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Aqueous two-phase extraction of nickel dimethylglyoximato complex and its application to spectrophotometric determination of nickel in stainless steel

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Abstract

A polyethylene glycol (PEG)-based aqueous two-phase system has been established for the extraction of Ni-dimethylglyoximato complex. Appropriate amounts of PEG solution and solid $(NH_4)_2SO_4$ were added to the Ni-dimethylglyoximato complex which had been formed in the presence of sodium tartrate and $K_2S_2O_8$ at pH 12 in a separatory funnel and shaken vigorously for about 1 min. The mixture was allowed to stand for 10 min and then the absorbance of the extracted complex in the upper PEG-rich phase was measured at 470 nm. Beer's law was obeyed over the range of 0.26–2.1 ppm Ni. The proposed extraction method has been applied to the determination of Ni in steel. A steel sample was decomposed with an appropriate acid mixture. An aliquot of the sample solution was taken, treated with H_3PO_4 and most of the iron and copper were removed by hydroxide precipitation using solid $BaCO_3$ to control the pH of the sample solution in advance of the extraction of Ni. The analytical results obtained for Ni in steel certified reference material JSS 650-10 (The Japan Iron and Steel Federation), BCS 323 (Bureau of Analysed Samples Ltd.) and NIST SRM 361 and 362 (National Institute of Standards and Technology) were in good agreement with certified values.

Keywords: Nickel; Aqueous two-phase extraction; Dimethylglyoximato complex; Steel analysis

1. Introduction

In recent years, use of toxic organic solvents, such as chloroform, dichloroethane and others containing chlorine, for extraction of metal-complexes is strictly limited by law. Therefore, the development of new types of extraction systems for metal ions has been required from point of view of environmental protection and an aqueous two-phase extraction is one of the most promising techniques for this purpose [1]. The last decades have seen very development in a separation or purification of biological materials using the aqueous two-phase systems. However, the aqueous two-phase systems have so far been hardly applied to the extraction of metal ions.

Wang et al. studied the extraction of Cu(II) with the two-phase aqueous system isopropyl alcohol–ammonium sulphate–ammonium thiocyanate and applied the proposed system to speciation of serum copper [2]. Akama et al. reported the selective extraction of Cd from Co, Cu, Fe and Zn [3] and Cr(VI) [4] by water-based two-phase system of tetrabutylammonium bromide. The effect of temperature on phase equilibrium and on partitioning of Cu(II)-1,10-phenannthroline-sulfate complex in poly(ethylene glycol)-based aqueous biphasic systems was determined by Fonta and Ricci [5]. Extraction behaviour of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Li(I) ions in aqueous polyethylene glycol–sodium sulphate two-phase systems in the presence of iodide and thiocyanate ions was studied extensively by Shibukawa et al. [6]. A selective separation of Cd(II) was carried out by using iodide ion as an extracting reagent

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for Cd(II) and an ammonium buffer as a masking reagent for Cu(II). The extraction of Au(I) cyanide in polyethylene glycol-based aqueous biphasic systems was proved by Zhang et al. to provide a potential technique for Au separation from alkaline cyanide solution with cleaner and safer advantages [7].

In this work, we have studied the extraction of Ni(II)-dimethylglyoximato complex in an aqueous polyethylene glycol (PEG)–$(NH_4)_2SO_4$ system and applied the proposed system to the spectrophotometric determination of nickel in steel.

2. Experimental

2.1. Apparatus and reagent

A spectrophotometer Hitachi (Tokyo) U-3210 was used for the absorbance measurement of nickel dimethylglyoximato complex. An ICP–AE spectrometer Seiko (Tokyo) SPS 1700H was also used for the determination of nickel in aqueous PEG phase after appropriate dilution with water.

The pH was measured by a TOA (Tokyo) HM-7E meter with a combined glass electrode.

