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Determination of Traces of Constituents with Schiff Bases. III.[1] Extraction-Spectrophotometric Determination of Nickel with Salicylidene-*o*-aminophenol

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A method was established for the spectrophotometric determination of microgram amounts of nickel after the extraction of nickel(II) as a salicylidene-*o*-aminophenol (SAP) complex from an alkaline aqueous solution into chloroform. Nickel(II) reacts with SAP to form a complex which can be extracted into organic solvents such as benzene, chloroform, methyl isobutyl ketone, *etc.*, in the presence of ammonium ions. The extraction of nickel was almost quantitative, and a maximum and constant absorbance was obtained in the pH range from 8.5 to 9.8. The complex extracted was very stable and had an absorption maximum at 418 mμ. The composition of the complex was confirmed to be 1 to 1 (metal to ligand). A linear relationship was maintained between the concentration of nickel and the absorbance. The molar extinction coefficient and the sensitivity for $\log(I_0/I)=0.001$ at 418 mμ were 17000 and 3.5×10^{-3} μg Ni/cm^2, respectively. Several ions such as cobalt(II), copper(I and II), chromium(III), lead(II), manganese(II) and citrate interfered with the determination.

Recently, salicylidene-*o*-aminophenol (SAP), a Schiff base obtained by the condensation of salicylaldehyde with *o*-aminophenol, has been used for the spectrofluorimetric determination of aluminum[2-7] and gallium[7] and for the separation and indirect spectrophotometric determination of copper.[8] The authors have previously reported the direct spectrophotometric determination of copper using the complex formation of SAP with copper(II).[1] This reagent was found to react also with nickel(II) in an alkaline aqueous medium to form a complex which could be extracted in the presence of ammonium ions into organic solvents such as benzene, chloroform, carbon tetrachloride, methyl isobutylketone (MIBK), *etc.* This paper will describe a direct spectrophotometric method for the determination of traces of nickel after extraction of it as a SAP complex into chloroform.

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8) K. Isagai, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **82**, 1172 (1961).

Experimental

Apparatus. The recording of absorption spectra and all the other spectrophotometric measurements were made with a Hitachi Model EPS-3T automatic recording spectrophotometer and a Hitachi Model 139 spectrophotometer, respectively, using 10 mm matched cells. The pH measurements were made with a Toa Dempa glass-electrode Model HM-5A pH meter. The shaking was done with an Iwaki Model KM shaker.

Reagents. *Standard Nickel(II) Solution.* A stock solution containing about 1000 μg of nickel per m*l* was prepared by dissolving nickel chloride in water, followed by adding a small amount of hydrochloric acid enough to give approximately 0.1 N hydrochloric acid solution. Standardization was made by titration with a 0.01 M EDTA solution. The stock solution was appropriately diluted to make working solutions of nickel(II).

SAP Solution. A 0.01% solution was prepared by dissolving 25 mg of SAP in 250 m*l* of chloroform. SAP used in this work was synthesized and purified by the method proposed by Dagnall *et al.*[2]

Buffer Solutions. Buffer solutions were prepared by mixing a 1 M ammonium chloride solution and a 1 M aqueous ammonia solution in the ratios required.

Extracting Solvent. Commercial chloroform of analytical reagent grade was used without further purification.

Recommended Procedure. In a 50 m*l* separatory funnel, an aliquot of the sample solution containing less than 30 μg of nickel(II) is taken. Add 1 m*l* of the buffer solution (pH 9), and dilute to 30 m*l* with distilled water. Add 10.0 m*l* of a 0.01% SAP solution in chloroform, and shake vigorously for 10 min. After the phase separation, transfer the organic phase into a 50 m*l* flask containing about 1 g of anhydrous sodium sulfate. Then transfer the organic solution into a cell and measure the absorbance at 418 mμ using a reagent blank as a reference. The amount of nickel can be obtained from the calibration curve.

Results and Discussion

Selection of Extracting Solvent. Nickel(II) is extracted as its SAP complex from an alkaline aqueous solution into organic solvents such as benzene, chloroform, carbon tetrachloride, MIBK, *etc.* in the presence of ammonium ions. Among them, chloroform seemed to be the best for the present purpose, because of the relatively high extractability of the complex and the good separability of two phases; an aqueous and an organic phases. For this reason, chloroform was used as the extracting solvent in this work.

