MATERIALS:  Automatic zero burets, 100 and 25 mL graduated cylinders, evaporating dish, 0.050 M HNO₃, indicator solutions of phenolphthalein, methyl purple, bromphenol blue and diphenylcarbazone (labeled ‘chloride indicator’), 0.0050 M Hg(NO₃)₂, 250 mL Erlenmeyer flask, two 100 mL volumetric flasks, 0.0200 M Na₂S₂O₃, 2 M MnSO₄, 10 M KOH containing 100 g KI per liter (labeled KOH-KI solution), conc. H₂SO₄, 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 using 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).

PRE-LAB:  Complete Smartwork5 Pre-Lab Assignment before going to lab.

DISCUSSION:  Aboard ship, fresh water is obtained by reverse osmosis or by distilling sea water in evaporators. A typical arrangement of a tank freshwater system is shown in Figure 1. The portion of this system set aside for use in boilers is known as makeup feedwater. The water that is actually in use within the boiler is called boiler water. Makeup feedwater is deionized water that has been deaerated to get rid of oxygen and other gases that cause corrosion. 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 run on makeup 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 = 10.50.

2. Conductivity (not tested in this lab):  This test is performed continuously with installed conductivity cells and is done to check for evaporator carryover or for leaks in the salt water cooled condensers.

3. Hardness (not tested in this lab):  This test monitors the concentration of calcium ions, Ca²⁺, and magnesium ions, Mg²⁺, 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 makeup 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.
Boiler water is treated with a mixture of Na$_2$HPO$_4$, commonly called disodium phosphate or DSP, and Na$_3$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 10.50. Recall that a buffer is a mixture of a weak acid, HA, and its conjugate base, A$^-$. DSP serves as the weak acid and TSP serves as the conjugate base. Also, the presence of phosphates causes the precipitation of Mg$^{2+}$ and Ca$^{2+}$ ions as a soft sludge that prevents the formation of hard boiler scale. (For more details on the reasons for phosphate addition, see the Naval Applications of Chemistry, Water Treatment: https://intranet.usna.edu/ChemDept/_files/documents/navapps/ARCHIVE/Water%20Treatment%20Chapter.pdf)

The tests run on boiler water samples are essentially the same as those run on the makeup 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 word on concentration units for dilute solutions, such as a solution of boiler water

For very dilute solutions, parts per million (ppm) is a convenient unit to use:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \quad (1)$$
Because the solution is very dilute and has a density that is effectively that of pure water (1.00 g/mL), and the mass of the solute is minuscule compared to that of the solvent, parts per million can also be expressed as

\[
\text{ppm} = \frac{\text{mg of solute}}{\text{L of solution}}
\]  

(2)

It follows that molarity (mol of solute/L of solution) can easily be converted to ppm. For all calculations, assume boiler water has a density of 1.00 g/mL.

A. Total Phosphate and Emergency pH

The objective here is to determine the total phosphate concentration in the sample of boiler water to determine whether the buffer is still present and working or if it needs to be replenished, i.e., determine the total concentration of \(\text{HPO}_4^{2-}\) and \(\text{PO}_4^{3-}\). Because the presence of these two species complicates the analysis slightly, converting one species to the other first would simplify the measurement.

Consider the titration of \(\text{PO}_4^{3-}\) with HNO\(_3\), Figure 2. With zero-added HNO\(_3\), the predominant species is \(\text{PO}_4^{3-}\). As HNO\(_3\) is added, \(\text{PO}_4^{3-}\) is converted to \(\text{HPO}_4^{2-}\), \(\text{HPO}_4^{2-}\) to \(\text{H}_2\text{PO}_4^-\), and \(\text{H}_2\text{PO}_4^-\) to \(\text{H}_3\text{PO}_4\). Thus, it is first necessary to convert all of the phosphate ions to hydrogen phosphate ions by adding H\(^+\) (by addition of HNO\(_3\)), following by conversion of \(\text{HPO}_4^{2-}\) to \(\text{H}_2\text{PO}_4^-\), also by adding H\(^+\). It is worth mentioning that as \(\text{PO}_4^{3-}\) is converted to \(\text{HPO}_4^{2-}\), the TSP/DSP buffer system is produced, as indicated on the titration curve.

The phosphate present is first titrated with H\(^+\) according to the equation:

\[
\text{PO}_4^{3-}(aq) + \text{H}^+(aq) \rightarrow \text{HPO}_4^{2-}(aq)
\]  

(3)

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. The hydrogen phosphate ion, \(\text{HPO}_4^{2-}\), reacts with H\(^+\) ions in a second step according to the equation:

\[
\text{HPO}_4^{2-}(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{PO}_4^-(aq)
\]  

(4)

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 phosphate ions converted to hydrogen phosphate in the first step (reaction 1). The “total phosphate concentration” will be calculated from data from this titration step only, and the calculated molarity will be converted to parts per million (ppm) of phosphate.

