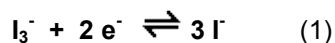

Iodometric Determination of Copper

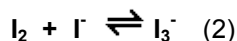
Adapted from Day and Underwood, "Quantitative Analysis", 6th Edition

Introduction: The iodine (triiodide) - iodide redox system,



is a weak oxidizing agent. On the other hand, iodide ion can be a strong reducing agent. Analytical reactions using iodine as the oxidizing agent are called iodimetry while procedures using iodide ion as the reducing agent are called iodometry. Since triiodide is such a weak reducing agent, there are few iodimetric determinations of analytical interest. Iodide ion is a strong enough a reducing agent that many oxidizing agents can react completely with the iodide ion resulting in many useful iodometric processes. The usual procedure involves the addition of an excess of iodide ion to the oxidizing agent analyte, which produces iodine, which can be titrated with standard sodium thiosulfate solution. The iodine-thiosulfate reaction is quite fast and the equilibrium is far to the product side.

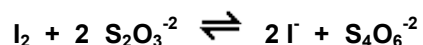
Iodine is slightly soluble in water (0.00134 mol/L at 25 °C) but is soluble in solutions containing iodide ion. Iodine forms the triiodide complex with iodide,



with $K > 500$ at 25 °C. Normally, excess potassium iodide is added to the reaction mixture to increase the solubility of iodine and to decrease its volatility. It is possible to prepare primary standard iodine solutions by direct weighing.

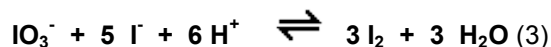
Sodium Thiosulfate

Sodium thiosulfate is commonly used as the pentahydrate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$, and solutions are standardized against a primary standard. Thiosulfate solutions are not stable over long periods of time, and frequently borax or sodium carbonate is added as a preservative. Iodine oxidizes thiosulfate to the tetrathionate ion:

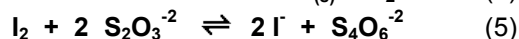
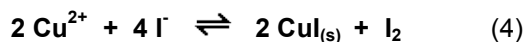


The reaction of iodine with thiosulfate is fast and goes to completion. The equivalent weight of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ is the molecular weight, 248.17, since one electron per molecule is lost.

Iodine is rarely used as a primary standard for thiosulfate because it presents a problem in weighing and maintaining its solution concentration. Potassium iodate oxidizes iodide quantitatively to iodine in acid solution:



Pure copper is used as a **primary standard** for sodium thiosulfate and is recommended when the thiosulfate is to be used for the determination of copper. Upon addition of excess iodide to a solution of Cu(II), a precipitate of CuI is formed along with I₂. The liberated iodine is then titrated with standard sodium thiosulfate.



Formation of the precipitate and the addition of excess iodide forces the equilibrium to the right. The pH of the solution must be maintained between pH 3 and 4 by the addition of a buffer. It has been found that iodine is adsorbed onto the surface of the copper(I) iodide precipitate and must be displaced to obtain correct results. Potassium thiocyanate is usually added just before the end point is reached to displace the adsorbed iodine. *Note that the net stoichiometry of the react is 1:1 since 2 moles of copper requires 2 moles of thiosulfate.*

Before you come to lab:

- Write the chemical equations 3, 4 & 5 (above) in your lab notebook.
- Write the atomic mass of copper in your notebook.
- List all of the reagents (formulas and names) in your notebook. Familiarity with the reagents will help you avoid costly mistakes during the experiment.

Important Note: Use of the wrong reagent during any step will ruin the sample and you will have to start all over. Some reagent names are given in **bold type** – this is to **emphasize exactly** what to use. Don't use the wrong concentration or reagent!

Reagents:

- 6 M HNO₃
- 4 M NH₃
- acetic acid (glacial)
- 9 M H₂SO₄
- urea
- sodium thiosulfate
- potassium iodide
- sodium thiocyanate
- starch solution
- Cu wire (99.99%)
- sodium carbonate

Preparation of a 0.1 M Sodium Thiosulfate Solution

Only prepare this solution if you did not do so last week.

Make this solution in your 1 L plastic bottle and label it with tape. Dissolve about 25 g of sodium thiosulfate pentahydrate crystals in 1 liter of distilled water. Add about 0.2 g of sodium carbonate as a preservative. Shake to ensure complete dissolution and mixing.