All chemicals used were of analytical-reagent grade from Wako Pure Chemicals (Tokyo) or Kanto Chemicals (Tokyo). Distilled, deionized water was further purified by a Milli-Q (Millipore, Benford, MA, USA) to be used for preparation of all the solutions. Nickel standard solution (1010 mg l^{-1}) for atomic absorption spectrometry and dimethylglyoxime (DMG) used were from Merck (Germany) and Wako Pure Chemicals, respectively. A solution of DMG was prepared by dissolving 1.0 g in 100 ml of 0.01 mol l^{-1} sodium hydroxide solution and was kept in a refrigerator. Polyethylene glycol (PEG) used was obtained from Kanto Chemicals (Tokyo) and its mean molecular weight was 400.

Stainless steel samples used were provided by Japan Iron and Steel Federation, Bureau of Analysed Samples Ltd. and National Institute of Standards and Technology.

2.2. General procedure

To adequate volume of sample solution, 5 ml of 20% sodium tartrate, 10 ml of 4% $K_2S_2O_8$ and 1 ml of 1% dimethylglyoxime were added and adjusted pH to 12.0 ± 0.1 with 10 mol l^{-1} of NaOH. Then, the sample solution containing nickel-dimethylglyoximato complex was poured into a separatory funnel of 100 ml and diluted to about 25 ml with water, followed by standing for 20 min. Ten milliliter of PEG and 9 g of $(NH_4)_2SO_4$ were added to the separatory funnel. The mixture was shaken for 1 min. After complete phase separation was performed, the absorbance of Ni-dimethylglyoximato complex extracted into the upper PEG-rich phase was measured at 470 nm versus reagent blank. The volume of the upper PEG-rich phase was 20 ml.

2.3. Analysis procedure of steel

2.3.1. JSS 650-10

About 100 mg of steel was weighted and dissolved in 4 ml of aqua regia. The sample solution was evaporated to dryness on a hot plate and the residue was taken up in 2 ml of HCl, followed by dilution to 100 ml in a volumetric flask. A 5 ml aliquot of the sample solution was transferred to a 20 ml beaker and was evaporated to dryness on a hot plate. The residue was dissolved in 2 ml of HNO_3 and evaporated again to dryness. This treatment was repeated three times and the sample solution was evaporated nearly to dryness. The sample was diluted to 20 ml with water to 20 ml. About 0.5 g of $BaCO_3$ was gently added and the solution was allowed to stand for 12 h [8]. The sample solution was vigorously stirred by a glass rod and permitted to stand for at least 30 min. The resulting Fe(III) hydroxide precipitate was filtered off with a No. 5A filter paper. One milliliter of H_3PO_4 was added to the filtrate and evaporated to expel HNO_3. The sample solution was then subjected to the extraction of Ni-dimethylglyoximato complex (see Section 2.2).

2.3.2. BCS 323

About 130–270 mg of steel was taken and dissolved in a mixture of 1 ml of H_2SO_4, 2 ml of HF and 10 ml of (1:1) HNO_3 by heating on a hot plate. Ten milliliters of (1:1) HCl were added and heated to dissolve the gelatinous substances. The sample solution was diluted to 100 ml with water. Four milliliters of aqua regia was added to a 5 ml aliquot of the sample solution and was evaporated to about 1 ml on a hot plate. Four milliliters of HCl was added and was again evaporated to about 1 ml. Four milliliters of water was added and evaporated to dryness on a water bath. The residue was dissolved in 20 ml of water by heating. About 0.5 g of $BaCO_3$ was added and the solution was allowed to stand for 12 h. The sample solution was vigorously stirred by a glass rod and permitted to stand for at least 30 min. The resulting Fe(III) hydroxide was filtered off with a No. 5A filter paper. The sample solution was vigorously stirred by a glass rod and permitted to stand for at least 30 min. The resulting Fe(III) hydroxide precipitate was filtered off with a No. 5A filter paper. The pH of the filtrate was adjusted to 1.0 ± 0.1 with (1:1) H_2SO_4 and the sample solution was boiled for 1 min. After cooling to room temperature, $BaSO_4$ precipitate was filtered off with a No. 5C filter paper. The filtrate was evaporated to the fume of H_2SO_4 and then treated to eliminate a black or brown colour with 2 ml of H_2O_2. After cooling to room temperature, 1 ml of H_3PO_4 was added and subjected to the extraction of Ni-dimethylglyoximato complex (see Section 2.2).