Absorption Spectra. Figure 1 shows the absorption spectra of SAP and its nickel(II) complex extracted in chloroform at pH 9. The absorption maximum of the complex appears at 418 mμ, while that of SAP, at 354 mμ. This maximum absorption wavelength of 418 mμ, which was used for the determination of nickel, did not shift in either case, when pH value of the aqueous phase was varied from 7 to 10.5 or when the molar ratio

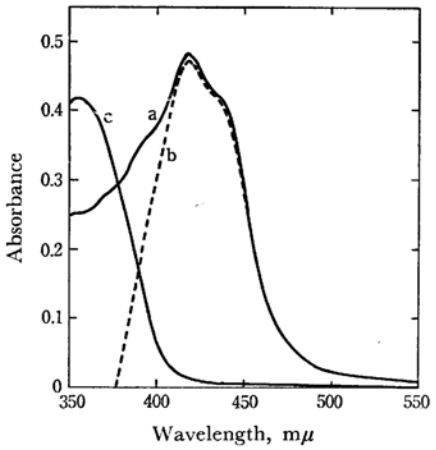

Fig. 1. Absorption spectra of SAP and its nickel-(II) complex.
Ni: 16.5 μg, SAP: 4.3×10^{-7} mol/10 m*l* of chloroform, pH : 9, $V_{aq}/V_{org}=1$, Shaking time: 30 min.
a : Ni(II)-SAP complex measured against chloroform
b : Ni(II)-SAP complex measured against a reagent blank
c : SAP alone (reagent blank) measured against chloroform

of nickel to SAP was varied 1 : 5 to 5 : 1. Taking this fact and those described in the subsequent paragraph into account, it was considered that only one species of the complex was extracted into chloroform under the conditions studied. The absorption spectra of the complex in benzene and in MIBK were essentially similar to that in chloroform, except that the absorbancepeak occurred at 424 mμ in benzene and 420 mμ in MIBK, respectively.

The Effect of pH Value. The effect of pH value on the absorbance at 418 mμ was examined over a pH range from 6.8 to 10.3. As shown in Fig. 2, it can be seen that a maximum and constant absorbance is obtained in the pH range from 8.5

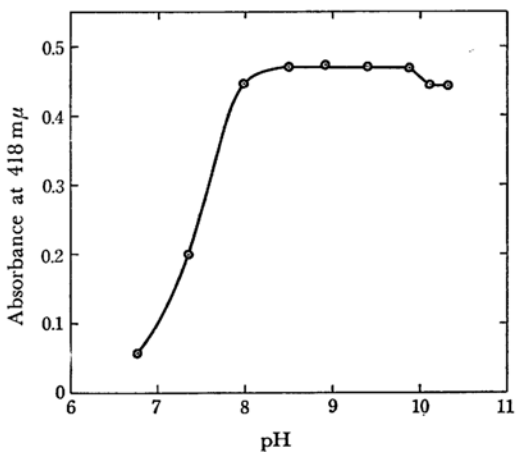

Fig. 2. Effect of pH.
Ni: 16.5 μg, $V_{aq}/V_{org}=1$

to 9.8. In subsequent experiments, therefore, the extraction of nickel was carried out at about pH 9.

The Effect of the Amount of SAP. Figure 3 shows the effect of the amount of SAP on the absorbance. About an 8-fold molar excess of the reagent over the amount of nickel is necessary to obtain a maximum and constant absorbance. Therefore, 10 m*l* of a 0.01% solution of the reagent in chloroform was used. This corresponds to 4.7×10^{-6} mol, and it is about an 8-fold molar excess over the highest point on the calibration curve in Fig. 4, *i. e.*, 33 μg of nickel.

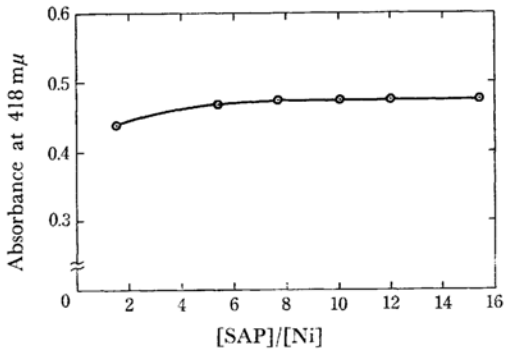

Fig. 3. Effect of amount of SAP.
Ni: 16.5 μg, $V_{aq}/V_{org}=1$

The Effect of the Shaking Time. The variation of shaking time from 1 to 30 min revealed that a 5-min shaking was enough to attain a good extraction under the recommended conditions, although the shaking time must be increased with the decrease of the ratio of SAP to nickel. The extraction of nickel was reproducible and 93.1% of it present in an aqueous phase were extracted by a single extraction. Therefore, one extraction seems to be sufficient for the determination of nickel.

The Effect of Volume of the Aqueous Phase. The absorbance of the extract was decreased with increasing the volume of the aqueous phase to that of organic phase. Considering this fact and the application of the method to the analysis of practical sample, the volume ratio of the aqueous to the organic phase was kept 3 in the recommended procedure.

The Stability of the Color. The absorbance of the extract did not change at all for at least 12 hr. The complex, therefore, seems to be very stable in chloroform.