Additionally, an emergency pH will be estimated by comparing the volume of added HNO\(_3\) in the second titration to volumes of HNO\(_3\) in a standard table of pH’s.

![Figure 2. Titration of phosphate ion with nitric acid.](image)
B. Chloride (Salinity)

The salinity of boiler water is determined by titrating the chloride ions present with a standard Hg(NO₃)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 HNO₃ 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(NO₃)₂ solution, the mercury(II) ions combine with the chloride ions to form HgCl₂:

\[ \text{Hg}^{2+}(aq) + 2 \text{Cl}^-(aq) \rightarrow \text{HgCl}_2(aq) \]  

(5)

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:

\[ \text{Hg}^{2+} + \text{diphenylcarbazone} \rightarrow \text{blue-violet complex} \]

(6)

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. (Recall that the pressure dependence is given by Henry’s law. 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, I⁻, to iodine, I₂, in the presence of manganese(II) salts. In basic solution, manganese(II) hydroxide, Mn(OH)₂, is oxidized to hydrated manganese(IV) oxide, MnO₂. This compound in acidic solution oxidizes iodide ion to free iodine and the manganese(IV) oxide is reduced to the original Mn²⁺. Since the manganese(II) ions are present at both the beginning and the end of the process in the same valence state, Mn²⁺, 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, Na₂S₂O₃, 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).

\[ \text{O}_2(aq) + 4 \text{KI}(aq) + 2 \text{H}_2\text{SO}_4(aq) \rightarrow 2 \text{K}_2\text{SO}_4(aq) + 2 \text{H}_2\text{O}(l) + 2 \text{I}_2(aq) \]  

(7)

\[ 2 \text{I}_2(aq) + 4 \text{Na}_2\text{S}_2\text{O}_3(aq) \rightarrow 2 \text{Na}_2\text{S}_4\text{O}_6(aq) + 4 \text{NaI}(aq) \]  

(8)

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 was 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.

\[ a \text{ Henry’s law: } s_g = k_H P_g, \text{ where } s_g \text{ is the solubility of the gas, } k_H \text{ is the Henry’s law constant for the gas, and } P_g \text{ is the pressure of the gas above the solution.} \]
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 HNO₃. 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 PO₄³⁻ to HPO₄²⁻. Record the volume of acid added in the DATA SECTION. Save this solution for the next step.

2. Re-zero 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 HNO₃. Be sure 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 HNO₃; this step is to ensure an acidic solution for the following titration.

3. Zero the automatic buret containing 0.0050 M Hg(NO₃)₂. Be sure the buret tip is filled with liquid. To the solution from Step 2, add the 0.0050 M Hg(NO₃)₂ 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(NO₃)₂ 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(NO₃)₂ 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 instructor 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. Record the temperature of the water in the DATA SECTION. To each sample, add 10 drops of KOH-KI solution and then 10 drops of MnSO₄ 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 H₂SO₄ to each water sample. Invert each capped flask to mix the solution thoroughly. Describe any changes in appearance which indicate 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 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 Na₂S₂O₃ until the solution is pale yellow (original orange color should be gone). Note: Do not let the pale yellow disappear; err on the side of ”not so pale” vs pale. 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, with stirring, 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 Na₂S₂O₃ 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.
DATA SECTION
Experiment 14

Part A. Total Phosphate and Emergency pH

Volume of boiler water sample tested: ________________ mL

1. PO$_4^{3-}$ Titration
   (to phenolphthalein end point)

   Volume of 0.050 M HNO$_3$ added
   __________   __________   __________

2. HPO$_4^{2-}$ Titration
   (from phenolphthalein to methyl purple end point)

   Volume of 0.050 M HNO$_3$ added
   __________   __________   __________

Part B. Chloride (Salinity)

Volume of boiler water sample tested: ________________ mL

Volume of 0.0050 M Hg(NO$_3$)$_2$ added
   __________   __________   __________

Part C. Dissolved Oxygen.

Volume of tap water tested: ________________ mL   temperature __________ °C

Observations:

- Initial precipitate: __________________________________________________________

- Precipitate after 10 minutes: _______________________________________________

- Upon addition of concentrated sulfuric acid: _________________________________

   Volume of 0.0200 M Na$_2$S$_2$O$_3$ added
   __________   __________   __________
Part A. Total Phosphate and Emergency pH

(A.1) Using the average volume of 0.050 M HNO₃ added in the PO₄³⁻ titration and Table 1 on page E14-12, 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 (4), 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 HPO₄²⁻) 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 HPO₄²⁻).

