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Spectrophotometric Studies on Complexation Reaction of Some Water-Soluble 5-Nitro-2-pyridylhydrazones with Nickel(II) and Determination of Trace Nickel with α-(2-Benzimidazolyl)-α-(5-nitro-2-pyridyl)hydrazono-3-toluenesulfonic Acid

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The complexation reaction of four water-soluble hydrazones, α-(5-nitro-2-pyridyl)hydrazono-α-(2-quinolyl)-3-toluenesulfonic acid (NPHQTS), α-(5-nitro-2-pyridyl)hydrazono-α-(2-thiazolyl)-3-toluenesulfonic acid (NPHTTS), α-(2-benzothiazolyl)-α-(5-nitro-2-pyridyl)hydrazono-3-toluenesulfonic acid (BTNPHTS) and α-(2-benzimidazolyl)-α-(5-nitro-2-pyridyl)hydrazono-3-toluenesulfonic acid (BINPHTS), with nickel(II) has been studied spectrophotometrically. These hydrazones react with nickel(II) to form a stable 1:2 (metal:ligand) complexes with high molar absorptivities. A sensitive and selective spectrophotometric method for the determination of nickel with BINPHTS has been developed. The nickel-BINPHTS complex is formed quantitatively in the pH range 6.5—8.9 and its absorption spectrum shows a maximum at 498 nm. Beer's law is obeyed over the range 0.02—0.8 μg cm^{-3} of nickel and the apparent molar absorptivity of the complex is 8.67×10^{4} dm^{3}mol^{-1}cm^{-1} at 498 nm. The proposed method was applied to the determination of nickel in manganese nodule samples, satisfactory results being obtained. Furthermore, the overall formation constants of nickel complexes of the four hydrazones were also determined spectrophotometrically.

In a previous work[1)] we synthesized 4 new water soluble hydrazones, α-(5-nitro-2-pyridyl)hydrazono-α-(2-quinolyl)-3-toluenesulfonic acid (NPHQTS), α-(5-nitro-2-pyridyl)hydrazono-α-(2-thiazolyl)-3-toluenesulfonic acid (NPHTTS), α-(2-benzothiazolyl)-α-(5-nitro-2-pyridyl)hydrazono-3-toluenesulfonic acid (BTNPHTS) and α-(2-benzimidazolyl)-α-(5-nitro-2-pyridyl)hydrazono-3-toluenesulfonic acid (BINPHTS), studied their properties and color reactions with metal ions, and reported that these hydrazones are very useful as highly sensitive spectrophotometric reagents for metals, especially for cadmium(II), cobalt(II), nickel(II), palladium(II), and zinc(II). Thus to start with, the complexation reaction of these four hydrazones with nickel(II) has been investigated in detail and compared with that of α-(5-nitro-2-pyridyl)hydrazono-α-(2-pyridyl)-3-toluenesulfonic acid (NPHPTS), synthesized in an earlier work,[2)] with nickel(II). A highly sensitive and practical spectrophotometric method for the determination of nickel with one of these hydrazones, BINPHTS, have been developed and applied to the analysis of real samples in this work.

Experimental

Reagents. BINPHTS solution, 1.0×10^{-3} M (1 M=1 mol dm^{-3}). Prepared by dissolving the required mass of BINPHTS synthesized in a previous work[1)] in 0.01 M sodium hydroxide solution. This solution was further diluted with water if necessary.

Standard Nickel(II) Solution. Prepared by dissolving 2.5 g of nickel nitrate [$Ni(NO_3)_2\cdot 6H_2O$] in about 100 cm^{3} of water, adding 10 cm^{3} of nitric acid (1+1) and diluting to 500 cm^{3} with water. This solution was standardized by EDTA titration with copper 1-(2-pyridylazo)-2-naphtholate (Cu-PAN) as an indicator. Working solutions were prepared by diluting this solution with water.