Standardization of a 0.1 M Sodium Thiosulfate:

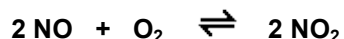
1. Weigh three pieces of clean copper wire or foil using about 0.20 to 0.25 g each and place them in 250-mL Erlenmeyer flasks.
2. Add to each flask 5 mL of **6 M nitric** acid and dissolve the copper by warming the solution on a hot plate. *Do not let the solution go dry since some metal oxides are quite insoluble once they have formed.* The volume of the solution can be increased by adding distilled water but be sure to allow the solution to cool before adding any reagents. *Never add a reagent to a sample on the hot plate.* If necessary, add a few more mL of the 6 M nitric acid to complete the dissolution of the copper.
3. After the copper has dissolved, add 25 mL of water and boil the solution for a few minutes.
4. Add 5 mL of **urea** solution (1 g in 20 mL of water) and continue boiling for another minute (Note 1).
5. Cool the solution and neutralize the excess acid with **4 M ammonia** *in the hood*. Use a dropper to add the ammonia carefully until a pale blue precipitate of copper(II) hydroxide is obtained. This is somewhat like a titration (Note 2). The amount of ammonia to be added depends on how much acid was used and how much was vaporized during the heating process. *If you overshoot the precipitate, the solution will turn royal blue. Boil the solution to remove excess ammonia and see your instructor.*
6. Add 5 mL of glacial acetic acid to dissolve the precipitate. Cool the solution if it is warm.

At this point, you should prepare and titrate your samples one at a time.

7. To the first sample, add 3 g of potassium **iodide**, cover the flask with a watch glass, and allow to stand for 2 min.
8. Then titrate with thiosulfate solution until the brownish color of iodine is almost gone or a light tan or "mustard" color (Grey Poupon, not French's) is obtained (Note 3).
9. Add 5 mL of starch solution and 2 g of sodium **thiocyanate** (Note 4).
10. Swirl the flask for about 15 seconds and complete the titration, adding thiosulfate dropwise.
11. At the end point the bluish-gray color of the solution disappears and the precipitate appears white, or slightly gray, when allowed to settle (Note 4).
12. Treat the second and third samples in the same manner and titrate with thiosulfate.
13. Calculate the molarity of the thiosulfate solution.

Notes

1. Boiling removes oxides of nitrogen which result from the following reactions:



and is decomposed by urea according to the equation



2. If excess ammonia is added, copper(II) hydroxide redissolves, forming the deep blue copper(II) ammonia complex, $\text{Cu}(\text{NH}_3)_4$. If the excess of ammonia is large, a large quantity of ammonium acetate will be produced later; this may keep the reaction between copper(II) and iodide ions from being complete. The excess ammonia can be removed by boiling, and the precipitate will re-form.
3. After the first titration, calculate the approximate volume required for the other samples. Then titrate to within 0.5 mL of this volume before adding the starch indicator and the sodium thiocyanate. The thiocyanate displaces adsorbed iodine from the precipitate.
4. The end-point precipitate is never completely white but there should be a sharp color change.

Determination of Copper in an Ore

Note: Since the range of the percentage of copper is relatively large, your instructor will give you a “ballpark” estimate of the % Cu in your sample. Use this to calculate the sample size needed for titration with 35 mL of the thiosulfate solution. See #1 below.

1. Accurately weigh three samples of appropriate size (consult the instructor) of the finely ground ore into 250-mL Erlenmeyer flasks.
2. Add approximately 5 mL of **9 M sulfuric** acid and cover the beaker with a watch glass and heat. In some samples, a white residue of silica remains. Add a few mL more of the H_2SO_4 if the sample does not dissolve after a few minutes of heating.
3. Cool the solution and carefully add 25 mL of water.
4. Add **4 M ammonium** carefully until the deep blue color of the copper-ammonia complex is just formed.
5. Add 5 mL of glacial acetic acid which should remove the copper(II)-ammonia complex.

At this point, you should prepare and titrate your samples one at a time.

6. Add about 3 g of potassium **iodide** to the solution.
7. Titrate the liberated iodine at once with thiosulfate until the brownish color of the iodine is almost gone (a light tan color is ideal.)
8. Then add 5 mL of starch solution and 2 g of sodium **thiocyanate**.
9. Swirl the flask gently for about 15 seconds and complete the titration, adding the thiosulfate titrant dropwise.
10. At the end point the bluish-gray color of the solution disappears, and the precipitate appears white, or slightly gray, when allowed to settle.

Report the result in terms of the percentage of copper (**% Cu**) in your unknown. The range on unknown values should be between 4% to 22%.