NOTES

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The Spectrophotometric Determination of Nickel(II) in a Solution Containing Cobalt(II), Utilizing EDTA and Bismuth as the Masking Reagent and the Demasking Reagent

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When hydrogen peroxide is added to a solution mixture of cobalt(II)-EDTA and nickel(II)-EDTA, the former chelate is easily oxidized to the cobalt(III)-EDTA chelate. This mixture in an acidic solution releases nickel(II) upon the addition of a bismuth(III) solution as the result of the nickel(II) in the EDTA chelate being replaced by bismuth(III), because, at pH 2.0, the apparent stability constants of nickel(II)-EDTA and bismuth(III)-EDTA $\log K'$ are 6.1 and 8.6 respectively.[1] Consequently, the exchange reaction between nickel(II)-EDTA and bismuth(III) should thermodynamically proceed almost quantitatively. The cobalt(III)-EDTA chelate does not participate in such an exchange reaction and is not replaced by bismuth(III). When the pH rises above 2.0, the difference in the apparent stability constants gradually decreases; consequently, the exchange is not quantitative. On the other hand, at a pH below 2.0, the formation of the bismuth(III)-EDTA chelate is not complete.

After the above exchange reaction had taken place, 4-(2-pyridylazo)-resorcinol(PAR) was added to the reaction mixture at pH 9.5, and the absorbance of the nickel(II)-PAR chelate was measured at 496 nm.

Bismuth(III) also reacts with PAR under these conditions, but the resulting bismuth(III)-PAR chelate is converted to the bismuth(III)-EDTA chelate by the addition of EDTA. On the other hand, the nickel(II)-PAR chelate, once formed, is stable upon the addition of EDTA.[2]

Thus, trace amounts of nickel(II) in a solution containing cobalt(II) can be determined sensitively by this method, although the procedure for determination is slightly complicated.

Experimental

Apparatus. All the spectrophotometric measurements were made with a Hitachi EPS-3-type recording spectrophotometer, using a 1-cm quartz cell. All the pH measurements were conducted with a Mitamura pH-mV meter.

Reagents. Cobalt and nickel metals with a purity of 99.99% were employed as the perchlorates. A bismuth(III) stock solution was prepared by dissolving GR-grade nitrate salt in a solution containing 1.0 N free nitric acid. Commercial PAR was used as the colorimetric reagent for nickel (II). All the other reagents were GR-grade materials.

Procedure. A series of nickel(II)-EDTA solutions of appropriate concentrations containing cobalt(II)-EDTA were placed in a 10-m*l* measuring flask; 0.5 m*l* of 30% hydrogen peroxide was then added. The pH was maintained at about 8.0 with a 0.2 N sodium hydroxide solution. To completely oxidize the cobalt(II)-EDTA chelate, the reaction mixture was allowed to stand for 15—20 min at 50°C. A 2-m*l* portion of a 5.86×10^{-4} M bismuth(III) was then added, and the pH was maintained at 2.0 with 0.2 N nitric acid and 0.2 N sodium hydroxide so that the exchange reaction proceeded in an acidic solution. The reaction mixture was warmed in a water bath at about 70°C for 40 min to complete the exchange reaction. To destroy the excess hydrogen peroxide, 1 m*l* of a 0.5 M sodium sulfite solution was added. After cooling with ice water to prevent the reversal of the reaction between bismuth(III)-EDTA and nickel(II), 1 m*l* of 0.047 M sodium borate and 1 m*l* of 2.00×10^{-3} M PAR were added. Any excess bismuth(III) present also reacts with PAR. Therefore, after the solution had stood for 5—10 min, a 2-m*l* portion of 2.2×10^{-2} M EDTA was added to convert the bismuth(III)-PAR chelate into the bismuth(III)-EDTA chelate. Absorbance measurements were made at 496 nm against a solution containing the same concentration of PAR as a blank.

In the above procedure, if the addition of bismuth(III) is omitted and the PAR solution is added directly to the nickel(II)-EDTA complex solution, the nickel(II)-PAR chelate is not formed, for the apparent stability constant of the nickel(II)-EDTA chelate is larger than that of the nickel(II)-PAR chelate.

Results

Absorption Spectra. The absorption curves of PAR and the nickel(II)-PAR chelate are shown in Fig. 1. PAR shows a maximum absorption at 415 nm, and the reddish nickel(II)-PAR chelate, at 496 nm.

Effect of the Heating Time on the Exchange Reaction. The exchange reaction between the nickel(II)-EDTA chelate and bismuth(III) is very slow at room temperature; it requires 40 min at pH 2.0 and 70°C to proceed quantitatively under the above experimental conditions.

Decomposition of Hydrogen Peroxide. The excess hydrogen peroxide, which destroys the nickel(II)-PAR chelate, must be decomposed before the addition of PAR to a reaction mixture. It was impossible to decompose the hydrogen peroxide completely by heating it for 40 min at 70°C. Thus, sodium sulfite was used to decompose the excess hydrogen peroxide.

