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Synthesis and Chromogenic Properties of Some Phthalazinylhydrazones and Extractive Spectrophotometric and Analogue-Derivative Spectrophotometric Determination of Trace Amounts of Nickel with Di-2-pyridylmethanone 1-Phthalazinylhydrazone

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Four kinds of 1-phthalazinylhydrazones have been synthesized and their chromogenic properties and reactivities with metal ions investigated. Of the synthesized hydrazones, di-2-pyridylmethanone 1-phthalazinylhydrazone (DPPhH) proved to be the best chromogenic reagent for nickel. It reacts with nickel(II) at pH above 2.5 to form a 1:2 (nickel–ligand) complex extractable into various organic solvents. The extracted species into benzene has an absorption maximum at 500 nm and gives a maximum and constant absorbance in the pH range 4.3—10.7. Beer's law is obeyed over the range 0.1—1.0 μg cm^{-3} of nickel. The molar absorptivity (ε) and the sensitivity for an absorbance of 0.001 are 5.4×10^4 dm^3 mol^{-1} cm^{-1} and 1.08 ng cm^{-2} at 500 nm, respectively. A sensitive and selective extraction-spectrophotometric method for the determination of nickel at μg cm^{-3} levels is proposed and has been applied successfully to the analysis of iron and steel samples. The proposed method can be made more sensitive by the introduction of an analogue-derivative spectrophotometric technique.

Since Lions et al.[1,2] first reported the preparation of hydrazones derived from 2-pyridylhydrazine and the properties of their metal complexes, a lot of nitrogen-containing heterocyclic hydrazones[3-6] have been synthesized and proposed as analytical reagents. On the other hand, we have prepared, over the period of more than 10 years, a series of hydrazones derived mainly from 2-benzothiazolylhydrazine[7-10] and proposed them as sensitive and useful reagents for metals. As for the phthalazinylhydrazone, however, only a few compounds[11,12] were prepared to date, since furfural 1-phthalazinylhydrazone and its analogue[13] were first synthesized and proposed as sensitive chromogenic reagents by us.

In the work presented here, 4 new hydrazones derived from 1-phthalazinylhydrazine, 2-pyridinecarbaldehyde 1-phthalazinylhydrazone (PAPhH), 1-(2-pyridyl)ethanone 1-phthalazinylhydrazone (MPPhH), phenyl(2-pyridyl)methanone 1-phthalazinylhydrazone (PPPhH), and di-2-pyridylmethanone 1-phthalazinylhydrazone (DPPhH) were synthesized and their chromogenic properties and reactivities with metal ions investigated and compared, as part of our continuing studies on the analytical application of hydrazones. Of the synthesized hydrazones, DPPhH was superior to the others as a spectrophotometric reagent for nickel(II) in terms of both sensitivity and selectivity. A sensitive and practical extraction-spectrophotometric method for the determination of trace amounts of nickel with DPPhH has been developed and successfully applied to the analysis of iron and steel samples. Further sensitization of the method by employing an analogue-derivative technique was feasible.

Experimental

Synthesis of Hydrazones. In 40 cm^3 of 5% hydrochloric acid dissolve 0.01 mol of 1-phthalazinylhydrazine, then add 20 cm^3 of ethanol solution containing 0.01 mol of the corresponding aldehyde or ketone. Heat the solution under reflux for 3 h. After cooling to room temperature, neutralize the solution with dilute aqueous ammonia. Filter off the resultant crystalline product with suction, recrystallize twice from ethanol and dry in vacuo.

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

Hydrazone solutions, 2.5×10^{-3} M (1 M=1 mol dm^{-3}). Prepared by dissolving the required mass of each synthesized hydrazone in ethanol. These solutions were stable for at least several months when stored in an amber bottle.

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.

Buffer solutions. Buffers consisting of 1 M chloroacetic acid–1 M sodium chloroacetate, 1 M acetic acid–1 M sodium acetate, M/15 potassium dihydrogenphosphate–M/15 disodium hydrogenphosphate, (0.2 M boric acid+0.05 M sodium chloride)–0.05 M sodium borate, and 1 M aqueous ammonia–1 M ammonium chloride systems were used according to the pH values required.

