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Synthesis and Chromogenic Properties of Disulfonated (1-Naphthyl)(2-quinolyl)methanone 5-Nitro-2-pyridylhydrazone and Its Application to the Spectrophotometric and Analogue-Derivative Spectrophotometric Determination of Trace Amounts of Zinc[†]

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A water-soluble hydrazone, disulfonated (1-naphthyl)(2-quinolyl)methanone 5-nitro-2-pyridylhydrazone (NQNPH), in which one nitro group and two sulfo groups are introduced for the purpose of increasing sensitivity and solubility in water, has been synthesized and its chromogenic property and reactivity with metal ions investigated. NQNPH reacts with various metal ions including zinc(II) to form 1:2 (metal:ligand) colored stable complexes with high molar absorptivities. On this basis, sensitive and practical spectrophotometric and analogue-derivative spectrophotometric methods for the determination of trace amounts of zinc with NQNPH have been proposed. The zinc(II)–NQNPH complex is formed quantitatively in the pH range 6.9—9.6 and its absorption spectrum shows an absorption maximum at 516 nm. Beer's law is obeyed over the range 0.07—1.5 ppm of zinc and the apparent molar absorptivity of the complex is 4.33×10^4 dm^3 mol^{-1} cm^{-1} at 516 nm. The proposed method was applied to the determination of zinc in Kuroko and water samples, with satisfactory results. In addition, the acid dissociation constants of NQNPH and the overall formation constant of its zinc complex were also determined spectrophotometrically.

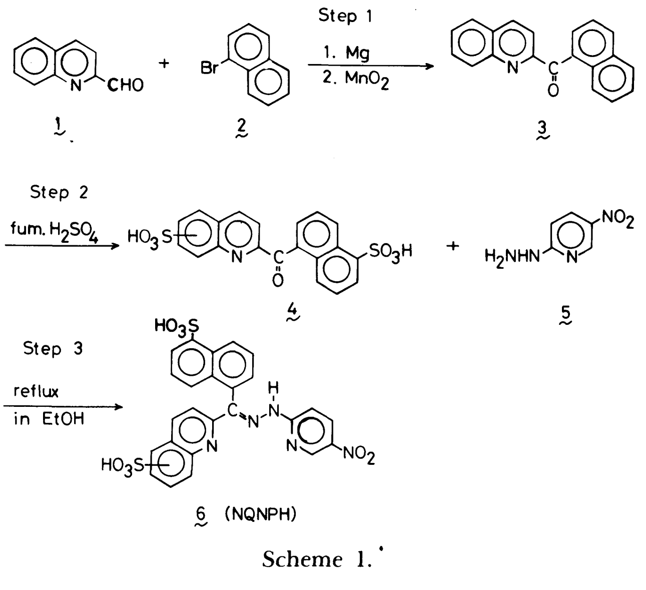
In the course of a series of studies on the synthesis of hydrazone compounds as highly sensitive and selective reagents and their analytical application, recently we synthesized five kinds of water-soluble hydrazones derived from 2-(3-sulfobenzoyl)pyridine[1,2] and reported that one of them, (2-pyridyl)(3-sulfophenyl)methanone 2-pyrimidylhydrazone, is a very useful reagent for the determination of iron at sub-ppm levels by spectrophotometry[1] and flow injection analysis.[3] Furthermore, we also synthesized a series of water-soluble hydrazones, in which various substituents were introduced to the 5-position of the pyridine ring in the hydrazine moiety of (2-pyridyl)(3-sulfophenyl)methanone 2-pyridylhydrazone synthesized by Going et al.,[4] and found that, of those hydrazones, (2-pyridyl)(3-sulfophenyl)methanone 5-nitro-2-pyridylhydrazone having an electron-withdrawing nitro group is a very favorable spectrophotometric reagent in both sensitivity and selectivity for the determination of metals, especially for that of cobalt.[5]

In the work presented here disulfonated (1-naphthyl)-(2-quinolyl)methanone 5-nitro-2-pyridylhydrazone (NQNPH) which has one nitro group and two sulfo groups in its molecule was synthesized from a viewpoint of the development of the hydrazone reagent which is more soluble in water as well as sensitive to metal ions and properties of the hydrazone and its metal complexes were investigated in detail. On the basis of the results, a spectrophotometric method for the determination of trace amounts of zinc has been developed and applied successfully to the determination of zinc in Kuroko, a kind of mineral containing copper, lead and zinc as major constituents, and water samples, as examples. Further, the proposed method could be made more sensitive by the introduction of an analogue-derivative spectrophotometric technique.

Experimental

Synthesis of NQNPH. NQNPH was synthesized according to Scheme 1 as follows.

Synthesis of 2-(1-Naphthoyl)quinoline (3): Manganese dioxide (activated under vacuum at 110 °C for 2 days, 67.6 g, 0.773 mol) was added to the chloroform solution (300 cm^3) of (1-naphthyl)(2-quinolyl)methanol (9.6 g, 0.034 mol) which was obtained by the Grignard method[6] using 1-bromonaphthalene (**2**) (16.6 g, 0.773 mol), magnesium turnings (3.86 g, 0.159 mol) and 2-quinolinecarbaldehyde (**1**) (10.5 g, 0.067 mol).[7] The reaction mixture was refluxed for 5 h. After cooling the mixture was filtered through a Celite pad and concentrated to yield a yellow solid, which was



Scheme 1.

