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MUHAMMAD IQBAL BHANGER

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WILLIE L. HINZE

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# Determination of Ni(II) with picolinaldehyde-4-phenyl-3-thiosemicarbazone used as a chromogenic reagent in a nonionic micellar system

Aamna BALOUCH<sup>1</sup>, Muhammad Iqbal BHANGER<sup>1,\*</sup>, Farah Naz TALPUR<sup>1</sup>,  
Willie L. HINZE<sup>2</sup>

<sup>1</sup>*National Centre of Excellence in Analytical Chemistry, University of Sindh,  
Jamshoro-PAKISTAN*

*e-mail: dbhanger2000@yahoo.com*

<sup>2</sup>*Department of Chemistry (Salem-Hall), Wake Forest University,  
Winston-Salem, NC-USA*

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Spectrophotometric determination of Ni(II) was carried out using picolinaldehyde-4-phenyl-3-thiosemicarbazone (PAPT) as a complexing/chromogenic reagent. The possibility of using a micellar system was explored to enhance the degree of detection and allow a more sensitive spectrophotometric method for the determination of nickel ions. The anionic surfactant Triton X-100 greatly enhanced the molar absorptivity and limit of detection relative to that observed with bulk water or an organic solvent. The linear calibration graphs were obtained for 0.5-2.0 mg L<sup>-1</sup> and 0.001-1.0 mg L<sup>-1</sup> of Ni(II) in aqueous and surfactant media, respectively. Using this approach, the limit of detection for the PAPT-Ni(II) complex (based on 3σ of blank absorbance/slope) was found to be 0.0008 mg L<sup>-1</sup> with a micellar enhancement reagent. The interference from over 50 cations, anions, and complexing agents was studied at 0.50 mg L<sup>-1</sup> of Ni(II); most metal ions can be tolerated in considerable amounts in aqueous micellar solutions.

**Key Words:** Spectrophotometry, surfactant, Ni(II), PAPT

## Introduction

The toxicity of nickel is well known in causing asthma and cancer of the nose, lungs, and intestine<sup>1-3</sup> when individuals are exposed to Ni-containing jewelry, cooking utensils, and clothing fasteners. Studies showed

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\*Corresponding author

that the accumulation of Ni in the body may lead to lung fibrosis and cardiovascular and kidney diseases, in addition to the most serious concerns related to nickel's carcinogenic activity.<sup>4</sup> It was confirmed that the tissues of cardiac patients had high levels of Ni, indicating its possible detrimental effects.<sup>5-6</sup> Therefore, trace analysis of nickel continues to be significant. Several researchers<sup>7-9</sup> have reported on the atomic absorption spectroscopy (AAS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) methods for nickel determination; however, all such methods suffer from limitations including high cost, particularly in laboratories with limited budgets in developing countries. Chemiluminescent methods<sup>10,11</sup> based on the catalytic action of Ni(II) are subject to interference from various metal ions capable of activating or inhibiting the reactions. Spectrophotometric methods also suffer from limitations in sensitivity and selectivity, but are still widely used due to their rapidity and simplicity. Their selectivity and sensitivity depend on the type of reaction and the chromogenic reagent used.<sup>12</sup> Picolinaldehyde-4-phenyl-3-thiosemicarbazone (PAPT) is a convenient reagent reported for spectrophotometric determination of nickel and cobalt in mixtures and of nickel alone by the extraction method with low sensitivity.<sup>13,14</sup> In addition, PAPT has been employed for the simultaneous spectrophotometric determination of iron, vanadium, and cobalt in crude petroleum oil in an acidic medium.<sup>15</sup> However, metal- PAPT complexes are sparingly soluble in aqueous media,<sup>13,16,17</sup> necessitating the use of such toxic organic solvents as chloroform, benzene, or carbon tetrachloride for the extraction step.<sup>18,19</sup>

Metal ion determination through solvent extraction suffers from some inherent disadvantages, being environmentally undesirable, expensive, and time-consuming, and often lacking selectivity and sensitivity. To eliminate the need for organic solvents, aqueous micellar solutions can be utilized to solubilize insoluble chelating agents along with their metal complexes, and they are compatible with many analytical techniques.<sup>20</sup> Surfactant solutions solubilize the species of interest, enhance the sensitivity of the analytical method by their catalytic potential, and also offer many advantages, including low cost, environmental friendliness, and a high capacity to concentrate a wide variety of analytes of varying nature with high recoveries and a high concentration factor.<sup>21-25</sup>

The aim of the present study was to develop a simple and selective spectrophotometric method for the trace determination of nickel with PAPT reagent in the presence of nonionic micelles, such as polyoxyethylene octyl phenyl ether (Triton X-100 [TX-100]), in aqueous solutions.