Apparatus. For measurements of the absorbance and the absorption spectrum, a Hitachi 139 and a Hitachi 200-10 spectrophotometer, respectively, were used. To obtain the derivative spectrum, a modified Hitachi 200-0576 derivative unit composed of two analogue differentiation circuits (each having six different time constants from 0.07 to 2.0 s) was connected in series between the output of a Hitachi 556 dual-wavelength spectrophotometer and the input of a Hitachi 057 X-Y recorder, the former being used as an ordinary double-beam spectrophotometer. The details of this apparatus and the principle and characteristics of analogue-derivative spectrophotometry have already been described.[14,15]

Procedures. Ordinary Spectrophotometry: Place a sample or standard solution containing up to 10 μg of nickel(II) in a 50-cm³ separating funnel and add suitable masking agents if necessary, 2 cm³ of 2.5×10⁻³ M DPPhH solution, followed by 2 cm³ of 1 M acetate buffer (pH 5.0) and dilute to approximately 20 cm³ with water. Extract the nickel complex into 10 cm³ of benzene by shaking mechanically for a few minutes. Allow the phases to separate and transfer the organic phase into a flask containing about 1 g of anhydrous sodium sulfate in order to dehydrate it. Measure the absorbance of the extract at 500 nm against a reagent blank prepared under the same conditions using 1-cm cells.

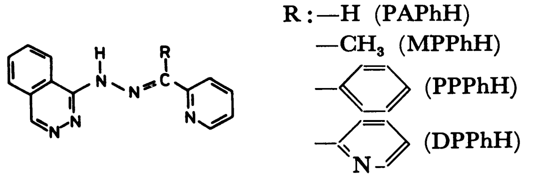
Second-Derivative Spectrophotometry: When the nickel content of the extract prepared by the procedure described above is too low to give a measurable absorbance, record the second-derivative spectrum from 550 to 380 nm against a reagent blank by using a combination of both first- and second-order differentiation circuits of No. 6 and a scan speed of 150 nm min⁻¹ and measure the second-derivative value (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 Iron and Steel Samples: Prepare 100 cm³ of the sample solution by decomposing about 0.1 g of the sample with aqua regia and perchloric acid and then removing iron by extraction with 4-methyl-2-pentanone, by the same way as described earlier.[13] Use 2 cm³ or other appropriate aliquot of the resultant solution for the determination.

Results and Discussion

Identification of the Hydrazones. The infrared spectra of the synthesized hydrazones, PAPhH, MPPhH, PPPhH, and DPPhH, were measured with potassium bromide tablets in order to confirm their structures. The spectra had absorption peaks assigned to the stretching vibration of an azomethine bond (-N=C<) around 1600 cm⁻¹.[16] On the basis of these results and those of the elemental analysis shown in Table 1, the synthesized hydrazones are presumed to have the structures shown in Table 1.

Table 1. Structures and Physical Properties of Hydrazones



	$Mp(\theta_m/°C)$	$\nu_{C=N}/cm^{-1}$	Elemental analysis/%[a]		
			C	H	N
PAPhH	181	1610	67.2 (67.5)	4.3 (4.5)	28.0 (28.1)
MPPhH	191	1590	68.2 (68.4)	5.0 (5.0)	26.6 (26.6)
PPPhH	176	1585	73.7 (73.8)	4.6 (4.7)	21.0 (21.5)
DPPhH	235	1600	69.9 (69.9)	4.3 (4.3)	25.8 (25.8)

a) Results in parentheses indicate calculated values.

Properties and Characteristics of the Hydrazones. PAPhH, MPPhH, PPPhH, and DPPhH are insoluble in water but soluble in organic solvents such as benzene, chloroform, and 4-methyl-2-pentanone.

As is evident from the structures of these hydrazones, at least 4 species, H_3L^{2+}, H_2L^+, HL, and L^-, are involved in their acid dissociation equilibria, depending on the pH:

$$H_3L^{2+} \overset{K_{a3}}{\rightleftharpoons} H_2L^+ \overset{K_{a2}}{\rightleftharpoons} HL \overset{K_{a1}}{\rightleftharpoons} L^-$$

Where L denotes the undissociable part of the hydrazone and K_{a1}, K_{a2}, and K_{a3} are the acid dissociation constants. The pK_a values were determined by extraporating the linear ethanol concentration (10—40%) versus apparent pK_a plot to the intercept. The apparent pK_a values were determined spectrophoto-

