Experiment 14D  

NAVY BOILER WATER CHEMICAL TESTS AND TREATMENTS

MATERIALS: Automatic zero burets, 100 and 10 mL graduated cylinders, 400 mL beaker, magnetic stir bar, 50-mL buret, evaporating dish, two 100 mL volumetric flasks, 250 mL Erlenmeyer flasks, boiler water, 0.010 M HNO₃, 0.050 M HNO₃, 0.0050 M Hg(NO₃)₂, 0.0200 M Na₂S₂O₃, 2.0 M MnSO₄, KOH – KI solution, 0.060 M Na₂SO₃ (must be fresh), 18 M H₂SO₄, 2% starch solution, phenolphthalein, methyl purple, chloride indicator, pH meter, thermometer, magnetic stirrer; conductivity meter.

PURPOSE: The purpose of this experiment is to familiarize the student with the chemical tests used for Navy boiler water systems, and to demonstrate the chemical principles associated with some of the tests and treatments used for these critical 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. Explain the process of an acid/base titration and the use of indicators.
3. Standardize and use a pH meter.
4. Convert concentration units of molarity to ppm (parts per million).
5. Explain the role of chloride ion testing and conductivity monitoring for boiler water.
6. Describe a chemical treatment for removing dissolved oxygen from water.

PRE-LAB: Complete the pre-lab prior to lab.

DISCUSSION - NAVY BOILER WATER TESTS

All Naval vessels use boilers to prepare steam. Depending on the type of vessel, the steam from the boilers is needed for a variety of purposes including catapults, propulsion and support activities, such as food preparation. Read the following resources on prevention of corrosion and scale formation in boilers:

Boiler Chemistry Corrosion Control
Boiler Scale Prevention

Aboard ship, fresh water is obtained by reverse osmosis. A typical arrangement of a tank freshwater system is shown in Figure 1. The portion of the fresh water that 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 deionized water, but in practice some contamination is always present. 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. Scale is the buildup of insoluble calcium and magnesium compounds on the inside of the boiler tubes. Corrosion is the conversion of the iron in the stainless steel to rust. Either of these processes can lead to catastrophic failure of the boiler and must be prevented. This laboratory describes some tests that can be run on boiler water and feedwater to ensure that conditions in the system are appropriate for minimizing corrosion and scale formation.
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:** This test is performed continuously with installed conductivity cells and is done to check for contamination of the feed water with sea water. Conductivity is typically expressed in units of microsiemens/cm (μS/cm) or micromhos/cm (μmhos/cm), which are equivalent units.

3. **Hardness (not tested in this lab):** This test monitors the concentration of calcium ions, Ca\(^{2+}\), and magnesium ions, Mg\(^{2+}\), that are the major cations responsible for 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 seawater enters the make-up feedwater. Boiler technicians report chloride in units of equivalents per million (epm)

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. Oxygen concentrations are reported in units of parts per million (ppm).

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 Na₂HPO₄, commonly called disodium phosphate or DSP, and Na₃PO₄, 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 Mg²⁺ and Ca²⁺ 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. In this experiment, we will run the three chemical tests as they are done aboard ship.

**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 PO₄³⁻ with HNO₃ (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, A⁻. As seen in the titration curve, the conjugate acid for this buffer system is hydrogen phosphate, HPO₄²⁻, and the conjugate base is phosphate ion, PO₄³⁻. 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:

\[ \text{H}^+ (aq) + \text{PO}_4^{3-} (aq) \rightarrow \text{HPO}_4^{2-} (aq) \]  (1)

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 initial pH of the boiler water will have an effect on how much HNO₃ is required to perform the first titration step, since a higher pH will have a greater proportion of PO₄³⁻ to HPO₄²⁻. This idea is used in reverse to obtain an approximate value of pH of the starting mixture. This determination provides an important check on the electronic pH indicators installed in the water system onboard ship.

The hydrogen phosphate ion, HPO₄²⁻, reacts with nitric acid in a second step according to the equation:

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

(2)

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.

