## Analysis of Hypochlorite in Bleach

(Redox titrations are cool!)
This experiment allows you to determine the percentage ( $\mathrm{w} / \mathrm{v}$ ) of active ingredient, sodium hypochlorite ( NaOCl ) in common commericial bleaches. We won't do it directly, but we will use some cool chemistry and we will be able (or should be able) to determine percentages pretty accurately.

THE CHEMISTRY: (for more a more detailed description see your lab manual)

$$
\begin{align*}
& \mathrm{OCl}^{-}{ }_{(\mathrm{aq})}+2 \mathrm{H}^{+}{ }_{(\mathrm{aq})}+2 \mathrm{I}_{(\mathrm{aq})}^{-} \rightarrow \mathrm{I}_{2(\mathrm{aq)}}+\mathrm{Cl}^{-}{ }_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}  \tag{1}\\
& 2 \mathrm{~S}_{2} \mathrm{O}_{3}{ }^{2-}+\mathrm{I}_{2} \rightarrow 2 \mathrm{I}^{-}+\mathrm{S}_{4} \mathrm{O}_{6}{ }^{2-}  \tag{2}\\
& \mathrm{I}_{2(\mathrm{aq)}}+\mathrm{I}^{-}{ }_{(\mathrm{aq)}} \rightarrow \mathrm{I}_{3}{ }^{-}{ }_{(\mathrm{aq})} \quad \text { (occurs rapidly and completely) } \tag{3}
\end{align*}
$$

So when $\mathrm{I}^{-}$is in excess:

$$
\begin{gather*}
2 \mathrm{~S}_{2} \mathrm{O}_{3}{ }_{(\text {(aq })}^{2-}+\mathrm{I}_{3}^{-}{ }_{\text {(aq) }} \rightarrow 3 \mathrm{I}_{(\text {aq })}^{-}+\mathrm{S}_{4} \mathrm{O}_{6}^{2-}{ }_{(\text {aq })}  \tag{4}\\
\mathrm{I}_{3}-_{(\text {aq })}+\text { starch } \rightarrow \text { deep-blue complex } \quad \text { (also occurs rapidly) } \tag{5}
\end{gather*}
$$

Our problem: The analysis of $\mathrm{OCl}^{-}$by titration with $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ requires that we know the concentration of the $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ solution. Unfortunately, sodium thiosulfate $\left(\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}\right)$ is not a primary standard, so we must standardize the sodium thiosulfate solution. A similar series of reactions is used for the standardization, only potassium iodate $\left(\mathrm{KIO}_{3}\right)$ is used to oxidize iodide ( $\mathrm{I}^{-}$) to iodine $\left(\mathrm{I}_{2}\right)$ :

$$
\begin{equation*}
\mathrm{IO}_{3}^{-}{ }_{(\mathrm{aq})}+5 \mathrm{I}_{(\mathrm{aq})}^{-}+6 \mathrm{H}^{+}{ }_{(\mathrm{aq})} \rightarrow 3 \mathrm{I}_{2(\mathrm{aq})}+3 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \tag{6}
\end{equation*}
$$

So we'll titrate a known amount of $\mathrm{KIO}_{3}$ (the limiting reagent), in the presence of excess of $\mathrm{I}^{-}$, with our $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ solution. Using the stoichiometry of reaction 6, we can calculate the $\mathrm{I}_{2}$ generated (theoretically) and then using the stoichiometry of reaction 2 (this gives us moles $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ used in each titration) and the titration volumes we can calculate $\left[\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}\right]$.

## THE EXPERIMENT:

1) Standardize $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}{ }_{(\mathrm{aq})} \Rightarrow$ Solves problem.