Total phosphate, ppm = ________________

Part B. Chloride (Salinity)

(B.1) From the molarity and the average volume of the Hg(NO₃)₂ 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 (remember to include the states):

\[ \text{_____ MnSO}_4(\ ) + \text{_____ KOH}(\ ) \rightarrow \text{_____ Mn(OH)}_2(\ ) + \text{___________}(\ ) \]

\[ \text{_____ Mn(OH)}_2(\ ) + \text{_____ O}_2(\ ) \rightarrow \text{_____ MnO}_2(\ ) + \text{_____ H}_2O(\ ) \]

(C.2) What is the precipitate that first appears in the flask when the 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) What did you do in lab to dissolve the precipitate (in C.3)?

___________________________________________________________________________

(C.5) Write the overall balanced redox reaction that results from these two half-reactions.

(A redox reaction involves the transfer of electrons. The two half-reactions show electrons explicitly being lost and gained.)

\[ 2 \text{I}^- \rightarrow \text{I}_2 + 2 \text{e}^- \] oxidation half-reaction

\[ \text{MnO}_2 + 4 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Mn}^{2+} + 2 \text{H}_2\text{O} \] reduction half-reaction

\[ \rightarrow \] overall reaction
(C.6) From the molarity and the average volume of sodium thiosulfate used in the titration, calculate the number of moles of iodine consumed in reaction 6 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 = ______________
Note: For some questions, you will need to refer to the Naval Applications of Chemistry, Water Treatment: https://intranet.usna.edu/ChemDept_files/documents/nanapps/ARCHIVE/Water%20Treatment%20Chapter.pdf

A.1a) Based on your determination of total phosphate concentration in your water, is the boiler water you tested within the control limits of pH and phosphate concentration for Type A boilers? For type B boilers?

A.2a) What is boiler scale?

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

A.2c) How does the presence of phosphate help to minimize boiler scale?

B.1) What problem does a significant concentration of Cl\(^-\) ion boiler water indicate? What negative impact does this have on boiler performance?

C.1) The monogram below can be used to determine the percent oxygen saturation in your boiler water sample. To use the monogram, connect the temperature of the boiler water to the oxygen concentration, in ppm using a straight edge such as a ruler.

temperature of boiler water: _____________ °C

percent oxygen saturation: _____________
<table>
<thead>
<tr>
<th>mL of Nitric Acid</th>
<th>Approximate pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.2 or less</td>
</tr>
<tr>
<td>0.1</td>
<td>8.3 to 9.7</td>
</tr>
<tr>
<td>0.2</td>
<td>9.80</td>
</tr>
<tr>
<td>0.3</td>
<td>9.90</td>
</tr>
<tr>
<td>0.4</td>
<td>10.00</td>
</tr>
<tr>
<td>0.5</td>
<td>10.10</td>
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<tr>
<td>0.6</td>
<td>10.20</td>
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<tr>
<td>0.7</td>
<td>10.25</td>
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<td>0.8</td>
<td>10.30</td>
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<td>11.10</td>
</tr>
<tr>
<td>6.4</td>
<td>11.20</td>
</tr>
</tbody>
</table>
1. Why is dissolved oxygen a problem in boiler water system?
   a. It changes the pH of boiler water too much.
   b. It can cause corrosion inside the boiler.
   c. It reacts with calcium ions to form soft sludge.
   d. It can cause boilers to explode.

2. At approximately what pH must boiler water be maintained to prevent scale formation and corrosion?

3. What TWO chemical species are added to boiler water to maintain this pH?
   a. Na$_3$PO$_4$
   b. Ca$^{2+}$
   c. Hg(NO$_3$)$_2$
   d. NaH$_2$PO$_4$
   e. Na$_2$HPO$_4$
   f. H$_3$PO$_4$
   g. Mg$^{2+}$

   a. They accelerate the rate of corrosion.
   b. They can lead to boiler tube rupture.
   c. They make the pH of boiler water too basic.
   d. They act as insulators and reduce heat transfer.

5. A 25.0 mL sample of boiler water containing Cl$^-$ is titrated with 0.0050 M Hg(NO$_3$)$_2$.
   a. If 5.43 mL of the Hg(NO$_3$)$_2$ solution are required to reach the end point of the titration, what is the molarity of chloride (Cl$^-$) ions in the original water sample?
   b. What is the concentration of chloride ions in the original boiler water sample, in ppm? Note that, for dilute aqueous species, 1 ppm is approximately 1 mg/L.