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; 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.

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

(3)

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:

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

(4)

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. (The value in epm is related to the value in ppm by the equivalent weight of chloride, 35.45 g/equivalent.)

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, 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 (5) and (6).
“fixing” the oxygen by a redox reaction forming molecular iodine:

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

(5)

titrating the iodine (related to the original amount of oxygen) with standard thiosulfate:

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

(6)

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.

DISCUSSION - BOILER WATER/FEEDWATER CHEMICAL PRINCIPLES

The chemical tests used by the Navy to evaluate boiler water/feedwater chemistry all involve titrations. Performing a titration is simply running a chemical reaction in a quantitative way, i.e., treating the test sample (the analyte) by adding a small amount of reactant at a time, until the reaction is complete, and there is no analyte remaining. The key to knowing when to stop is to have an appropriate indicator for the specific titration being performed. Here we will discuss some properties of these compounds, and explore their uses in the tests performed in the lab.

**Indicators.** There are two broad categories of indicators used in many chemical analyses: acid-base indicators and chemical indicators. Most indicators change color in response to changes in the titration solution. By selecting the appropriate indicator, one can have the indicator change color at a certain point in the titration (e.g., near the equivalence point in an acid/base titration). Obviously, indicators must be molecules that absorb different wavelengths of light depending on the chemical state of the indicator.

**Acid-Base Indicators.** Acid-base indicators are generally organic weak acids where the neutral acid form absorbs one set of wavelengths (hence, makes solutions appear a certain color), and the conjugate base form absorbs a different set of wavelengths (hence, makes solutions appear a different color). As with the all weak acids, there is an acid dissociation constant, \( K_a^{\text{In}} \), associated with the equilibrium:

\[
\text{HInd}_{\text{color1}} + \text{H}_2\text{O} \leftrightarrow \text{Ind}_{\text{color2}} + \text{H}_3\text{O}^+
\]  

(7)

The equilibrium constant expression, including reference to the colors of the acid and conjugate base forms, is

\[
K_a^{\text{In}} = \frac{[\text{Ind}_{\text{color2}}]}{[\text{HInd}_{\text{color1}}]} 
\]  

(8)

Normally, indicators are added to a solution in such small quantities that the impact on the acidity of the solution is negligible. However, the pH of the solution to which the indicator has been added has a significant impact on the predominant form of the indicator, and hence on the color of the solution. This is best illustrated by transforming Equation 2 to the following form:

\[
pH = pK_a^{\text{In}} + \log \left( \frac{[\text{Ind}_{\text{color2}}]}{[\text{HInd}_{\text{color1}}]} \right)
\]  

(9)

From this equation, we see that if the pH of the solution is, for example, 1 unit higher than the \( pK_a^{\text{In}} \), the concentration of the conjugate base form of the indicator, \( \text{Ind}^- \), will be ten times larger than that of the acid form, \( \text{HIn} \). For this case, the solution will appear to be color 2. Similarly, if the pH of the solution is 1 unit lower than the \( pK_a^{\text{In}} \), the acid form will be ten times more concentrated than the base form, with the solution appearing to be color 1. If the pH of the solution were \( \sim pK_a^{\text{In}} \), the solution would be a mixture of color 1 and color 2. During the course of a titration, if the pH of the solution were to change from one unit below the \( pK_a^{\text{In}} \)}
to one unit above, the solution’s color would change from color 1 to color 2. From this, we see that a given acid-base indicator “indicates” when the pH of a solution changes from pH values just below its pK\(_a^{in}\) to those just above.

There are hundreds of different indicators, each with a unique value of K\(_a^{in}\). The selection of an indicator for use in a particular titration depends on the value of pH at which the color change is needed. For example, if the indicator was intended for use to “indicate” the equivalence point of a titration, an indicator whose pK\(_a^{in}\) value was close to the pH of the equivalence point would be selected (Figure 3).

