

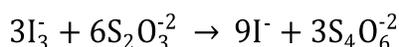
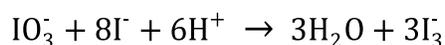
Analysis of Hypochlorite in Commercial Bleach: Iodometric Titrimetry

Introduction

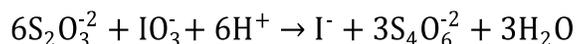
The oxidizing power (percent NaOCl) of commercial bleach is determined iodometrically by reacting it with an excess of iodide in acetic acid solution and titrating the triiodide ion produced (I_3^- is formed in the presence of excess iodide) with standard sodium thiosulfate solution. The sodium thiosulfate is standardized against primary standard potassium iodate, and a starch indicator is used for the endpoint detection.

Equations that govern the complex equilibrium of this iodometric titration:

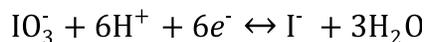
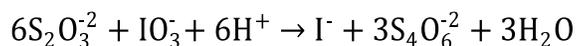
Standardization of $Na_2S_2O_3$:



In the reaction six thiosulfate ions ($S_2O_3^{2-}$) react for every iodate (IO_3^-) ion reacted.



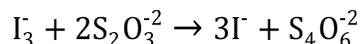
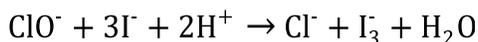
Why do we call this an oxidation/reduction reaction?



The thiosulfate is oxidized and the iodate is reduced.

DETERMINATION OF A HYPOCHLORITE SAMPLE

I_3^- is generated using ClO^- in a 1 to 1 mole ratio and is then reacted with the standardized thiosulfate solution. The following two reactions govern the iodometric titration of hypochlorite:



In the reaction two thiosulfate ions ($S_2O_3^{2-}$) react for every hypochlorite (ClO^-) ion reacted. The thiosulfate is oxidized and the hypochlorite is reduced.

Solutions needed for this experiment:

Solutions prepared by the student:	Solutions provided by the instructor:
0.01 M KIO_3 standard	Glacial acetic acid
0.1 M $Na_2S_2O_3$	Reagent sulfuric acid
6 M HCl	Reagent hydrochloric acid
1 M H_2SO_4	Starch solution

Experimental Procedure:

Preparation of KIO_3 :

- Dry about 1.5 g of the primary standard KIO_3 at $120^\circ C$ for 1-2 hours and cool in a desiccator for 30-40 minutes.
- Accurately weigh out (to the nearest 0.0001g) 1.0 to 1.4 g of the salt (by difference) and dissolve in a small amount of distilled water in a 200 ml beaker.
- Quantitatively transfer, with rinsing to a 500 ml volumetric flask using a glass funnel ensuring all solution and any solid are transferred to the flask.
- Dilute to the mark.
- Calculate the molarity of the solution.

Preparation of 0.1M $Na_2S_2O_3$:

- Boil about 700 ml of distilled water for 5-10 minutes to ensure sterility and to expel carbon dioxide. (*Sodium thiosulfate solutions are subject to bacterial attack, which may change the molarity after some time. Therefore, all water and glassware used to prepare and store the solution should be sterilized. If any turbidity or bacteria or mold growth appears, the solution should be discarded. Removal of carbon dioxide is also beneficial, because thiosulfate is more stable in neutral solution.*)

- Cool to room temperature.
- Sterilize a 1-liter bottle with concentrated H_2SO_4 ; rotate the bottle so that the acid contacts the entire interior wall. **Caution! Highly Corrosive! Use the minimum amount necessary.**
- Rinse very thoroughly with tap water, then with distilled water, and finally with the boiled distilled water.
- Using a rough balance (i.e., a top-loader), weigh out on weighing paper or weighing boat 12.5 g of sodium thiosulfate crystals, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.
- Transfer to the liter bottle, add about 500 mL of the freshly boiled and cooled distilled water, add 0.05 g sodium carbonate, and shake thoroughly until the solution is homogenous. (*A small amount of sodium carbonate is added to keep the solution neutral or slightly alkaline and thereby stabilize it against decomposition to elemental sulfur.*)
- Store this solution in a dark, cool place (your locker).

