connect the two values)

TABLE 1

Correlation of Phosphate Titrant Volume and Boiler Water pH  
(NAVSEA S9086-GX-STM-020/CH-220 V2 R3)

| <u>mL of Nitric Acid</u> | <u>Approximate pH</u> |
|--------------------------|-----------------------|
| 0.0                      | 8.2 or less           |
| 0.1                      | 8.3 to 9.7            |
| 0.2                      | 9.80                  |
| 0.3                      | 9.90                  |
| 0.4                      | 10.00                 |
| 0.5                      | 10.10                 |
| 0.6                      | 10.20                 |
| 0.7                      | 10.25                 |
| 0.8                      | 10.30                 |
| 0.9                      | 10.35                 |
| 1.0                      | 10.40                 |
| 1.1                      | 10.45                 |
| 1.2                      | 10.50                 |
| 1.3                      | 10.51                 |
| 1.4                      | 10.54                 |
| 1.5                      | 10.57                 |
| 1.6                      | 10.61                 |
| 1.7                      | 10.63                 |
| 1.8                      | 10.65                 |
| 1.9                      | 10.68                 |
| 2.0                      | 10.70                 |
| 2.1                      | 10.72                 |
| 2.2                      | 10.74                 |
| 2.3                      | 10.76                 |
| 2.4                      | 10.78                 |
| 2.5                      | 10.80                 |
| 2.6                      | 10.81                 |
| 2.7                      | 10.84                 |
| 2.8                      | 10.85                 |
| 2.9                      | 10.86                 |
| 3.0                      | 10.88                 |
| 3.1                      | 10.89                 |
| 3.2                      | 10.90                 |
| 3.3                      | 10.92                 |
| 3.4                      | 10.93                 |
| 3.5                      | 10.94                 |
| 3.6                      | 10.95                 |
| 3.7                      | 10.97                 |
| 3.8                      | 10.98                 |
| 3.9                      | 10.99                 |
| 4.0                      | 11.00                 |
| 5.0                      | 11.10                 |
| 6.4                      | 11.20                 |