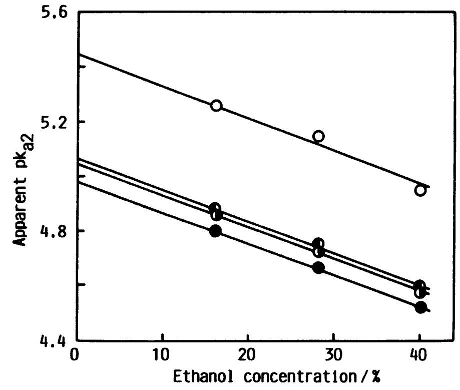


Fig. 1. Plots of apparent pK_{a2} vs. ethanol concentration. Hydrazone: 2.5×10⁻⁴ M, ionic strength: 0.2. temperature: 25±0.1 °C. —○—: MPPhH, —◐—: PPPhH, —◑—: DPPhH, —●—: PAPhH.

Table 2. Acid Dissociation Constants of the Hydrazones. Ionic Strength = 0.2; and Temperature = 25±0.1 °C

Hydrazone	pK_{a_1}[a] (Imino group)	pK_{a_2} (Pyridine nitrogen)	pK_{a_3} (Phthalazino nitrogen)
MPPhH	14.6_6	5.4_4	2.4_9
PAPhH	14.6_0	4.9_8	2.5_4
PPPhH	14.6_1	5.0_6	2.4_1
DPPhH	14.4_5	5.0_5	1.8_7

a) Ionic strength = 3.0, calculated by simplex method with a personal computer.

metrically at an ionic strength of 0.2, at 25±0.1 °C and at various ethanol concentrations. As an example, typical plots of apparent pK_{a2} of the 4 synthesized hydrazones versus ethanol concentration are shown in Fig. 1. The pK_a values of all the hydrazones thus obtained are summarized in Table 2. The pK_{a1} corresponds to the deprotonation of the secondary amino group, whereas the pK_{a2} and pK_{a3} correspond to that of the protonated pyridine-nitrogen and phthalazine-nitrogen, respectively.

Reactivities of the Hydrazones with Metal Ions. The reactivities of the synthesized hydrazones with metal ions and the extractabilities of the resultant complexes into benzene from aqueous media of pH 4,

Table 3. Extractability of Metal-PAPhH Complexes

Complex	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)	—	—	—	—	—	—
Al(III)	—	—	—	—	—	—
Ca(II)	—	—	—	—	—	—
Cd(II)	—	—	—	—	478	37000
Co(II)	—	—	—	—	—	—
Cr(III)	—	—	—	—	—	—
Cr(VI)	—	—	—	—	—	—
Cu(II)	—	—	455	9800	455	34000
Fe(II)	464 638	31000 8000	464 638	33000 8000	464 638	33000 8000
Hg(II)	—	—	466	17000	—	—
Mg(II)	—	—	—	—	—	—
Mn(II)	—	—	—	—	—	—
Ni(II)	—	—	470	52000	470	54000
Pb(II)	—	—	—	—	—	—
Pd(II)	538	9000	—	—	—	—
Ti(IV)	—	—	—	—	—	—
V(IV)	—	—	—	—	—	—
V(V)	—	—	—	—	—	—
Zn(II)	—	—	—	—	473	43000

Table 4. Extractability of Metal-MPPhH Complexes

Complex	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)	—	—	—	—	—	—
Al(III)	—	—	—	—	—	—
Ca(II)	—	—	—	—	—	—
Cd(II)	—	—	—	—	476	59000
Co(II)	—	—	—	—	—	—
Cr(III)	—	—	—	—	—	—
Cr(VI)	—	—	—	—	—	—
Cu(II)	—	—	—	—	468	24000
Fe(II)	442 653	19000 10000	460 653	24000 11000	460 653	28000 11000
Hg(II)	—	—	466	31000	466	18000
Mg(II)	—	—	—	—	—	—
Mn(II)	—	—	—	—	483	34000
Ni(II)	—	—	487	48000	487	52000
Pb(II)	—	—	—	—	—	—
Pd(II)	532	6000	532	6000	—	—
Ti(IV)	—	—	—	—	—	—
V(IV)	—	—	—	—	—	—
V(V)	517	8000	517	6000	—	—
Zn(II)	—	—	474	46000	474	66000

7, and 10 were investigated. The results are summarized in Table 3—6. Every hydrazone is found to react with cadmium(II), copper(II), iron(II), nickel(II), zinc(II), etc. to give colored complexes having large molar absorptivities. Of these, the reaction of DPPhH with nickel(II) proceeds over the wide pH region from weakly acidic to alkaline media to give a complex having large molar absorptivity (ε) and in addition, one can expect not only high sensitivity but also high selectivity when this complexation reaction in the weakly acidic medium is utilized to the determination of nickel, so the conditions for this complexation were examined in detail in subsequent experiments.