[†] Presented in part at the 48th Symposium on Analytical Chemistry, Toba, June, 1987.

recrystallized from benzene to give a pure pale yellow 2-(1-naphthoyl)quinoline (**3**) [9.21 g (92.8%)]. Mp: 139 °C. Found: C, 84.76; H, 4.81; N, 5.39%. Calcd. for $C_{20}H_{13}ON$: C, 84.78; H, 4.63; N, 5.65%. IR (KBr): $\nu_{C=O}$ 1650 cm^{-1}.

Synthesis of Disulfonated 2-(1-Naphthoyl)quinoline (4): 2-(1-Naphthoyl)quinoline (**3**) (6 g, 0.021 mol) and fuming sulfuric acid (25% SO_3, 30 cm^3) were placed in a round bottom flask with a tight stopper and the mixture was stirred at 90 °C for 138 h. Fuming sulfuric acid (20 cm^3) was added, the temperature was raised to 110 °C and the stirring was continued for additional 72 h. Furthermore fuming sulfuric acid (10 cm^3) was added. After the stirring was continued for additional 27 h, the reaction mixture was cooled and cautiously poured into ethanol (120 cm^3) under cooling. Addition of ethyl acetate (6 dm^3) with sufficient stirring caused the precipitate as a dark brown solid. The mixture was filtered, washed with acetone and dried overnight at 60 °C under reduced pressure to yield a dark brown solid (**4**) (13 g), which still contained water and sulfuric acid. This material was used in the next step without purification. IR (KBr): $\nu_{C=O}$ 1670 cm^{-1}, ν_{SO_2} 1240—1140, 1040—1020 cm^{-1}.

Synthesis of Disulfonated (1-Naphthyl)(2-quinolyl)-methanone 5-Nitro-2-pyridylhydrazone (NQNPH) (6): 5-Nitro-2-pyridylhydrazine (**5**) (2.09 g, 0.014 mol) in hot ehtanol (450 cm^3) was added to a hot ethanol solution (100 cm^3) of disulfonated 2-(1-naphthoyl)quinoline (**4**) (7 g) and the mixture was refluxed for 5 h. After cooling a dark brown solid was obtained by concentration of the mixture. This solid was purified in a column of silica gel by elution with 2-propanol–ethyl acetate–water (2+3+1, v/v). Appropriate fractions [R_f=0.42 in 2-propanol–ethyl acetate–water (2+3+2, v/v)] were collected and concentrated to afford an orange yellow solid. This purification was repeated for several times to give 3.5 g in total. Mp>350 °C, IR (KBr): $\nu_{C=O}$ 1670 cm^{-1} (disappeared), ν_{NO_2} 1540, 1340 cm^{-1}, ν_{SO_2} 1240—1180, 1040 cm^{-1}.

Reagents. All reagents used were of analytical-reagent grade unless stated otherwise. All solutions were prepared with distilled, deionized water.

NQNPH solution. A 1.25×10^{-3} M (1 M=1 mol dm^{-3}) aqueous solution was prepared using synthesized NQNPH. This solution was standardized by photometric titration with a standard copper(II) solution at pH 5.5 and at 530 nm.

Standard zinc(II) solution. A 1×10^{-2} M stock solution was prepared by dissolving metallic zinc (99.999% pure) in a sufficient volume of hydrochloric acid (1+1) to give an acidity of about 0.1 M in the final solution. Working solutions were prepared by dilution of this solution with water.

Buffer solutions. 1 M Chloroacetic acid–1 M sodium chloroacetate, 1 M acetic acid–1 M sodium acetate, 0.5 M tris(hydroxymethyl)aminomethane–0.5 M hydrochloric acid, 1 M aqueous ammonia–1 M ammonium chloride or 0.5 M boric acid–0.5 M sodium carbonate system was used according to the pH value required.

Apparatus. For measurements of the absorbance, the absorption spectrum and the derivative absorption spectrum, the same instruments as those stated in an earlier paper[5] were used. Infrared spectra were obtained on a JASCO A-3 IR spectrometer. Thin-layer chromatography (TLC) was carried out on 0.2-mm E. Merck 60F-254 precoated silica-gel plates. For column chromatography, E. Merck silica gel 60 (70—230 mesh) was used.

Procedures. Determination of Zinc by Ordinary Spectrophotometry: Place a sample or standard solution containing up to 30 μg of zinc(II) in a 25-cm^3 calibrated flask. Add 5 cm^3 of 0.5 M tris(hydroxymethyl)aminomethane–0.5 M hydrochloric acid buffer solution (pH 7.2), suitable masking agents if necessary and 2 cm^3 of 1.25×10^{-3} M NQNPH solution, and dilute to the mark with water. After allowing to stand for about 10 min, measure the absorbance of the resultant solution at 516 nm against a reagent blank prepared under the same conditions using 1-cm cells.

Determination of Zinc by Second-Derivative Spectrophotometry: When the zinc content of the solution prepared by the procedure described under ordinary spectrophotometry is too low to give a measureable absorbance, record the second-derivative spectrum from 600 to 400 nm against a reagent blank by using a combination of both first- and second-order differentiation circuits (No. 6 of Refs. 8 and 9) and a scan speed of 300 nm min^{-1} and measure the second-derivative absorbance (the vertical distance from a peak to a trough or that from the base line to a trough of the peak).

