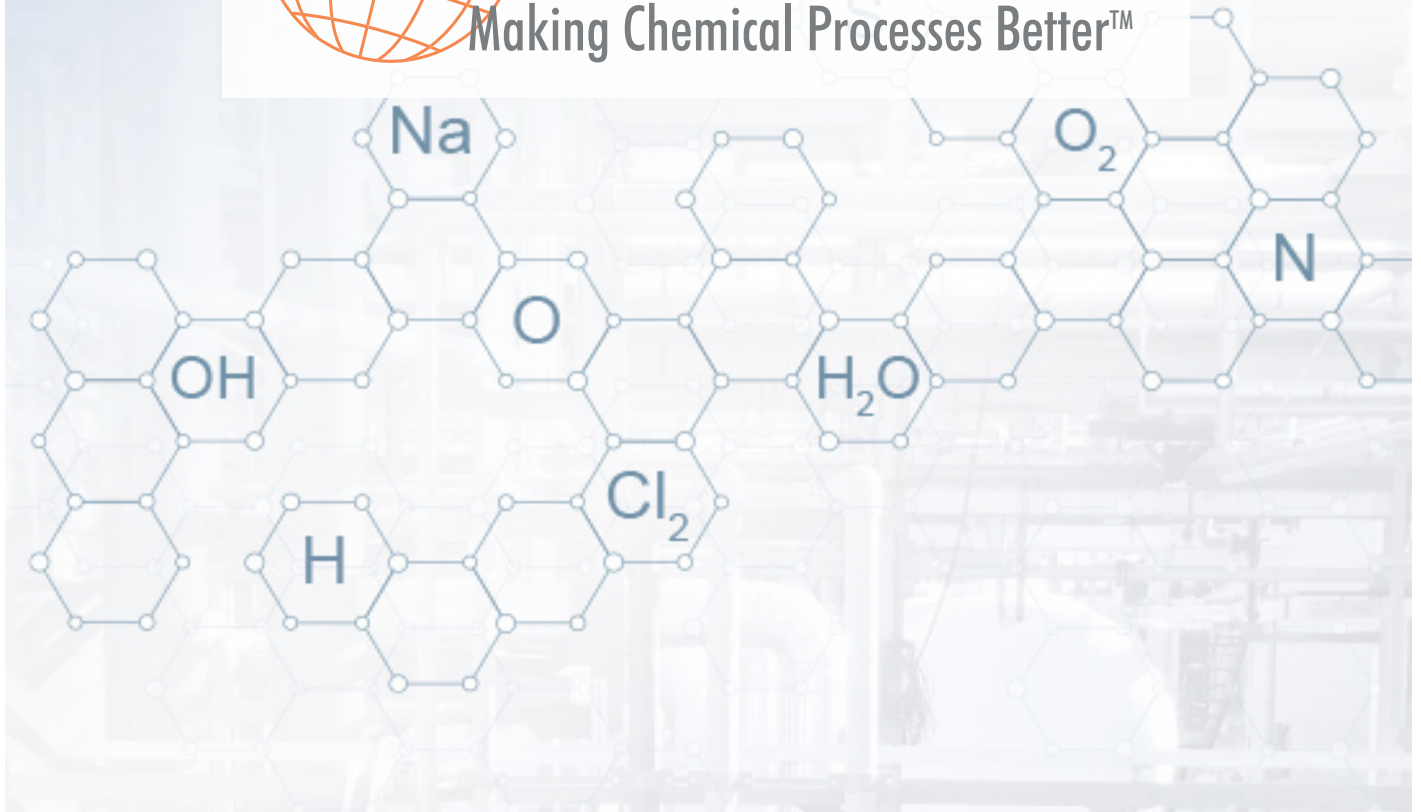




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A TITRATION METHOD

MEASURING CHLORATE ION IN
CONCENTRATED BLEACH SOLUTIONS



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The minimization of bleach loss is a high priority for sodium hypochlorite producers. The largest source of bleach loss during production is process related with the subsequent formation of chlorate ion.

The most accurate measurement method for determining the chlorate ion concentration in bleach is ion chromatography (IC). Because this measurement requires specialized equipment and training, most bleach producers are unable to measure the chlorate ion concentration (and the subsequent bleach loss) at the production site. Thus, a titration method has been developed for on-site use to estimate the chlorate ion concentration in 10-15% bleach solutions.