## Experimental

### Apparatus

All absorbance measurements were conducted using a PerkinElmer UV-Lambda 2 spectrophotometer. A Nicolet 5700 FT-IR spectrophotometer (Thermo Electron Corporation, MA, USA) with a total attenuated reflectance accessory was employed for IR measurements. A WTW (Weilheim, Germany) pH meter with a combination glass-Ag/AgCl electrode was used for the pH measurements. Elemental analysis was carried out on a CHNS analyzer (Series 1112 FLASH, Thermo Electron Corporation). A HITACHI 180-50 atomic absorption spectrophotometer (HITACHI, Tokyo, Japan) with an air-acetylene or nitrous oxide-acetylene flame was used for comparison of our method with results obtained from AAS.

## Reagents, standards, and samples

All standard solutions were prepared from analytical-grade salts of respective materials. Ultrapure water (conductivity:  $0.050 \mu\text{S cm}^{-1}$ ) was obtained from a Milli-Q purification system (PURELAB Prima 7 BP, PURELAB Classic UV) used for the preparation of all samples, standards and blanks. Glassware was cleaned by soaking in acidified solutions of  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ , followed by washing with concentrated  $\text{HNO}_3$  and rinsing with water.

## Synthesis procedure for picolinaldehyde-4-phenyl-3-thiosemicarbazone

The chelating agent, PAPT, was synthesized according to the reported method.<sup>14</sup> Briefly, 0.01 mol (1.07 g) of pyridine-2-carboxaldehyde was dissolved in 10.0 mL of methanol and mixed with a methanolic solution of 4-phenyl-3-thiosemicarbazide (0.01 mol, 1.67 g). Next, 2.00 mL of concentrated acetic acid was added and the contents were refluxed for 30 min at  $80.0^\circ\text{C}$ . The mixture was cooled to room temperature and the yellowish solid precipitate obtained was filtered, recrystallized from ethanol, dried, and stored in an amber bottle. The melting point of the solid was found to be  $195.0^\circ\text{C}$ , which is in good agreement with the reported literature value ( $196.0^\circ\text{C}$ ).<sup>26</sup> Elemental analysis of the PAPT ( $\text{C}_{13}\text{H}_{12}\text{N}_4\text{S}$ ) was as follows: calculated% C = 60.94, H = 4.69, N = 21.88, and S = 12.50; found% C = 60.91, H = 4.65, N = 22.11, and S = 12.01. The FT-IR spectrum exhibited major peaks at the following wave numbers ( $\text{cm}^{-1}$ ): 3306.61 (*v* N-H), 1595.41 (*v* C=N), 1548.3, 1523.03, 1497.35, 1467.39 (*v*-ring breathing vibration of phenyl and pyridine), and 1187.07 (*v* C=S).

## Preparation of nickel ion standards solutions

Stock solutions ( $1000 \text{ mg L}^{-1}$ ) of nickel were prepared by dissolving the appropriate amount of nickel sulfate (Merck, Germany) in water acidified to a pH of approximately 5 with the addition of 2.00 mL of 0.001 M  $\text{H}_2\text{SO}_4$  and dilution to a final volume of 100.0 mL.

## Preparation of surfactant solution

A 10% (v/v) solution of polyoxyethylene octyl phenyl ether (TX-100) was freshly prepared by dissolving 10.0 mL of pure polyoxyethylene octyl phenyl ether (Merck) in 30 mL of ultrapure deionized water sonicated for 15 min, then diluted up to the mark in a 100.0-mL volumetric flask.

## Preparation of sodium hydroxide and sulfuric acid solution

A sodium hydroxide solution of 1.0 M was prepared by dissolving the appropriate amount in 40 mL of deionized water, then increasing the volume up to the mark in a 100.0-mL volumetric flask with deionized water and standardizing by the standard titration procedure. Less concentrated solutions were prepared by series dilution.

