August, 1987] NOTES *Bull. Chem. Soc. Jpn.*, ***60***, *3077—3079 (1987)* 3077

Improved Spectrophotometric Determinations of Cobalt(II) and Nickel(II) with Zincon in the Surfactants Micellar

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(Received December 13, 1986)

Synopsis. Reactions between Zincon and cobalt(II) in the presence of *N*-hexadecylpyridinium chloride (cationic surfactant), and between Zincon and nickel(II) in the presence of poly(vinyl alcohol) (nonionic surfactant) are discussed in terms of the development of simple, sensitive and improved spectrophotometric determinations of cobalt(II) and nickel(II). The calibration graphs were rectilinear in the ranges 0—2.2 μg 10 $\mathrm{cm^{-3}}$ cobalt(II) with a Sandell sensitivity of 0.00015 $\mu\mathrm{g\,cm^{-2}}$ at 550 nm and 0—42.0 μg 10 $\mathrm{cm^3}$ nickel(II) with that of 0.0047 $\mu\mathrm{g\,cm^{-2}}$ nickel(II) at 470 nm. The proposed methods were relatively sensitive in comparison with the methods in the absence of surfactants with apparent molar extinctions of 4.6×10^5 for cobalt(II) and 2.4×10^4 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ for nickel (II). Separative assays of cobalt(II) and various metals (nickel(II), zinc(II), copper(II), and iron(III)) were possible by selections of analytical wavelengths, respectively.

The spectrophotometry of micro amounts of cobalt(II) or nickel(II) has recently attracted much attention regarding heavy metal pollution in enviromental areas. For cobalt(II) or nickel(II), various spectrophotometric determinations using Dithizone,[1)] 4-(2-pyridylazo)resorcinol(PAR),[2)] nitroso R salt,[3)] dimethylglyoxime.[4)] Chrome Azurol S,[5)] etc., have already been reported. However, most methods are relatively complicated and therefore organic solvent extractions are necessary using a toxic organic solvent such as chloroform. Although determinations of cobalt(II) and nickel(II) using Zincon are comparatively sensitive,[6—9)] these methods lack selectivity, stability and reproducibility. On the other hand, we found that the reaction systems between cobalt(II) and Zincon in the presence of a cationic surfactant micellar(such as *N*-hexadecylpyridinium chloride (HPC)) and between nickel(II) and Zincon in the presence of a nonionic surfactant micellar(such as poly(vinyl alcohol) (PVA)) posessed many advantages over these reaction systems (binary complex) in the absence of surfactants: highly sensitive, stability and a wide coloring pH ranges under these experimental conditions.

In this paper, simple, sensitive and improved spectrophotometric determinations of cobalt(II) using Zincon in the presence of HPC, and of nickel (II) using Zincon in the presence of PVA are, respectively, discussed and proposed in water-soluble surfactants micellar media.

Experimental

Reagents and Apparatus. Standard cobalt(II) and nickel(II) solutions, a stock solution containing 1.0×10^{-2} M ($1\ \mathrm{M}=1\ \mathrm{mol\,dm^{-3}}$) of cobalt(II) or nickel (II), were prepared by dissolving cobalt nitrate or nickel nitrate in water. The concentrations of these stock solutions were determined by chelatometric titration.[10)] A working solution (5.0×10^{-4} M) was prepared by a suitable dilution of this stock solution. A 1.0×10^{-3} M Zincon solution was prepared by dissolving Zincon(Merck Chemical Co., Ltd.) in methanol according to a previous report.[11)] A 1.0×10^{-2} M solution of HPC was prepared by dissolving HPC in water. A 1.0% PVA, solution was prepared by dissolving PVA (n=2000) in water. A Sörensen phosphate buffer solution was used for the pH adjustments.

All the other reagents and materials were of analytical grade and were used without further purification. Twice-distilled water was used throughout this work.

Shimadzu Model UV-200, recording spectrophotometer with 1.0-$\mathrm{cm^3}$ quartz cells was used for the absorption spectra and absorbance measurements. A Hitachi-Horiba Model F-7AD glass electrode pH meter was used for the pH measurements.