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1) A. Ringbom, "Complexation in Analytical Chemistry," Interscience Pub., New York (1963), p. 360.

2) Yoshio Shijo and Tsugio Takeuchi, *Bunseki Kagaku*, **14**, 511 (1965).

Table 1. Determination of nickel(II) in the presence of cobalt(II)

Amount taken Ni(II) (M)	Amount added Co(II) (M)	Molar ratio Co(II)/Ni(II)	Ni(II) found (M)	Error (%)
1.95×10^{-6}	5.04×10^{-6}	2.58	1.90×10^{-6}	−2.6
4.00×10^{-6}	2.00×10^{-5}	5.00	4.01×10^{-6}	+0.25
4.00×10^{-6}	3.90×10^{-5}	9.75	5.51×10^{-6}	+37.8
6.31×10^{-6}	1.59×10^{-5}	2.52	6.53×10^{-6}	+0.63
8.31×10^{-6}	8.10×10^{-6}	0.98	8.24×10^{-6}	−0.84
9.30×10^{-6}	2.38×10^{-5}	2.56	9.33×10^{-6}	+0.32
1.48×10^{-5}	4.12×10^{-5}	2.78	1.42×10^{-5}	−4.5

Table 2. Determination of nickel(II) in the presence of divers ions

Ion	Amount added (M)	Molar ratio M/Ni(II)	Ni(II) (M)		Error (%)
			Taken	Found	
Al(III)	4.20×10^{-5}	10.5	4.00×10^{-6}	4.02×10^{-6}	+0.50
Cd(II)	1.00×10^{-5}	2.5	4.00×10^{-6}	3.90×10^{-6}	−2.5
Cu(II)	5.00×10^{-6}	1.25	4.00×10^{-6}	4.01×10^{-6}	+0.25
Cu(II)	1.10×10^{-5}	2.75	4.00×10^{-6}	4.80×10^{-6}	+20.0
Hg(II)	5.00×10^{-5}	12.5	4.00×10^{-6}	4.01×10^{-6}	+0.25
Mn(II)	2.51×10^{-5}	6.28	4.00×10^{-6}	a)	
Pb(II)	1.00×10^{-5}	2.5	4.00×10^{-6}	4.01×10^{-6}	+0.25
Zn(II)	2.80×10^{-4}	70.0	4.00×10^{-6}	3.93×10^{-6}	−1.8

a) Very much interfere

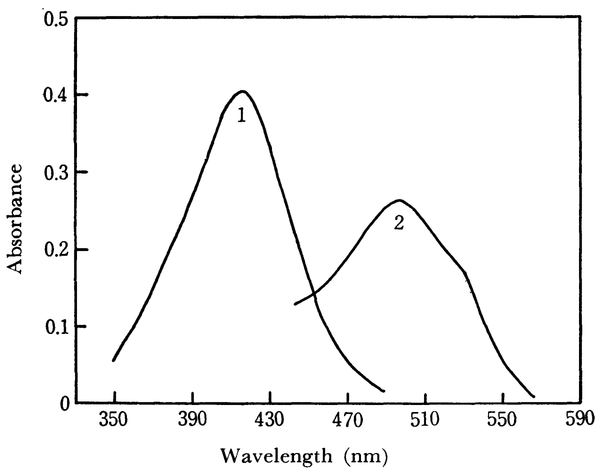

Fig. 1. Absorption spectra of PAR and Ni(II)-PAR chelate.
1. PAR 1.11×10^{-5} M
2. Ni(II)-PAR chelate 3.56×10^{-6} M
pH=9.5

With the addition of 1 m*l* of 0.5 M sodium sulfite to a reaction mixture, the change in the absorbance was not appreciable.

Concentration of EDTA. Bismuth(III) forms a reddish chelate with PAR, so a large excess of free bismuth(III) in a reaction mixture interferes seriously. Such an interference, however, can be avoided by using EDTA as a masking agent. EDTA displaces PAR easily from the bismuth(III)-PAR chelate. The addition of EDTA is also necessary for the masking of some foreign interfering elements, for example, cadmium(II), copper(II), and zinc(II). A 2-m*l* portion of 2.2×10^{-2} M EDTA was used as a masking agent.

Determination of Nickel(II). The nickel(II) was determined by the procedure described above. Beer's law was obeyed within the concentration range of 1.95×10^{-6} M to 1.48×10^{-5} M of nickel(II). The molar extinction coefficient was 7.3×10^{4}, and the sensitivity was very high. Table 1 shows the results of determinations in the presence of cobalt(II). When the concentration of the cobalt(II) becomes about ten times as much as the nickel(II), a large error was observed.

Effect of Diverse Ions. The effects of diverse ions on the colorimetric determination of nickel(II) utilizing the nickel(II)-PAR chelate were previously investigated by Shijo.[2] In the present experiments, the authors examined the effect of diverse ions which are highly sensitive in their reactions with PAR. These results are shown in Table 2. It was found that the interference of manganese(II) and copper(II) was very pronounced, but other metal ions did not interfere.