

# Synthesis of 4-Benzyl-1-Piperazineglyoxime and its Use in the Spectrophotometric Determination of Nickel

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A new reagent, 4-benzyl-1-piperazineglyoxime(BPGH<sub>2</sub>), was synthesized and used for developing a simple and rapid extractive method for the spectrophotometric determination of nickel. This method is based on the selective extraction of nickel complex from aqueous solution into carbontetrachloride and the measurement of the absorption at 267 nm. The method was applied to the determination of nickel ion in some standard and practical samples.

## Introduction

The most widely used reagents for nickel have been the *vic*-dioximes, compounds containing the group -C(=NOH)-C(=NOH)-, which reacts selectively with nickel and other transition group metals. The gravimetric procedures involving these reagents are well known<sup>1</sup>, and a large number of oximes are used as spectrophotometric reagents for trace determination of metal ions in various materials<sup>2</sup>. Only in the last forty years has the reagent been used for the extraction-spectrophotometric determination of nickel; the complex dissolves in benzene and isoamyl alcohol<sup>3</sup>, but dissolves more easily in chloroform, which has been preferred by most researchers<sup>2</sup>.

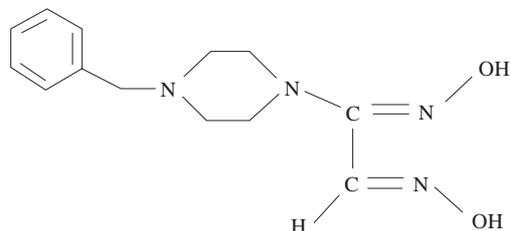
A newly synthesized 4-benzyl-1-piperazineglyoxime was used for developing a sensitive and simple spectrophotometric method. The structures of the ligand and its complex with Ni(II) are shown in Figure 1. The bis(4-benzyl-1-piperazineglyoxime) nickel complex has four well-defined maxima at 267, 323, 373 and 471 nm in carbontetrachloride (Fig. 2). The use of the sharp peak at 267 and 323 nm should be preferable to the broader peak at 373 and 471 nm. The ligand is not extracted into carbontetrachloride phase under these conditions. The peak at 267 nm provides better sensitivity than the others. Thus the 267 nm maximum was employed in the proposed determination of nickel in some standard and metal mixtures.

## Experimental

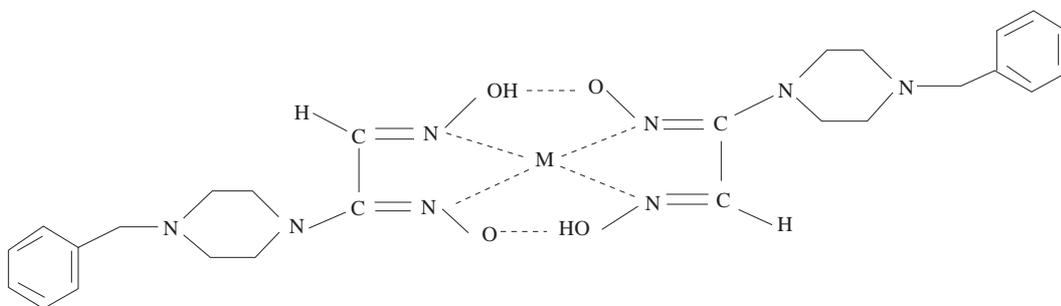
### Apparatus

A UNICAM UV/VIS spectrometer UV2 was used for recording the absorption spectra and pH measurements were done with a Crison Micro 2000 pH-meter. IR spectra were recorded by a MATTSON 1000 FTIR

spectrophotometer with samples prepared in KBr pellets. The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were taken on a AC-200 Bruker FT-NMR spectrometer 200 MHz. Elemental analyses were performed by a Perkin-Elmer 240 C elemental analyzer.