## Real sample digestion method

### Chocolates and candies

The chocolate and candy samples were digested by the conventional digestion method (CDM) for nickel analysis. About 0.5 g of each selected sample, 1 of each chocolate and candy ( $n = 3$ ), was weighed in separate Pyrex flasks (50 mL in capacity) and the contents of the flasks were treated with a mixture of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{O}_2$  (1:1:1, v/v/v) for decomposition.

The contents of the flasks were heated on an electric hotplate at 80 °C for 2-3 h, until clear. After the cooling of the digestion flask, the resulting solutions were evaporated until semidried, and then 5.0-8.0 mL of water was added and the pH of the solution was adjusted to approximately 7 by the addition of 0.01 M NaOH. The final volume was increased to 25.0 mL. An aliquot of 0.5-2.0 mL was then taken and analyzed for its nickel contents.

### Water samples

Water samples were collected from Manchar Lake, Sindh, Pakistan, and from a domestic tap. In both cases 100.0 mL of each water sample was filtered with Whatman No. 40 filter paper and evaporated to near dryness. In order to dissolve the salts 5.0 mL of concentrated  $\text{HNO}_3$  and 10.0 mL of water were added and the solution was heated in a fume hood. The solution was cooled and neutralized with 0.01 M NaOH solution. The resulting solution was then filtered and quantitatively transferred to a 25.0-mL volumetric flask and diluted to the mark with water. An aliquot (1.02.0 mL) of this solution was pipetted into a 10.0-mL calibrated flask and the nickel content was determined.

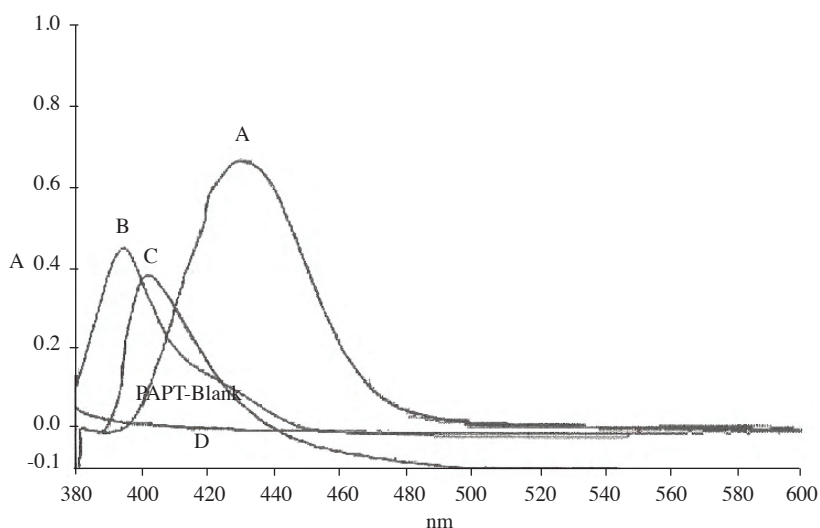
### Experimental procedures for calibration data

Slightly acidic solutions (pH of approximately 5.00) containing 0.50-100.0  $\mu\text{g}$  of nickel ion were added to 10.0-mL volumetric flasks followed by the addition of 2.00 mL of 0.05% (w/v) PAPT solution in dimethylformide and 0.10 mL of 0.01 M NaOH (pH of approximately 10-11), and then diluted to a final volume with 10% (v/v) TX-100 solution. After mixing the solution, the absorbance of the metal-PAPT complex was measured versus an appropriate blank solution within 10-15 min at 430 nm.

## Results and discussion

### Absorption spectra

The absorption spectra of PAPT and its nickel complex in the micellar solution are shown in Figure 1. Maximum absorbance of the PAPT-Ni(II) complex was observed at 390 nm in acetic acid-acetate buffer and at 400 nm in chloroform;<sup>13</sup> however, in the aqueous TX-100 micellar solution, the wavelength maximum bathochromically shifted to 430 nm.



**Figure 1.** Absorption spectra of PAPT-Ni(II) complex in micellar solution (curve A); PAPT-Ni(II) complex in acetic acid-acetate buffer (curve B); PAPT-Ni(II) complex in chloroform extract (curve C); and reagent blank (curve D) in TX-100. Conditions: final Ni(II) ion concentration was  $0.50 \text{ mg L}^{-1}$ ;  $[\text{PAPT}] = 0.001171 \text{ M}$ ,  $[\text{TX-100}] = 1.0\% \text{ (v/v)}$ ;  $\text{pH} = 10.2$  at  $25 \text{ }^\circ\text{C}$ .

