

## Experiment 8

# ANALYSIS OF HYPOCHLORITE IN BLEACH

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### PURPOSE

The percent sodium hypochlorite by mass in an unknown sample of bleaching solution will be determined by iodimetric titration.

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#### WHAT IS BLEACH?

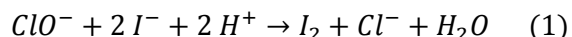
Commercial bleaching agents are made by reaction of chlorine with a base. In bleaching solutions, the base is sodium hydroxide and the product is sodium hypochlorite, NaClO. In bleaching powders, the base is calcium hydroxide and the product may be either Ca(OH)ClO or Ca(ClO)<sub>2</sub>, or a mixture of the two.

Sodium and calcium hypochlorites owe their bleaching ability to the presence of chlorine in an oxidized state, the +1 state. Bleaching by hypochlorite is an oxidation-reduction reaction in which the victim molecule is oxidized, usually to a less-colored form, by the +1 oxidation state chlorine, ClO<sup>•</sup>. In the process, the chlorine is reduced to Cl<sup>-</sup>.

Notice, that because it is the ClO<sup>•</sup> species which is the actual oxidizing agent, or oxidant, a mole of bleaching agent consisting of Ca(ClO)<sub>2</sub> has twice the bleaching ability of a mole of Ca(OH)ClO. Commercially, the former is called "low test", and the latter "high test," bleaching powder. These products are often called "swimming pool chlorine."

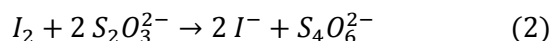
#### HOW DO WE ANALYZE BLEACH?

Because there is no good direct analysis for ClO<sup>•</sup>, an indirect, two-step procedure is used. The hypochlorite is first reacted under acidic conditions with an excess of the reducing agent, iodide ion. (Do not confuse iodide, I<sup>-</sup>, with iodine, I<sub>2</sub>.) Under these conditions, the following reaction goes to completion:



The appearance of a reddish-brown color due to the product iodine is a visible sign the reaction has occurred. From the reaction, we can see that the moles of I<sub>2</sub> produced will equal the moles of ClO<sup>•</sup> that were present in the sample.

The moles of iodine are determined by titrating it with thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) solution of known concentration, using the following reaction:



where we can see that two moles of thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) are required for every mole of iodine (I<sub>2</sub>).

The endpoint of the titration is when the last trace of yellow color from the iodine disappears. Because this change from pale yellow to colorless is not very distinct, a small quantity of starch solution is added near the endpoint. Any iodine still present combines with the starch to form a deep blue complex, so the endpoint will be more clearly signaled by the disappearance of the blue color.

Although, to a chemist, the molarity of NaClO in the bleach is simpler to determine, the concentration of bleach is normally reported as percent by mass (or weight percent). As you know conversion between molarity and percent by mass requires knowing the density of the solution. (Your instructor will give you the density of the particular bleach sample you will be using.)

## IN THIS EXPERIMENT

A specific volume of commercial bleaching solution will be diluted in water, treated with an excess of iodide, acidified, and titrated with standard thiosulfate solution. From these titration data, the moles of hypochlorite ion will be determined. Since this is equal to the number of moles of sodium hypochlorite (NaClO), the corresponding mass of sodium hypochlorite in a sample can be calculated.

The mass of the bleach solution sample will be calculated from the volume and density of the sample. Knowing the mass of NaClO in a sample and the mass of the sample, it will then be easy to calculate the concentration of the bleach solution as percent NaClO by mass.

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## PRE-LABORATORY PREPARATION

1. Read over the procedure and data analysis sections of the experiment
2. Complete the computer-generated PRELAB assignment. Refer to the procedure and data analysis sections of the experiment as needed. The prelab questions for this experiment exactly replicate the questions in the data analysis section.
3. Construct a complete, organized data sheet.

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## EXPERIMENTAL SECTION

### REAGENTS PROVIDED

Bleach unknown.  
 Standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (approximately 1 M).  
 6.0 M HCl.  
 0.6 M KI.  
 Starch indicator solution.

### Hazardous Chemicals

Hypochlorite solutions make white spots on colored clothing, and erode skin and eye tissue.  
 Acids are, as usual, hazardous. Iodide and thiosulfate are mildly toxic.

### WASTE DISPOSAL

None of the wastes from this experiment are serious pollutants. The exhausted or excess solutions may be washed down the sinks.

### SPECIAL EQUIPMENT

This is the first experiment where you will use **volumetric flasks**. Like volumetric pipets, when filled to the calibration line, they contain precise amounts of solution (to 3 or 4 significant figures). A 50-mL volumetric flask has a volume of 50.0 mL and a 100-mL volumetric flask has a volume of 100.0 mL. This is similar to pipets, where a 5-mL pipet typically delivers 5.00 mL and a 10-mL pipet delivers 10.00 mL.

