Experiment 5: DETERMINATION OF SODIUM HYPOCHLORITE IN BLEACH

Purpose: The mass percent of sodium hypochlorite in household bleach is determined by an oxidation-reduction titration with sodium thiosulfate.

Introduction: The active ingredient in standard laundry bleach is the hypochlorite ion (ClO\(^-\)). It acts as an oxidizing agent that decomposes many organic compounds such as those found in wine, chocolate, and other foods that commonly stain clothing. The decomposition products are smaller molecules that are generally more soluble in water and can then be washed away in the normal wash cycle. In this lab you will titrate a sample of bleach with sodium thiosulfate (Na\(_2\)S\(_2\)O\(_3\)) to determine the mass percent of the sodium hypochlorite.

In this analysis, the hypochlorite ion is first reduced with excess iodide under acidic conditions to form the chloride ion. In this reaction, the iodide is oxidized to form aqueous iodine, I\(_2\) (aq) as shown in Equation 1. Iodine is not very soluble in water but in the presence of iodide ions, it immediately converts to the triiodide ion (I\(_3^-\)) which is soluble and forms a deep yellow solution (Equation 2).

\[
\text{ClO}^- (aq) + 2\Gamma (aq) + H_2O(l) \rightarrow \text{Cl}^- (aq) + I_2 (aq) + \text{H}_2\text{O} \quad \text{Equation 1}
\]

\[
\Gamma (aq) + I_2 (aq) \rightarrow I_3^- (aq) \quad \text{deep yellow solution}
\]

The triiodide formed is then titrated with thiosulfate to form iodide and tetrathionate, as shown in Equation 3. With the hypochlorite ion as the limiting reactant (Equation 1), the amount of triiodide formed reflects how much hypochlorite was originally present in the bleach sample. How much triiodide is formed can be determined by the amount of thiosulfate needed to react with it in. Thus, the amount of thiosulfate indirectly gives us information on the amount of hypochlorite in the bleach.

\[
I_3^- (aq) + 2\text{S}_2\text{O}_3^{2-} (aq) \rightarrow 3\Gamma (aq) + \text{S}_4\text{O}_6^{2-} (aq) \quad \text{Equation 3}
\]

Theoretically, the disappearance of the yellow color of the triiodide could be used as an endpoint. However, the change in color is subtle and difficult to detect precisely. For this reason you will make use of the iodide/iodine already present in the solution as an indicator. Addition of starch to a solution that contains triiodide or iodine creates a reversible blue complex that is referred to as an “iodine-starch indicator.”

\[
I_3^- (aq) + \text{starch} \quad \rightleftharpoons \quad I_3^- - \text{starch} (aq) \quad \text{Equation 4}
\]

deep yellow \quad \text{deep blue}
During the titration (Equation 3), the triiodide (now complexed to the starch) is reduced to iodide. When all of the triiodide has reacted, the deep blue color of the complex will disappear, indicating that the endpoint has been reached. There is however a slight complication. If the starch is added to a solution with a high concentration of triiodide or iodine (as in the early stages of the titration), the triiodide-starch complex precipitates out irreversibly, preventing the triiodide from reacting with the thiosulfate. For this reason, the starch is not added until shortly before the endpoint is reached.

The actual reaction taking place in the titration near the endpoint is shown in Equation 5, indicating the change in color from deep blue to colorless.

\[
I_3^- - \text{starch} (aq) + 2S_2O_3^{2-} (aq) \rightarrow 3I^- (aq) + S_4O_6^{2-} (aq) + \text{starch} \quad \text{deep blue to colorless}
\]

In your calculations because the starch does not play a part in the stoichiometry it would be simpler to refer to Equation 3, which shows the molar ratio of triiodide to thiosulfate. The overall reaction is written by combining Equations 1, 2 and 3, and cancelling out what is in common on the left and right side of the equations.

\[
\begin{align*}
\text{ClO}^- (aq) + 2\text{I}^- (aq) + \text{H}_2\text{O} (l) &\rightarrow \text{I}_2 (aq) + \text{Cl}^- (aq) + 2 \text{OH}^- \quad \text{Equation 1} \\
\text{I}^- (aq) + \text{I}_2 (aq) &\rightarrow \text{I}_3^- (aq) \quad \text{Equation 2} \\
\text{I}_3^- (aq) + 2\text{S}_2\text{O}_3^{2-} (aq) &\rightarrow 3\text{I}^- (aq) + \text{S}_4\text{O}_6^{2-} (aq) \quad \text{Equation 3}
\end{align*}
\]

\[
\text{ClO}^- (aq) + 2\text{S}_2\text{O}_3^{2-} (aq) + \text{H}_2\text{O} (l) \rightarrow \text{Cl}^- (aq) + \text{S}_4\text{O}_6^{2-} (aq) + 2\text{OH}^- (aq) \quad \text{Equation 6}
\]

This overall equation gives the molar ratio of thiosulfate to hypochlorite, which is what we are aiming for. Your titration data will therefore allow you to calculate the number of moles of hypochlorite present in the sample based on the amount of thiosulfate added in the titration. Note that this is valid only because KI was in excess at the first step (Equation 1) so that at the endpoint, all of the hypochlorite has reacted. If this was not so, the endpoint would reflect only the amount of iodide that is present and not the hypochlorite.