## Factors influencing the chelating reaction and metal complex

To optimize the conditions for determination of Ni(II), such factors as pH, surfactant type and concentration, reagent concentration, and composition of complexes were evaluated.

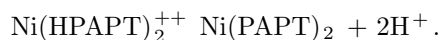
### Effects of surfactants

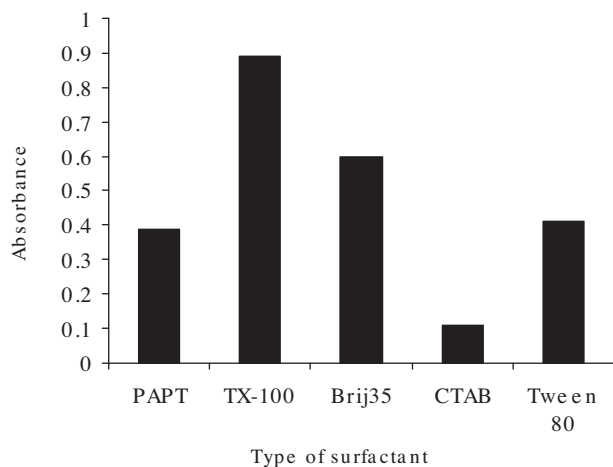
In the absence of surfactants, the chromogenic system gives a low analytical signal. To enhance the absorption (i.e., molar absorptivity), the effects of various surfactants on the PAPT-Ni(II) chromogenic system were examined. The order of the absorbance was TX-100 > Brij35 > Tween 80 > cetyltrimethylammonium bromide (CTAB), as illustrated in Figure 2. The absorbance of PAPT-Ni(II) increases considerably in the presence of a nonionic surfactant, which is attributed to the uncharged complex in basic media, as reported previously.<sup>13</sup> However, when anionic surfactant sodium dodecyl sulfate (SDS) was added, the solution turned turbid and the absorbance of the PAPT-Ni(II) complex was difficult to measure.

Figure 3 shows the effect of surfactant concentration on the absorbance of the PAPT-Ni(II) complex. A solution of 1.0 mL of 10% (v/v) TX-100 gave a constant and maximum absorbance, which was used for further study.

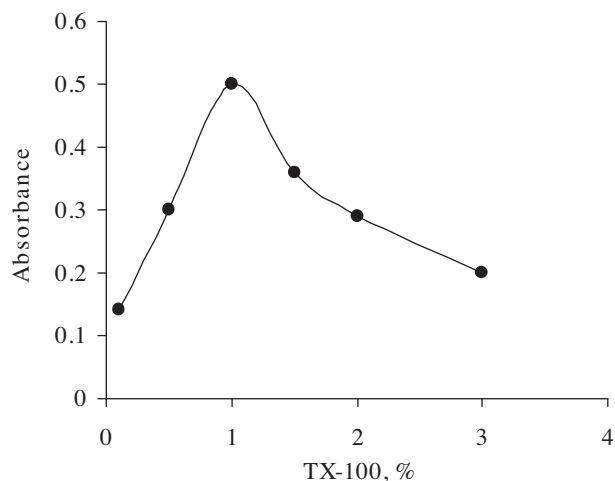
### Effect of pH

The color of the nickel complex had a maximum intensity in the basic medium at a pH greater than 10:





**Figure 2.** Effect of surfactant type on the absorbance of PAPT-Ni(II) complex and water alone. Conditions: final Ni(II) ion concentration was  $0.50 \text{ mg L}^{-1}$ ; [PAPT] =  $0.001171 \text{ M}$ , [CTAB] =  $0.06 \text{ M}$ , [TX-100] =  $2\%$ , [Brij35] =  $1\%$ , [Tween 80] =  $1\%$ ; pH =  $10.2$  at  $25 \text{ }^\circ\text{C}$ .



**Figure 3.** Effect of TX-100 concentration on the absorbance of PAPT-Ni(II) complex. Conditions: final Ni(II) ion concentration was  $0.50 \text{ mg L}^{-1}$ ; [PAPT] =  $0.001171 \text{ M}$ ; pH =  $10.2$  at  $25 \text{ }^\circ\text{C}$ .