## PROCEDURE

Work individually, unless told otherwise.

### PREPARATION OF 1/10 DILUTED $\text{Na}_2\text{S}_2\text{O}_3$

1. Use your graduated cylinder to obtain about 15-20 mL of the stock  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Record the actual concentration of the stock  $\text{Na}_2\text{S}_2\text{O}_3$  on your Data Sheet.

2. Rinse the 5 mL pipet with a couple mL of the stock  $\text{Na}_2\text{S}_2\text{O}_3$  solution and discard the rinsings into a 400-mL beaker (which will serve as a waste beaker).

3. Pipet 5.00 mL of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution into a clean (but not necessarily dry) 50.0 mL volumetric flask, fill with distilled  $\text{H}_2\text{O}$  until the bottom of the meniscus rests on the calibration mark on the flask's neck, cap the flask, and mix thoroughly by inverting at least five times.

*This solution will be used in the buret for the titration. It is the titrant.*

When filling volumetric flasks, it is often convenient to fill a plastic squeeze bottle with distilled water. The bottles are usually set out near the back sink. When you are trying to fill the volumetric flask to the calibration line, it is easier to control the flow of water from the squeeze bottle than from a faucet (so you will not overfill the flask).

**NOTE:** If either this dilution or the next one is done incorrectly, you will get poor results and you won't know it until you get your graded report back.

### PREPARATION OF 1/10 DILUTED BLEACH UNKNOWN

4. Bring a clean, dry 50-mL beaker to the laboratory assistant. You will receive about 15-20 mL of unknown.

*Record the unknown number and the density of the unknown bleach (from the board) on your Data Sheet.*

5. After rinsing the pipet with the unknown, pipet 5.00 mL of your unknown bleach sample into a clean (but not necessarily dry) 50 mL volumetric flask, dilute to the mark with distilled  $\text{H}_2\text{O}$ , cap the flask, and mix thoroughly by inverting the flask repeatedly.

*Aliquots (measured portions) of this solution will be titrated.*

### LOAD THE BURET

6. Rinse a clean 25 mL buret with the Dilute  $\text{Na}_2\text{S}_2\text{O}_3$  solution prepared in step 2.

First, close the stopcock and then add about 5-7 mL of  $\text{Na}_2\text{S}_2\text{O}_3$  to the buret. To avoid spilling, *always use a funnel when pouring solution into a buret.* Rinse the walls by tilting the buret and rolling the solution over the entire inner surface. Drain the  $\text{Na}_2\text{S}_2\text{O}_3$  through the stopcock into a waste beaker.

If you feel moisture in your shoe, one possibility is that you left the stopcock open during a tilt and roll maneuver.

7. Clamp the buret to a ring stand and, using a funnel, fill it with the dilute  $\text{Na}_2\text{S}_2\text{O}_3$  solution that you prepared and record the initial buret reading (to the nearest 0.01 mL).

To do this, initially add enough solution to fill the buret to about 1 cm above the top calibration mark. Then set your waste beaker under the buret and open the stopcock to flush air bubbles from the stopcock and delivery tip. Close the stopcock when the meniscus reaches the top calibration mark (0.00 mL), or shortly thereafter.

### PREPARATION OF FIRST BLEACH SAMPLE FOR TITRATION

8. Add about 100 mL of distilled water and about 5 mL of 0.6 M KI to a clean 250-mL beaker.

The 0.6 M KI will be dispensed by auto-pipet. One squirt should provide the 5 mL you need for a titration. This is added in excess, therefore approximate measurement is adequate.



Figure 1. An autopipet. The autopipets should have been calibrated before the start of lab, so please don't readjust them. If you don't believe the correct amount is being delivered, let the instructor know.

**9. Rinse a clean 10 mL pipet with some of the diluted bleach unknown you prepared, then transfer exactly 10.00 mL to the 250 mL beaker.**

Stir well with a glass stirring rod, leaving the rod in the beaker. The solution should turn a yellow-to-rusty orange color (depending upon the concentration of your unknown).

**10. Add about 2 mL of 6 M hydrochloric acid, and stir well.**

This will also be dispensed by auto-pipet. One squirt should provide the 2 mL you need for a titration. This is added in excess, therefore approximate measurement is adequate.

Note the immediate formation of iodine, which colors the solution reddish-brown. If it turns a muddy brown with precipitate in it, you used the wrong bleach solution (you should use the dilute solution you prepared in the volumetric flask) and should remake the sample.