Dissolution and Pretreatment of Kuroko Samples: Decompose sample and prepare the sample solution according to JIS method:[10] To 10—40 mg of sample add 15 cm^3 each of concentrated nitric and hydrochloric acids and heat to decompose the sample. Add 2 cm^3 of sulfuric acid (1+1) and evaporate to dryness. After cooling to room temperature, dissolve the residue in about 50 cm^3 of hydrochloric acid (1+50), heat for a few minutes to dissolve the soluble salts, filter into a 200-cm^3 calibrated flask, wash with hot water, and dilute to the mark with water after cooling to room temperature. Use an appropriate aliquot of the resultant solution to the determination.

Results and Discussion

Identification of the Hydrazone. Identification of the product was carried out at two stages in the course of synthesis.

Disulfonated 2-(1-Naphthoyl)quinoline (4): A TLC test on the product obtained at step 2 revealed that the product consists of two position isomers of the sulfo group on quinoline ring [R_f=0.26 and 0.18 respectively in 2-propanol–ethyl acetate–water (2+3+2, v/v)]. The faster-migrating product was obtained mainly on a reaction mixture sulfonated for 23 h and decreased gradually with the addition of fuming sulfuric acid and the passage of time. On the other hand, the slower-migrating one increased gradually and became main finally. The faster- and slower-migrating products presumed to be 2-(5-sulfo-1-naphthoyl)-5-quinolinesulfonic acid and 2-(5-sulfo-1-naphthoyl)-8-quinolinesulfonic acid, respectively, because 5-sulfoquinoline migrated faster (R_f=0.45) than 8-sulfoquinoline (R_f=0.39) in 2-propanol–ethyl acetate–water (2+3+2, v/v). However, the position of sulfo group on quinoline ring could not be decided.

NQNPH (6): Neither of the elemental analysis, the determination of water content by Karl Fischer's method, the mass spectrum (FAB) and the NMR spectrum of the final product gave reliable results in spite of trials because the product is hygroscopic and has large molecular weight and two sulfo groups. However, the hydrolysis of this product with concentrated nitric acid at room temperature for two days gave the starting ketone, disulfonated 2-(1-naphthoyl)-quinoline (**4**). On the basis of the result, this product is presumed to be a target hydrazone.

The number of sulfo groups of NQNPH (**6**) was determined by the ion-pair extraction method with zephiramine as an ion-pair-forming reagent, that is, solutions of pH 7.8 containing a fixed amount of NQNPH and various amounts of zephiramine were shaken for 24 h with an equal volume of benzene to the aqueous phase and then the absorbances of the organic and aqueous phases were measured, in which the absorbance of the latter was measured after the addition of sufficient amounts of zinc(II) as a color-forming reagent. The results are shown in Fig. 1, from which the composition of the ion pair of NQNPH and zephiramine is found to be 1:2. This indicates that the number of sulfo groups of NQNPH is two.

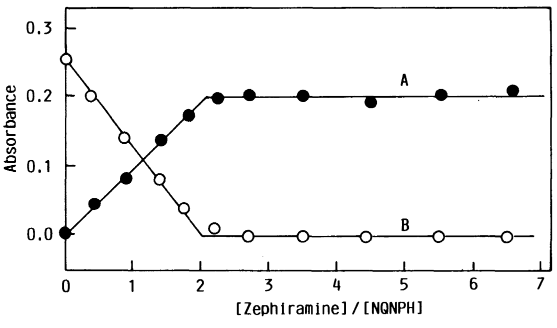


Fig. 1. Determination of the number of sulfo groups of NQNPH by the ion-pair extraction method. NQNPH, 7.2×10^{-5} M; pH 7.8; shaking time, 24 h. A, Benzene phase measured at 430 nm against benzene; B, water phase measured at 516 nm against water.

Properties and Characteristics of the Hydrazone. NQNPH is hygroscopic, but remains unchanged for more than one year when stored in a desiccator. It is very soluble in water as expected beforehand and also soluble in polar solvents such as ethanol, *N,N*-dimethylformamide, and dimethyl sulfoxide, but insoluble in less or nonpolar solvents. Its aqueous solution is very stable.

As is apparent from the structure, NQNPH is a tribasic acid as well as a triacidic base, having six dissociable hydrogens in acidic solutions above 1 M. However, in less acidic solutions, the de-protonations from the C=N nitrogen and the sulfo groups are complete. Hence NQNPH exists in solution in any of the following forms, depending on pH:

$$H_3L \overset{K_{a4}}{\rightleftharpoons} H_2L^- \overset{K_{a5}}{\rightleftharpoons} HL^{2-} \overset{K_{a6}}{\rightleftharpoons} L^{3-} \qquad (1)$$

where L denotes the undissociable part of the hydrazone and K_{a4}, K_{a5}, and K_{a6} are the acid dissociation constants.

The acid dissociation constants were determined spectrophotometrically at ionic strengths of 0.2 for K_{a5} and K_{a6} and 3.0 for K_{a4}, and at 25±0.1 °C. The values obtained for K_{a4}, K_{a5}, and K_{a6} were $10^{-0.80}$, $10^{-4.80}$, and $10^{-10.93}$, respectively. The K_{a4} and K_{a5} may be assigned to the de-protonation of the protonated pyridine-nitrogen and quinoline-nitrogen, respectively, whereas the K_{a6} corresponds to that of the secondary amino group. The contribution of the electron-withdrawing nitro group on the pyridine ring to the value of K_{a4} is found to be remarkable. A species distribution diagram of NQNPH prepared on the basis of these acid dissociation constants is shown in Fig. 2.