Operating Procedure. Determination of Cobalt(II): A standard solution containing up to 2.2 μg of cobalt(II) was placed in a 10-$\mathrm{cm^3}$ volumetric flask; then, 1.0 $\mathrm{cm^3}$ of a 1.0×10^{-2} M HPC solution, 2.0 $\mathrm{cm^3}$ of a Sörensen phosphate buffer solution (pH 8.5), and 2.0 $\mathrm{cm^3}$ of 1.0×10^{-3} M Zincon solution were added. The solution was diluted to the mark with water, mixed well, kept at 60 °C for 30 min, and then cooled in water at room temperature for 10 min. The difference of absorbance at 550 nm between the Zincon-cobalt(II) solution (Solution A) and the Zincon solution (Solution B) was measured against water.

Determination of Nickel(II): A standard solution (0—42.0 μg of nickel (II)) was placed in a 10-$\mathrm{cm^3}$ volumetric flask; 1.0 $\mathrm{cm^3}$ of a 1.0% PVA solution, 2.0 $\mathrm{cm^3}$ of a Sörensen buffer solution (pH7.0), and then 2.0 $\mathrm{cm^3}$ of a 1.0×10^{-3} M Zincon solution were added. The solution was diluted to the mark with water, mixed well (Solution A′), kept at room temperature for 20 min together with Zincon solution (Solution B′). The absorbance difference at 470 nm between Solutions A′ and B′ was measured against water. The concentrations of cobalt(II) or nickel(II) were determined by using a calibration graph.

Results and Discussion

Reaction between Zincon and Cobalt(II) or Nickel(II). The reaction systems between cobalt(II) or nickel(II) and Zincon in the presence or absence of a surfactant (cationic—HPC, anionic—sodium dodecyl sulfate, nonionic—PVA, amphoteric—sodium *N*-lauroylsarcosine) were studied at room temperature or by heating at 60 °C. The reaction systems in the absence were unstable, inconvenient and insensitive in comparison with the reaction systems in the presence of a surfactant. The absorption spectra of Zincon-cobalt(II) and Zincon solutions in the presence of HPC (Solutions A and B), and Zincon-nickel(II) and Zincon solutions in the presence of PVA (Solutions A′ and B′) are shown in Figs. 1 and 2. The Zincon-cobalt(II) solution in the presence of a cationic surfactant such as HPC was more easily decomposed by heating at 60 °C

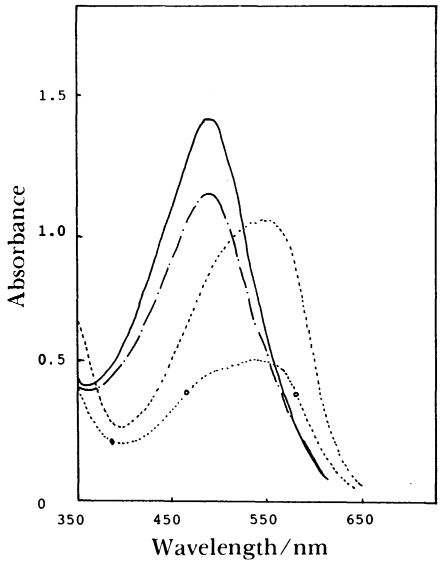

Fig. 1. Absorption spectra of Zincon-cobalt(II) and Zincon solutions in the presence of HPC or in the presence of Tween (0.1%) under the operating procedure. Cobalt(II), 2.0×10^{-6} M; Reference, water. ---o---: Zincon-cobalt(II)-HPC (Solution A); ------: Zincon-HPC solution (Solution B); —·—·—: Zincon-cobalt(II)-Tween 20; ——: Zincon-Tween 20.