Other reagents used were the same as those used in a previous work.[1)]

Procedures. Determination of Nickel: To an aliquot containing up to 70 μg of nickel(II) in a 25-cm^{3} calibrated flask were added 1 cm^{3} of 50% w/v potassium fluoride solution, 1 cm^{3} of 30% w/v sodium citrate solution and/or 1 cm^{3} of 10% w/v sodium thioglycollate solution as masking agents if necessary, 2 cm^{3} of 0.2 M 2,4,6-trimethylpyridine–0.2 M perchloric acid buffer solution of pH 7 and 5 cm^{3} of 5×10^{-4} M BINPHTS solution. The solution was diluted to the mark with water. After allowing to stand for about 5 min, the absorbance of the solution was measured at 498 nm against a reagent blank.

Dissolution and Pretreatment of Manganese Nodule Sample: The sample was decomposed and the sample solution was prepared as follows, consulting to JIS method:[3)] To 100 mg of the sample were added 15 cm^{3} each of concentrated hydrochloric and nitric acids. The mixture was heated to decompose the sample. After adding 2 cm^{3} of sulfuric acid (1+1), the mixture was evaporated to dryness and cooled to room temperature. To the residue was added about 50 cm^{3} of hydrochloric acid (1+100) and the mixture was heated for a few minutes to dissolve the soluble salts and filtered into a 200-cm^{3} calibrated flask. The insoluble residue was washed with hot water. The filtrate and washings in the flask were diluted to the mark with water after cooling to room temperature. An appropriate aliquot of this solution was used to the determination of nickel.

When more than 100 μg of iron(III) was contained in the aliquot taken, it was transferred into a separating funnel. Sufficient amounts of concentrated hydrochloric acid to give an acidity of about 6 M and 10—20 cm^{3} of 4-methyl-2-

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pentanone were added, and then the mixture was shaken for 5 min to remove the iron(III). The aqueous phase was transferred into an evaporating dish and heated to remove the majority of the acid. The content of the dish was transferred into a 25-cm^3 calibrated flask and used for the determination of nickel.

Results and Discussion

Absorption Spectra of Complexes and Influence of pH on the Complexation. Figure 1 shows absorption spectra of the complexes of the five hydrazones, including NPHPTS for comparison, with nickel(II) at pHs where the complexes are formed quantitatively, and Fig. 2 the influence of pH on the complexation. The absorption maxima of the complexes and the optimal pH ranges for the complexation are summarized in Table 1. These results indicate that BTNPHTS is the most sensitive and gives the largest shift in wavelength by the complexation, followed by BINPHTS. However, the rate of formation of the BTNPHTS-nickel complex is very slow and no suitable accelerator could be found, whereas that of the BINPHTS-nickel complex was remarkably accelerated by the addition of thioglycollate, as stated below. Therefore, since BINPHTS seemed to be the most preferable spectrophotometric reagent for nickel(II) among these hydrazones, its complexation reaction with nickel(II) was mainly investigated in the subsequent work.

As can be seen from Fig. 2 and Table 1, a constant and maximum absorbance is obtained over the pH range 6.5—8.9 for the BINPHTS complex, so that the use of 0.2 M 2,4,6-trimethylpyridine-0.2 M perchloric acid buffer of pH 7 was recommended for the nickel determination with BINPHTS.

Rate of Complex Formation and Stability of the Complex. The rate of complexation of the hydrazones with nickel(II) was not so rapid as expected. Two examples for the complexations of BTNPHTS and BINPHTS with nickel(II) are shown in Fig. 3, which reveals that more than 30 min is required to attain to each constant and maximum absorbance in either case. Accelerators for the complexation reactions were therefore sought and thioglycollate was found to accelerate the complexation reaction of

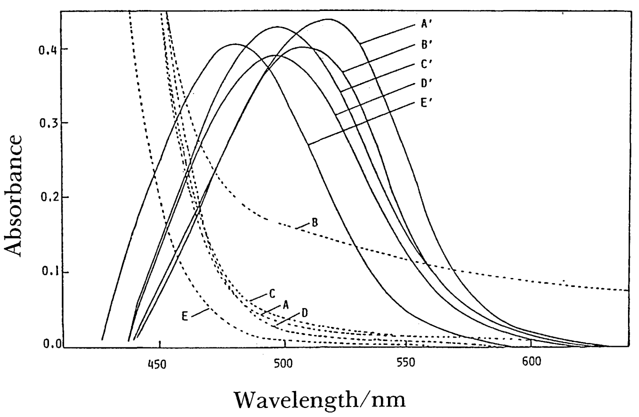

Fig. 1. Absorption spectra of hydrazones and their nickel complexes. Hydrazones, 5.0×10^{-5} M; Ni(II), 5.0×10^{-6} M; A—E, hydrazone against water; A′—E′, complex against reagent blank; A,A′, BTNPHTS (5.8); B,B′, NPHQTS (7.6); C,C′, BINPHTS (6.8); D,D′, NPHTTS (8.5); E,E′ NPHPTS (7.8), where figures in parentheses indicate pH values.