Table 1. Reactivity of NQNPH with Metal Ions

Metal ion	pH 4		pH 7		pH 10	
	λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{max}/nm	ε/M^{-1} cm^{-1}
Ag(I)	—	—	—	—	515	32800
Cd(II)	—	—	519	18700	519	47100
Co(II)	521	1000	521	37400	521	20300
Cr(III)	—	—	—	—	515	2700
Cr(VI)	—	—	—	—	525	5700
Cu(II)	530	33900	530	33900	530	28400
Fe(II)	—	—	513	41100	498	14200
Fe(III)	—	—	500	3100	—	—
Hg(II)	494	7800	485	8600	445	17700
Mn(II)	—	—	519	2600	519	44900
Ni(II)	524	2900	524	47100	524	42000
Pb(II)	—	—	525	15600	—	—
Pd(II)	592	22000	592	22000	592	21100
Ti(IV)	—	—	—	—	—	—
V(IV)	—	—	—	—	510	4000
V(V)	—	—	—	—	490	1500
Zn(II)	—	—	516	43300	516	41400

Standing time: 30 min.

Reactivity of the Hydrazone. The reactivity of NQNPH with various metal ions at pH 4, 7, and 10 were investigated, the results being summarized in Table 1. NQNPH is found to react with cadmium(II), cobalt(II), copper(II), iron(II), nickel(II), palladium(II), zinc(II), etc. to form colored stable complexes with high molar absorptivities. So the complexation reaction of NQNPH with these metal ions was investigated somewhat in detail. Absorption spectra of the complexes are shown in Fig. 3. Experimental results concerning the effect of pH on the complexations are indicated in Fig. 4. Absorption maxima of the complexes and optimum pH ranges for the complexations obtained from these results are summarized in Table 2 along with apparent molar absorptivities and compositions of the complexes determined by both the continuous variation and the molar ratio methods. These results suggest that NQNPH may be useful for the sensitive determination of these metals. Hence conditions for the complexation with zinc(II) and spectrophotometric determination of zinc at sub-ppm levels utilizing this complexation were investigated in detail at the outset in the subsequent work.

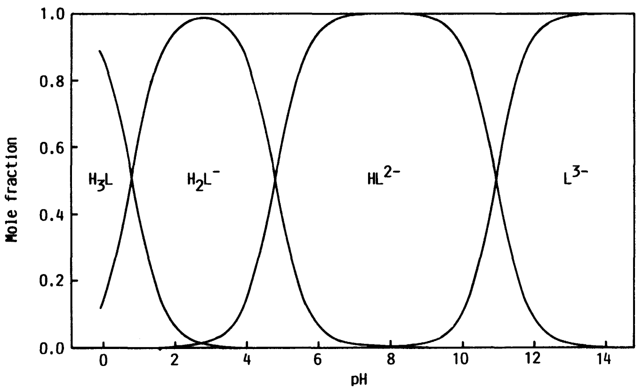


Fig. 2. Species distribution diagram of NQNPH.

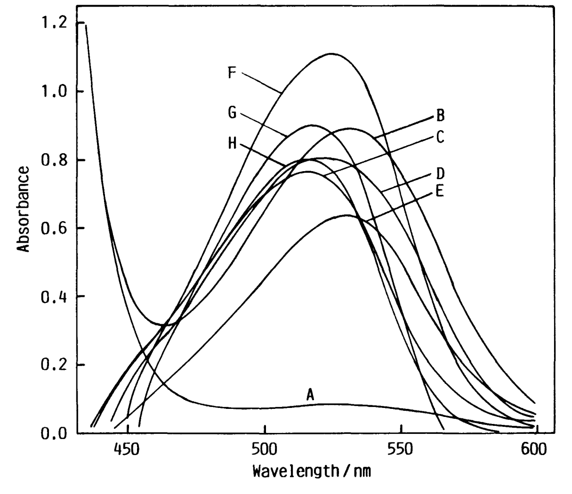


Fig. 3. Absorption spectra of (A, B) NQNPH and (C–H) its metal complexes. NQNPH, 2.50×10^{-4} M; metal ions, 1.87×10^{-5} M; pH, 7.5 (except for 9.0 for B and G); standing time, 30 min (except for 12 h for F); reference—A and B, water; C—H, reagent blank. A and B, NQNPH (reagent blank) at pH 7.5 and 9.0, respectively; C, iron(II); D, cobalt(II); E, copper(II); F, nickel(II); G, cadmium(II); H, zinc(II) complex.

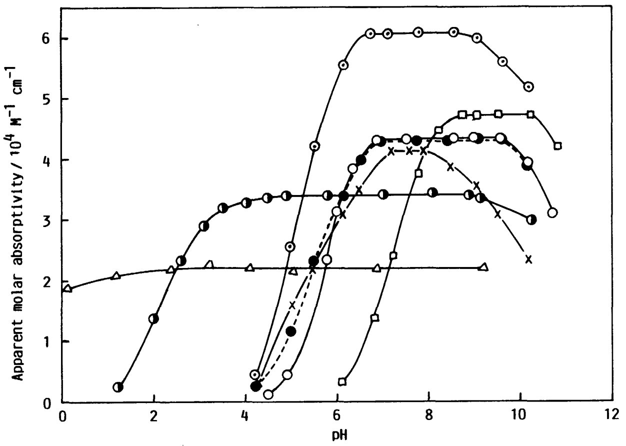


Fig. 4. Effect of pH on the complexation. Reference, reagent blank.