4-Benzyl-1-piperazineglyoxime (BPGH<sub>2</sub>)



M: Ni(II); Bis(4-benzyl-1-piperazineglyoximate) nickel [(BPGH<sub>2</sub>)<sub>2</sub>Ni]

**Figure 1.** The Structure of the Ligand and the Complex

## Reagent

The reagent, 4-benzyl-1-piperazineglyoxime (BPGH<sub>2</sub>), was prepared by adding a solution of anti-chloroglyoxime<sup>5,6</sup> (20 mmol, 2.45 g) in 25 ml of ethanol to a solution of 4-benzylpiperazine (20 mmol, 3.52 g) in 10 ml of the solution at  $-10^\circ\text{C}$ . The mixture was stirred for 4 hours at under  $0^\circ\text{C}$ . After adjusting the pH of the mixture to 6-7 with 0.1 N KOH; the contents were stirred for 4 hours at  $0^\circ\text{C}$  and further stirring for 4 hours was performed at  $0^\circ\text{C}$ . To the mixture, 20 ml carbontetrachloride was added and the contents were mixed for 3 hours. The resulting precipitate was filtered and then washed with ethanol. The white product was dried and recrystallized from ethanol. Yield was 68%; m.p.  $185^\circ\text{C}$  (decomposed).

Elemental analysis for BPGH<sub>2</sub> (C<sub>13</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>): C 59.56, H 6.87, N 21.37; Found: C 59.47, H 6.95, N 21.63 %.

The compound BPGH<sub>2</sub> is soluble in ethanol, pyridine, DMF, DMSO, dioxane and slightly soluble in water and insoluble in carbontetrachloride.

UV-VIS. (ethanol): 291 nm ( $\epsilon=3000$ ), 210 nm( $\epsilon=14283$ ).

IR (KBr):  $\nu$  max  $3250\text{ cm}^{-1}$  ( $\nu$  O-H),  $3080\text{-}2700\text{ cm}^{-1}$  ( $\nu$  C-H),  $1630\text{ cm}^{-1}$  ( $\nu$  C=N),  $986\text{ cm}^{-1}$  ( $\nu$  N-O)

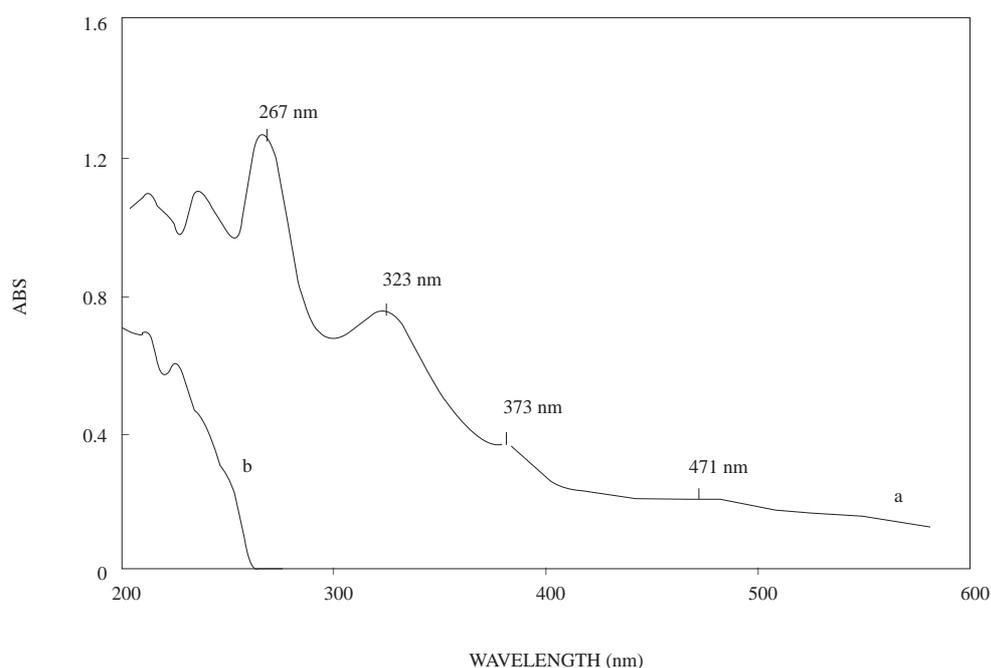
$^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ ):  $\delta$  3.5 (2H, s), 2.4(4H, t), 3.1(4H, t), 7.1-7.4 (5H, m), 7.9 (1H, s), 10.4 (1H, s), 11.7(1H, s).