![Figure 3](image)

Figure 3. The equivalence point for this acid/base titration occurs at pH ~ 7. The indicator shown changes color between pH ~ 6 (it is blue below pH ~ 6) and pH ~ 8 (it is yellow above pH ~ 8). The pK\(_a^{in}\) of this indicator is about 7, and is therefore ideal for signaling this particular equivalence point. When the pH is between 6 and 8, the two colors are mixed together, yielding green.

In the titration of the boiler water sample, two different indicators were used, because their color changes had to occur in two different pH range, one which coincides with the PO\(_4^{3-}\) → HPO\(_4^{2-}\) conversion, and one for the HPO\(_4^{2-}\) → H\(_2\)PO\(_4^{-}\) conversion. What does that suggest about the pK\(_a^{in}\) values of the phenolphthalein and methyl purple indicators?

**Removing Oxygen from Water** One of the key steps in minimizing corrosion in a boiler is the removal of dissolved oxygen from the feedwater. This can be accomplished through both physical and chemical means.

**Deaeration: Henry’s Law and Temperature Effects on Gas Solubility.** All dissolved gases obey Henry’s Law, which for the case of oxygen, is:

\[
[O_2] = K_H P_{O_2}
\]

(10)

where \(P_{O_2}\) is the partial pressure of oxygen gas above the solution and \(K_H\) is the Henry’s Law constant for oxygen in an aqueous solution. In addition, all dissolved gases become less soluble in water at higher temperatures. A water sample can be physically deaerated (i.e., have its dissolved oxygen removed) by first heating the water, and then reducing the pressure of gas above the water, as with a vacuum system. Fortunately, a sample of water which has been deaerated will, if re-exposed to the normal atmosphere, take several hours to become saturated with dissolved oxygen again. The percent saturation of dissolved oxygen in water for any temperature can be determined with a nomogram, a simple chart that cleverly combines the pressure and temperature dependence of the solubility of oxygen into one chart. A discussion of the ecological significance of dissolved oxygen and a nomogram (Fig. 5) can be found within the document at the website [http://waterontheweb.org/under/waterquality/oxygen.html](http://waterontheweb.org/under/waterquality/oxygen.html). To use the nomogram, simply draw a straight line between the mg/L (ppm) of dissolved oxygen and the temperature of the water. The % saturation can then be read directly where the line crosses the slanting middle scale.

![Fig. 5](image)

**Oxygen Scavengers.** Physical deaeration is effective at removing the majority of dissolved oxygen in a water sample. However, chemical means are required to remove the remainder of the dissolved oxygen. There are many types of oxygen scavengers that are used in actual boiler water treatment schemes. This experiment focuses on the use of the sulfite ion, $\text{SO}_3^{2-}$, which reacts with dissolved oxygen according to:

\[
2 \text{SO}_3^{2-} (\text{aq}) + \text{O}_2 (\text{aq}) \rightarrow 2 \text{SO}_4^{2-} (\text{aq}) \tag{11}
\]

In principle, addition of some $\text{Na}_2\text{SO}_3$ solution to a water sample should result in oxygen removal. However, the rate of this reaction is extremely slow. For practical purposes, therefore, a catalyst is required in order to effectively use sulfite ion as an oxygen scavenger. The $\text{Co}^{2+}$ ion acts as a catalyst for this reaction, based on the following two-step process:

\[
\text{O}_2 + 4 \text{Co}^{2+} + 2 \text{H}_2\text{O} \rightarrow 4 \text{Co}^{3+} + 4 \text{OH}^- \tag{12}
\]

\[
2 \text{Co}^{3+} + 2 \text{OH}^- + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + 2 \text{Co}^{2+} + \text{H}_2\text{O} \tag{13}
\]

The net result of the two-step process is the same as Equation 11 above, but the rate at which it occurs is much faster.