Experimental results demonstrated that the optimal reaction pH value for nickel with PAPT was  $10.2$  in a micellar system, as shown in Figure 4.

### Effect of chelate (PAPT) concentration

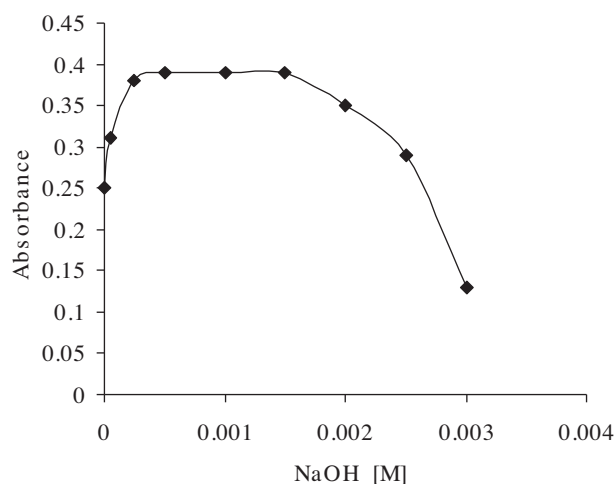
The PAPT reagent concentration was varied under otherwise identical conditions ( $0.50 \text{ mg L}^{-1}$  metal ion,  $0.001 \text{ M NaOH}$ ,  $1.0 \text{ mL}$  of  $10\%$  TX-100 (v/v)). Figure 5 shows the effect of the reagent PAPT concentration on the absorbance of the PAPT-Ni(II) complex within a range of from  $7.8 \times 10^{-5}$  to  $2.3 \times 10^{-3} \text{ M}$ . An increase in reagent concentration enhanced the absorbance up to a concentration of from  $3.9 \times 10^{-4}$  to  $1.5 \times 10^{-3} \text{ M}$ , after which a decrease was observed. For up to  $10 \text{ mg}$  of Ni(II),  $1.5 \times 10^{-3} \text{ M}$  reagent solutions were enough for complete reaction. Therefore, a final PAPT concentration of  $1.5 \times 10^{-3} \text{ M}$  was selected as optimum and utilized in the recommended procedure.

### Stability of the chromogenic system

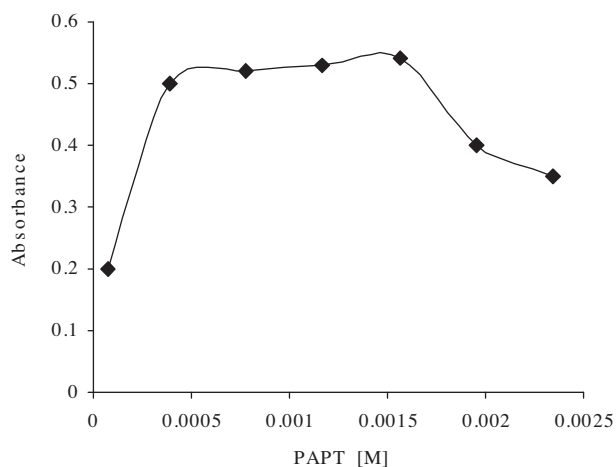
The absorbance of the PAPT-Ni(II) chromogenic system reaches a maximum value within  $10 \text{ min}$  at room temperature and remains stable for at least  $24 \text{ h}$ . The temperature did not affect the stability of the complex at up to  $50 \text{ }^\circ\text{C}$ .

### Calibration graph and sensitivity

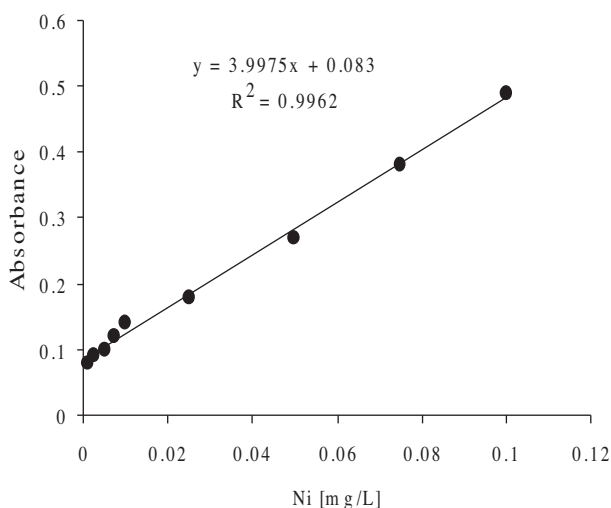
The effect of metal concentration was studied over  $0.001\text{-}1.0 \text{ mg L}^{-1}$ , distributed in 2 different sets ( $0.001\text{-}0.10$  and  $0.10\text{-}1.0 \text{ mg L}^{-1}$ ) for convenience of measurement. The calibration graph (Figures 6a and 6b) was