**STANDARDIZATION OF SODIUM THIOSULFATE**

Sodium thiosulfate is a *secondary standard*, one which is unstable and its concentration will easily change over time. Before the bleach titration can be performed, it is necessary to standardize the sodium thiosulfate solution. In other words, you must first determine the concentration of the sodium thiosulfate solution for yourself, rather than trusting what is on the label. To do this, you will make use of a *primary standard*, one that is stable and its concentration does NOT change significantly over time.

The primary standard you will use is potassium iodate (KIO$_3$). The titration is similar to the one described previously for the bleach sample (with IO$_3^-$ in place of ClO$^-$. The iodate is first reduced with excess potassium iodide to form iodine.
EXPERIMENT 5: SODIUM HYPOCHLORITE IN BLEACH

\[ \text{IO}_3^- (aq) + 6\text{H}^+ (aq) + 5\text{I}^- (aq) \rightarrow 3 \text{I}_2(aq) + 3 \text{H}_2\text{O} (l) \]  
Equation 7

Again, the iodine reacts with iodide to form triiodide which is then titrated with thiosulfate, and starch is added near the endpoint. The overall reaction is shown in Equation 8.

\[ \text{IO}_3^- (aq) + 6\text{S}_2\text{O}_3^{2-} (aq) + 6\text{H}^+ (aq) \rightarrow \text{I}^- (aq) + 3\text{S}_4\text{O}_6^{2-} + 3\text{H}_2\text{O} (l) \]  
Equation 8

This equation gives you the stoichiometric ratio of iodate to thiosulfate and allows you to calculate the molarity of the thiosulfate solution needed for the bleach titration.

**Safety Precautions:**
- WEAR YOUR GOGGLES AT ALL TIMES!
- Bleach is a corrosive liquid. It is harmful if swallowed or inhaled, causes irritation to eyes and respiratory tract, causes substantial but temporary eye injury. Keep it off your clothing as it will bleach it!
- Iodine is poisonous and corrosive. It causes severe irritation or burns to every area of contact. It may be fatal if swallowed or inhaled. Vapors cause severe irritation to skin, eyes and respiratory tract. It is a strong oxidizer. Contact with other material may cause fire. It affects the cardiovascular and central nervous systems and may cause allergic skin or respiratory reaction.
- Sodium thiosulfate may be harmful if swallowed or inhaled, cause irritation to skin eyes and respiratory tract.
- Sulfuric acid is corrosive and can cause severe burns to all body tissue. It may be fatal if swallowed or contacted with skin, harmful if inhaled.
- Iodine-starch indicator solution may cause eye, skin and respiratory tract irritation.

**Procedure:** Work individually on all parts of this experiment.

**Standardization of the sodium thiosulfate:**

1. The concentration of the KIO₃ solution is approximately 0.009 M. Record the actual concentration listed on the bottle which is given in 3 significant figures.
2. Using a 10-mL pipet [Warning! Do not pick up the 5-mL pipet by mistake!!!], transfer 10.00 mL of the KIO₃ solution into a 250-mL Erlenmeyer flask fitted with a magnetic stir bar. *This must be done accurately.* If you don’t remember how to use a pipet, seek help from your instructor. Using a 10-mL graduated cylinder, deliver \( \approx \)10 mL of deionized water and then 5.0 mL of 1.0 M sulfuric acid. Weigh about 1 g of solid KI and add it to the flask. This solution will be brown in color due to triiodide present. **Note the difference in precision needed for each of the measurements described above:** 10.00 mL, 10 mL, 5.0 mL, 1 g. *How does that affect what you do?*
3. Fill a buret with Na₂S₂O₃ (approximately 0.02 M but labeled as “unknown concentration”). If you do not remember how to set up the apparatus for a titration from General Chemistry I lab, you should ask your instructor. This is not the time to be shy! Place the Erlenmeyer flask over the center of a stir plate. The stirrer should be at a rate that ensures thorough mixing without splattering. Record the initial buret reading.
Titrating the KIO₃ solution until it is a pale yellow indicating that most of the triiodide is gone. With a clean (not necessarily dry) graduated cylinder, deliver ≈3 mL of a 2% starch solution. A blue color should immediately form. (If it does not, that means you have already passed the endpoint and you will have to repeat the titration with a fresh solution of KIO₃ solution.) Continue titrating until the blue color disappears. Remember to frequently wash down the sides of the flask and the tip of the buret with the wash bottle of deionized water as you get near to (but before) the end point. At the end point, record the final buret reading. Remember not to allow the level of the Na₂S₂O₃ solution to go below the 50.00 mL mark!