	Complex	Standing time	Wavelength	[NQNPH]/[Metal]
—□—	Cd(II) complex	30 min	519 nm	17.3
—●—	Co(II) complex	1 h	521 nm	17.9
—◑—	Cu(II) complex	30 min	530 nm	19.8
—×—	Fe(II) complex	30 min	513 nm	17.0
—⊙—	Ni(II) complex	12 h	524 nm	18.1
—△—	Pd(II) complex	30 min	592 nm	4.7
—○—	Zn(II) complex	30 min	516 nm	9.5

Table 2. Properties of Metal-NQNPH Complexes and Optimum pH Ranges for the Complexations

Complex	Absorption maximum/nm	Apparent molar absorptivity/M^{-1} cm^{-1}	Composition (metal: ligand)	Optimum pH range
Cd(II)-NQNPH	519	47100	1:2	8.7—10.2
Co(II)-NQNPH	521	43000	1:2	7.0— 9.6
Cu(II)-NQNPH	530	33900	1:2	4.9— 8.9
Fe(II) -NQNPH	513	41100	1:2	7.2— 7.9
Ni(II)-NQNPH	524	60600	1:2	6.7— 8.6
Pd(II)-NQNPH	592	22000	1:2	2.8— 9.2
Zn(II)-NQNPH	516	43300	1:2	6.9— 9.6

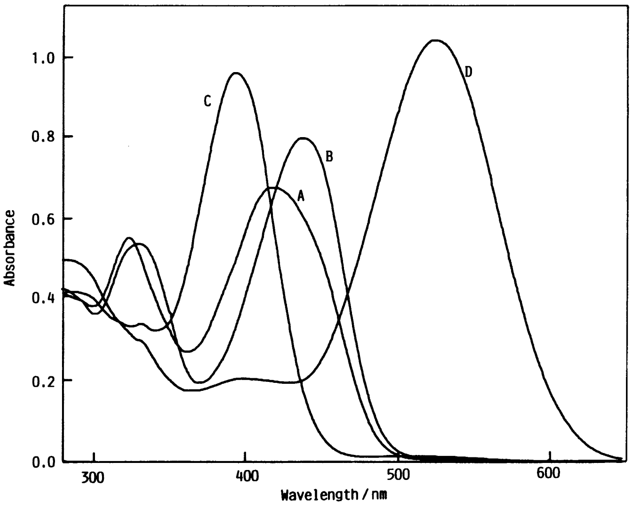


Fig. 5. Absorption spectra of NQNPH at pH (A), 0; (B), 3; (C), 8; and (D), 13.7. NQNPH, 4.1×10^{-5} M; reference, water.

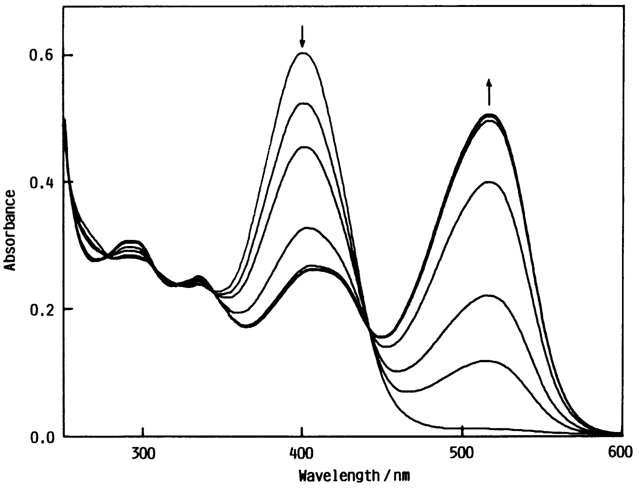


Fig. 6. Absorption spectra of the zinc(II)-NQNPH system. NQNPH, 2.3×10^{-5} M; pH, 7.0; reference, water. Arrows indicate spectral trends observed when changing the NQNPH to zinc(II) ratio from 1:0 to 1:3.2.

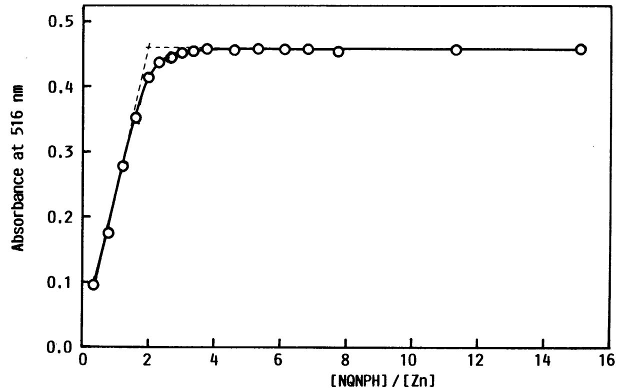


Fig. 7. Effect of NQNPH concentration. Zn(II), 693 ppb (1.1×10^{-5} M); pH, 7.2; reference, reagent blank.

Studies of the Zinc(II)-NQNPH System. Absorption Spectra: Figure 5 shows absorption spectra of NQNPH at pH 0, 3, 8, and 13.7, in which spectra A, B, C, and D correspond to H_3L, H_2L^-, HL^{2-}, and L^{3-}, respectively, taking Fig. 2 into consideration. Figure 6 exhibits the spectral change in the complexation between zinc(II) and NQNPH at pH 7.0, from which it is found that the absorption maximum shifts from 400 to 516 nm on complexation. In addition, the absorption due to NQNPH itself is very small at the latter wavelength, which is favorable for the zinc determination.

Effect of pH: As shown in Fig. 4 and Table 2, a constant and maximum absorbance is obtained over the pH range 6.9—9.6. The use of tris(hydroxymethyl)aminomethane-hydrochloric acid buffer (pH 7.2) is recommended because the phosphate buffer interferes with the zinc determination.