$^{13}\text{C-NMR}$  ( $\text{DMSO-d}_6$ ):  $\delta$  47.5, 52.1, 126.8, 128.8, 137.7, 138.2, 152.9.

Stock solution of 0.5 % of the reagent  $\text{BPGH}_2$  was prepared by dissolving at ( $50^\circ\text{C}$ ) the appropriate amount of it in a ethanol-water (1:1) mixture. Stock solution of Ni(II) (10 mg/L) was prepared by dissolving the appropriate amount of nickel chloride hexahydrate in distilled and deionized water.

The buffer solution used was  $\text{KH}_2\text{PO}_4$ -NaOH for pH 8.

All solvents and reagents used were of analytical grade.



**Figure 2.** Absorption Spectra of  $(\text{BPGH})_2\text{Ni}$  Complex ( $3\ \mu\text{g/ml}$  Ni(II)) (a), and the Reagent blank (b) in Carbondtetrachloride.

## Synthesis of Nickel Complex

The reagent  $\text{BPGH}_2$  (10 mmol, 2.62 g) was dissolved in 30 mL of ethanol-water mixture (1:1) and a solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5 mmol, 1.18 g) in water (10 mL) was added to this solution while stirring at about  $30\text{-}40^\circ\text{C}$ . The pH of this solution was adjusted to 8.0 with the addition of 0.1 M KOH solution. The resulting rose red compound was extracted from the mixture to the chloroform phase (30 mL) and recrystallized from chloroform and dried in vacuo. Yield was 85 %; m.p.  $190^\circ\text{C}$ . The complex was soluble in chloroform, tetrachloromethane, DMSO, pyridine and slightly soluble ethanol and water.

UV-VIS (Tetrachloromethane): 267 nm ( $\epsilon=22493$ ), 323 nm ( $\epsilon=12892$ ), 471 nm ( $\epsilon=2040$ ).

IR (KBr):  $\nu$  max  $3100\text{-}2720\ \text{cm}^{-1}$  ( $\nu\text{C-H}$ ),  $1800\ \text{cm}^{-1}$  ( $\delta\text{O-H.O}$ ),  $1620\ \text{cm}^{-1}$  ( $\nu\text{C=N}$ ),  $993\ \text{cm}^{-1}$  ( $\nu\text{N-O}$ ).

Anal. cal. for  $\text{Ni}(\text{C}_{13}\text{H}_{17}\text{N}_4\text{O}_2)_2$ : C 53.74, H 5.86, N 19.28; Found: C 53.84, H 5.95, N 19.44 %