2.3.3. NIST SRM 361 and 362

About 30–90 mg of sample was taken and dissolved in a mixture of 1 ml of H_2SO_4, 2 ml of HCl and 2 ml of HNO_3 by heating. After cooling to room temperature, the sample solution was diluted to 100 ml with water. A 5 ml aliquot of the sample solution was taken and evaporated to fume of H_2SO_4.

About 20 ml of water was added and 0.5 g of $BaCO_3$ was added. Fe(III) hydroxide and $BaSO_4$ precipitates were filtered off and a black or brown colour was discharged with H_2O_2 as in the case of BCS 323. After addition of 1 ml of H_3PO_4, the solution was to the extraction of Ni-dimethylglyoximato complex (see Section 2.2).

Standard solutions for construction of a calibration graph contained almost the same amount of iron as that in the sample solution and treated in a similar manner as above.

3. Results and discussion

3.1. Extraction of nickel dimethylglyoximate

Nickel-dimethylglyoximato complex was extracted into the upper phase of an aqueous two-phase system containing PEG and $(NH_4)_2SO_4$. The absorption spectrum of the complex (brown color) has two peaks at wavelengths of 365 and 470 nm (Fig. 1). The absorption peak at 470 nm is higher than that at 365 nm and the absorbance at 470 nm was therefore used for the determination of Ni in the subsequent experiments.

It is well-known that the system based on $(NH_4)_2SO_4$ in the presence of significant amounts of bases results in a strong salting-out effect [1]. Therefore, it was used as a salting-out agent throughout the work.

The aqueous two-phase extraction system of nickel-dimethylglyoximato complex has many parameters such as volume and pH of sample solution, amounts of $(NH_4)_2SO_4$, dimethylglyoxime, oxidizing agent and masking agents. The sample volume was kept at 25.0 ml for convenience; whereupon the optimum amount of $(NH_4)_2SO_4$ to lead to rapid phase separation was found to be 9.0 g.

3.1.1. Effect of pH

The effect of pH on the extraction of Ni-dimethylglyoximato complex was examined over the range from 8 to 13 by using 25 ml of sample solution (25 μg Ni), 1 ml of dimethylglyoxime solution and 10 ml of PEG. After the phase separation, Ni in the upper phase was determined by ICP–AES. The results are shown in Fig. 2. The extractability of nickel-dimethylglyoximato complex into the upper phase showed a maximum at pH 12. Therefore, Ni-dimethylglyoximato complex was formed at pH 12 hereinafter.

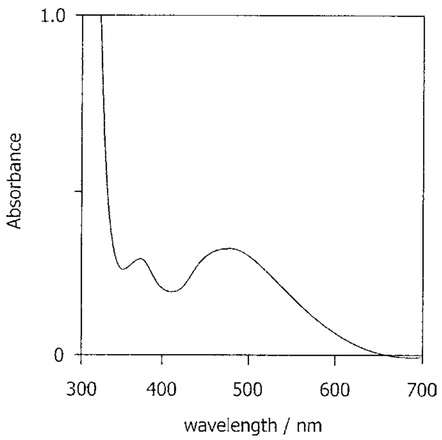

Fig. 1. Absorption spectrum of Ni-dimethylglyoximato complex in polyethylene glycol–water vs. blank; Ni, 2.75 μg/ml.

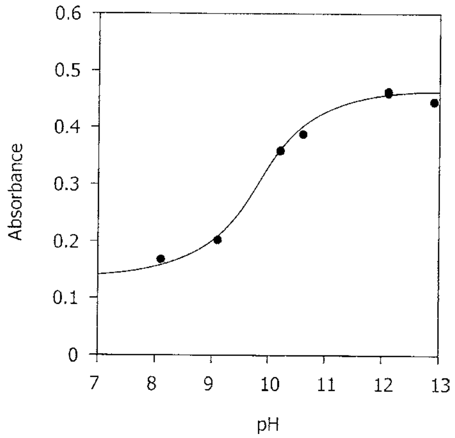

Fig. 2. Effect of the pH values on the extraction of Ni-dimethylglyoximato complex into the upper polyethylene glycol-rich phase. Sample volume, 25.0 ml; Ni, 25.3 μg; PEG solution, 10.0 ml; $(NH_4)_2SO_4$, 9.0 g.