The stoichiometry is important:
$1{\text { mole } \mathrm{IO}_{3}{ }^{-}=3 \text { mole } \mathrm{I}_{2}}^{1 \text { mole }_{2}=2 \text { mole } \mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}} \quad[2]$
So after titrations are completed (volumes), you can find $\left[\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}\right]$.
You need at least 3 titration volumes within 0.05 mL .
2) Determine $\% \mathrm{NaOCl}$ in bleach $(\mathrm{w} / \mathrm{v})$

You need at least 3 titrations within 0.05 mL .
$\left[\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}\right] \times$ titration vol. of $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}=$ mole $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$
1 mole $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}=1 / 2$ mole $\mathrm{I}_{2}$
$1 \mathrm{~mole}^{2}=1 \mathrm{~mole}_{2} \mathrm{OCl}^{-}(=$mole NaOCl$)$ [1]
Convert to mass NaOCl (g) (MW NaOCl $=74.44 \mathrm{~g} /$ mole)
Find (g/sample vol.) x $100 \%$
sample vol. $=0.10 \mathrm{~mL} \Rightarrow 5.00 \mathrm{~mL}$ of orignal bleach solution $/ 250.0 \mathrm{~mL}$, so, stock bleach solution is 0.02 ( or $1 / 50$ ) of original bleach solution.
For each titration $\Rightarrow 5.00 \mathrm{~mL} \times 0.02($ or $5.00 \mathrm{~mL} / 50)=0.10 \mathrm{~mL}$

## SAMPLE CALCULATIONS:

1) Standardization of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ :
$\left(0.2000 \mathrm{~g} \mathrm{KIO}_{3}\right)\left(1 \mathrm{~mole} \mathrm{KIO}_{3} / 214.00 \mathrm{~g} / \mathrm{mole}\right)=9.346 \times 10^{-4} \mathrm{~mole} \mathrm{KIO}_{3}$
You made up $\mathrm{KIO}_{3}$ stock solution in a 100.0 mL volumetric flask and for each titration you used 5.00 mL of your stock solution

So.... for each titration you used 1/20 of your stock solution:
$\mathrm{KIO}_{3}$ used in each titration $=9.346 \times 10^{-4} \mathrm{~mole}_{\mathrm{KIO}}^{3}$ /20
$\mathrm{KIO}_{3}$ used in each titration $=4.67 \times 10^{-5} \mathrm{~mole}_{\mathrm{KIO}}^{3}$
1 mole $\mathrm{KIO}_{3}=3$ mole $\mathrm{I}_{2} \Rightarrow 1.40 \times 10^{-4} \mathrm{~mole}_{2}$
1 mole $\mathrm{I}_{2}=2$ mole $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3} \Rightarrow 2.80 \times 10^{-4} \mathrm{~mole}_{\mathrm{Na}}^{2} \mathrm{~S}_{2} \mathrm{O}_{3}$
e.g. For a titration volume $=5.61 \mathrm{~mL}$ (from experimental data) :
$2.80 \times 10^{-4}$ mole $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3} / 0.00561 \mathrm{~L}=0.0500 \mathrm{M} \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$
2) Analysis of Bleach (Clorox)
e.g. For a titration volume $=3.44 \mathrm{~mL}$ (from experimental data)
$\left(0.00344 \mathrm{~L} \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}\right)\left(.0500 \mathrm{~mole} / \mathrm{L} \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}\right)=1.72 \times 10^{-4} \mathrm{~mole}_{\mathrm{Na}}^{2} \mathrm{~S}_{2} \mathrm{O}_{3}$
1 mole $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}=1 / 2$ mole $_{2} \Rightarrow 8.68 \times 10^{-5} \mathrm{~mole}_{2}$
1 mole $\mathrm{I}_{2}=1$ mole mole $\mathrm{NaOCl} \Rightarrow 8.68 \times 10^{-5}$ mole NaOCl
mass $\mathrm{NaOCl}=\left(8.68 \times 10^{-5}\right.$ mole NaOCl$)(74.44 \mathrm{~g} /$ mole $)=0.00640 \mathrm{~g} \mathrm{NaOCl}$
$\% \mathrm{NaOCl}(\mathrm{w} / \mathrm{v})=(0.00640 \mathrm{~g} \mathrm{NaOCl} / 0.10 \mathrm{~mL}$ bleach $) \times 100 \%=6.40 \% \mathrm{NaOCl}$
$\operatorname{RMD}(\mathrm{ppt})=($ mean deviation $/$ mean $) \times 1000$

