Spectrophotometric Determination of Nickel with Sarcosinexylenol Blue

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Synopsis. Sarcosinexylenol Blue (SXB) was synthesized and the possibility of using SXB as a spectrophotometric reagent was examined. The fundamental conditions for the photometric determination of nickel which gave relatively strong coloration with SXB were studied. The simultaneous determination of nickel and zinc was also studied.

In a series of sulfophthalein derivatives, there are many useful compounds utilized as the spectrophotometric reagents for various metal ions.[1,2] The authors have newly synthesized Sarcosinexylenol Blue, 3,3′-bis[*N*-(carboxymethyl)methylaminomethyl]-*p*-xylenolsulfophthalein, as sulfophthalein derivative and examined its color reactions with metal ions. It was found that this reagent generally does not react as sensitively as Xylenol Oragne[1] which is a representative sulfophthalein reagent. However it gives relatively strong colors with some metal ions such as nickel, cobalt, cadmium, and iron(III), and there is a possibility to use this reagent as the photometric reagent for those ions. Nickel gave the strongest color, and we have studied in detail the best conditions for its use for the photometric determination of this ion and for the simultaneous determination of nickel and zinc. The usefulness of SXB in comparison with Glycinethymol Blue, Glycinecresol Red, and Methylthymol Blue[3] has been established, these have a similar structure to that of SXB, but SXB is more sensitive than those reagents. It also has relatively good selectivity for the diverse ions. The results obtained are shown below.

Experimental

Reagents. Standard Metal Solutions: A solution containing about 1 mg cm^{-3} of nickel or zinc was prepared by dissolving guaranteed reagent grade metal nitrate in a small amount of nitric acid and diluted with distilled water. The solutions were standardized by complexometric titration.

SXB Solution: A 0.05% SXB solution was prepared by dissolving in distilled water a weighed amount of SXB. The SXB was synthesized from Paraxylenol Blue, sarcosine, and formaldehyde by the Mannich condensation,[1] and separated from the reaction mixture on a cellulose column by 1-butanol saturated with 10% acetic acid. Then, the SXB was passed through a column of cation-exchange resins to convert it to the free acid form. The SXB, obtained as on orange compound has mp 137—140 °C. The result of the elemental analysis was as follows. Found: C, 56.52; H, 6.33; N, 4.12; S, 5.15%. Calcd for $C_{31}H_{36}O_9N_2S \cdot 2H_2O$: C, 57.41; H, 6.17; N, 4.32; S, 4.94%.

Buffer Solution: The pH was adjusted with 0.1 mol dm^{-3} borax–0.1 mol dm^{-3} hydrochloric acid and 0.1 mol dm^{-3} borax–0.1 mol dm^{-3} sodium hydroxide.

All the other reagents used were of guaranteed reagent grade.

Results and Discussion

Absorption Curves of SXB. The absorption spectra of 6.2×10^{-5} mol dm^{-3} SXB solution at various pH are shown in Fig. 1. The SXB solution colors reddish-orange in 4 mol dm^{-3} nitric acid. The color of the solution changes to yellow with increasing pH, but, over the pH range from 1.8 to 5.0, there is no color change and the solutions show almost the same absorption curves having an absorption maximum at 439—443 nm. On increase of the pH, however, the color of the solution changes again, and it becomes yellow-green at pH 6.0, blue-violet at pH 10.8, violet at pH 11.7, and blue at 13.4. With these color changes, the absorption maximum at 439—443 nm decreases, accompanied by an increase of that at 599—602 nm. At pH 13.4, the absorption maximum of the solution shifts to 611—614 nm.

Complexes of SXB and Metal Ions. The color reactions between SXB and metal ions were investigated. The results are summarized in Table 1, nickel, cobalt, cadmium, and iron(III) gave relatively strong colors whose molar absorptivities are $1—2 \times 10^4$. The chemical formula of the nickel complex obtained by mole ratio method is $Ni(SXB)_2$. In the case of zinc, there are two complexes, $Zn(SXB)_2$ at 650 nm and $Zn(SXB)_3$ at 580 nm. Cobalt forms $Co(SXB)_2$. Concerning the compositions of the cadmium and iron(III) complexes, no clear results could be obtained.

Determination of Nickel. Standard Procedure: A sample solution containing up to 60 μg of nickel is

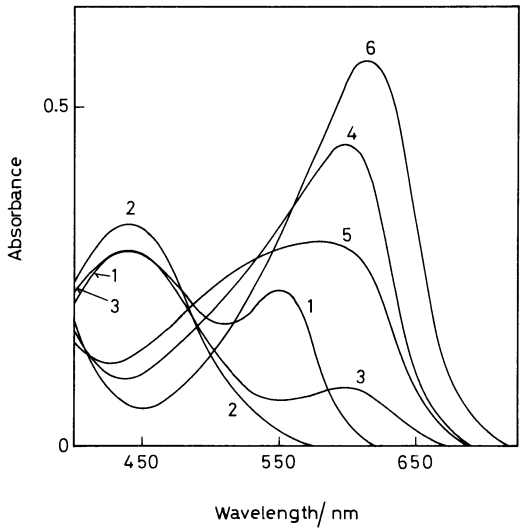

Fig. 1. Absorption curves of SXB.
[SXB] = 6.2×10^{-5} mol dm^{-3}, reference: water, 1 : 4 mol dm^{-3} HNO_3, 2: pH 1.8—5.0, 3: pH 6.0, 4: pH 10.8, 5: pH 11.7, 6: pH 13.4.