Table 5. Extractability of Metal-PPPhH Complexes

Complex	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)	—	—	—	—	—	—
Al(III)	—	—	—	—	—	—
Ca(II)	—	—	—	—	—	—
Cd(II)	—	—	486	55000	486	68000
Co(II)	493	16000	493	12000	488	19000
Cr(III)	—	—	—	—	—	—
Cr(VI)	—	—	—	—	—	—
Cu(II)	503	16000	482	41000	482	52000
Fe(II)	475 657	32000 13000	475 657	32000 13000	475 657	32000 13000
Hg(II)	—	—	477	31000	477	28000
Mg(II)	—	—	—	—	—	—
Mn(II)	—	—	—	—	495	45000
Ni(II)	484	53000	484	53000	484	57000
Pb(II)	—	—	—	—	—	—
Pd(II)	545	6000	545	8000	—	—
Ti(IV)	—	—	—	—	—	—
V(IV)	535	8000	535	12000	—	—
V(V)	535	21000	535	12000	—	—
Zn(II)	—	—	486	37000	486	57000

Table 6. Extractability of Metal-DPPhH Complexes

Complex	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)	—	—	—	—	—	—
Al(III)	—	—	—	—	—	—
Ca(II)	—	—	—	—	—	—
Cd(II)	—	—	485	27000	485	76000
Co(II)	—	—	—	—	—	—
Cr(III)	—	—	—	—	—	—
Cr(VI)	—	—	—	—	—	—
Cu(II)	500	7000	480	41000	480	54000
Fe(II)	474 653	32000 18000	474 653	32000 18000	474 653	32000 18000
Hg(II)	475	9000	475	29000	475	41000
Mg(II)	—	—	—	—	—	—
Mn(II)	—	—	—	—	496	64000
Ni(II)	500	54000	500	54000	500	54000
Pb(II)	—	—	—	—	—	—
Pd(II)	—	—	—	—	—	—
Ti(IV)	—	—	—	—	—	—
V(IV)	—	—	—	—	—	—
V(V)	533	14000	—	—	—	—
Zn(II)	—	—	485	71000	485	74000

Spectrophotometric Studies for the Determination of Nickel with DPPhH. Extraction Solvent, Effect of pH and Absorption Spectra: Nickel(II) reacts rapidly with DPPhH to form a red complex in weakly acidic to alkaline media. The complex is insoluble in water but soluble in organic solvents such as benzene, chloroform, 4-methyl-2-pentanone, and 1,2-dichloroethane. Of these, benzene was the most preferred extraction solvent, because the benzene extract gave the highest molar absorptivity. As shown in Fig. 2, the complex gave a constant, maximum absorbance when extracted from aqueous media of pH 4.3—10.7. Thus a pH of 5.0 is recommended. Figure 3 illustrates the absorption spectra of DPPhH and its nickel complex in benzene, together with the corresponding second-derivative spectrum. The complex has an absorption maximum at 500 nm, whereas the absorption of DPPhH at this wavelength is almost negligible.

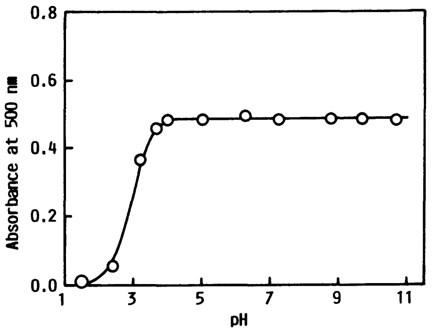


Fig. 2. Effect of pH. Ni(II): 5.1 μg/10 cm^3, DPPhH: 2.5×10^{-4} M, reference: reagent blank.