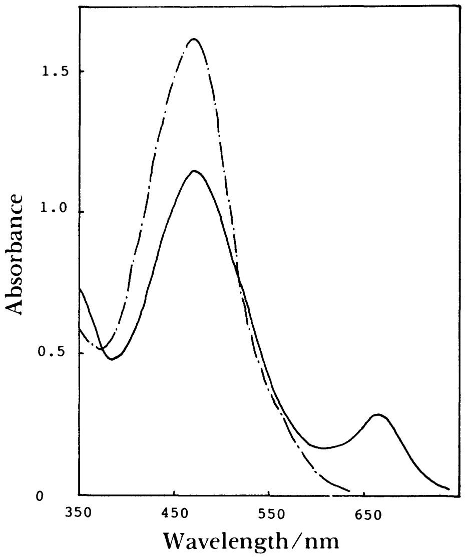

Fig. 2. Absorption spectra of Zincon-nickel(II) and Zincon solutions in the presence of PVA under the operating procedure. Ni(II), 2.5×10^{-5} M; PVA, 0.1%; Reference, water.
——: Zincon-nickel(II) (Solution A′); —·—·—: Zincon (Solution B′).

than the Zincon-cobalt(II) solution in the absence of surfactant. There was a large distinct difference of absorbance between Solutions A and B at 550 nm. The difference of absorbances at 470 and 665 nm between Solutions A′ and B′ in the presence of a nonionic surfactant (such as PVA) at room temperature was stable and abundant in reproducibility compared with reaction systems in the absence of a surfactant. Consequently, the later measurements were carried out by measuring the absorbance of 550 and 470 nm.

A maximum and constant absorbance was obtained in the pH range of 8.0—9.0 for a determination of cobalt(II), and 6.0—8.3 for a determination of nickel(II), by using 2.0 cm^3 of a Sörensen phosphate buffer solution. Later measurements were carried out at pH 8.5 for the assay of cobalt(II) and at pH 7.0 for the assay of nickel(II).

For the determinations of these metal ions, the effects of various surfactants(cationic—HPC, hexadecyltrimethylammonium chloride, zephiramine, benzylhexadecylmethylammonium chloride, nonionic—PVA, poly(oxyethylene) 6-methylheptyl ether, poly(oxyethylene) sorbitan monolaurate(Tween 20), poly(oxyethylene) dodecyl ether, and poly(*N*-vinylpyrrolidone) were studied. The uses of HPC for cobalt(II), and PVA for nickel (II) were best regarding sensitivity and stability. A maximum and constant absorbance could be obtained by the addition of 0.5—2.0 cm^3 of a 1.0×10^{-2} M HPC solution for the determination of cobalt(II), and 0.5—3.0 cm^3 of a 1.0% PVA solution for a determination of nickel(II), at final volume of 10 cm^3.

The effect of the amount of Zincon on the operating procedure was studied while keeping the amounts of cobalt(II) or nickel(II) constant. Though the molar ratio of nickel(II) to Zincon regarding the reaction system was found to be 2:1 by the molar ratio and continuous variation methods, the maximum and almost constant difference of the absorbance was obtained by using 0.5—2.0 cm^3 for the assay of nickel(II), and 1.25—2.5 cm^3 of a 1.0×10^{-3} M Zincon solution for the assay of cobalt(II) in the final 10 cm^3. Although a further investigation is necessary, the molar ratio of Zincon to cobalt(II) could not be explicitly defined.

Effect of Temperature and Time. A study of the influence of temperature on the reaction system was performed at 15—80 °C. The reaction rate (for times between 0 and 60 min) increased with the temperature, and a reproducible absorbance was obtained at 60 °C for 30 min. On the other hand, the reaction system between Zincon and nickel(II) was the best regarding stability and reproducibility at room temperature. From these results, the conditions of 60 °C for 30 min for cobalt(II) and at room temperature for 20 min for nickel(II) were chosen.

Calibration Graphs and Reproducibilities. Calibration graphs for the determinations of cobalt(I) and nickel(II) were obtained by the operating procedure. Beer's laws were followed up to 0—2.2 μg 10 cm^{-3} of cobalt(II), and 0—42.0 μg 10 cm^{-3} of nickel(II). Sandell sensitivities were 0.00015 μg, cm^{-2} cobalt(II) and 0.0047 μg cm^{-2} nickel(II). This proposed method for cobalt(II) was especially about 20 times as sensitive as the method$^{7)}$ using Zincon alone. Also, the relative standard deviations for cobalt(II) and nickel(II) (n=5) were to be 0.33 and 0.95%, respectively (relatively good values).