Table 1. Reactions of SXB with Metal Ions

Ion	pH	Color of complex	Wavelength nm	Molar absorptivity	Composition (M:SXB)
Al^{3+}	5.9	Reddish brown*			
Ga^{3+}	5.9	Reddish brown	517—521	8.5×10^3	
In^{3+}	5.9	Reddish brown	513—518	7.3×10^3	
Sn^{4+}	10.1	Reddish violet*			
Pb^{2+}	10.1	Blue violet*			
Cu^{2+}	5.3	Blue violet	554—564	5.2×10^3	
Zn^{2+}	10.1	Blue	649—651	9.1×10^3	1:2
	10.1	Blue	579—582	7.2×10^3	1:3
Cd^{2+}	10.7	Blue	573—575	1.9×10^4	
	10.7	Blue	640	5.6×10^3	
Hg^{2+}	10.1	Blue*			
Cr^{3+}	5.0	Reddish brown*			
Mn^{2+}	10.1	Violet*			
Fe^{3+}	5.3	Reddish violet	524—529	1.4×10^4	
Co^{2+}	9.8	Blue	649—650	1.6×10^4	1:2
Ni^{2+}	10.1	Blue	640—642	2.2×10^4	1:2

Alkali metals, alkaline earth metals, bismuth(III), scandium, yttrium, thorium, zirconium, molybdenum(VI), and tungsten(VI) did not react with SXB. * Weak color.

placed in a 25 cm^3 volumetric flask. Then, 10 cm^3 of buffer solution and 5 cm^3 of 0.05% SXB solution are added. After making up the volume to 25 cm^3 (the final pH: 10.1), the absorbance is measured at 641 nm against a reagent blank.

Absorption Curves of Nickel Complex: The colored solution of the nickel complex has an absorption maximum at 640—642 nm which is nearly constant at pH 10.0—10.5.

The Effect of the Amount of SXB: The maximum and almost constant absorbance was obtained by adding from 3 to 7 cm^3 of 0.05% SXB solution for 20 μg of nickel.

Calibration Curves: Beer's law is observed up to 2.4 μg cm^{-3} of nickel. The relative standard deviation for five determinations was 0.91%.

Simultaneous Determination of Nickel and Zinc: The colored solution of the zinc complex has two absorption maxima at 579—582 and 649—651 nm. On the other hand, that of the nickel complex has only one absorption maximum at 640—642 nm. As a result, the absorbance at 649—651 nm of the zinc complex is affected by the absorbance of the nickel complex, but the absorbance at 579—582 nm of the zinc complex is not affected by that of nickel complex. Utilizing these facts, the simultaneous determination of these two elements has been investigated. Satisfactory results were obtained for a solution containing 5—25 μg of nickel and 20—50 μg of zinc. The procedure is as follows. The sample solution containing nickel and zinc is placed in a 50 cm^3 Erlenmeyer's flask. Then, 10 cm^3 buffer solution and 6 cm^3 of 0.05% SXB solution are added. After being kept for a few minutes in about 50 °C water bath, the solution is cooled with running water, transferred to a 25 cm^3 volumetric flask, and diluted to the mark with distilled water (the final pH: 10.1). The absorbance is measured at 580 and 650 nm within 15 min against a reagent blank. Zinc is determined from the absorbance at 580 nm, then, nickel is determined by subtracting the absorbance due to zinc from the total absorbance at 650 nm.

The Effect of Diverse Ions: The effect of thirty-seven diverse ions on the determination of 20 μg of nickel and 50 μg of zinc has been examined. Concerning anions, the presence of 10 mg each of oxalate, citrate, tartrate, phosphate, and sulfate, and 1 mg of fluoride does not interfere with either the nickel or the zinc determinations. For cations, nickel can be determined within 5% error in the presence of 500 μg each of alkali metals, alkaline earth metals, aluminium, gallium, gold, scandium, yttrium, lanthanoids, thorium, molybdenum(VI), and tungsten(VI), 100 μg each of indium, antimony(III), and manganese(II), and 20 μg each of bismuth(III), mercury(II), and palladium. But beryllium, tin(IV), lead, copper, zinc, cadmium, chromium(III), iron(III), and cobalt interfere with the determination. For the zinc determination, the presence of 500 μg each of alkali metals, alkaline earth metals, aluminium, gallium, bismuth(III), gold, scandium, yttrium, lanthanoids, thorium, molybdenum(VI), tungsten(VI), and palladium, 100 μg each of indium, antimony(III), and manganese(II), and 50 μg of mercury(II) does not interfere with the determination. Beryllium, tin(IV), lead, copper, cadmium, chromium(III), iron(III), cobalt, and nickel interfere when the measurements are carried out at 650 nm, but the interference from cobalt and nickel can be eliminated by the measurements at 580 nm.

References

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