4. Repeat the standardization a second time with a clean (not necessarily dry) flask. Examine how much Na₂S₂O₃ solution was needed for the first trial and check to see whether your buret needs to be refilled before your second trial. If your results from the two trials are widely different (more than 0.1 mL apart), you may have to repeat a third time. If your standardization is not reproducible, there is not much point in continuing to the bleach analysis.

**Bleach analysis:**

5. The bleach solution is too concentrated for the titration. Prepare a one to ten dilution of the bleach by using a 10-mL pipet and a 100-mL volumetric flask. Note the precision: A 10-mL pipet delivers 10.00 mL, and a 100-mL volumetric flask holds 100.00 mL. If you do not remember how to use these lab apparatus, ask your instructor! It would be a waste of time to continue if you do this dilution incorrectly.

**Pipeting Technique:**

Good demo video: [http://tinyurl.com/PipetTech](http://tinyurl.com/PipetTech)

(Note: We use a pipet pump instead of a pipet bulb.)

Use Parafilm as a seal for the volumetric flask. Mix thoroughly by inverting the volumetric flask at least 30 times.

6. With a 5-mL pipet, transfer 5.00 mL of the diluted bleach into a 250-mL Erlenmeyer flask. Using a graduated cylinder, add 10 mL of 1.0 M sulfuric acid and 25 mL of deionized water. Weigh out approximately 1 g of KI and add it to the flask.

7. Titrating this bleach solution with sodium thiosulfate solution, exactly as you did in the standardization (titrate first to a pale yellow before adding 3 mL of the 2% starch indicator). Perform 3 trials of this titration, but DO NOT prepare them all at once. You should prepare one bleach sample (starting at Step 6) and complete the titration before preparing the second bleach sample.

**Determination of the density of the diluted bleach:**

Figure out how to determine the density of your diluted bleach using 10.00 mL of the solution and describe it clearly in your lab notebook in full sentences. Record your measurements and calculate the density.

From the first semester of General Chemistry you should know how to do this. You know you need to have the mass and volume of the solution. What size sample would you use? If your sample size is too small, the uncertainty in your measurement would be too significant. For example if you decide to use 1.0 mL and you have an uncertainty of 0.1 mL, that would...
give you 10% error. However if you use 10.0 mL with the same uncertainty of 0.1 mL, that would give you only 1% error. What volume of the diluted bleach did you use in your titration? Based on the density you just determined, what is the mass of the diluted bleach? You will need this figure in your final calculations.

**Calculations:**
Perform the calculations as stipulated on your Calculations & Results page.

**Special Instructions for a Formal Lab Report:** Review the comments from the first formal lab report that has been returned to you. Again, follow the format described in Appendix 6 & 7 in writing your report. Since this is your second formal lab report, you are expected to do a better job at writing a scientific report than the first time.

In your error analysis, include a calculation of the standard deviation and relative standard deviation (see Appendix 3) of the number of moles of sodium hypochlorite in each of the three trials and explain what it tells you. As one of the three likely sources of error, include the possibility that if you used a pipet that is wet with water when measuring out the 10.00 mL of potassium iodate in the standardization, how that would affect your molarity of sodium thiosulfate, and how that would affect your reported mass % of sodium hypochlorite. Would your percent be too high or too low. Explain carefully. In addition to this error, give two other possible errors.

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Prepare your lab notebook.

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**STANDARDIZATION OF Na$_2$S$_2$O$_3$**

<table>
<thead>
<tr>
<th>Conc. of KIO$_3$</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol of KIO$_3$ used in each trial</td>
<td>=</td>
<td>=</td>
<td>=</td>
</tr>
</tbody>
</table>

(should be within _____)

**BLEACH ANALYSIS**

How bleach was diluted: (describe)

Volume of diluted bleach used in each trial =

<table>
<thead>
<tr>
<th>Trial #</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final Buret Reading</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Buret Reading</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vol Na$_2$S$_2$O$_3$ added</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**DENSITY OF DILUTED BLEACH**

Mass of diluted bleach =

Volume of diluted bleach =

Description of how these measurements were made (in full sentences):
**Preparation for Pre-Lab Quiz:**

1. Be familiar with the names and formulas of ions and compounds involved in this reaction.
   a) Give the names of the following: Cl\(^-\) ClO\(^-\) I\(_3^-\) I\(_2\) IO\(_3^-\) S\(_2\)O\(_3^{2-}\) S\(_4\)O\(_6^{2-}\)
   b) Give the formulas of the following: potassium iodate, sodium thiosulfate, sodium hypochlorite

2. If 25.00 mL of 0.0500 M sodium thiosulfate were used to titrate a bleach solution, how many moles of sodium thiosulfate were used? How many moles of ClO\(^-\) must have been in this bleach solution? How many moles of sodium hypochlorite must have been there?

