The Precipitation-Spectrophotometric Determination of Dithionate Ions with Bis(diethylenetriamine)nickel(II) Chloride Solution

Tsugio Sato* and Taijiro Okabe
Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Sendai 980
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Synopsis. A solution containing dithionate ions is treated with bis(diethylenetriamine)nickel(II) chloride solution to precipitate dithionate as [Ni(dien)₂]S₂O₄ complex. After centrifugation, the concentration of nickel(II) ions in the supernatant is spectrophotometrically determined by dimethylglyoxime method. There is no interference from SO₄²⁻, SO₂⁻, S₂O₄²⁻, S₄O₆²⁻, HN(SO₃)₂⁺, S²⁻, or Fe³⁺.

Special attention has been recently devoted to the chemical behavior of dithionate because dithionate is often produced in various industrial processes using sulfate solutions, such as wet type desulfurization and hydrometallurgy, and causes pollution problems. However, the analysis of dithionate by classical methods such as redox titration²⁻⁸ or gravimetry⁴⁻⁶ after disproportionation of dithionate to sulfate and sulfite in hot acidic solutions that were used in previous studies are very tedious operations, especially in the cases where other sulfur compounds coexist.

Recently Maru et al.² reported that dithionate forms slightly soluble salts with metal(II) ethylenediamine complexes and with metal(II) 1,2-propanediamine complexes, where metals are nickel, cadmium, copper, and zinc. They have proposed a gravimetric method for determining dithionate as these amine complexes. The method can be used to determine dithionate in the presence of sulfate and sulfite, but high amounts of polythionates interfere. In the proceeding study,⁹ we have shown the solubility of many kinds of metal(II) alkylamine complexes and have reported that the solubility of [Ni(dien)₂]S₂O₄ is extremely small. Therefore, it may be more useful for the determination of dithionate ions. The present paper is concerned with a simple and selective spectrophotometric determination of dithionate ions using bis(diethylenetriamine)nickel(II) chloride as precipitant.

Experimental

Apparatus. The spectrophotometric measurements were made with a Hitachi 101 spectrophotometer.

Reagents. Sodium dithionate, potassium tetrathionate, and potassium imidobis(sulfate) were prepared by Pfannstiel's method,⁸ Martin's method,⁶ and Säuber's method,⁹ respectively.

Bis(diethylenetriamine)nickel(II) Chloride Solution: Dissolve 6.0 g of nickel(II) chloride hexahydrate in 150 cm³ of distilled water, and add 50 cm³ of diethylenetriamine and 800 cm³ of ethyl alcohol.

Dimethylglyoxime Solution: Dissolve 1 g of dimethylglyoxime in 500 cm³ of 0.25 M (M=mol dm⁻³) sodium hydroxide solution.

All other chemicals were of analytical grade and were used without further purification.

Procedures. Transfer 5 cm³ of sodium dithionate solution (0—20 mM) to a 15 cm³ centrifuge tube, add 5 cm³ of bis(diethylenetriamine)nickel(II) chloride solution, seal it to prevent evaporation of solvent and place the tube in an ice bath. After 30 min, remove the tube from the ice bath and centrifuge it at 2000 min⁻¹ for 10 min. Transfer 100 mm³ of supernatant to a 50 cm³ volumetric flask, then add 2 cm³ of 20 wt% potassium sodium tartrate solution, 0.5 g of ammonium peroxosulfate, 1 cm³ of dimethylglyoxime solution and 2.5 cm³ of 5 M sodium hydroxide. Dilute the solution to the mark with distilled water. After 30 min, measure the absorbance of the solution at 465 nm in a 10 mm thick glass cell against a water blank.

Results and Discussion

The analytical method described above consists of the separation of dithionate as a slightly soluble bis(diethylenetriamine)nickel(II) dithionate complex by double decomposition as shown in Eq. 1, and the Na₂S₂O₄ + [Ni(dien)₂]Cl₂ ---→ [Ni(dien)₂]S₂O₄ + 2NaCl, (1) determination of nickel(II) ions remaining in the solution. For the determination of nickel(II) ion, dimethylglyoxime method¹⁰ was adapted because it seems to be the simplest method. Therefore in the present study, a series of tests was carried out to investigate the precipitation behavior of dithionate.

Four different organic solvents (dioxane, acetone, methyl alcohol, and ethyl alcohol) were tested for the precipitation of [Ni(dien)₂]S₂O₄ at 30 °C. The results are shown as Fig. 1. It is seen that solubility of [Ni(dien)₂]S₂O₄ under these experimental conditions is 1.47 mM in water, but rapidly decreases with increasing concentrations of organic solvents. Subsequently, ethyl alcohol–H₂O system was chosen because it showed the smallest solubility of [Ni(dien)₂]S₂O₄ complex. The solubility product of this complex in 40 vol% ethyl alcohol is 1.6×10⁻⁷; hence, more than

![Fig. 1. Solubility of [Ni(dien)₂]S₂O₄ in mixed organic solvent-H₂O solutions. O: Dioxane, □: acetone, ●: methyl alcohol, ■: ethyl alcohol, temperature: 30 °C, ionic strength: 0.5 M.](image-url)
99% of dithionate in the range of concentrations 2—20 mM can be precipitated by the above-mentioned procedure.

The effect of standing time in the precipitation step was examined and constant absorbances were obtained after standing for 15 min.

The absorbance was measured as a function of the pH value at double decomposition reaction in the range of pH 7.0—12.5. As is shown in Fig. 2, constant absorbances were obtained at pH values above 8.5. The precipitant, bis(diethylenetriamine)nickel(II) chloride solution, contains much free diethylenetriamine, so that it is not necessary to neutralize the sample solutions unless the acid concentrations are more than 2.5 M.

On the basis of the above results, a standard procedure was evolved, by which the linear calibration graph was obtained in the range of dithionate concentrations in the sample solution 0—20 mM, as shown in Fig. 3. The coefficient of variation for the ten replicated experiments was satisfactory (2.5% for 15.4 mM of $S_2O_3^{2-}$).

The interferences due to various ions were also examined, as is shown in Table 1. Thiosulfate caused considerable errors, but no other compounds showed interference. It is significant that sulfate and sulfite which usually coexist with dithionate showed no interference even at such high concentrations as 800 mM. In the presence of thiosulfate, the amounts of dithionate found were larger than those added: it means that a part of thiosulfate coprecipitates with dithionate as nickel(II) diethylenetriamine complex. However, thiosulfate can be oxidized by iodide to tetrathionate which shows no interference for the determination of dithionate. Therefore the interference due to thiosulfate may be overcome by modifying the procedure as follows. After the same volume (5 cm$^3$) of the sample solution is placed in a 15 cm$^3$ centrifuge tube, add 1 cm$^3$ of adequate concentration of iodide solution to oxidize thiosulfate, and then carry out the same procedures. The results shown in Fig. 4 were thus as expected, and excess iodide showed no interference.

References