Method 253

# THIOSULFATE

## INTRODUCTION

Thiosulfate can be found in many industrial waste discharges, particularly those of the petroleum industry. It imposes an excessive and rapid chlorine demand in wastewater treatment processes.

Three methods are offered for the analysis of thiosulfate. The first method is a direct iodometric titration in which both thiosulfate and sulfite are determined as thiosulfate. The second method is similar to the direct iodometric titration with the exception that any sulfite present is first attached to an aldehyde to prevent reaction with iodine. The third method is a cyanolysis method in which thiosulfate is converted to thiocyanate in the presence of cupric chloride and sodium cyanide. The thiocyanate is then measured. Sulfite does not interfere, but the thiocyanate originally present must be subtracted.

## Procedure 253A: Direct Iodometric Titration (11-17-97)

1. Scope and Application

    1.1 This procedure measures CSDLAC parameter 253, Thiosulfate.

    1.2 This procedure is applicable to most wastewater samples.

    1.3 This procedure is less sensitive than the CSDLAC cyanolysis procedure 253C.

    1.4 The procedure is directed toward the total iodine demand of a sample or, specifically, the thiosulfate-sulfite combination. The result can be considered thiosulfate only if sulfite is known to be absent.

2. Summary

    2.1 The sample is treated with $ZnCl_2$ conditioning buffer and filtered to remove interferences.

    2.2 The sample pH is adjusted to 7 with dilute HCl.

    2.3 The sample is titrated with a standard iodine solution to a starch-iodine endpoint.

3. Sampling Handling and Preservation

    3.1 Samples should be refrigerated at 4°C and analyzed as soon as practical.

4. Interferences

4.1 If present, sulfite ion will titrate as thiosulfate, giving false results.

4.2 Sulfide will be oxidized to elemental sulfur during the titration and therefore, consume iodine if it is not removed.

4.3 Any other substances which impose an iodine demand should be absent during the titration.

5. Apparatus

5.1 200 mL volumetric flask

5.2 25 mL buret

5.3 White ribbon filter paper

6. Reagents

6.1 Ammoniacal $ZnCl_2$ conditioning buffer. Dissolve 50 g $ZnCl_2$ in 500 mL of distilled water. Add 125 mL of $NH_4OH$ and 50 g $NH_4Cl$.

6.2 Hydrochloric acid, 0.1N

6.3 Methyl Red Indicator

6.4 Starch Solution, 0.5%. Dissolve 5 g of soluble starch in 1 L of boiling distilled water, cool to room temperature and let stand overnight. Use clear supernatant.

6.5 Stock Iodine Solution, 0.1N. Dissolve 40 g KI in 25 mL of distilled water, add 13 g re-sublimed iodine and stir until dissolved. Transfer to a 1 liter volumetric flask and dilute to the mark with distilled water.

6.5.1 Standardize the iodine against the standardized $Na_2S_2O_3$ solution prepared in Step 6.7.

6.6 Standard Iodine Titrant, 0.01N. Dissolve 25 g KI in a little distilled water contained in a 1 L volumetric flask, add proper amount of the standardized stock solution and dilute to the mark.

6.7 Standard Thiosulfate Solution, 0.112 mg/mL $S_2O_3^{2-}$. Dissolve 0.124 g $Na_2S_2O_3 \bullet 5H_2O$ in distilled water and dilute to 500 mL. Add 3 mL chloroform as preservative.

Standardize as follows:

6.7.1 Dissolve 1.226 g $K_2Cr_2O_7$ (dried two hours at 103°C) in distilled water and dilute to 1 L in a volumetric flask. Add 2 g KI to an erlenmeyer flask containing 100 to 150 mL distilled water. Add 10 mL 1 + 9 $H_2SO_4$ and pipet 10 mL of the standard $K_2Cr_2O_7$ solution into the flask. Dilute to 200 mL and titrate liberated iodine with the thiosulfate solution to a starch-iodine endpoint. Add the starch when the solution is pale yellow. Calculate the normality of the thiosulfate solution.

$$N_1V_1 = N_2V_2$$

Where: $N_1$ = normality of $K_2Cr_2O_7$
$V_1$ = Volume (mL) of $K_2Cr_2O_7$
$N_2$ = normality of $Na_2S_2O_3$
$V_2$ = volume (mL) of $Na_2S_2O_3$

$$\text{mg } S_2O_3^{2-}/\text{mL} = (\text{N } S_2O_3^{2-})(112.12 \text{ g/mole})$$

6.8 Thiosulfate spiking solution, 0.112 mg/mL $S_2O_3^{2-}$. Dissolve 0.124 g $Na_2S_2O_3 \bullet 5H_2O$ in distilled water and dilute to 500 mL. Add 3 mL chloroform as preservative. Do <u>not</u> use this solution to standardize the iodine solution. The solid reagent used to prepare this solution must be from a different vendor, or lot number different from that used to prepare the Standard Thiosulfate Solution.

7. Procedure

7.1 Pipet 50 mL of sample into a 200 mL volumetric flask containing 50 mL distilled water.

7.1.1 Set up a blank (with 0.1 g KI added to insure a sharp endpoint), laboratory control spike, duplicate, and matrix spike for each sample batch of ten or less. Use 5 or 10 mL of the thiosulfate spiking solution to produce a spike of 0.56 mg or 1.12 mg.

7.2 Add an excess of ammoniacal conditioning buffer until no additional precipitation is noted (approximately 5-10 mL).

7.3 Dilute to the mark with distilled water.

7.4 Complete determination as rapidly as possible. Shake vigorously and filter through a dry, white ribbon medium porosity filter.

7.5 Measure 100 mL of filtrate into an Erlenmeyer flask.

7.6 Neutralize to the methyl red endpoint with 0.1N HCl.

7.7 Add a few drops of starch solution and titrate with 0.01N iodine solution until the first faint blue color appears.

8. Calculations

8.1

$$S_2O_3\,(mg/L) = \frac{(A - B)(N)(112.12\ g/eq)(1000\ mL/L)}{mL\ sample}$$

Where: A = mL $I_2$ titrant used for sample
B = mL titrant used for blank
N = normality of standard iodine solution

8.2

$$S\,(mg/L) = \frac{(mg/L\ S_2O_3)(32.06\ g/g\text{-}atom\ S)(2\ mole\ S)}{(112.12\ g/mole\ S_2O_3)(mole\ S_2O_3)}$$

9. Quality Assurance Guidelines

9.1 Run a duplicate and a spike with each sample batch of ten or less. Calculate relative percent difference (RPD) to assess precision, and % spike recovery to assess accuracy. The values obtained must be within established acceptance limits. If not, corrective action must be performed to determine the cause/s of the discrepancyy.

10. Method Performance

10.1 Analysis of five replicates of San Jose Creek primary effluent samples containing 28.45 mg/L $S_2O_3^{2-}$, and $SO_3^{2-}$ equivalent to 21.39 mg/L $S_2O_3^{2-}$ produced a standard deviation of " 0.263 and a relative standard deviation of 0.54%.

10.2 The CSDLAC QA program shows, for samples containing between 0.1 and 100 mg/L,

an average relative percent difference (RPD) between duplicates of 1.09 and an average percent recovery of 100.1.

11. Reference

11.1 This procedure is according to Henry Kendall, Determination of Thiosulfate and Sulfite by Iodometry, San Jose Creek Water Quality Laboratory Memo, July 2, 1975.