Effect of NQNPH Concentration: The effect of the NQNPH concentration on the complexation was investigated. The results was shown in Fig. 7, from which it is found that a 4-fold molar excess of NQNPH is necessary for the complete complexation and an excess of NQNPH does not interfere. In addition, this result suggests the formation of a 1:2 (metal: ligand) complex.

Stability of the Complex: Under the recommended conditions, zinc(II) reacts almost instantaneously with NQNPH to form a complex at room temperature. The complex formed is very stable, the absorbance remaining constant even after 20 h.

Calibration Graph, Sensitivity and Precision: A linear calibration graph passing through the origin

Table 3. Tolerance Limits for Other Metal Ions in the Determination of 15.9 µg of Zinc

Tolerance limit		No masking agent added	Masking agent added
Above	1000 µg	Mg(II), Cr(VI)	Ag(I),[a] Hg(II)[a]
	500 µg	Ca(II), V(V)	
	200 µg	Al(III)	Fe(III),[b] Cu(II)[c]
	100 µg	Cr(III)	
	50 µg	Ti(IV)	V(IV),[d] Mn(II),[b] Pd(II),[c] Pd(II)[a]
	20 µg		Co(II),[e] Ni(II),[f] Cd(II)[a]
	10 µg	Mn(II), Ag(I), Hg(II)	V(IV),[b] Co(II)[f]
	5 µg	V(IV)	
	2 µg	Pd(II), Pb(II)	
	1 µg	Fe(III), Cd(II)	
Below	1 µg	Fe(II), Co(II), Ni(II), Cu(II)	
Above	100 mg	Br^-, Cl^-, I^-, ClO_4^-, NO_3^-, SCN^-, SO_4^{2-}, Acetate	
	50 mg	F^-, $S_2O_3^{2-}$	
	20 mg	Tartrate	
	10 mg	PO_4^{3-}	
	1 mg	Oxalate	
Below	1 mg	Citrate, EDTA	

a) 3 ml of 50% potassium iodide solution was added. b) 4 ml of 4% sodium fluoride solution was added. c) 5 ml of 10% thiourea solution was added. d) 1 ml of 2.5% sodium tartrate solution was added. e) 1 ml of 10% sodium perborate solution and 1.5 ml of sodium acetate solution were added. f) 0.7 ml of 5×10^{-3} M *N*-(dithiocarboxy)sarcosine solution was added.

was obtained by the recommended procedure. The equation for the line obtained by a least-squares treatment was

$$\mathrm{Zn(ppm)} = 1.51A \tag{2}$$

where A is the absorbance. The optimum range for the zinc determination is 0.1—1.5 ppm in the solution measured. The apparent molar absorptivity calculated from Eq. 2 is 4.33×10^4 M^{-1} cm^{-1}.

Ten standard solutions containing 638 ppb of zinc(II) were analyzed by the recommended procedure. The results gave a relative standard deviation of 0.29%.

Effect of Diverse Ions: The effect of diverse ions on the determination of zinc were studied by adding a known amount of the ion in question to a solution containing 15.9 µg of zinc(II) and following the recommended procedure. An error of ±3% in the absorbance reading was considered tolerable. The results are summarized in Table 3. Many ions including cadmium(II), cobalt(II), copper(II), iron(II and III), lead(II), manganese(II), mercury(II), nickel(II), palladium(II), silver(I), vanadium(IV), oxalate, citrate, and EDTA interfered with the determination when no masking agent is added, but the other ions scarcely or did not interfere. Of these interfering ions, iron(III), manganese(II) and a small amount of vanadium(IV) can be masked with sodium fluoride, cadmium(II), lead(II), mercury(II), and silver(I) with thiourea, nickel(II) and a small amount of cobalt(II) with *N*-(dithiocarboxy)sarcosine, vanadium(IV) with sodium tartrate, and cobalt(II) with sodium perborate and ammonium acetate.

In addition, the removal of interferences caused by several ions which coexist at the same time was also examined. For example, a calibration graph prepared in the presence of each 30 µg of copper(II), iron(III), and lead(II) and by using thiourea, sodium fluoride, and potassium iodide as masking agents for these ions was in good agreement with that prepared in the absence of these interferents within an error of 3%. This suggests that the selectivity in the proposed method can be improved enough to apply it to the analysis of practical samples.

Use of Analogue-Derivative Spectrophotometry to Improve Sensitivity. Derivative spectrophotometry using the analogue differentiation circuit enhances the sensitivity of ordinary spectrophotometry,[8,9] so second-derivative spectrophotometry was applied here to the determination of zinc.

Selection of Conditions for Measurements: In second-derivative spectrophotometry both the time constant of the analogue differentiation circuit and the scan speed of the spectrophotometer considerably affect the sensitivity and selectivity, so both need to be optimized to give a well resolved large peak. Figure 8 shows the second-derivative spectra of the zinc(II)–NQNPH complex measured with various scan speeds and circuit numbers. A combination of circuit No. 6 (which has the largest time constant, 2.0 s, the time constant increasing with circuit number in our apparatus) and a scan speed of 300 nm min^{-1} was found to give the best sensitivity and resolution (i.e., selectivity) for the zinc determination.