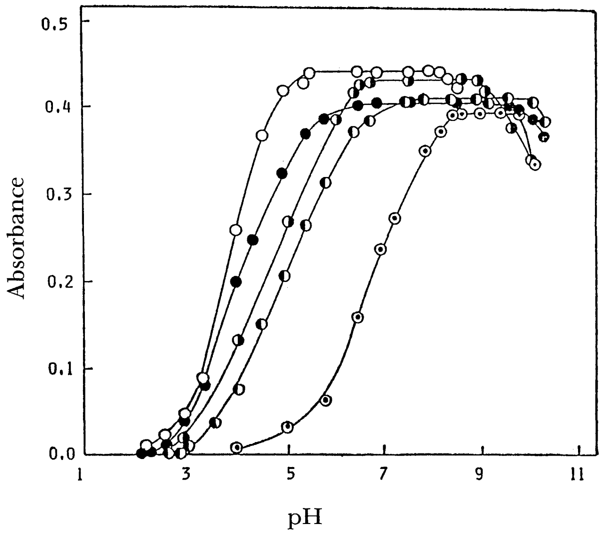

Fig. 2. Influence of pH on the complexation. Hydrazone, 1.0×10^{-4} M; Ni(II), 5.0×10^{-6} M; standing time, 30 min; reference, reagent blank. ○ BTNPHTS (517); ● NPHQTS (510); ◑ BINPHTS (498); ◐ NPHPTS (480); ⊙ NPHTTS (496), where figures in parentheses indicate wavelengths (nm) measured.

Table 1. Optimal pH Ranges for Complex Formation of Hydrazones with Nickel(II) and Characteristics of the Complexes

Complex	Optimal pH range	Absorption maximum/nm	Apparent molar absorptivity/M^{-1}cm^{-1}	Composition (M:L)
NPHPTS complex	7.5—10.0	480	8.2×10^4	1:2
NPHQTS complex	6.5— 9.5	510	8.1×10^4	1:2
NPHTTS complex	8.4— 9.7	496	7.9×10^4	1:2
BTNPHTS complex	5.5— 8.2	517	8.8×10^4	1:2
BINPHTS complex	6.5— 8.9	498	8.7×10^4	1:2

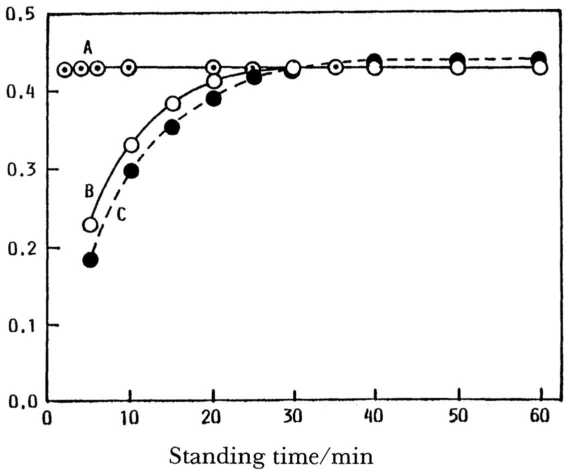

Fig. 3. Influence of standing time on the complexation of BINPHTS and BTNPHTS with nickel(II). Hydrazone, 1.0×10^{-4} M; Ni(II), 5.0×10^{-6} M; pH, 7.0; reference, reagent blank; wavelength/nm—A, B, 498; C, 517; A, B, BINPHTS complex; C, BTNPHTS complex; A, in the presence of sodium thioglycollate of 0.04% w/v; B, C, in the absence of thioglycollate.