Standardization of the $\text{Na}_2\text{S}_2\text{O}_3$ solution. **READ THIS PROCEDURE BEFORE STARTING!! TIME DEPENDENT!!!!**

1. Rinse the 50 ml burette several times with small portions of the thiosulfate solution and fill it with thiosulfate solution. Adjust the volume near the zero mark and record the volume reading to the nearest 0.01 ml. Pipette a 50.00 ml aliquot of the potassium iodate solution into a clean 250 ml Erlenmeyer flask. Add about 2 g of solid potassium iodide and swirl to dissolve. Add, with thorough, rapid mixing, 5 ml of 1 M H_2SO_4 . ***Once you have added the acid, you must be prepared to titrate!!***
2. Titrate immediately with the thiosulfate solution. In strongly acidic solutions the excess iodide is rapidly air-oxidized to I_3^- . Therefore, the titration must be performed quickly without long delay times. Thorough, continuous mixing by swirling the flask is required throughout the titration with the addition of each aliquot. The thiosulfate must not be allowed to accumulate in local excess in the acid solution or else some decomposition into H_2SO_3 and S may occur. Titrate until the yellow color (due to I_3^-) almost disappears. The solution will become pale yellow. To ensure that you see this place a white sheet of paper under the titration vessel. Once you observe the pale yellow color add 2 to 3 ml of the starch indicator to the vessel and titrate until the blue color just disappears. This should occur within the addition of the first 0.5 ml of sodium thiosulfate after the starch indicator addition. If the solution does not turn blue then you have over titrated your first trial and you should discard it and try again.
3. Titrate two more 50.00 mL aliquots of potassium iodate. Calculate the molarity of the $\text{Na}_2\text{S}_2\text{O}_3$ solution based on your trials. Provide the mean, standard deviation, and relative standard deviation.

Determination of Hypochlorite in an Unknown.

Bleach solutions are inherently unstable with storage, so do not prepare your bleach solution unless you are prepared to titrate it the exact same lab period. When you are ready to prepare and titrate the bleach solution, get an unknown from your instructor.

1. Wash and thoroughly dry a weighing bottle. Using the analytical balance, weigh the empty weighing bottle to the nearest 0.0001 gram. The hypochlorite (bleach) solution to be analyzed will be supplied by the instructor. Pipette 10.00 mL of the bleach solution into the weighing bottle; it is essential that the upper portion of the bottle, particularly the ground glass rim remain dry. Replace the stopper and weigh to the nearest 0.0001 gram.
2. Empty the weighing bottle into a 250 ml volumetric flask containing about 100 ml of water using a funnel. Wash out the weighing bottle and the funnel with water from your wash bottle, catching the rinse in the volumetric flask. Dilute to the mark and mix thoroughly. From this point on, handle each sample individually throughout the remainder of the procedure.
3. Fill your burette with the standardized 0.1 M sodium thiosulfate solution. Measure out and have ready 10 ml of glacial acetic acid and 2 g of potassium iodide. When ready to titrate, pipette a 50.00 mL aliquot of the diluted bleach solution in a clean 250 mL Erlenmeyer flask containing about 50 mL of water. Rinse down the walls of the flask in such a way as to form a layer of water above the sample. Add the acid to the sample, mix, add the potassium iodide, and titrate immediately, swirling the flask constantly. When the color has faded to a pale yellow, add 2 ml of starch solution and then continue to titrate drop by drop until the solution becomes colorless. Titrate two additional 50.00 mL aliquots the same way.
4. Calculate the percentage by weight of NaOCl in the solution. Note: Fresh commercial bleach should contain at least 5% NaOCl. If less than 5%, it cannot legally be called bleach. Nevertheless, the bleach sample used in class may contain less than this. Report the mean, standard deviation, and relative standard deviation for your analysis.

Report

Report the percent NaOCl in the unknown. Show all calculations and propagation of error for one sample from start to finish. Calculate the mean, standard deviation, and relative standard deviation for at least three samples. If you have questions regarding any of the calculations required, please see the instructor.