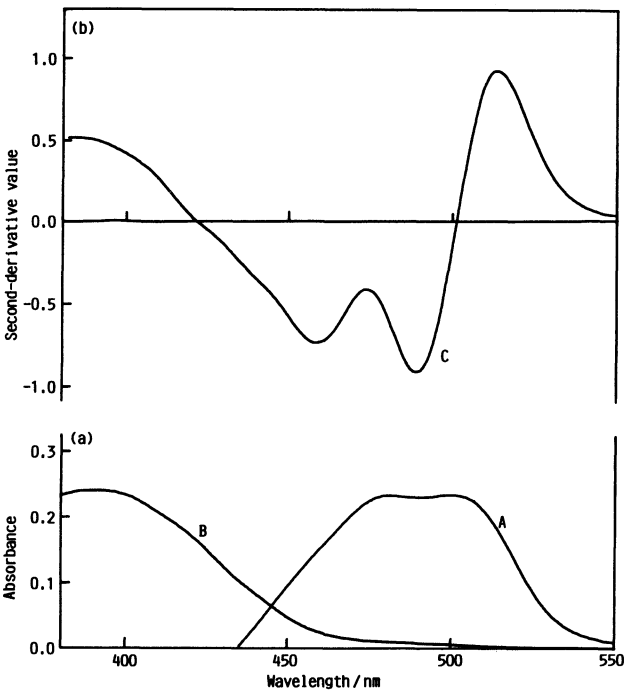


Fig. 3. (a) Absorption spectra of DPPhH and its nickel complex and (b) second-derivative spectrum of nickel–DPPhH complex in benzene. Ni(II): 2.53 μg/10 cm^3, DPPhH: 1.25×10^{-5} M, pH: 5.0, A, C: complex against reagent blank, B: reagent blank against benzene. Second-derivative spectrum was measured with scan speed 150 nm min^{-1} and circuits all No. 6.

Effects of DPPhH Concentration and Shaking Time: A 3-fold molar excess of DPPhH was the minimum required for obtaining constant absorbance, and excess of DPPhH did not interfere. Shaking for a few minutes was sufficient for quantitative extraction of the complex.

Effect of Other Variations in Extraction: Variations in temperature from 15 to 30 °C, the ethanol concentration up to 15% in aqueous phase and the organic to aqueous phase ratio from 1 : 1 to 1 : 5 did not affect the absorbance. The absorbance of the extract remained constant even after several hours, which suggests that the extracted complex is very stable.

Composition of the Complex: The composition of the extracted complex was determined by the continuous variation method. The result, which is shown in Fig. 4, revealed that the metal to ligand ratio of the complex was 1 : 2. So DPPhH is considered to act presumably as a tridentate ligand, but no further detailed experiments to confirm this were carried out.

Calibration Graph, Sensitivity, and Precision: The calibration graph obtained by the recommended procedure was linear over the range 1—10 μg of nickel and passed through the origin. The equation for the line obtained by least-squares treatment was

$$\mathrm{Ni}(\mu\mathrm{g}) = 10.8A \qquad (1)$$

where A is the absorbance. The molar absorptivity and the sensitivity for an absorbance of 0.001 calculated from Eq. 1 were 5.4×10^4 dm^3 mol^{-1} cm^{-1}

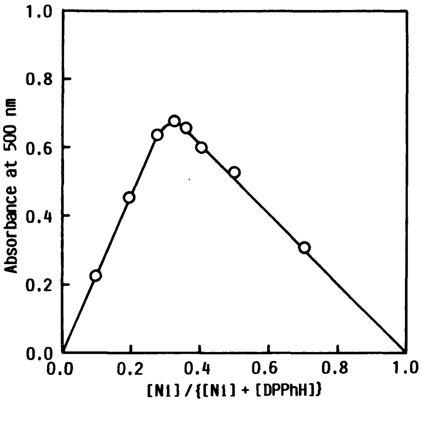


Fig. 4. Continuous variation graph for the nickel–DPPhH system. [Ni]+[DPPhH]=1.72×10^{-4} M, pH: 5.0.

and 1.08 ng cm^{-2}, respectively. These values indicate that the proposed method is extremely superior in sensitivity to that with 5-methylfurfural 1-phthalazinylhydrazone reported previously by us.[13] The relative standard deviation for 5.1 μg of nickel was 0.7%.