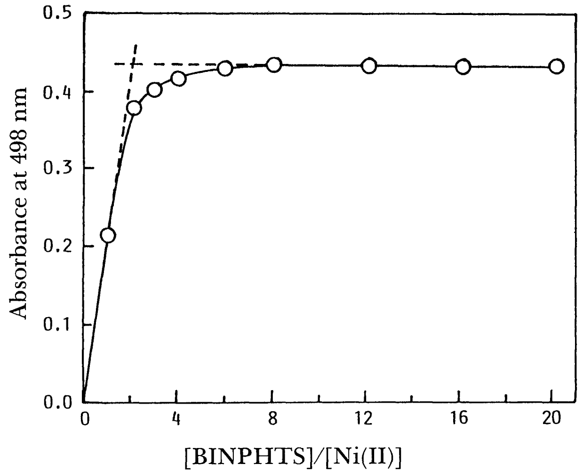

Fig. 4. Influence of BINPHTS concentration. Ni(II), 5.0×10^{-6} M; pH, 7.0; reference, reagent blank.

Table 2. Influence of Other Ions[a)]

Ion	Tolerance limit
Ag(I), Al(III), Bi(III), Ca(II) Cd(II), Cr(III), Cu(I, II), Ga(III) Hg(II), In(III), Mn(II), Mg(II) Pb(II), Ti(IV), V(IV, V), Zn(II)	≧1000 μg
Pd(II)	500 μg
Fe(III)[b)]	100 μg
Co(II)	30 μg
Fe(III)	5 μg
Fe(II)	<1 μg
Br^-, Cl^-, ClO_4^-, F^-, I^-, NO_3^-, PO_4^{3-} SCN^-, SO_4^{2-}, Acetate, Citrate Oxalate, Tartrate, NH_4^+	≧100 mg
EDTA	<1 mg

a) Tolerable error: ±3%, Nicke(II) taken: 7.29 μg.
b) One cm^3 of 50% w/v potassium fluoride solution was added.

BINPHTS with nickel(II), the complexation being complete within a few minutes in the presence of a small amount of it as also shown in Fig. 3. However, thioglycollate had no effect on the acceleration of the complexation reaction of BTNPHTS with nickel(II).

The BINPHTS-nickel complex formed was very stable, no measurable change in absorbance being noticed for more than 5 h.

Influence of BINPHTS Concentration. The influence of the BINPHTS concentration was examined. The results were shown in Fig. 4, from which it is found that an 8-fold molar excess of BINPHTS is the minimum required for obtaining a constant absorbance and an excess of BINPHTS does not interfere. Further, this result suggests the formation of a 1 : 2 (metal : ligand) complex.

Calibration Graph, Sensitivity, and Precision. The calibration graph for the determination of nickel with BINPHTS was prepared by the recommended procedure. The graph conformed to Beer's law and gave a straight line passing through the origin in the range 0.02—0.8 $\mu g\,cm^{-3}$ of nickel. The equation of the line obtained by a least-squares treatment was

$$\mathrm{Ni}(\mu g\,cm^{-3}) = 0.677\,A, \qquad (1)$$

where A is the absorbance. The apparent molar absorptivity and Sandell's sensitivity calculated from this equation were 8.67×10^4 $M^{-1}cm^{-1}$ and 0.677 $ng\,cm^{-2}$ of Ni, respectively.

The precision of the proposed method was determined by analysing 10 standard solutions containing 7.29 μg of nickel(II), the coefficient of variation being 0.32%.

Influence of Foreign Ions. Since BINPHTS reacts with many metal ions to form complexes,[1)] the interference from these ions was anticipated in the determination of nickel. However, thioglycollate added as an accelerator for the complexation of nickel(II) with BINPHTS was very effective also for the masking of metal ions classified as so-called soft or border-line acids and moreover the addition of citrate was effective for those classified as hard acids. Hence, in the determination of nickel the addition of citrate prior to the addition of thioglycollate is recommended. Table 2 shows the influence of other ions in the determination of 7.29 μg of nickel by the recommended procedure. An error of ±3% in the absorbance reading was considered tolerable. Only iron(II) interfered with the

Table 3. Determination of Nickel in Manganese Nodules

Sample	Nickel content/%	
	Proposed method	Atomic absorption spectrometry
A	1.22_0 1.21_9	1.21_9
B	0.71_5 0.71_5	0.71_5
C	0.39_4 0.39_3	0.39_3
D	0.79_6 0.79_7	0.79_7
E	0.74_9 0.74_8	0.74_8

determination, but this interference can be removed by adding fluoride after oxidizing to iron(III). Thus the proposed method can be regarded as very selective as well as highly sensitive for nickel.