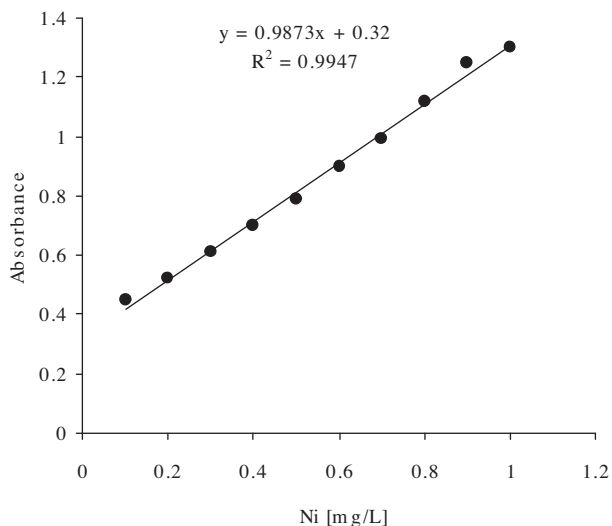
**Figure 4.** Effect of NaOH concentration on the absorbance of PAPT-Ni(II) complex. Conditions: final Ni(II) ion concentration was  $0.50 \text{ mg L}^{-1}$ ; [PAPT] =  $0.001171 \text{ M}$ , [TX-100] =  $1.0\%$  (v/v); pH = 10.2 at  $25 \text{ }^\circ\text{C}$ .



**Figure 5.** Effect of reagent (PAPT) concentration on the absorbance of PAPT-Ni(II) complex. Conditions: final Ni(II) ion concentration was  $0.50 \text{ mg L}^{-1}$ ; [TX-100] =  $1.0\%$  (v/v); pH = 10.2 at  $25 \text{ }^\circ\text{C}$ .



**Figure 6a.** Linear calibration graph from  $0.001$  to  $0.1 \text{ mg L}^{-1}$  of Ni(II). Conditions: [PAPT] =  $0.001171 \text{ M}$ , [TX-100] =  $1.0\%$  (v/v); pH = 10.2 at  $25 \text{ }^\circ\text{C}$ .



**Figure 6b.** Linear calibration graph from  $0.1$  to  $1.0 \text{ mg L}^{-1}$  of Ni(II). Conditions: [PAPT] =  $0.001171 \text{ M}$ , [TX-100] =  $1.0\%$  (v/v); pH = 10.2 at  $25 \text{ }^\circ\text{C}$ .

constructed following the general procedure. The absorbance was linear for  $0.5\text{-}2 \text{ mg L}^{-1}$  and  $0.001\text{-}1.00 \text{ mg L}^{-1}$  of Ni(II) in organic and surfactant media, respectively. The linear regression equation was  $A = 3.9877C_{Ni} + 0.0837$  with a correlation coefficient of  $r = 0.9975$  for the concentration range of  $0.001\text{-}0.1 \text{ mg L}^{-1}$  and  $A = 0.9873C_{Ni} + 0.32$  with a correlation coefficient of  $r = 0.9962$  for the concentration range of  $0.1\text{-}1.0 \text{ mg L}^{-1}$  of nickel, where  $A$  = absorbance and  $C_{Ni}$  = the concentration of Ni(II) in  $\text{mg L}^{-1}$ . Beer's law was obeyed in



the range of 0.001-1.00 mg L<sup>-1</sup> of Ni(II). From the slope of the calibration graph, the molar absorptivity for PAPT-Ni(II) in TX-100 was found to be  $2.41 \times 10^5$  and  $5.79 \times 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup> for 0.001-0.1 and 0.1-1.0 mg L<sup>-1</sup>, respectively, as compared to  $3.0 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup> in its absence, under optimized conditions. The limit of detection for the PAPT-Ni(II) complex (based on  $3\sigma$  of blank absorbance/slope) was found to be 0.0008 mg L<sup>-1</sup> using the micellar enhancement reagent. The optimized parameters are summarized in Table 1. This proposed PAPT method is simple and rapid (nonextractive), convenient, and more selective relative to the existing spectral absorption methods<sup>25,27-31</sup> for the determination of nickel.