The titration method is based on the method proposed by Aieta, Roberts and Hernandez (AWWA, 1984, 76(1):64). The bleach sample is prepared by removing the available chlorine by reaction with hydrogen peroxide. The measurement is based on the titration of iodine by sodium thiosulfate. At pH 2, a number of oxidizing species in the sample are titrated (e.g. chlorite ion). Under highly acidic conditions, chlorate ion is titrated along with the oxidizing species titrated at pH 2. The chlorate ion concentration is calculated by taking the difference of the titrations.

This method is to be used for chlorate ion concentrations between 1,000 – 10,000 mg/L.

Chemistry Background

The pertinent chemistry for this method is 3-fold:

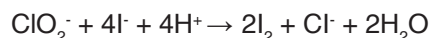
- the removal of chlorine
- reactions at pH 2
- reactions under very acidic conditions

Chlorine is removed by treating the bleach sample with hydrogen peroxide as shown below:

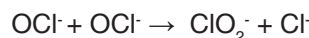


This step removes chlorine as a potential interference in the method. As hydrogen peroxide reacts with KI to form iodine, the treated sample is heated to remove any residual hydrogen peroxide.

At pH 2, any number of oxyhalogen species that might be present in bleach solutions can react with KI. Thus it is important to account for the presence of these species in the final calculation. For example, chlorite ion (ClO_2^-):

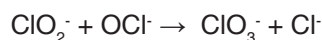


Chlorite ion is a steady-state intermediate species that is formed when bleach decomposes -- 2 hypochlorite ions react to form chlorite ion:



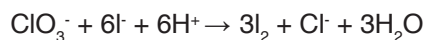
This means that for every “mole” of chlorite ion present in bleach, 2 “moles” of hypochlorite ion are lost.

As an intermediate species, chlorite ion will readily react with hypochlorite ion to form chlorate ion:



This means that for every “mole” of chlorate ion present in bleach, 3 “moles” of hypochlorite ion are lost. Thus, a high concentration of chlorate ion might represent a substantial bleach loss.

Under very acidic conditions, chlorate ion reacts with iodide ion to form iodine



A difficulty that can present itself under highly acidic reaction conditions is the oxidation of iodide ion to iodine resulting in a positive bias. To minimize this potential problem, bromide ion is used as the reducing agent. Bromide ion is not oxidized by oxygen under these conditions. After the reaction is completed (20 min), iodide ion is added to the sample and iodine is formed following reaction with bromine resulting from the reduction of the chlorine species originally present in the sample. Rapid dilution of the sample with sodium phosphate lowers the acidity of the sample thus minimizing unwanted side reactions.

Sample Preparation

The following laboratory equipment/chemicals are required:

- 100 ml volumetric flask
 - Stir bar
 - Heated Stir Plate
 - 5 ml disposable plastic pipette
 - 30% Hydrogen Peroxide
 - 20 ml pipette
1. Accurately pipette 20 ml of the concentrated bleach sample into a 100 ml volumetric flask
 2. Place the volumetric flask on the heated stir plate and place the stir bar in the flask
 3. Turn on the stir plate so that the stir bar revolves in a controlled manner
 4. Using the 5 ml plastic pipette, slowly and carefully add the hydrogen peroxide. For 10-15% bleach, expect to add 4-6 ml of 30% hydrogen peroxide. When the appropriate volume of hydrogen peroxide has been added, the solution in the flask will turn colorless and the addition of hydrogen peroxide will not generate oxygen.

CAUTION! The addition of hydrogen peroxide to bleach can be a violent reaction. The addition must be done slowly so that the evolution of oxygen is controlled and the reaction is contained in the volumetric flask. When the hydrogen peroxide is added too quickly, the reaction will “bubble-out” of the flask. Appropriate eye wear and protective clothing must be used at all times.

5. Turn the stir plate heater on and continue to stir the solution. Allow the solution to boil for 15 minutes in a controlled manner.
6. Remove the flask from the hot plate and allow the solution to cool to room temperature. NOTE: Adding 40 ml of distilled water to the volumetric flask and placing the flask in an ice bath will speed up the cooling process.
7. Remove the stir bar and bring the solution to volume with distilled water.

Measurements

The following laboratory equipment/chemicals are required:

- 125 ml Erlenmeyer flask
- 1 ml pipette
- 3 ml pipette
- 10 ml pipette (2)
- Stir bar
- Stir Plate
- 50 ml burette
- 100 ml volumetric flask (2)
- 25 ml graduated cylinder
- Potassium bromide crystals
- Potassium iodide
- Conc hydrochloric acid
- 2.5 N hydrochloric acid
- Sodium phosphate
- Sodium thiosulfate

Prepare the following solutions:

Potassium Bromide (5%): Dissolve 5g KBr in a 100 ml volumetric flask and dilute to volume with distilled water. Store the solution in a brown glass-stoppered bottle. This solution should be made fresh daily.