Since the sulfite ion, $\text{SO}_3^{2-}$, is a medium-strength conjugate base of a weak acid, whereas the sulfate ion, $\text{SO}_4^{2-}$, is an extremely weak base, the progress of the oxygen scavenging can be detected through the use of a pH meter. As the sulfite ion is consumed in Equation 11, the pH of the water sample will steadily fall.
PROCEDURE - NAVY BOILER WATER/FEEDWATER TESTS:

Part A. Phosphate Acid-Base Titration – Determining the Titration Curve.

1. Your instructor will demonstrate the use of the pH meter, including standardizing the meter and taking measurements of pH. Make any notes for future reference.

2. Rinse and fill a 50-mL buret with 0.010 M HNO₃ solution.

3. Use a graduated cylinder to obtain a 100.0 mL sample of boiler water, and place the sample in a 400-mL beaker. Place the beaker on a magnetic stirrer and add the clean, dry stir bar. Place the pH meter probe in the boiler water sample; set the height within the solution to ensure that the stir bar will not hit the probe during use. Install the buret with your 0.010 M HNO₃ solution in place for a titration.

4. Add 2 drops of phenolphthalein indicator solution to the boiler water sample. Start the stirrer and begin the titration, taking pH readings and noting the color at approximately 0.5 mL intervals (or smaller if the pH is changing rapidly). The pH reading may drift somewhat, but you should only wait a few seconds after each addition before taking a pH reading. Immediately after the first color change, add 2 drops of methyl purple indicator solution and continue the titration, recording pH and color until you have added a total of about 40 mL of titrant.

Part B. 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. 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 C. Chloride (Salinity).

At any time during the course of the day, obtain about a 60 mL sample of boiler water in a 100 mL beaker. Bring the sample to the conductivity meter, which should already be operational. Take the probe out of the distilled water bath, and put the probe in your boiler water sample. Let it stand in the solution until the reading stabilizes. Record the conductivity in μS/cm (which is equal to μmho/cm). RETURN THE PROBE TO THE DISTILLED WATER BATH.

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 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 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 that 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.

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 D. Dissolved Oxygen.**

1. Using two 100 mL volumetric flasks, obtain from the same water tap, two consecutive 100 mL samples of tap water (NOT boiler water). 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.

2. CAREFULLY add 1 mL (20 drops) of concentrated H₂SO₄ to each water sample. Invert each capped flask to mix the solution thoroughly. Record your observations of any changes in appearance which indicate that a chemical reaction has taken place.

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. Include any distilled water rinsings to assure complete transfer.

4. Zero the automatic buret containing the 0.0200 M standard sodium thiosulfate (Na₂S₂O₃) 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 Na₂S₂O₃ 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 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.
Part A. Phosphate Acid-Base Titration – Determining the Titration Curve.

Record Volume of 0.010 M HNO₃ added, pH and color changes on this page.
Part B. Total Phosphate and Emergency pH.

Volume of the boiler water sample tested

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Average Volume</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
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</tbody>
</table>

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

Volume of 0.050 M HNO$_3$ added

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
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<tbody>
<tr>
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</table>

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

Volume of 0.050 M HNO$_3$ added

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
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<tbody>
<tr>
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</table>

Part C. Chloride (Salinity).

Conductivity of boiler water sample.

Volume of the boiler water sample tested

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
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</table>

Part D. Dissolved Oxygen.

Volume of the tap water sample tested

Observations:

Initial precipitate:

Precipitate after 10 minutes:

Upon addition of concentrated sulfuric acid:

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
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</table>

Volume of 0.0200 M Na$_2$S$_2$O$_3$ added

Average volume used

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
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<td></td>
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</tbody>
</table>
DATA ANALYSIS:

PART A.
(A.1) Use Excel to produce a clearly labeled pH vs. volume HNO₃ plot of your titration curve. Indicate (a) the equivalence points and (b) the pH ranges of the various colors observed.

PART B. Total Phosphate and Emergency pH.
(B.1) Calculate the average volume of HNO₃ titrant used for the two phenolphthalein indicator titrations. Using the phenolphthalein titration data and the table below, determine the approximate pH of the solution.