Practical Application. To confirm the usefulness of the proposed method, nickel in manganese nodules was determined. The results are given in Table 3 together with those by atomic absorption spectrometry carried out for comparison. Both sets of results are in good agreement.

Composition of the Complex. As was already anticipated from Fig. 4, the molar composition of the BINPHTS-nickel complex formed under the conditions for the nickel determination was determined to be 1 : 2 (metal ; ligand) by both the molar ratio and the continuous variation methods, the results of the latter method being shown in Fig. 5. The composition of the complexes of the other hydrazones was also determined by the same ways. The results indicated the formation of the 1 : 2 complex in every hydrazone as shown already in Table 1.

Formation Constant of the Complexes. The formation constant of the BINPHTS-nickel complex was determined spectrophotometrically by the equilibrium shift method.[4)]

Taking into consideration the proton dissociation constants ($pK_{a3}=0.70$, $pK_{a4}=3.58$, $pK_{a5}=10.61$, and $pK_{a6}=12.61$) of BINPHTS reported in a previous paper,[1)] BINPHTS exists as the species of H_2L^- under the recommended conditions for the complexation, so that the complexation equilibrium between BINPHTS and nickel(II) may be expressed as

$$Ni^{2+} + n\ H_2L^- \rightleftarrows Ni(HL)_n^{(2n-2)-} + n\ H^+, \tag{2}$$

$$K_{eq} = [Ni(HL)_n^{(2n-2)-}][H^+]^n/[Ni^{2+}][H_2L^-]^n, \tag{3}$$

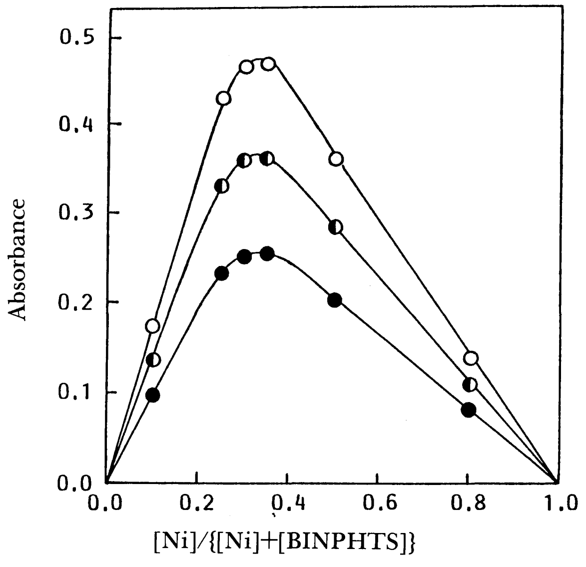

Fig. 5. Determination of composition of the BINPHTS-Ni complex by continuous variation method. [Ni(II)]+[BINPHTS]=2.0×10^{-5} M; pH, 7.3; standing time, 60 min; reference, reagent blank; wavelength/nm—○ 498; ◐ 472; ●538.