SAMPLE REPORT

Analysis of Hypochlorite in Commercial Bleach:
Iodometric Titrimetry
Ben Affleck
Unknown # Π

Standardization of Sodium Thiosulfate:

	1 st	2 nd	3 rd
M, KIO ₃	0.01009	0.01009	0.01009
mL KIO ₃	50.00	50.00	50.00
Initial buret mL	0.05	0.23	1.01
Final buret mL	30.02	30.15	30.89
mL, S ₂ O ₃ ⁻²	29.97	29.92	29.88
mmoles, KIO ₃	0.5045	0.5045	0.5045
mmoles, S ₂ O ₃ ⁻²	3.027	3.027	3.027
M, S ₂ O ₃ ⁻²	0.1010	0.1012	0.1013
Mean S ₂ O ₃ ⁻²		0.1012	
Sx		0.0002	
RSD		0.2%	

Sample calcs for standardization:

1. $\text{mmoles KIO}_3 = \text{mL KIO}_3 \times \text{M, KIO}_3$
 $0.5045 \text{ mmoles} = 50.00 \text{ mL} \times 0.01009 \text{ M}$
2. $\text{mmoles S}_2\text{O}_3^{-2} = \text{mmoles KIO}_3 \times (6 \text{ S}_2\text{O}_3^{-2} / 1 \text{ KIO}_3)$
 $3.027 \text{ mmoles S}_2\text{O}_3^{-2} = 0.5045 \text{ mmoles KIO}_3 \times (6 \text{ S}_2\text{O}_3^{-2} / 1 \text{ KIO}_3)$
3. $\text{M, S}_2\text{O}_3^{-2} = \text{mmoles, S}_2\text{O}_3^{-2} / \text{Volume, S}_2\text{O}_3^{-2}$
 $0.1010\text{M} = 3.027 \text{ mmoles S}_2\text{O}_3^{-2} / 29.97 \text{ mL S}_2\text{O}_3^{-2}$

Titration of Bleach:

Mass of undiluted bleach solution used: 10.8035 g

	1 st	2 nd	3 rd
mL diluted bleach solution	50.00	50.00	50.00
Initial buret mL	0.05	0.23	1.01
Final buret mL	29.02	29.15	29.89
mL, S ₂ O ₃ ⁻²	28.97	28.92	28.88
M, S ₂ O ₃ ⁻²	0.1012	0.1012	0.1012
mmoles S ₂ O ₃ ⁻²	2.932	2.927	2.923
mmoles ClO ⁻	1.466	1.463	1.461
mmoles ClO ⁻ in undiluted bleach	7.329	7.317	7.307
Mass NaOCl in undiluted bleach	0.5456 g	0.5447 g	0.5439 g
% NaOCl	5.050	5.042	5.034
Avg % NaOCl		5.042	
Sx		0.008	
RSD		0.2%	

Sample calculations:

- $$\text{mmoles S}_2\text{O}_3^{2-} = \text{mL, S}_2\text{O}_3^{2-} \times \text{M, S}_2\text{O}_3^{2-}$$

$$2.932 \text{ mmoles S}_2\text{O}_3^{2-} = 28.97 \text{ mL, S}_2\text{O}_3^{2-} \times 0.1012 \text{ M, S}_2\text{O}_3^{2-}$$
- $$\text{mmoles ClO}^- = \text{mmoles S}_2\text{O}_3^{2-} \times (1 \text{ ClO}^- / 2 \text{ S}_2\text{O}_3^{2-})$$

$$1.466 \text{ mmoles ClO}^- = 2.932 \text{ mmoles S}_2\text{O}_3^{2-} \times (1 \text{ ClO}^- / 2 \text{ S}_2\text{O}_3^{2-})$$
- $$\text{mmoles ClO}^- \text{ in undiluted bleach} = \text{mmoles ClO}^- \times (250.00 \text{ mL diluted bleach} / 50.00 \text{ mL aliquot})$$

$$7.329 \text{ mmoles ClO}^- \text{ in undiluted bleach} = 1.466 \text{ mmoles ClO}^- \times (250.00/50.00)$$
- $$\text{Mass NaOCl in undiluted bleach} = 7.329 \text{ mmoles ClO}^- \text{ in undiluted bleach} \times (\text{FW NaOCl}/1000)$$

$$0.5456 \text{ g NaOCl in undiluted bleach} = 7.329 \text{ mmoles ClO}^- \text{ in undiluted bleach} \times (74.44/1000)$$