ANALYSIS OF BLEACH BY THIOSULFATE TITRATION

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The determination of free chlorine in bleach is possible by a redox titration. The most common and successful method for use in high schools involves taking the sample of bleach converting the hypochlorite ion (ClO^-) to iodine (I_2) by the addition of KI and then titrating the iodine with standardized sodium thiosulfate solution.

Step 1: Preparing a standard solution of potassium iodate (KIO_3)
Procedure: To make an approximately 0.033 M solution of potassium iodate, accurately weigh approximately 0.7 g KIO_3 (dried at 120˚C for at least 2 hours prior to weighing) and make up to 100 mL in a volumetric flask.

Sample results and calculations:
Mass of KIO_3 = 0.715 g

$$C(KIO_3) = \frac{n}{V} = \frac{m/M}{V} = \frac{0.715/214.0}{0.100} = 0.0334\ M$$

Step 2: Prepare a solution of approximately 0.2 M $Na_2S_2O_3$ solution
Weigh out approximately 12.5 g of sodium thiosulfate pentahydrate crystals into a 250 mL volumetric flask and add approximately 0.025g sodium carbonate. Make up to the mark with distilled water.

Sample results and calculations:
Mass of sodium thiosulfate = 12.62 g

$$C(KIO_3) = \frac{n}{V} = \frac{m/M}{V} = \frac{12.62/248.21}{0.250} = 0.2033\ M$$

Note: this is only approximate as sodium thiosulfate is not a primary standard (it has to be standardized against potassium iodate). However, in schools, this solution is sometimes treated as an accurate concentration.

Step 3: Standardize sodium thiosulfate solution against standard KIO_3 solution.
Theory: The overall reaction is as follows:
$IO_3^- + 6\ H^+ + 6\ S_2O_3^{2-} \rightarrow I^- + 3\ S_4O_6^{2-} + 3\ H_2O$

$$n(iodate) = \frac{n(thiosulfate)}{6}$$

$$C(iodate) \times V(iodate) = \frac{C(thiosulfate) \times V(thiosulfate)}{6}$$

Pipette out a 25 mL aliquot of the standard potassium iodate solution into a conical flask and add 10 mL of 10% sulfuric acid solution and 2 g of KI. Titrate with thiosulfate solution (in the burette), adding starch as colour fades to straw yellow.

Sample results and calculations:
C(iodate) = 0.0334 M
V(iodate) = 25.0 mL (pipette)
V(thiosulfate) = 20.15 mL (titre)

$$C(iodate) \times V(iodate) = \frac{C(thiosulfate) \times V(thiosulfate)}{6}$$

$$0.334 \times 25.0 = \frac{C(thiosulfate) \times 20.15}{6}$$

$$C(thiosulfate) = \frac{0.0334 \times 25.0 \times 6}{26.15} = 0.192\ M$$

Step 4: Preparing the bleach

Theory: Commercial bleach is approximately 5.25% NaClO by mass (approx 0.7 M) and is too concentrated to titrate with the 0.2M thiosulfate solution. It is advisable to dilute the bleach by a factor of 1 in 10. We'll call this diluted bleach solution "chlorine water".

Procedure: Prepare the diluted bleach ('chlorine water') solution by pipetting 10 mL of bleach into a 100 mL volumetric flask and filling to the mark with distilled water. Stopper and invert several times to mix.

Step 5: Titrating sodium hypochlorite (free chlorine) in bleach solution

Theory: Chlorine water cannot be titrated against the standard thiosulfate solution because the end point is not easily detectable. The standard procedure in schools is to react the chlorine water with an excess of acidified KI which converts all of the ClO^- to I_2 which can be detected. (This in turn combines with iodide ion to form the very visible soluble brown tri-iodide ion I_3.)

$$\underset{\text{(faint yellow)}}{ClO^-} + \underset{\text{(colourless)}}{2I^-} + 2\,H^+ \rightarrow \underset{\text{(brown)}}{I_2} + Cl^- + H_2O \qquad (1)$$

As we can't detect an end-point for the reaction above, the (brown) I_2 product is titrated with thiosulfate. As the iodine is used, the brown colour due to the tri-iodide ion fades to yellow, and then disappears. This is a hard endpoint to detect, so when the brown starts to fade to yellow, starch can be added. Starch forms a blue complex with I_2, and this colour disappears when the stoichiometric amount of thiosulfate has been added to the flask.

$$2\,S_2O_3^{2-} + I_2 \rightarrow 2\,I^- + S_4O_6^{2-} \qquad (2)$$

From equations (1) and (2), it can be seen that 1 mole of ClO^- reacts to form 1 mole I_2, which consumes 2 moles of $S_2O_3^{2-}$. Hence, 1 mole of hypochlorite is equivalent to 2 moles of thiosulfate.

$$n(hypochlorite) = \frac{n(thiosulfate)}{2}$$

$$C(hypochlorite) \times V(hypochlorite) = \frac{C(thiosulfate) \times V(thiosulfate)}{2}$$

Procedure:

Prepare an acidified KI solution (14.0 g KI + 40 mL glacial acetic acid in 1 L).

Prepare a 1% starch suspension.

Rinse a 25 mL pipette with the chlorine water solution and transfer an aliquot into a conical flask.

Measure 50 mL of the acidified potassium iodide solution in a measuring cylinder and add to the chlorine water in the flask. It should go brown. If it does not, check the bleach – it decomposes over time.

Rinse and fill the burette with the standard 0.20 M $Na_2S_2O_3$ solution and titrate until the brown colour fades to a straw yellow. Add a few drops of starch indicator. A blue starch-iodine complex should form.

Continue adding $Na_2S_2O_3$ to the flask until the blue colour disappears.

Sample results and calculations:

Volume of chlorine water (pipette) = 25.00 mL

Titre of thiosulfate solution (burette) = 10.25 mL

$$C(hypochlorite) \times V(hypochlorite) = \frac{C(thiosulfate) \times V(thiosulfate)}{2}$$

$$C(hypochlorite) \times 25.00 = \frac{0.192 \times 10.25}{2}$$

$$C(hypochlorite) = \frac{0.192 \times 10.25}{2 \times 25.00} = 0.03936\ M$$

[Note: this is the concentration of the ClO^- in the ‘chlorine water’].

Concentration of original bleach would be 0.3936 M (because of the 1:10 dilution)

Additional calculations:

If you want to express the conc of the hypochlorite ion in the chlorine water in other forms (mg/L) then you will have to convert molarity (M) to g/L and then to mg/L:

$$C(ClO^-) = \frac{n(ClO^-)}{V(ClO^-)} = \frac{m / M}{V} = \frac{m}{M \times V}$$

$$m(ClO^-) = C(ClO^-) \times M \times V$$

$$= C(ClO^-) \times M \quad [g\ in\ 1\ L]$$

$$m(ClO^-) = C(ClO^-) \times M \times 1000 \quad [mg\ in\ 1\ L]\ \ Note: mass\ is\ now\ in\ milligrams$$

Sample results and calculations:

$$m = C(ClO^-) \times M \left[g\ in\ 1L\right]$$

$$m = C(ClO^-) \times M \times 1000 \ \left[mg\ in\ 1L\right]$$

$$m = 0.03936 \times 51.5 \times 1000 \left[mg\ in\ 1L\right]$$

$$C\ (mg/L) = 2030\ mg/L\ (\ in\ the'chlorine\ water')\ (\ 3\ significant\ figures)$$