Titrimetric Determination of Ferricyanide and Persulfate in Ferricyanide Bleach

ECR-1113D

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PRINCIPLE

Zinc sulfate is added to a sample of ferricyanide bleach to precipitate the ferricyanide and ferrocyanide. The persulfate remains in solution. The mixture is then centrifuged and the supernatant liquid is decanted.

The combined zinc ferricyanide and ferrocyanide precipitate is dispersed in acid and excess potassium iodide. Iodide equivalent to the amount of ferricyanide present is oxidized to iodine. A titration of the liberated iodine with standard sodium thiosulfate gives an indirect measure of the ferricyanide content. This ferricyanide determination is valid in the presence of persulfate and other oxidizing agents. Although sodium ferricyanide is usually purchased as a hydrate, it is reported here as anhydrous sodium ferricyanide, Na₃Fe(CN)₆.

The persulfate remaining in the decanted supernatant liquid is determined by treatment with a known excess of ferrous ion. The unoxidized ferrous ion is titrated in an acid solution with standardized 0.01 N sulfato cerate using Ferroin indicator.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS’s are available from your chemical supplier.

SPECIAL APPARATUS

- Centrifuge, with head to accommodate 50-mL centrifuge tubes
- 50-mL Centrifuge Tubes, glass- or rubber-stoppered

Note: Use pipets and volumetric glassware meeting the “Class A” definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 7.0 N Sulfuric Acid, H₂SO₄
- 50 g/L Zinc Sulfate, ZnSO₄
- Potassium iodide, KI
- 0.1 N Sodium Thiosulfate, Na₂S₂O₃ (standardized to 4 decimal places)
- Starch Indicator
- 0.10 N Ferrous Ammonium Sulfate, Fe(NH₄)₂(SO₄)₂
- Ferroin Indicator
- 0.01 Sulfato Cerate (standardized to 4 decimal places)

Note: The concentration of the ferrous ammonium sulfate must be determined daily since its strength decreases because of aerial oxidation.

PROCEDURE

Separation from Persulfate

1. Pipet (wipe the pipes before leveling) 5.00 mL of sample into a 50-mL centrifuge tube.
2. Add 3 mL of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 20 mL of 50 g/L zinc sulfate from a tip-up pipet.
4. Stopper the tube and shake it vigorously for 15 seconds. Rinse the stopper with distilled water into the centrifuge tube.
5. Stopper the tube and centrifuge for two minutes.
6. Carefully decant the supernatant liquid into a 250-mL conical flask. (Do not pour the solution too slowly since this promotes a greater loss of precipitate.)
7. Add from a tip-up pipes 20-mL of distilled water to the precipitate.
8. Stopper and shake the tube until the precipitate has completely broken up. Shake for an additional 10 seconds. Rinse the stopper with distilled water into the centrifuge tube.
9. Stopper the tube and centrifuge for two minutes.
10. Carefully decant the rinse into the conical flask containing the previously decanted liquid. (Do not pour the solution too slowly since this promotes a greater loss of precipitate.) Save the decanted liquid for the section Persulfate Determination.
**Ferricyanide Determination**

1. Add from a tip-up pipes 5 mL of 7.0 N sulfuric acid to the precipitate remaining after Step 10 of the *Separation from Persulfate* section above.
2. Add 6 g of potassium iodide crystals.
3. Stopper the tube and shake it until the precipitate is completely dispersed.
4. Quantitatively transfer the mixture into a 250-mL conical flask, using distilled water from a wash bottle.
5. Rinse the stopper and sides of the centrifuge tube with distilled water and add the rinses to the flask.
6. Add distilled water to the 250-mL conical flask to attain an approximate volume of 125 mL.
7. Titrate with standardized 0.1 N sodium thiosulfate to a light yellow color.
8. Add 5 mL of starch indicator and continue the titration until the blue color just disappears. Any precipitate present does not interfere.

### Calculations

**Potassium Persulfate**

\[
K_2S_2O_8, \text{ g/L} = \frac{(N \text{ sulfato cerate})(A - B)(\text{eq wt } K_2S_2O_8)(1000)}{(mL \text{ sample})(1000)}
\]

**Ammonium Persulfate**

\[
(NH_4)_2S_2O_8, \text{ g/L} = \frac{(N \text{ sulfato cerate})(A - B)(\text{eq wt } (NH_4)_2S_2O_8)(1000)}{(mL \text{ sample})(1000)}
\]

**Persulfate Determination**

1. Pipet (wipe the pipet before leveling) 4.00 mL of 0.10 N ferrous ammonium sulfate into the 250-mL conical flask containing the decanted liquid from Step 10 of the *Separation from Persulfate* section.
2. Swirl the flask and allow it to stand for one minute.
3. Add 10 mL of 7.0 N sulfuric acid from a tip-up pipet.
4. Add four drops of Ferroin indicator to the flask.
5. Titrate with standardized 0.01 N sulfato cerate to the first blue color that persists for 15 seconds. The volume of sulfato cerate required is “A” in the calculations below.

**Note:** If the volume of titrant required for the decanted liquid is 5 mL or less, repeat the *Separation from Persulfate* section and this section, pipetting 10.0 mL of 0.10 N ferrous ammonium sulfate.

6. Once daily, determine the strength of the ferrous ammonium sulfate using approximately 20 mL of distilled water in place of the decanted liquid. Repeat Steps 1 through 5 of this section as you did with the decanted liquid. The volume of sulfato cerate required is “A” in the calculations below.