Hydrochloric Acid (2.5 N): Cautiously add 20 ml of concentrated HCl to 50 ml of distilled water with mixing in a 100 ml volumetric flask and dilute to volume.

Sodium phosphate (Saturated Solution): Prepare a saturated solution of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ with cold distilled water (Add enough sodium phosphate so that undissolved crystals are observable in the flask).

Standard Sodium Thiosulfate (0.1 N): This solution is typically available from chemical supply companies. We recommend that this solution be purchased. If purchasing the prepared solution is not possible, prepare the solution as follows: dissolve 25g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 1L of freshly boiled distilled water and standardize against potassium bi-iodate or potassium dichromate after at least a two-week storage. This initial storage is necessary to allow oxidation of any bisulfite ion present. Use boiled distilled water and add a few milliliters of chloroform to minimize bacterial decomposition.

Titration at pH 2

- Add 1 g of KI and 10 ml of distilled water to a 125 ml Erlenmeyer flask
- Add 3 ml of 2.5 N HCl to the flask
- Add 20 ml of prepared sample to the flask
- Cover the flask and let the solution stand for 5 min in the dark
- Titrate the solution with 0.1 N sodium thiosulfate (NTS)
- Record the number as B (B = ml titrant /ml sample)

Titration at pH <0.1

- Add 1 ml of 5% KBr and 10 ml of conc HCl to a 125 ml Erlenmeyer flask
- Add 10 ml of sample to the flask and let the solution stand in the dark for 20 minutes
- Add 1 g of KI to the flask and shake vigorously for 5 seconds
- Immediately add 25 ml of saturated sodium phosphate to the flask and stir
- Titrate the solution with 0.1 N sodium thiosulfate (NTS)
- Record the number as A (A = ml titrant /ml sample)

Calculations

The calculation for determining the chlorate ion concentration takes into account that chlorate ion is reduced to chloride ion (a 6-electron change). Thus, the equivalent weight of chlorate ion is divided by 6 to give 13,909 mg/equivalent.

$$\text{ClO}_3^- \text{ (mg/L)} = (\text{A} - \text{B}) (\text{N NTS}) (13,909) (5)$$

N, normality, of the sodium thiosulfate (NTS) is 0.1 N. (5) is the dilution factor of the original solution -- 20 ml of bleach was diluted to 100 ml.

To convert to g/L NaClO₃ divide by 1000 and multiply by 1.28:

$$\text{g/L NaClO}_3 = (\text{mg/L ClO}_3^-) (1.28/1,000)$$

The method is to be used for concentrations between 1,000 and 10,000 mg/L. If the calculated concentration exceeds 10,000 mg/L, the prepared sample should be diluted or a smaller sample size evaluated (for example, 5 ml instead of 20 ml).

Sample Data (The A values were calculated using a 9 ml sample volume. The B values were calculated using a 20 ml sample volume)

Sample Bleach #1

$$\text{A} = 1.6/9 = 0.178$$

$$\text{ClO}_3^- \text{ (mg/L)} = (\text{A} - \text{B}) (\text{N NTS}) (13,909) (5)$$

$$\text{B} = 0.7/20 = 0.035$$

$$\text{ClO}_3^- \text{ (mg/L)} = (0.178 - 0.035) (0.1) (13,909) (5) = 994$$

Titration value: 994

IC value: 908

109% agreement

$$\text{g/L NaClO}_3 = (994) (1.28 / 1,000) = 1.27$$

Sample Bleach #2

$$\text{A} = 13.7/9 = 1.522$$

$$\text{ClO}_3^- \text{ (mg/L)} = (\text{A} - \text{B}) (\text{N NTS}) (13,909) (5)$$

$$\text{B} = 6.9/20 = 0.345$$

$$\text{ClO}_3^- \text{ (mg/L)} = (1.522 - 0.345) (0.1) (13,909) (5) = 8,185$$

Titration value: 8,185

IC value: 8,874

92% agreement

$$\text{g/L NaClO}_3 = (8,185) (1.28 / 1,000) = 10.48$$

The average standard deviation of multiple titrations was less than 5%.