Calibration Graph: The calibration graph prepared under the recommended conditions by plotting the second-derivative absorbance versus the zinc concentration is linear and passes through the origin

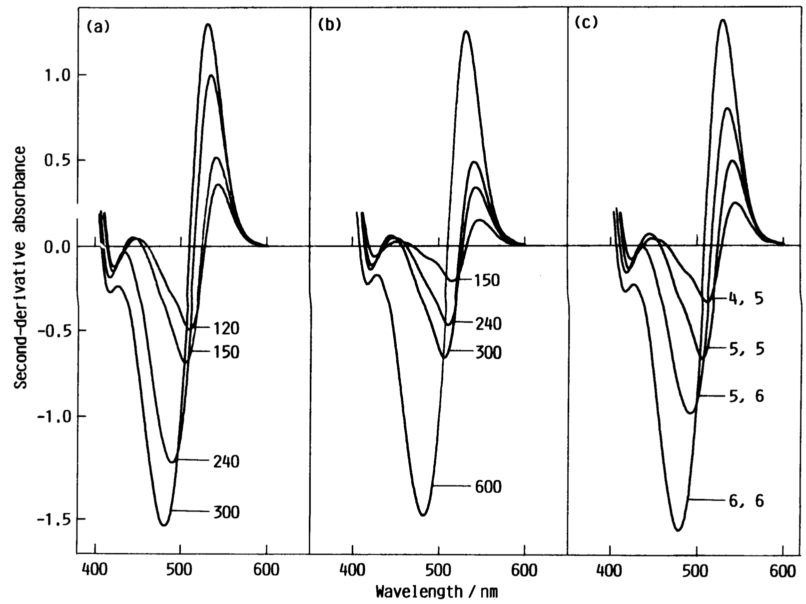


Fig. 8. Influence of (a), (b) scan speed [with circuits all No. 6 in (a) and all No. 5 in (b)] and (c) circuit number (with scan speed 300 nm min^{-1}) on second-derivative spectra of zinc(II)-NQNPH complex solution. Zn(II), 319 ppb (4.9×10^{-6} M); NQNPH, 1.0×10^{-4} M; pH, 7.2; reference, reagent blank. Numerical values indicate scan speeds in (a) and (b) and first- and second-differentiation circuits in (c).

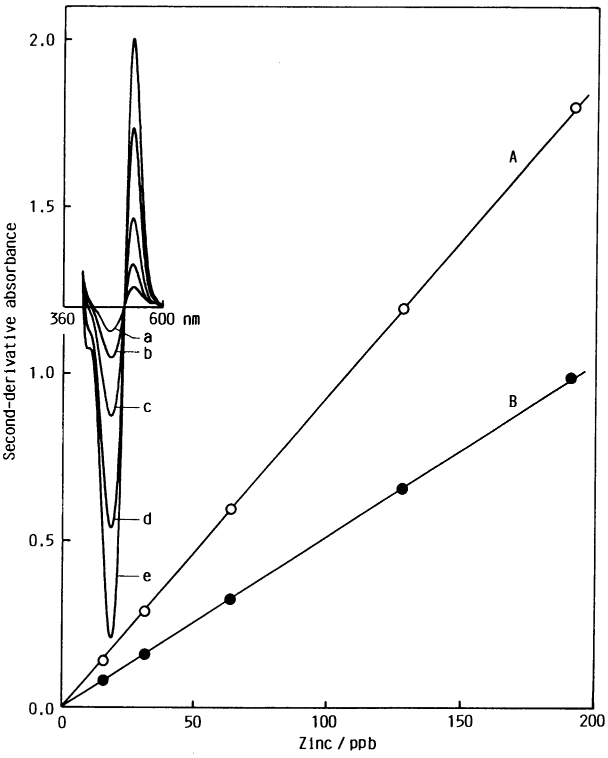


Fig. 9. Calibration graph for zinc in second-derivative spectrophotometry. A, Peak-to-trough values plotted; B, base line-to-trough values plotted. Circuits, all No. 6; scan speed, 300 nm min^{-1}; slit width, 1 nm; recorder sensitivity, ×1; reference, reagent blank; NQNPH, 1.0×10^{-4} M. Zn(II)—a, 15.9; b, 31.9; c, 63.8; d, 128; and e, 191 ppb.

when either the peak to trough values or the base line to trough values are plotted, as shown in Fig. 9. The equation for the lines were

$$\text{Zn(ppb)} = 107D \qquad (3)$$

$$\text{Zn(ppb)} = 194D \qquad (4)$$

where D is the second-derivative absorbance converted into absorbance. It will be seen that zinc at levels as low as 16 ppb can easily be determined in this way.

Practical Applications. To confirm the usefulness of the proposed method, zinc in Kuroko and water samples was determined. The results are summarized in Table 4 together with those by atomic absorption spectrometry carried out for comparison. Both sets of results are in good agreement.

Composition of the Complex. The molar composition of the zinc(II)-NQNPH complex formed under the conditions for the determination of zinc was examined by both the molar ratio and the continuous variation methods. Both method indicated the formation of a 1:2 (metal:ligand) complex. As an example, the result by the continuous variation method is shown in Fig. 10.

Formation Constant of the Complex. The formation constant of the zinc(II)-NQNPH complex formed under the recommended conditions was determined spectrophotometrically by the equilibrium shift method.[11]

Table 4. Determination of Zinc in Kuroko and Water Samples

Sample	Zinc content		
	Proposed method		Atomic absorption method[a]
	Individual values	Average	
Kuroko A	19.4% 18.8%	19.1%	19.0%
Kuroko B	9.19% 8.90%	9.05%	9.07%
Tap water	34 ppb 34 ppb 33 ppb	34 ppb	35 ppb[b]
Hirose river water	18 ppb 19 ppb 19 ppb	19 ppb	20 ppb[b]

a) By JIS K-0102 (1981) p. 155. b) Before the determination samples were concentrated by evaporation to 1/20 of the initial volume.