Effect of Diverse Ions: In order to study the effect of other ions on the determination of nickel, a fixed amount (5.1 μg) of nickel(II) was taken with various amounts of foreign ions and the recommended procedure was followed. An error of ±3% in the absorbance reading was considered tolerable. Tolerances for various foreign ions are shown in Table 7. Copper(II), iron(II,III), mercury(II), vanadium(IV,V), and zinc(II) interfere when no masking agent is added, whereas the other ions do not interfere. These interferences except that by iron(II) can be removed by the addition of masking agents noted in Table 7. Interference from iron(II) can be eliminated by masking with fluoride after oxidizing it to iron(III). Interference from a large amount of iron(III) can easily be removed by extracting it with 4-methyl-2-pentanone prior to the nickel determination, as mentioned already. On the other hand, most anions do not interfere, although the tolerance limit for iodide is somewhat low in comparison with those for other anions. The proposed method, therefore, may be regarded as very selective as well as sensitive for nickel.

Application to Actual Samples: In order to confirm the usefulness of the proposed method, it was applied to the determination of nickel in standard iron and steel samples. The results, shown in Table 8, are in good agreement with certified values.

Sensitization by Employing Analogue-Derivative Spectrophotometry. As described in earlier papers[14,15] the determination limit of ordinary spectrophotometry can remarkably be lowered by the introduction of a derivative spectrophotometric technique using the analogue differentiation circuit. As an example of sensitization, the second-derivative spectrophotomet-

Table 7. Tolerance Limits for Other Ions

Ion	Tolerance limit
Al(III), Ca(II), Mg(II)	1000 μg[a)]
Ag(I), Cd(II), Co(II), Cr(III), Cu(II)[b)], Fe(III)[c)], Hg(II)[d)], Pb(II), Ti(IV), V(IV)[e)], V(V)[f)], Zn(II)[b)]	100 μg
Fe(II)	below 5 μg
Br$^-$, Cl$^-$, ClO$_4^-$, NO$_3^-$, H$_2$PO$_4^-$, SCN$^-$, SO$_4^{2-}$, Tartrate, Citrate	0.04 M[a)]
I$^-$	0.02 M

Nickel(II) taken: 5.1μg a) Maximum tested. b) One cm^3 of 10% mercaptoacetic acid was added. c) One cm^3 of 1 M sodium fluoride was added. d) One cm^3 of 1 M sodium thiosulfate was added. e) One cm^3 of 0.1 M oxalic acid was added. f) One cm^3 of 1% ascorbic acid and 1 cm^3 of 0.1 M oxalic acid were added.

Table 8. Determination of Nickel in Standard Iron and Steel Samples

Sample	Sample taken	Nickel content/%	
	g	Proposed method	Certified value
Carbon steel[a)] (JSS-162)	0.1013	0.31_1	0.31
	0.1013	0.31_2	
	0.2103	0.30_0	
	0.2103	0.30_1	
	Average	0.30_6	
Carbon steel[a)] (JSS-163)	0.1017	0.10_8	0.11
	0.1017	0.11_4	
	0.1998	0.11_5	
	0.1998	0.11_4	
	Average	0.11_3	

a) JSS: Japan Standard Sample of Iron and Steel.