<table>
<thead>
<tr>
<th>Phosphate Titrant Volume - Boiler Water pH Correlation</th>
<th>(NAVSEA S9086-GX-STM-020/CH-220 V2 R3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL HNO₃</td>
<td>approx pH</td>
</tr>
<tr>
<td>0.0</td>
<td>&lt;8.2</td>
</tr>
<tr>
<td>0.1</td>
<td>8.3-9.7</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>
</tr>
<tr>
<td>0.6</td>
<td>10.20</td>
</tr>
<tr>
<td>0.7</td>
<td>10.25</td>
</tr>
<tr>
<td>0.8</td>
<td>10.30</td>
</tr>
<tr>
<td>0.9</td>
<td>10.35</td>
</tr>
</tbody>
</table>

Average emergency pH = _______________

(B.2) Using the stoichiometry for the second step of the phosphate titration (reaction (2)), the volume of nitric acid used in Part B.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 = ____________

(B.3) Using the definition of parts per million (ppm), convert the units of molarity to ppm phosphate (as HPO₄²⁻).

Total phosphate, ppm = _________________
Part C. Chloride (Salinity).

(C.1) From the molarity and the average volume of the Hg(NO$_3$)$_2$ 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 = ________________

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

Chloride ions, ppm = ________________

Part D. Dissolved Oxygen.

Using the discussion section and your observations, answer the following questions.

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

$$\text{____ MnSO}_4 + \text{____ KOH} \rightarrow \text{____ Mn(OH)}_2 + \text{____}$$

$$\text{____ Mn(OH)}_2 + \text{____ O}_2 \rightarrow \text{____ MnO}_2 + \text{____ H}_2\text{O}$$

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

______________________________________________________________________________

(D.3) (1) Why does the precipitate become darker in a short time? (2) What is the new precipitate that forms? Give its chemical formula and its proper chemical name.

(1)________________________________________________________________________________

(2)________________________________________________________________________________

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

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

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

What did you do in lab to dissolve the precipitate (in D.3)? ________________________________

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(D.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 = ______________

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

Moles of oxygen present = ______________

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

Dissolved oxygen, molarity = ______________

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

Dissolved oxygen, ppm = ______________
Post-Lab Questions (Optional)

1. The $K_a$ values for phenolphthalein and methyl purple are $5.5 \times 10^{-10}$ and $7.9 \times 10^{-6}$, respectively. Show why these indicators are good choices for detecting the equivalence points of this titration from the titration curve generated in part A of this experiment.

2. Based on your data, determine the ratio of the concentrations of the phosphate ion and the hydrogen phosphate ion in the original boiler water sample.

3. The rate for redissolving oxygen gas in water is very slow. Why is this fact helpful when doing experiments that measure the amount of dissolved oxygen in water?

4. Discuss the negative consequences if $\text{Cl}^-$ levels or dissolved $\text{O}_2$ levels are not kept to a minimum in a boiler water system.

5. Discuss two positive effects that the phosphate/hydrogen phosphate ions have on a boiler water system.
PRE-LAB QUESTIONS
Experiment 14B

Complete these questions prior to attending lab.

1. Why is dissolved oxygen a problem in boiler water systems?
   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 a 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. Na₃PO₄   b. Ca²⁺   c. Hg(NO₃)₂   d. NaH₂PO₄   e. Na₂HPO₄
   f. H₃PO₄   g. Mg²⁺

4. Why are deposits of boiler scale a problem in boiler systems? Select ALL that apply.
   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 water containing Cl⁻ is titrated with 0.0050 M Hg(NO₃)₂. It requires 5.43 mL of Hg(NO₃)₂ solution to reach the end point of the titration. (HINT: Look in the lab for the equation of the net ionic reaction first.)
   a. What is the molarity of chloride ions in the original water sample?

   b. What is the concentration of chloride ions in the original water sample in ppm? Note that, for dilute aqueous species, 1 ppm is approximately 1 mg/L.