3.1.2. Effect of polyethylene glycol

The effect of the amount of PEG was examined under the conditions of 25 ml of sample solution (30 μg Ni) and 9 g of $(NH_4)_2SO_4$. The percentage of Ni extracted into the upper phase at 10 or 15 ml of PEG was found to be 99 or 102%, respectively (see Fig. 3). Therefore, the volume ratio of PEG/sample solution was kept at 10/25 in the subsequent experiments.

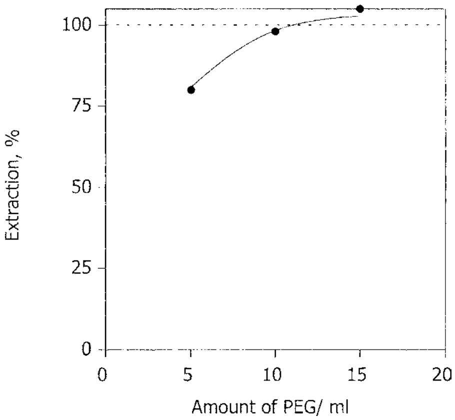

Fig. 3. Effect of the amount of PEG on the extraction of Ni-dimethylglyoximato complex. Sample volume kept at 25 ml; Ni, 30 μg; 20% sodium tartrate, 4 ml; 4% potassium peroxodisulfate, 10 ml; 15 mol l^{-1} H_3PO_4, 1 ml.

Table 1
Effect of mineral acids on the determination of nickel

Acid	Added (ml)	Ni (μg)	
		Added	Found
Hydrochloric acid, 12 mol l^{-1}	1.0	10.1	9.8
	0.1	10.1	10.1
Nitric acid, 16 mol l^{-1}	1.0	10.1	5.0
	0.1	10.1	10.1
Perchloric acid, 9 mol l^{-1}	1.0	10.1	9.8
	0.1	10.1	10.1
Sulphuric acid, 18 mol l^{-1}	1.0	10.1	10.1
	0.1	10.1	10.2

3.1.3. *Calibration graph and stability of the extracted complex*

Under the optimum conditions, a linear calibration graph was obtained over the range of 0.26–2.1 ppm of Ni, that corresponded to 2.5–40 μg of Ni in 25 ml of sample solution before the addition of PEG. The absorbance of Ni-dimethylglyoximato complex extracted into the upper phase was found to be constant for at least 40 min after the phase separation. In the conventional spectrophotometric method of Ni with dimethylglyoxime, the absorbance should be measured at 5 min after the colour development because of the instability of the Ni-dimethylglyoximato complex formed in the aqueous solution [9]. Therefore, the present method is convenient from a practical point of view.

3.1.4. *Interference study*

To evaluate the attainable selectivity of the proposed method, the interference effects of various ions such as Cl^-, NO_3^-, ClO_4^-, SO_4^{2-}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+} and Mn^{2+} were investigated. One milliliter of the mineral acids such as HCl, $HClO_4$, HNO_3 and H_2SO_4 were added to a 25 ml solution containing 10 μg of Ni. The cations such as Co^{2+}, Cr^{3+}, Fe^{3+} and Mn^{2+} were introduced into a solution containing 25 μg of nickel. The concentration of each of metal ions was about four times more than nickel contents. The results are shown in Tables 1 and 2. It was found that HCl, $HClO_4$, H_2SO_4, Co^{2+}, Cr^{3+}, Fe^{3+} and Mn^{2+} did not interfere, whereas HNO_3, 10 μg of Cu^{2+} and 500 μg of Fe^{3+} showed an interfering effect. Unfortunately, it is not clear why copper(II) give a serious negative error in Ni determinations. In the analysis of steel, HNO_3 was expelled by H_3PO_4 treatment and most of Fe and Cu were removed by precipitation before the aqueous two-phase extraction of Ni-dimethylglyoximato complex as described above. Copper might be removed by co-precipitation with iron(III) hydroxide.