Effects of Foreign Ions. Effects of various foreign ions were examined regarding interference. As described in Table 1, the coexistence of such elements as iron(III), copper(II), and zinc(II) showed positive errors owing to the reaction with Zincon. The coexist-

Table 1. Effect of Foreign Ions Under the Operating Procedure

Foreign ion	Added		Difference of absorbance	
	as	μg 10 cm^{-3}	Co(II) at 550 nm	Ni(II) at 470 nm
—	—	—	0.587	0.610
Co(II)	Nitrate	1.5	—	0.615
Ni(II)	Nitrate	0.8	0.615	—
Zn(II)	Nitrate	8.2	0.587	0.615
Cu(II)	Nitrate	7.9	0.592	0.675
Fe(III)	Chloride	0.7	0.590	0.615
Al(III)	Chloride	33.0	0.600	0.608
Pb(II)	Nitrate	10.4	0.569	0.618
Bi(III)	Nitrate	13.1	0.550	0.608
Mg(II)	Nitrate	60.8	0.580	0.609
NO_2^-	Sodium	57.5	0.481	0.609
I^-	Potassium	79.3	0.587	0.610
F^-	Sodium	238.0	0.587	0.610
$S_2O_3^{2-}$	Sodium	14.0	0.405	0.600
Citrate	Sodium	31.0	0.661	0.605
CN^-	Potassium	1.3	0.540	0.605

Ni(II) taken, 14.7 μg 10 cm^{-3}, Co(II) taken 0.9 μg 10 cm^{-3}.

ence of bismuth(III) or tin(IV) up to 2.5×10^{-5}—1.0×10^{-6} M over cobalt(II) or nickel(II) did not interfere. The coexsitence of such anions as sulfate, chloride, iodide, bromide, and nitrate ions did not entirely interfere. The coexistence of cyanide, thiosulfate or nitrite ions, excess over cobalt(II) or nickel(II) 1/2—5 molar ratios gave negative errors. Citrate or oxalate ion gave a positive error for cobalt(II), and a negative error for nickel(II), respectively.

Assay of Cobalt(II) in the Coexistence of Nickel(II) or Some Metal Ions. Although the absorbance at 615 nm of Zincon-cobalt(II) solution was relatively small, its value was not affected by the coexistence of nickel(II). The amounts of cobalt(II) in the coexistence of nickel(II) up to about 25-fold over cobalt(II) could be determined by measuring the absorbance differences at 615 nm between Solution A involving nickel(II) and Solution B prepared according to the operating procedure. On the other hand, the amounts of nickel(II) were calculated using the nickel(II)-calibration graph previously prepared in the coexistence of this assayed cobalt(II) concentrations. Moreover, the separative assay of cobalt(II) in the coexistence of some metal ions(zinc(II), copper(II), iron(III), etc.) was possible by measuring the absorbance on the cobalt(II)-mixed solution involving these each metal ion up to about 10—25-fold over cobalt(II) at proper wavelength; the absorbance difference at 595 nm in the coexsitence of zinc(II), at 580 nm in the coexistence of copper(II) and at 582 nm in the coexistence of iron(III), respectively.

In conclusion, reactions between Zincon and cobalt(II) in the presence of a cationic surfactant, and between Zincon and nickel(II) in the presence of a nonionic surfactant were the best concerning sensitivity and reproducibility. Accordingly, simple, sensitive and improved spectrophotometric determinations of cobalt(II) and nickel(II) were obtained, respectively, by using reaction of Zincon-cobalt(II) in the presence of HPC and Zincon-nickel(II) in the presence of PVA established at basic media. The sensitivity for cobalt(II) was about 20-times larger than that reported method by Gomez et al.[9] Also, the sensitivities on these proposed methods were about 8—10-times larger than the methods using nitrosonaphthol derivatives, etc.[3,8,12] Moreover, the separative assay of cobalt(II) in the coexistence of some metal ions-nickel(II), zinc(II), copper(II), or iron(III), etc. was possible by measuring at indivdual analytical wavelength.

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