## Recommended Procedure for the Determination of Nickel(II)

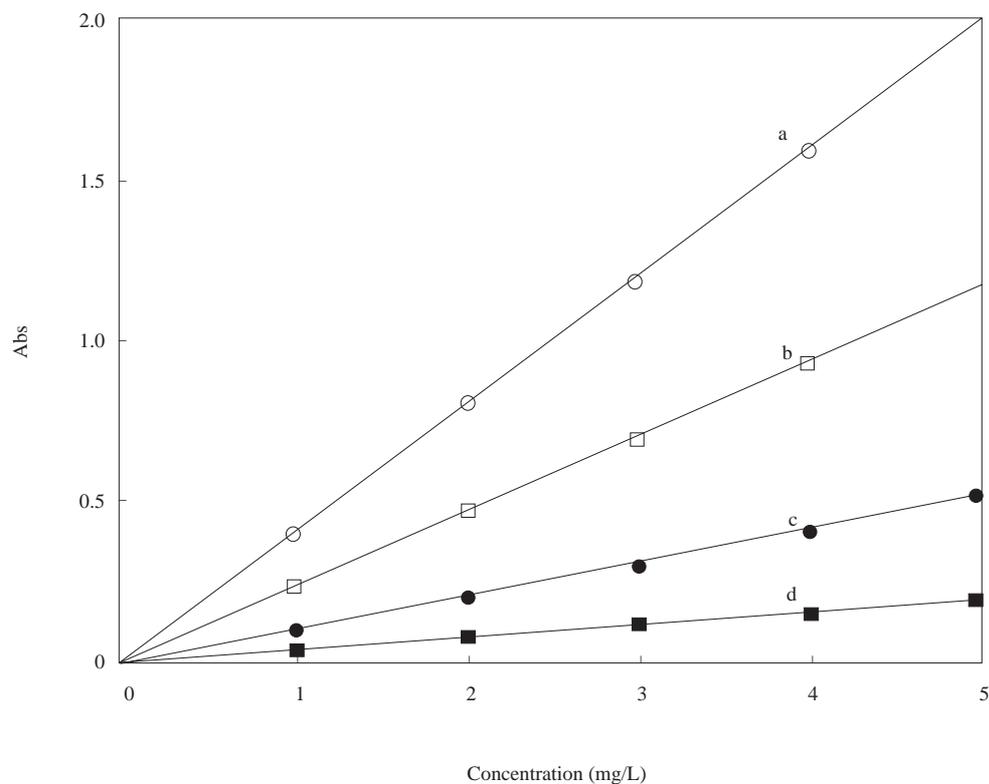
An aqueous sample (8 mL) containing not more than 5.0  $\mu\text{g/mL}$  of Ni(II) was transferred into a volumetric flask and the pH was adjusted to 8.0 by adding  $\text{KH}_2\text{PO}_4\text{-NaOH}$  buffer (1 mL). The solution (1 mL) of  $\text{BPGH}_2$  (0.5 %, at 50 °C) in ethanol-water (1:1) mixture and carbontetrachloride (10 mL) was added to the solution and stirred for 20 min. A blank solution was prepared in a similar way. The organic layer containing nickel complex was separated and its absorbance was measured at 267 nm. The nickel concentration of the sample solution was determined to be in the range 0.1-5  $\mu\text{g/mL}$  by comparing the measured absorbance value with a preconstructed calibration graph.

Nickel in synthetic and alloy samples was determined by the proposed procedure.

## Results and Discussion

### Spectroscopic Properties of the Reagent and Complex

The absorption spectra of the carbontetrachloride extracts of the  $(\text{BPGH})_2\text{Ni}$  complex and the reagent are shown in Figure 2. These results show that four absorption peaks of the complex were observed at 267, 323, 375 and 473 nm and at these wavelengths, the absorbance of the free ligand is negligible. The absorbance of the complex at 267 nm was more sensitive than the peaks at 323, 375 and 471 nm in Fig. 3. Therefore, the optimum wavelength 267 nm for the spectrophotometric determination of Ni(II) was preferred.



**Figure 3.** Standard Curves for Nickel Determination with 4-Benzyl-1-piperazineglyoxime in Carbontetrachloride: (a) at 267 nm, Correlation Coefficient 0.9999; (b) at 323 nm, Correlation Coefficient 0.9999; (c) at 373 nm, Correlation Coefficient 0.9999; (d) at 471 nm, Correlation Coefficient 0.9999.

In the  $^1\text{H-NMR}$  spectrum of  $\text{BPGH}_2$ , two chemical shifts were observed at 10.4 and 11.7 ppm for OH protons. The aldoxime CH proton which neighbors the oxime groups was observed at 7.9 ppm. the cyclic  $\text{CH}_2$  protons at 2.4-3.1 ppm and the aromatic CH proton at 7.1-7.4 ppm and benzyl  $\text{CH}_2$  at 3.5 ppm, respectively. The OH protons were identified by  $\text{D}_2\text{O}$  exchange.