3. Explain in your own words why the starch cannot be added at the beginning of the titration along with the potassium iodide, sulfuric acid and water.

4. In the Introduction section, we showed you how Equations 1, 2 and 3 can be combined to give us the overall reaction (Equation 6) for the bleach analysis. Combine Equations 2, 3 and 7 in a similar manner to give the overall reaction for the standardization of thiosulfate. You may need to make adjustments to some of the equations in order to have neither I\(_3^-\) nor I\(_2\) left over. HINT: What would you get if you multiplied Equation 3 by 3 before combining the equations?

\[
\begin{align*}
3\text{I}^- (aq) + 3\text{I}_2 (aq) & \rightarrow 3\text{I}_3^- (aq) & \text{Equation 2} \\
\text{I}_3^- (aq) + 2\text{S}_2\text{O}_3^{2-} (aq) & \rightarrow 3\text{I}^- (aq) + \text{S}_4\text{O}_6^{2-} (aq) & \text{Equation 3} \\
\text{IO}_3^- (aq) + 6\text{H}^+ (aq) + 5\text{I}^- (aq) & \rightarrow 3\text{I}_2(aq) + 3\text{H}_2\text{O} (l) & \text{Equation 7}
\end{align*}
\]

**Post-Lab Questions:**

1. The reactions in the titrations are oxidation-reduction reactions. Examine the equation involved in the standardization. To answer the questions, you may wish to review your chemistry textbook on how to calculate oxidation numbers.

\[
\text{IO}_3^- (aq) + 6\text{S}_2\text{O}_3^{2-} (aq) + 6\text{H}^+ (aq) \rightarrow \text{I}^- (aq) + 3\text{S}_4\text{O}_6^{2-} + 3\text{H}_2\text{O} (l)
\]
   a. What is the oxidation number of iodine in the iodate ion? (Hint: O has the oxidation number of –2.)
   b. What is the oxidation number of iodine in the iodide ion?
   c. Is the iodine in iodate gaining or losing electrons? How many electrons are transferred per mole of iodate?
   d. Is the iodate ion undergoing oxidation or reduction?
   e. What is the oxidation number of S in the thiosulfate ion? (Again, O is –2.)
   f. What is the oxidation number of S in the tetrathionate ion?
   g. Is the S in thiosulfate gaining or losing electrons? How many electrons are transferred per mole of thiosulfate?

2. In both the standardization and bleach analysis, you were asked to use 1 g of KI. Why wasn’t it necessary to record the mass? Explain in full sentences.

3. Optional (5 BONUS POINTS): Based on your standardization data, could you have used 0.500 g of KI in the standardization titration? Show your calculations and explain in full sentences.
STANDARDIZATION OF Na₂S₂O₃ SOLUTION

Calculate the concentration of the Na₂S₂O₃ solution using your standardization data and complete the table below. Show your calculation setups in the space below.

<table>
<thead>
<tr>
<th></th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3 (if necessary)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol of Na₂S₂O₃ used</td>
<td></td>
<td></td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>Concentration of Na₂S₂O₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

BLEACH ANALYSIS

Calculate the density of the diluted bleach solution. Show your calculation here. Be sure to include units in your setup.

Calculate the mass of the diluted bleach solution from the volume used in each titration. Show your calculation here.
Calculate from the volume of Na$_2$S$_2$O$_3$, the number of moles of hypochlorite ions in each of the diluted bleach solution that was titrated, and the mass % of NaClO in the diluted bleach solution, and finally, the average mass % NaClO. Show your calculation setups, clearly labeled, then complete the table below. (Use extra paper if necessary.)

<table>
<thead>
<tr>
<th></th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol of Na$_2$S$_2$O$_3$ used</td>
<td></td>
<td></td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td># mol NaClO in diluted bleach</td>
<td></td>
<td></td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>Mass % NaClO in diluted bleach</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Using the average mass % NaClO in the diluted bleach, calculate the mass % NaClO of the original undiluted bleach solution. Show your calculations here:

ANS. Mass % NaClO of original bleach solution = ______________

Manufacturer’s claim of the mass % NaClO in bleach = ______ (Obtain from instructor.) Calculate the error and % error in your mass percent. Show your setup here, and watch your SIGN AND SIG. FIG.

Error = ____________ % Error = ______________

Calculate the standard deviation of the relative standard deviation of the number of moles of NaClO in your three trials. Show your calculations on a separate sheet of paper.