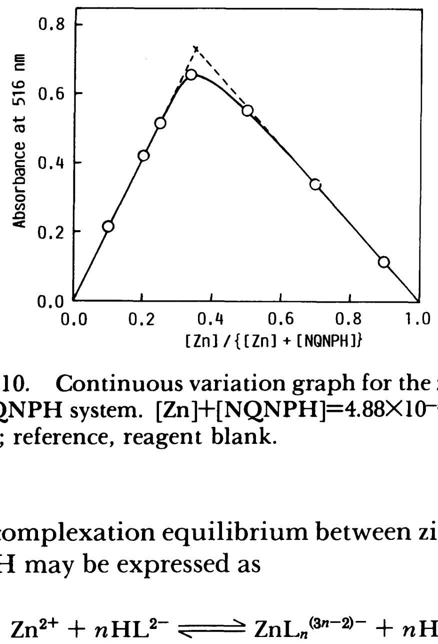


Fig. 10. Continuous variation graph for the zinc(II)–NQNPH system. [Zn]+[NQNPH]=4.88×10^{-5} M; pH, 7.2; reference, reagent blank.

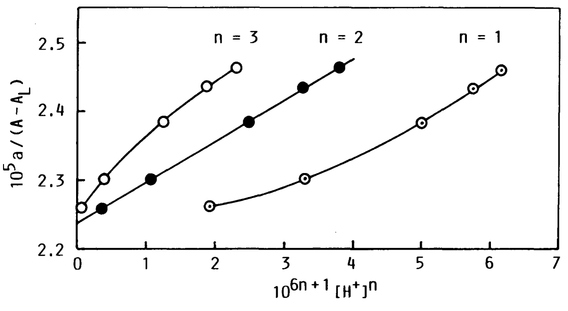


Fig. 11. Plots of $a/(A-A_L)$ versus $[H^+]^n$. Zn(II) (=a), 9.75×10^{-6} M; NQNPH (=b), 3.39×10^{-4} M; wavelength, 516 nm; ionic strength, 0.2 ($NaClO_4$); temperature, 25±0.1 °C.

The complexation equilibrium between zinc(II) and NQNPH may be expressed as

$$Zn^{2+} + nHL^{2-} \rightleftharpoons ZnL_n^{(3n-2)-} + nH^+ \qquad (5)$$

$$K_{eq} = [ZnL_n^{(3n-2)-}][H^+]^n/[Zn^{2+}][HL^{2-}]^n \qquad (6)$$

where K_{eq} denotes 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. 6 can be approximated as

$$K_{eq} = x[H^+]^n/(a-x)b^n \qquad (7)$$

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

$$A = \varepsilon_L(b-nx) + \varepsilon_C x \qquad (8)$$

where ε_L and ε_C are molar absorptivities of the ligand and the complex at a specified wavelength, respectively, and A is the total absorbance of the solution. From Eqs. 7 and 8, Eq. 9 can finally be obtained:

$$a/(A-A_L) = [H^+]^n/(\varepsilon_C - n\varepsilon_L)K_{eq}b^n + 1/(\varepsilon_C - n\varepsilon_L) \qquad (9)$$

where A_L is the absorbance of the solution of the ligand alone. Equation 9 implies 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. 11. This reveals the formation of a 1:2 (metal:ligand) complex, which is in accordance with the result by the continuous variation method indicated above. Thus the complexation reaction of zinc(II) with NQNPH may reasonably be expressed as

$$Zn^{2+} + 2HL^{2-} \rightleftharpoons ZnL_2^{4-} + 2H^+ \qquad (5')$$

$$K_{eq} = [ZnL_2^{4-}][H^+]^2/[Zn^{2+}][HL^{2-}]^2 \qquad (6')$$

The value of K_{eq} obtained from Eq. 9 and the experimental data when assuming $n=2$ in Fig. 11 was $10^{-4.49}$.

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

$$Zn^{2+} + 2L^{3-} \rightleftharpoons ZnL_2^{4-} \tag{10}$$

$$\beta_2 = [ZnL_2^{4-}]/[Zn^{2+}][L^{3-}]^2 \tag{11}$$

can be calculated from the values of K_{eq} and the acid dissociation constant of the ligand, K_{a6}, as follows:

$$\beta_2 = K_{eq}/K_{a6}^2 = 10^{-4.49}/(10^{-10.93})^2 = 10^{17.37}$$

Conclusion

A water-soluble hydrazone, NQNPH, was synthesized and its chromogenic properties and reactivity with metal ions were investigated. This hydrazone, the synthesis of which was somewhat complicated, was very soluble in water as expected beforehand and reacted with transition metal ions to give complexes with high molar absorptivities as well as water-soluble hydrazones reported earlier by us.[1,2,5] On the basis of results of fundamental experiments, spectrophotometric and analogue-derivative spectrophotometric methods for the determination of trace amounts of zinc have been proposed and applied successfully to the analysis of mineral and water samples. The proposed methods offer the advantages of simplicity, rapidity, reasonable selectivity and high sensitivity. Very high sensitivity was attained on employing second-derivative spectrophotometry. In addition, the acid dissociation constants of NQNPH and the formation constant of the zinc(II)–NQNPH complex were determined spectrophotometrically.

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