Adherence to Beer's Law. As is seen in Fig. 4, a linear relationship was maintained between the concentration of nickel and the absorbance up to at least 33 μg of nickel per 10 m*l* of the extract. The molar extinction coefficient was about 17000, and the sensitivity was 3.5×10^{-3} μg Ni/cm^2, which corresponds to $\log(I_0/I)=0.001$.

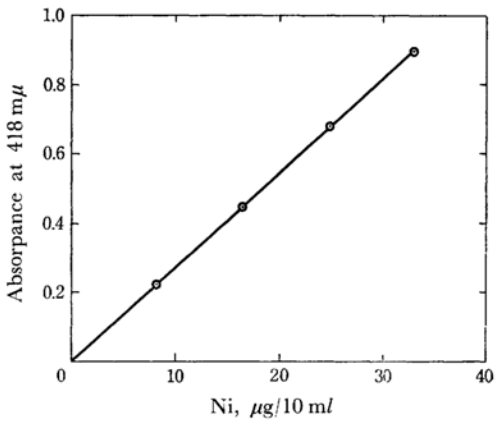

Fig. 4. Calibration curve for nickel.
pH: 9, $V_{aq}/V_{org}=3$

The Effect of Diverse Ions. The effect of diverse ions on the determination of nickel was examined at pH 9 and the results are summarised in Table 1. Cobalt(II), copper(I and II), chromium(III), lead(II), manganese(II) and citrate interfered with the determination. The interferences by these cations and citrate may be due to the complex formation with SAP and with nickel, respectively.

The Composition of the Complex. Although the composition of the complex has been already reported to be 1 to 1 (metal to ligand) from the analytical results of the isolated complex,[7] the authors also examined the composition in chloroform by means of the continuous variation and the molar ratio methods. Extraction was performed at pH 9, and the absorbance was measured at three wavelengths between 400 and 440 mμ. Both methods revealed that nickel(II) forms a 1-to-1 complex with SAP. As an example, the result of the continuous variation method is shown in Fig. 5.

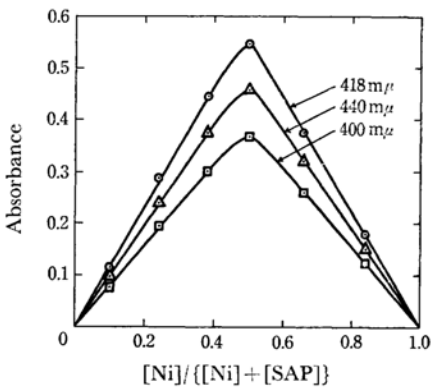

Fig. 5. Continuous variation method.
$[Ni]+[SAP]=7.0\times10^{-5}$ M, pH: 9,
$V_{aq}/V_{org}=1$, Shaking time: 30 min

TABLE 1. EFFECT OF DIVERSE IONS (Ni taken: 16.5 μg)

Ion	Added μg	Ni found μg	Relative error %	Ion	Added μg	Ni found μg	Relative error %
Al(III)	27.0	16.3	−1.2	Si(IV)	18.3	16.7	1.2
Ca(II)	40.1	16.7	1.2	Ti(IV)	16.5	16.5	0
Cd(II)	50.0	16.7	1.2	V(IV)	20.0	16.6	0.6
Co(II)	20.6	17.9	8.5	V(V)	20.0	16.6	0.6
Cr(III)	50.0	5.9	−64.2	W(VI)	52.6	16.7	1.2
Cr(VI)	25.0	16.6	0.6	Zn(II)	32.8	16.7	1.2
Cu(I)	5.0	30.0	81.8	Zr(IV)	18.2	16.8	1.8
Cu(II)	12.4	27.0	63.6	ClO_4^-	49.7*	16.6	0.6
Fe(II)	20.0	16.4	−0.6	NO_3^-	31.0*	16.5	0
Fe(III)	20.1	16.5	0	SO_4^{2-}	48.0*	16.5	0
Hg(II)	57.7	16.6	0.6	PO_4^{3-}	47.0*	16.7	1.2
Mg(II)	24.3	16.7	1.2	Acetate	29.5*	16.6	0.6
Mn(II)	3.6	36.0	118.2	Tartrate	37.0*	16.7	1.2
Mo(VI)	47.6	16.7	1.2	Citrate	31.5*	10.8	−34.5
Pb(II)	50.0	17.5	6.1				

*: In mg unit

Comparison with Other Methods. The proposed method has the following advantages: A relatively broad pH range is tolerable, the color of the extract is very stable, and the sensitivity is superior to that of other methods, *e. g.*, the dimethylglyoxime-oxidizing agent method (sensitivity: 4.2×10^{-3} μg Ni/cm^2).[9]

9) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York (1965), p. 669.