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The Precipitation-Spectrophotometric Determination of Dithionate Ions with Bis(diethylenetriamine)nickel(II) Chloride Solution[1)]

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Synopsis. A solution containing dithionate ions is treated with bis(diethylenetriamine)nickel(II) chloride solution to precipitate dithionate as $[Ni(dien)_2]S_2O_6$ complex. After centrifugation, the concentration of nickel(II) ions in the supernatant is spectrophotometrically determined by dimethylglyoxime method. There is no interference from SO_4^{2-} SO_3^{2-}, $S_2O_3^{2-}$, $S_4O_6^{2-}$, $HN(SO_3)_2^{2-}$, S^{2-}, or Fe^{3+}.

Special attention has been recently devoted to the chemical behavior of dithionate because dithionate is often produced in various industrial processes using sulfite solutions, such as wet type desulfurization and hydrometallurgy, and causes pollution problems. However, the analysis of dithionate by classical methods such as redox titration[2,3)] or gravimetry[4)] after disproportionation of dithionate to sulfite and sulfate in hot acidic solutions that were used in previous studies are very tedious operations, especially in the cases where other sulfur compounds coexist.

Recently Marcu *et al.*[5)] 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 sulfite and sulfate, but high amounts of polythionates interfere. In the preceeding study,[6)] we have shown the solubility of many kinds of metal(II) alkylamine complexes and have reported that the solubility of $[Ni(dien)_2]S_2O_6$ 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 Pfanstiel's method,[7)] Martin's method,[8)] and Sisler's method,[9)] respectively.

Bis(diethylenetriamine)nickel(II) Chloride Solution: Dissolve 6.0 g of nickel(II) chloride hexahydrate in 150 cm^3 of distilled water, and add 50 cm^3 of diethylenetriamine and 800 cm^3 of ethyl alcohol.

Dimethylglyoxime Solution: Dissolve 1 g of dimethylglyoxime in 500 cm^3 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 cm^3 of sodium dithionate solution (0—20 mM) to a 15 cm^3 centrifuge tube, add 5 cm^3 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 mm^3 of supernatant to a 50 cm^3 volumetric flask, then add 2 cm^3 of 20 wt% potassium sodium tartrate solution, 0.5 g of ammonium peroxodisulfate, 1 cm^3 of dimethylglyoxime solution and 2.5 cm^3 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

$$Na_2S_2O_6 + [Ni(dien)_2]Cl_2 \longrightarrow [Ni(dien)_2]S_2O_6 + 2NaCl, \quad (1)$$

determination of nickel(II) ions remaining in the solution. For the determination of nickel(II) ion, dimethylglyoxime method[10)] 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 $[Ni(dien)_2]S_2O_6$ at 30 °C. The results are shown as Fig. 1. It is seen that solubility of $[Ni(dien)_2]S_2O_6$ under these experimental conditions is 1.47 mM in water, but rapidly decreases with increasing concentrations of organic solvents. Subsequently, ethyl alcohol–H_2O system was chosen because it showed the smallest solubility of $[Ni(dien)_2]S_2O_6$ complex. The solubility product of this complex in 40 vol% ethyl alcohol is 1.6×10^{-7}; hence, more than

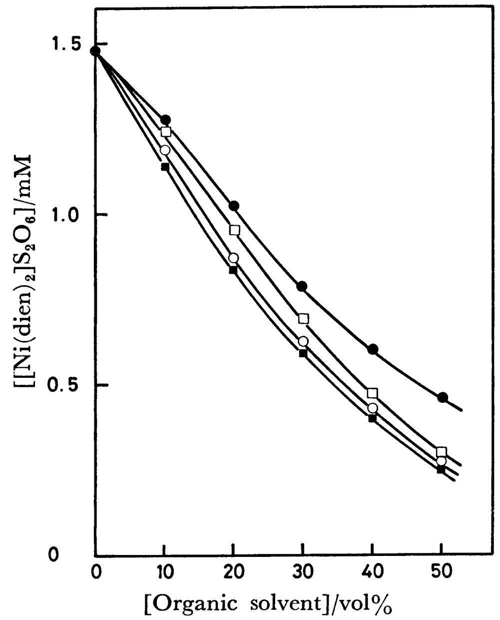

Fig. 1. Solubility of $[Ni(dien)_2]S_2O_6$ in mixed organic solvent-H_2O solutions. ●: Dioxane, □: acetone, ○: methyl alcohol, ■: ethyl alcohol, temperature: 30 °C, ionic strength: 0.5 M.

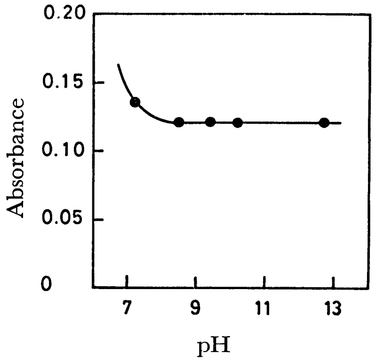

Fig. 2. Effect of pH variation. Concentration of $Na_2S_2O_6$: 15.4 mM.

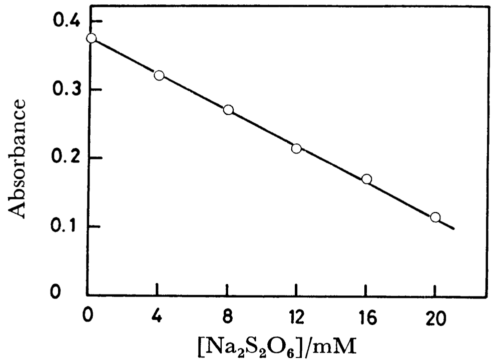

Fig. 3. Calibration curve.

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, contanins much free diethylentriamine, 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 $S_2O_6^{2-}$).

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 sulfite and sulfate 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.

TABLE 1. EFFECT OF FOREIGN SUBSTANCES

[Substances]/mM		$[S_2O_6^{2-}]$ found/mM
Na_2SO_4	20	15.6
	40	15.6
	60	15.9
	100	15.3
	500	15.5
	800	15.4
Na_2SO_3	20	15.2
	100	15.1
	800	15.0
$Na_2S_2O_3$	20	20.2
	40	21.7
	60	22.5
$Na_2S_4O_6$	20	15.4
	40	15.7
	60	15.6
$NH(SO_3K)_2$	20	15.3
	40	15.5
	60	15.1
Na_2S	20	15.4
	40	15.1
	60	15.2
$Fe_2(SO_4)_3$	10	15.3
	20	15.3
	30	15.6
$[Na_2S_2O_6]$ added/mM		15.4

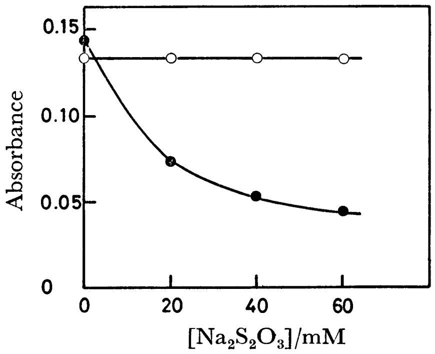

Fig. 4. Effect of the concentration of thiosulfate. Concentration of $Na_2S_2O_6$: 15.4 mM. ○: Added 1 cm^3 of 0.2 M iodide solution, ●: none.

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