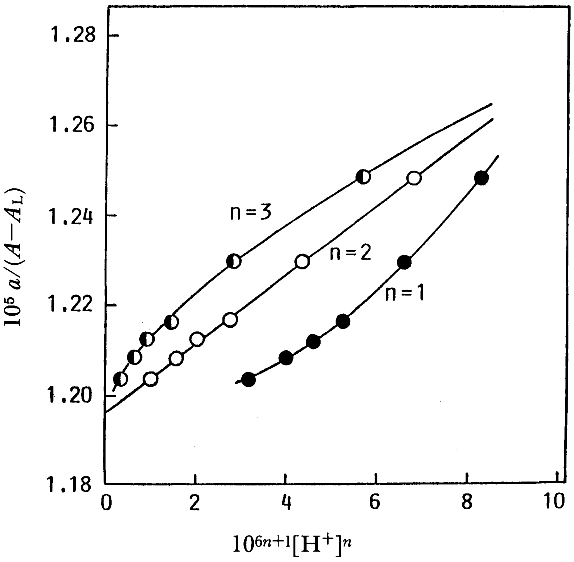

Fig. 6. Plots of $a/(A-A_L)$ vs. $[H^+]^n$. Ni(II) (=a), 1.7×10^{-6} M; BINPHTS (=b), 8.8×10^{-5} M; wavelength, 498 nm; ionic strength, 0.2 ($NaClO_4$); temperature, 25±0.1 °C.

Table 4. Equilibrium Constants of Complexation Reaction between Nickel(II) and Hydrazones and Overall Formation Constants of the Complexes[a)]

Complex	$\log K_{eq}$[b)]	$\log \beta_2$[b)]
NPHPTS complex	−2.36±0.03	20.60±0.09
NPHQTS complex	−1.59±0.04	21.49±0.11
NPHTTS complex	−4.03±0.04	17.27±0.10
BTNPHTS complex	−0.33±0.03	21.15±0.09
BINPHTS complex	−2.71±0.04	18.51±0.12

a) Temperature: 25±0.1 °C, Ionic strength: 0.2 ($NaClO_4$). b) Indicates the average value of three determinations.

where L denotes the undissociable part of BINPHTS and K_{eq} the equilibrium constant of the complexation reaction. If the initial concentration of the ligand, b, is much higher than that of the metal ion, a, Eq. 3 can be approximated as

$$K_{eq} = x[H^+]^n/(a-x)b^n, \qquad (4)$$

where x is the equilibrium concentration of the complex formed. As described above, since the system obeys Beer's law additively over the wavelength range of interest, Eq. 5 can be deduced

$$A = \varepsilon_L(b-nx) + \varepsilon_C x, \qquad (5)$$

where ε_L and ε_C are apparent molar absorptivities of the ligand and the complex at a specified wavelength, respectively, and A is the total absorbance of the solution. From Eqs. 4 and 5, Eq. 6 can finally be obtained:

$$a/(A - A_L) = [H^+]^n/(\varepsilon_C - n\varepsilon_L)K_{eq}b^n + 1/(\varepsilon_C - n\varepsilon_L), \qquad (6)$$

where A_L is the absorbance of the solution of the ligand alone. Eq. 6 means that at constant values of a and b there should be a linear relationship between the terms $a/(A-A_L)$ and $[H^+]^n$, from which the value of n can be estimated. Such a relation was experimentally obtained when assuming n is equal to 2, as shown in Fig. 6. This reveals the formation of a 1 : 2 (metal : ligand) complex, which is in accordance with the results by the continuous variation and the molar ratio methods stated already. Thus the complexation reaction of BINPHTS with nickel(II) may reasonably be expressed by

$$Ni^{2+} + 2\,H_2L^- \rightleftarrows Ni(HL)_2{}^{2-} + 2\,H^+, \qquad (2')$$

$$K_{eq} = [Ni(HL)_2{}^{2-}][H^+]^2/[Ni^{2+}][H_2L^-]^2. \qquad (3')$$

The value of K_{eq} obtained from Eq. 6 and the experimental data when assuming n=2 in Fig. 6 was $10^{-2.71}$.

The overall formation constant, β_2, of the complex defined by

$$Ni^{2+} + 2\,HL^{2-} \rightleftarrows Ni(HL)_2{}^{2-}, \qquad (7)$$

$$\beta_2 = [Ni(HL)_2{}^{2-}]/[Ni^{2+}][HL^{2-}]^2, \qquad (8)$$

can be calculated from the values of K_{eq} and the proton dissociation constant of the ligand as follows:

$$\beta_2 = K_{eq}/K_{a5}{}^2 = 10^{-2.71}/(10^{-10.61})^2 = 10^{18.51}.$$

The equilibrium constants of the complexation reactions between the other hydrazones and nickel(II) and the overall formation constants of the complexes were also determined in the same way, the results being summarized in Table 4.

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