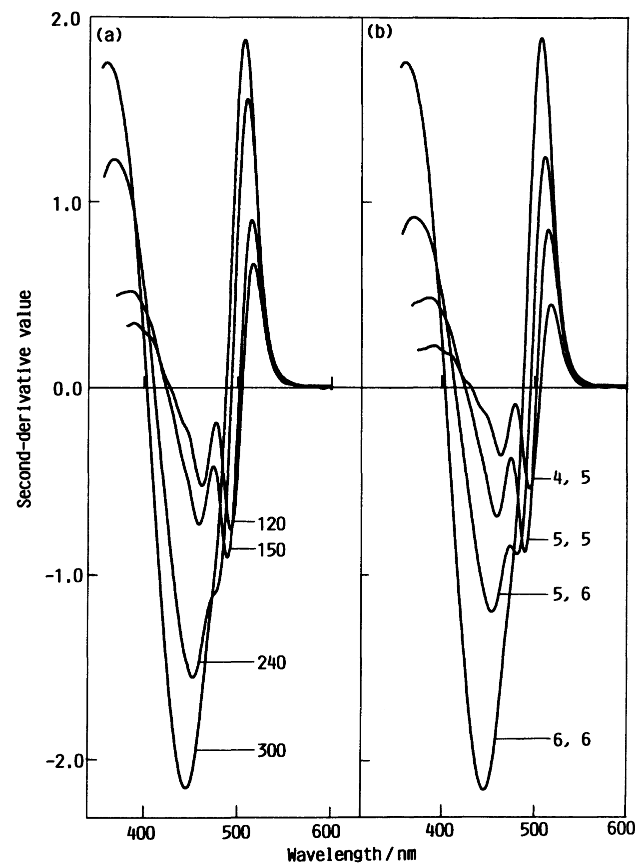


Fig. 5. Influence of (a) scan speed (with circuits all No. 6) and (b) circuit number (with scan speed 300 nm min^{-1}) on second-derivative spectra of the complex in benzene. Ni(II): 2.53 μg/10 cm^3, DPPhH: 1.25×10^{-5} M. pH: 5.0, slit width: 1 nm; recorder sensitivity: ×1/4, reference: reagent blank. Numerical values indicate scan speeds in (a) and first- and second-differentiation circuits in (b).

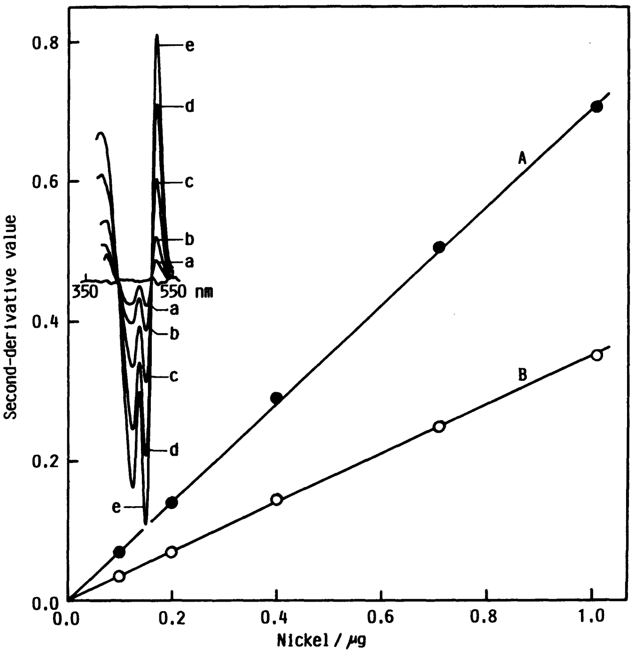


Fig. 6. Calibration graph for nickel in second-derivative spectrophotometry. Circuits: All No. 6, Scan speed: 150 nm min^{-1}, slit width: 1 nm, recorder sensitivity: ×1, reference: reagent blank. A: Peak-to-trough values are plotted, B: base line-to-trough values are plotted. Nickel (µg)—a: 0.10, b: 0.20, c: 0.40, d: 0.71, e: 1.01.

ric determination of nickel is described here.

Selection of Conditions for Merasurements: As the second-derivative value (the vertical distance from a peak to trough or that from the base line to a trough of the spectrum) depends on both the time constant of the analogue differentiation circuit and the scan speed of the spectrophotometer in second-derivative spectrophotometry, these need to be optimized to give a well resolved large peak (to give good selectivity and higher sensitivity). Figure 5 shows the second-derivative spectra of the nickel–DPPhH complex solution measured with varying circuit number or scan speed. A combination of circuit No. 6 (which has the largest time constant, 2.0 s, the time constant increasing with increasing circuit number in our apparatus) and a scan speed of 300 nm min^{-1} gives the highest sensitivity, but the resolution (i.e., selectivity) is poor in this combination. Taking both the sensitivity and selectivity into consideration, a combination of circuit No. 6 and a scan speed of 150 nm min^{-1} or that of No. 5 and 300 nm min^{-1} is recommended for the nickel determination.

Calibration Graph, Sensitivity, and Precision: The calibration graph prepared by plotting the second-derivative value versus the nickel concentration, an example of which is shown in Fig. 6, is linear and passes through the origin when either the peak-to-trough values or the base line-to-trough values were plotted. The equation for each line measured with a combination of circuit No. 6 and a scan speed of 150 nm min^{-1} was

$$\mathrm{Ni}(\mu\mathrm{g}) = 1.42\,D \tag{2}$$

$$\mathrm{Ni}(\mu\mathrm{g}) = 2.86\,D \tag{3}$$

respectively, where D is the second-derivative value represented by the conversion of the value into absorbance. It will be seen that as little at 100 ng or less of nickel can easily be determined in this way. Twelve standard solutions containing 400 ng of nickel(II) were analyzed. The results gave a relative standard deviation of 1.3%.

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