In the  $^{13}\text{C-NMR}$  spectrum of ligand, two different signals which are observed at 138.2 ( $\text{HC=N-OH}$ ) and 152.9 ( $\text{N-C=N-OH}$ ) ppm show the asymmetrically substituted vic-dioximes.

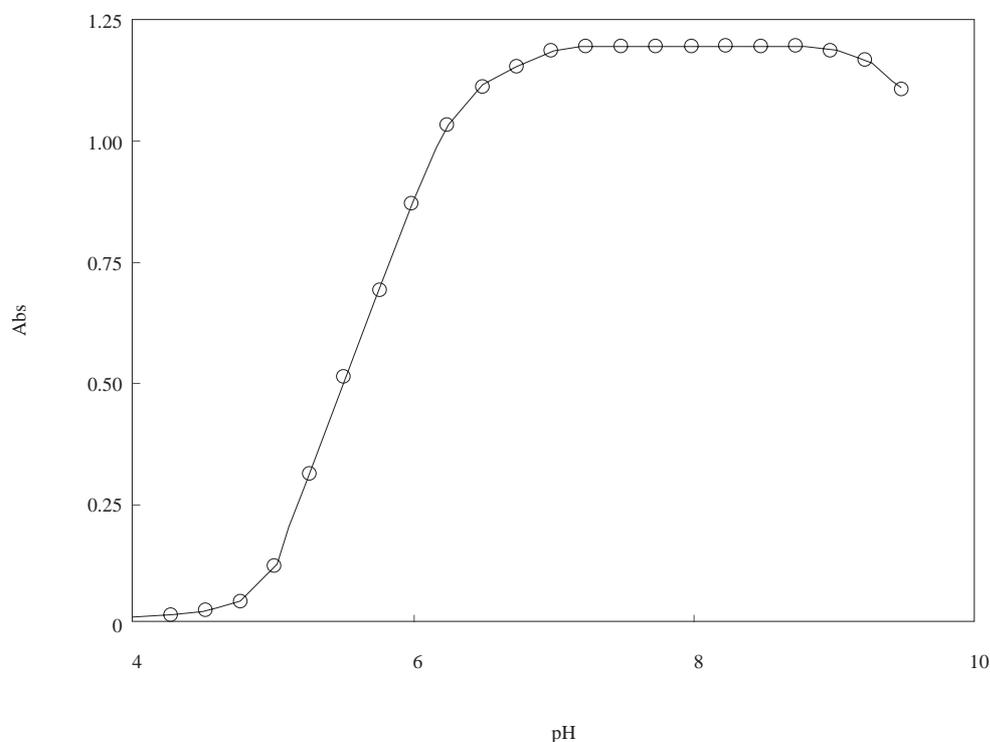
In the IR spectrum of  $\text{BPGH}_2$ , the O-H, C=N and N-O stretching vibrations are observed at 3250, 1630 and 986  $\text{cm}^{-1}$ , respectively. These data are in agreement with these previously reported vic-dioximes derivatives<sup>7-13</sup>. The IR spectra of nickel complex shows similar vibrations with the spectra of the ligand.

### Composition of the Ligand and Complex

The formula of the ligand ( $\text{BPGH}_2$ ) was investigated by IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  and elemental analysis techniques and that of the complex was investigated with spectrophotometry using the molar ratio method. The composition of the complex was found to be  $(\text{BPGH})_2\text{Ni}$ . The structures of the ligand and the complex are illustrated in Figure 1.

### The Effect of pH on the Extraction of the Complex

The effect of pH on the extraction of the nickel complex from aqueous solution into carbon-tetrachloride phase was investigated spectrophotometrically. As clearly seen in Figure 4, the complex is extracted completely at pH values of 7.5-8.5. Therefore, the pH value of 8.0 was chosen for the extraction of Ni(II) prior to the spectrophotometric determination.



