

Iodometric Titrations

Iodimetric Titrations: The titrations in which standardized iodine solution is used directly.

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Sodium Thiosulfate

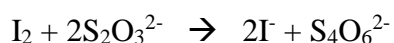
Thiosulfate ion ($\text{S}_2\text{O}_3^{2-}$) is a moderately strong reducing agent that has been widely used to determine oxidizing agents by an indirect procedure in which iodine is an intermediate.

With iodine, thiosulfate ion is oxidized quantitatively to tetrathionate ion ($\text{S}_4\text{O}_6^{2-}$) according to the half-reaction



The quantitative reaction with iodine is unique. Other oxidants can oxidize the tetrathionate ion to sulfate ion.

The scheme used to determine oxidizing agents involves adding an unmeasured excess of potassium iodide to a slightly acidic solution of the analyte. Reduction of the analyte produces a stoichiometrically equivalent amount of iodine. The liberated iodine is then titrated with a standard solution of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, one of the few reducing agents that is stable toward air oxidation.



The quantitative conversion of thiosulfate ion to tetrathionate ion requires a pH smaller than 7.

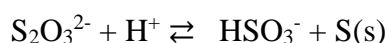
Detecting End Points in Iodine/Thiosulfate Titrations

Provided the analyte solution is colorless, the disappearance of the iodine color (red-brown) can serve as the indicator in titrations with sodium thiosulfate. Most often, iodine titrations are performed with a suspension of starch as an indicator. The deep blue color that develops in the presence of iodine is believed to arise from the absorption of iodine into the helical chain of β -amylose, a macromolecular component of most starches. The closely related α -amylose forms a red adduct with iodine. This reaction is not easily reversible and is thus undesirable. In commercially available soluble starch, the alpha fraction has been removed to leave principally β -amylose. Indicator solutions are easily prepared from this product.

Starch decomposes irreversibly in solutions containing large concentrations of iodine. Therefore, in titrating solutions of iodine with thiosulfate ion, as in the indirect determination of oxidants, addition of the indicator is delayed until the color of the solution changes from red-brown to yellow; at this point, the titration is nearly complete.

Stability of Sodium Thiosulfate Solutions

Although sodium thiosulfate solutions are resistant to air oxidation, they do tend to decompose to give sulfur and hydrogen sulfite ion:



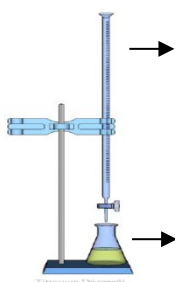
Variables that influence the rate of this reaction include

- pH,
- the presence of microorganisms,
- the presence of copper(II) ions,
- exposure to sunlight.

The rate of the decomposition reaction increases markedly as the solution becomes acidic.

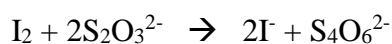
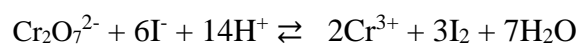
Experimental Procedure:

Standardizing Thiosulfate Solution with Potassium Dichromate

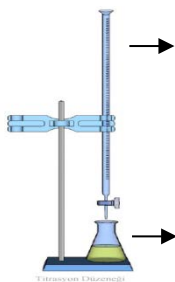


→ $\text{Na}_2\text{S}_2\text{O}_3$ solution

- 4-5 mL $\text{K}_2\text{Cr}_2\text{O}_7$ solution + 40 mL ~0.1 M HCl + KI
- Erlenmeyer is covered with paper. Because of the produced I_2 , the color of the solution becomes dark brown
- The solution is kept in the dark for 4 minutes
- The solution is titrated until the yellow-green color is observed in the solution
- + 3 mL starch solution (the color of the solution becomes dark blue)
- The solution is titrated until the light green color is observed in the solution

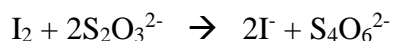
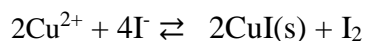


Copper Determination with Sodium Thiosulfate

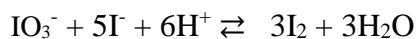


Standardized $\text{Na}_2\text{S}_2\text{O}_3$ solution

- Neutral or slightly acidic medium is required for copper determination
- Saturated Na_2CO_3 is added before diluting the sample, precipitate is formed (CuCO_3).
- The precipitate is dissolved with concentrated acetic acid.
- Erlenmeyer is covered with paper and kept in the dark for 3 minutes
- The solution is titrated until the yellow-green color is observed in the solution
- + 2 mL starch solution (the color of the solution becomes dark blue)
- The solution is titrated until the white color is observed in the solution



*** If it is kept for more than 4 minutes, iodide reacts with trace amount of iodate in the KI and iodine is formed.



*** It is kept in the dark with the cover, because the iodide reacts with the oxygen to form iodine. Sunlight catalyses this reaction.