#### TITRATION OF FIRST BLEACH SAMPLE

**11. While stirring continuously, begin adding  $\text{Na}_2\text{S}_2\text{O}_3$  from the buret.**

Add the thiosulfate solution from the buret in a fairly rapid stream, until the solution has a light yellow-orange color, indicating only a small quantity of iodine left in the solution. Once the orange is completely turned to yellow, you are only a couple of drops from the endpoint.

If you only use 1 or 2 mL to reach the endpoint, you put the wrong thiosulfate solution in the buret. It should contain the dilute  $\text{Na}_2\text{S}_2\text{O}_3$  solution you made in the volumetric flask.

**12. Add roughly 1 mL of starch solution (one squirt from an eyedropper), which will form the blue iodine-starch complex.**

The exact amount of starch is not important. The solution should become a dark, deep blue after the starch is added.

**13. Continue the titration with dropwise addition of thiosulfate solution, while stirring continuously.**

The disappearance of all color constitutes the endpoint. This is a very sharp endpoint that is easy to overshoot.

**14. Read and record the final buret reading (to the nearest 0.01 mL).**

#### ADDITIONAL TITRATIONS

**15. Refill the buret with the dilute thiosulfate solution you prepared and repeat steps 8-14 two additional times using 10.00 mL aliquots of your diluted bleach unknown.**

If the results vary considerably (have poor precision), there is some technique problem. If you can't identify the problem, tell your story to one of the instructors, who may be able to help.

If you are unhappy with your results, you can perform additional titrations, as time allows. Remake any solution if you run out.

**16. Clean, dry, and store your glassware. Clean up your bench space and wash your hands.**

With three (nearly identical, we hope) titrations recorded on the Data Sheet, we're now ready for the fun part...

\_\_\_\_\_  
Name

\_\_\_\_\_  
Station Used

\_\_\_\_\_  
Instructor/Day/Time

\_\_\_\_\_  
Station Checked & Approved

## DATA SHEET

Concentration of the stock  $\text{Na}_2\text{S}_2\text{O}_3$  provided: \_\_\_\_\_

Using the concentration of the stock  $\text{Na}_2\text{S}_2\text{O}_3$  and the volumes provided in procedure step 3, *perform a dilution calculation to obtain the concentration of the dilute  $\text{Na}_2\text{S}_2\text{O}_3$  you made:*

Concentration of the dilute  $\text{Na}_2\text{S}_2\text{O}_3$  prepared: \_\_\_\_\_

Construct a data table to be used for recording the titration data during the experiment:

## DATA ANALYSIS

All calculations must be clearly organized, make proper use of significant figures and include the units. Show a single sample calculation, for sample 1, for each question.

**1. Calculate the number of moles of  $\text{Na}_2\text{S}_2\text{O}_3$  used in each of the titrations.** Remember to convert mL to L and to use the concentration of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution that you actually used in the titrations.

sample 1 \_\_\_\_\_; sample 2 \_\_\_\_\_; sample 3 \_\_\_\_\_

**2. Calculate the number of moles of  $\text{ClO}^-$  in each of samples titrated.** Look at reaction (1) to see the mole relationship between  $\text{S}_2\text{O}_3^{2-}$  and  $\text{I}_2$  and then use reaction (2) to see it between  $\text{I}_2$  and  $\text{ClO}^-$ .

sample 1 \_\_\_\_\_; sample 2 \_\_\_\_\_; sample 3 \_\_\_\_\_

**3. Calculate the grams of NaClO in each of the titrated bleach samples.** Note that the moles of  $\text{ClO}^-$  equals the moles of NaClO. The molar mass of NaClO is 74.45 g/mole.

sample 1 \_\_\_\_\_; sample 2 \_\_\_\_\_; sample 3 \_\_\_\_\_

**4. Calculate the mass of the undiluted bleach that was in each sample titrated.** In step 5 of the procedure, a 50-mL solution was prepared from 5.00 mL of the undiluted bleach. 10-mL samples of this solution were then titrated. Clearly, each 10-mL sample contained one-fifth of the 50-mL of diluted bleach solution. Thus, each titration sample must also contain one-fifth of the original undiluted bleach. *Since 5.00 mL of undiluted bleach were originally used, each titration sample contains one-fifth of the 5.00 mL of undiluted bleach.* Trivially calculate the volume of undiluted bleach in each titration sample and then use the density of your unknown bleach to determine the grams of unknown in a titration sample.

mass of undiluted bleach in each sample \_\_\_\_\_

**5. Using the answers to 3 and 4, calculate the percent NaClO by mass in each undiluted bleach sample.**

sample 1 \_\_\_\_\_; sample 2 \_\_\_\_\_; sample 3 \_\_\_\_\_

**6. Average your percent NaClO by mass values.**

Average \_\_\_\_\_

Unknown Number \_\_\_\_\_