**Figure 4.** The Effect of pH on the Extraction of the Complex

**Table 1.** The Effect of Foreign Ions on the Determination of Nickel.

Salt or ion	added $\mu\text{g/mL}$	taken Ni(II) ( $\mu\text{g/mL}$ )	found* Ni(II) ( $\mu\text{g/mL}$ )	Relative error, %
...	...	3.00	3.00	0.00
Ag(I)	12.50	3.00	3.03	1.00
Zn(II) <sup>a</sup>	12.50	3.00	2.98	-0.67
Pb(II)	12.50	3.00	2.99	-0.33
Co(II)	12.50	3.00	3.07	2.33
Cu(II) <sup>b</sup>	12.50	3.00	3.04	+1.33
Cd(II) <sup>c</sup>	12.50	3.00	2.99	-0.33
Mn(II)	12.50	3.00	2.96	-1.33
Hg(II)	12.50	3.00	3.06	2.00
Fe(II)	12.50	3.00	2.98	0.67
Fe(III)	12.50	3.00	3.05	1.67
Cr(III) <sup>d</sup>	12.50	3.00	3.01	0.33
Al(III) <sup>e</sup>	12.50	3.00	2.97	-1.00
NaCl	19990.00	3.00	3.04	1.33
KI	9030.00	3.00	3.07	2.33
KNO <sub>2</sub>	10539.00	3.00	3.06	2.00
NaNO <sub>3</sub>	13263.00	3.00	3.03	1.00
KSCN	13114.00	3.00	2.94	-1.00
Na <sub>2</sub> SO <sub>4</sub>	11161.00	3.00	2.96	-1.33
NaCH <sub>3</sub> COO	13140.00	3.00	2.99	-0.33
K <sub>2</sub> CrO <sub>4</sub>	4784.00	3.00	3.05	1.66
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	11986.00	3.00	2.98	-0.66
KCN	3960.00	3.00	0.05	-98.33
KClO <sub>3</sub>	4883.00	3.00	3.03	1.00
Na-EDTA	2970.00	3.00	0.08	-97.33
Sodium tartrate	16109.00	3.00	2.92	-2.67

\*Three determinations

Masking agent was not added: Zn<sup>2+</sup> (2.5 mg/L, error > 10%); Cu<sup>2+</sup> (2.5 mg/L, error >20%); Cd<sup>2+</sup> (2.5 mg/L, error >5 %); Cr<sup>3+</sup> (2.5 mg/L, error>20 %); Al<sup>3+</sup> (2.5 mg/L, error>5 %); MX<sub>2</sub> and MX<sub>3</sub> (M=Ni(II), Cu(II), Al(III), ect., X=Cl).

Masking agent in the 10 ml sample solution:

a: Na-tartrate or Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (0.1-0.5 g) d: Na-tartrate (0.1-0.5 g)

b: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.1-0.5 g) e: 20 % TEA (triethanolamine) (1 ml)

c: Na-tartrate or Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.1-0.5 g)

**Table 2.** Determination of Nickel in Synthetic Mixtures (Mixtures: Cu(II)<sup>a</sup>, Co(II), Zn(II)<sup>b</sup>, Cd(II)<sup>c</sup>, Mn(II), Fe(II), Pb(II), Hg(II), Fe(III), Cr(III)<sup>d</sup>, Al(III)<sup>e</sup> 2.5 µg/mL and Standard MBH Reference Materials (Mild Steel, Inconel Type and Copper Base).