Table 2
Effect of foreign ions on the determination of nickel

Foreign ion	Added (μg)	Ni (μg)	
		Added	Found
Co(II)	100	25.3	25.3
Cr(III)	100	25.3	24.8
Cu(II)	10	25.3	7.5
	50	25.3	5.5
Fe(III)	100	25.3	25.7
	500	25.3	29.0
Mn(II)	100	25.3	25.4

Table 3
Determination of nickel in steel certified reference materials

Sample	Taken (mg)	Ni (%)		
		Found	Certified	Recovery
JSS 650-10[a]	110.0	0.385	0.39	98.7
	102.6	0.370		94.9
	103.7	0.390		100
	100.8[b]	0.367		94.1
	100.8[b]	0.407		104
BCS 323[c]	136.1	0.179	0.172	104.1
	146.3	0.157		91.3
	266.7	0.169		98.3
NIST SRM 361[d]	41.4	2.14	2.0	107.0
	40.4	1.93		96.5
	23.9	2.07		103.5
NIST SRM 362[d]	72.2	0.56	0.59	94.9
	61.6	0.52		88.1
	73.3	0.61		103.4

JSS 650-10 (SUS 430): C, 0.046; Si, 0.45; Mn, 0.44; P, 0.021; S, 0.0053; Ni, 0.39; Cr, 16.18; Mo, 0.021; Cu, 0.038; Co, 0.024% (m/m). BCS 323: Ni, 0.172; Cr, 0.22; Mo, 0.100, W, 0.25; Ti, 0.018; As, 0.058; Sn, 0.024% (m/m). NIST SRM 361: Al, 0.021; Sb, 0.0042; As, 0.017; Ca, 0.00010; C, 0.383; Ce, 0.0040; Cr, 0.694; Co, 0.032; Pb, 0.000025; Mg, 0.00026; Mn, 0.66; Mo, 0.19; Nd, 0.00075; Ni, 2.00; Nb, 0.022; P, 0.014; Si, 0.222; Ag, 0.0004, S, 0.0143; Ta, 0.020; Sn, 0.010; Ti, 0.020; W, 0.017; V, 0.011; Zr, 0.009% (m/m). NIST SRM 362: Al, 0.083; Sb, 0.013; As, 0.092; B, 0.0025; Ca, 0.00021; C, 0.160; Ce, 0.0019; Cr, 0.30; Co, 0.30; Cu, 0.50; Pb, 0.00048; Mg, 0.0007; Mn, 1.04; Mo, 0.068; Nd, 0.0008; Ni, 0.59; Nb, 0.29; P, 0.041; Si, 0.39, Ag, 0.0011; S, 0.0360; Ta, 0.20; Sn, 0.016; Ti, 0.097; W, 0.20; V, 0.040; Zr, 0.19% (m/m).

[a] Provided by The Japan Iron and Steel Federation.

[b] 2.4 mg of copper added.

[c] Provided by Bureau of Analysed Samples Ltd.

[d] Provided by National Institute of Standards and Technology.

3.2. *Determination of nickel in steel*

In order to test the applicability of the method, nickel in steel-certified reference materials was determined and the results obtained are shown in Table 3. The analytical values are in fairly good agreement with the certified value.

4. Conclusions

The PEG-based aqueous two-phase system was established for the extraction and spectrophotometric determination of Ni-dimethylglyoximato complex. The proposed system could be applied to the determination of Ni in stainless steel by combining hydroxide precipitation by $BaCO_3$ to remove the interference from Cu^{2+} and Fe^{3+}. The Ni-dimethylglyoximato complex was found to be relatively stable so that the present method is convenient for practical use.

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