mixture	Composition	Taken, Ni(II) (µg/mL)	Found*,Ni(II) (µg/mL)	Relative error, %
...	...	3.00	3.00	0.00
Mixture 1	Zn(II), Cd(II)	3.00	2.98	-0.67
Mixture 2	Cu(II), Co(II), Mn(II)	3.00	3.02	0.67
Mixture 3	Cu(II), Co(II), Mn(II), Cd(II), Fe(II)	3.00	3.07	2.33
Mixture 4	Cu(II), Co(II), Mn(II), Pb(II), Hg(II)	3.00	3.02	0.67
Mixture 5	Cu(II), Zn(II), Al(III), Fe(III)	3.00	3.04	1.33
Mixture 6	Cu(II), Zn(II), Al(III), Cr(III)	3.00	3.05	1.66
Mixture 7	Cu(II), Co(II), Cd(II), Zn(II), Fe(II)	1.00	1.01	0.33
Mixture 8	Cu(II), Co(II), Cr(III), Fe(III), Al(III)	1.00	0.99	-1.00
MBH- C12X3500 Mild Steel	C 0.18, Si 0.45, S 0.032, P 0.029, Mn 0.70, Ni 0.18, Cr 0.31, Mo 0.10 Cu 0.15, Co 0.005, Sn 0.03, Al 0.35, W 0.29, Ti 0.054, V 0.002, As 0.070 %	3.60	3.63	0.83
MBH- C28X71830 Inconel type alloy Ni/Cr/Fe	C 0.19, Si 0.18, S 0.05, Mn 0.4, Fe (REM.), Cr 17.78, Mo 3.31, Co 1.00, Ti 1.40, Al 1.77, Nb 5.44, Ni 54.8 %	3.28	3.31	0.92
MBH-C31XB20 Copper Base Brass	Sn 0.18, Pb 0.21, Zn (REM), Fe 0.035, Ni 0.21, Al 0.15, Si 0.10, Mn 0.20, Cu 60.8, As 0.115, Bi 0.09, Sb 0.05 %	3.15	3.18	0.95

\*Three determinations

a: Masked with 0.5-1.0 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>b: Masked with 0.1-0.5 g Na-tartrate or Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>c: Masked with 0.1-0.5 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> or Na-tartrate

d: Masked with 0.1-0.5 g Na-tartrate

e: Masked with 1mL 20 % TEA

### Applicability of Beer's Law, Molar Absorptivity and Sensitivity

The measured absorbance values of the extracts of the standard Ni(II) solution at 267 nm show that nickel obeys Beer's Law in the concentration range of 0.1-5.0 mg/L.

The average molar absorptivity ( $\epsilon$ ) of the complex calculated from the linear portion of Beer's Law plot is 22500 L.mol<sup>-1</sup>.cm<sup>-1</sup> at 267 nm and Sandell's sensivity of the reaction is 0.0026 µg/cm<sup>2</sup>

The complex has four well-defined maxima at 267, 323, 373 and 471 nm in carbontetrachloride. The peak at 267 nm is more sensitive than 323, 373 and 471 nm for the determination of nickel (Fig. 2). The ligand has absorbance at the complex's region (200-320 nm) in the ethanol, but it is not extracted into

carbontetrachloride phase. Thus the 267 nm maximum was employed in the proposed determination of nickel in standard, synthetic metal mixtures and alloys.

### Effect of Foreign Ions

Nickel(II) was extracted from several foreign ions in the same solution at pH 8.0 A solution was prepared which was 3 mg/L Ni(II) and 2.5 mg/L each in Ag(I), Co(II), Fe(II), Zn(II), Pb(II), Hg(II), Cd(II), Mn(II), Fe(III), Cr(III) and Al(III). The absorbance of the extracts were measured at 267 nm. Data for these extractions are given in Tables 1-2. Zn(II), Cu(II), Cd(II), Cr(III), and Al(III) have significant interference in the determination of nickel by the present method. The interference effect of Zn(II), Cu(II), Cd(II), Cr(III) and Al(III) can be eliminated by adding suitable masking agents of sodium tartrate or sodium oxalate, sodium thiosulphate, sodium tartrate or sodium thiosulphate, sodium tartrate, and triethanolamine, respectively.

No common anions such as chloride, nitrate, sulphate, acetate, thiosulphate, tartrate and chlorate interfere with the determination of nickel. Cyanate and ethylenediamine-tetraacetic acid ions show highly negative interference; and iodide, nitrite ions slightly and negatively interfere for determination of nickel.

Nickel in synthetic and alloy samples was determined by the proposed procedure. The results (Table 2) are in good agreement with previously reported values.

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