**Table 1.** Analytical parameters obtained after optimization.

Selected parameter		Micellar system	Organic system <sup>13</sup>
pH		10-12	8-9
Surfactant		TX-100, 1.0% (v/v)	Chloroform
Reagent (PAPT) M		0.001171	0.0039
Reagent (PAPT) %		0.0075	0.025
Time for reaction, min		10	10-15
Temperature °C		20-40	25
Calibration equation	0.001-0.1 mg L <sup>-1</sup>	Abs = 0.9873C + 0.32	NR*
	0.1-1.0 mg L <sup>-1</sup>	Abs = 3.9975C + 0.083	NR*
Wave length (nm)		430	400
Linear range (mg L <sup>-1</sup> )		0.001-1.0	0.5-2.0
Regression of calibration	0.001-0.1 mg L <sup>-1</sup>	0.9962	NR*
	0.1-1.0 mg L <sup>-1</sup>	0.9947	

\*NR: not reported

## Determination of PAPT-Ni(II) complex stoichiometry

Job's method of continuous variation<sup>32</sup> was applied for identifying the composition of the predominant complex. Equimolar  $1 \times 10^{-4}$  M solutions of nickel and PAPT were prepared and the classical procedure followed. The composition of the PAPT-Ni(II) complex was found to be 2:1.

## Interference study

The interference study was performed by analyzing fixed concentrations of Ni(II) ( $0.50 \mu\text{g mL}^{-1}$ ) in the presence and absence of different concentrations of each interfering ion. The reagent PAPT is a nonselective photometric reagent; its selectivity is improved by the selection of an appropriate pH (i.e., alkaline media). In addition, whereas the absorption maxima of many metal ions with PAPT complexes are at 410 nm, the PAPT-Ni(II) complex absorbs at 430 nm. The tolerance limits were taken as the concentration in mg L<sup>-1</sup> causing a relative error of 5% or less in the concentration of analyte. The tolerance limits for all ions examined are given in Table 2. A number of cations do not interfere, even when present at 50- to 100-fold excess in concentration.

**Table 2.** Effect of foreign species on proposed determination of nickel ion.

Species	Tolerance ratio (folds per mg L <sup>-1</sup> )
I, PO <sub>4</sub> , SCN	1000
Oxalate, Fe(II)/(III), Co(II)	250
Azide, Be(II), Br, F	
PO <sub>4</sub> <sup>3-</sup>	200
Al(III), AsO <sub>3</sub> <sup>3-</sup> , ascorbic acid, Ba <sup>2+</sup>	100
CO <sub>3</sub> <sup>2-</sup> , Cl <sup>-</sup> , NO <sub>3</sub>	
Tartrate, SO <sub>4</sub> <sup>2-</sup> , sulfide, Sb(III), Ag <sup>+</sup>	
Ca <sup>2+</sup> , Cr(III&VI)	
Ce(III&IV), Mn(II&VII), Mg(II), W(VI)	
Zn(II), Ga(III), Au(III), K <sup>+</sup>	
Se(II), Na <sup>+</sup> , Hg(II)	
Pb(II), Mo(VI), Pd(II), Sn(II), Tl(I), Cu(II)	50
Cd(II), In(III), 1,10-phenanthroline	25
EDTA	

Conditions: Final Ni(II) ion concentration was 0.50 mg L<sup>-1</sup>; [PAPT] = 0.001171 M, [TX-100] = 1.0% (v/v); pH = 10.2 at 25 °C.

## Applications

### Determination of Ni (II) in water and synthetic samples

In order to test the applicability of the proposed method to the analysis of real samples, the method was applied to Ni(II) ions in environmental water samples collected from Manchar Lake and a domestic tap. Spiked samples were analyzed by the proposed method and the results are summarized in Table 3. A synthetic mixture was also prepared to validate the method in the presence of all ions mentioned in Table 4 and to calculate the percentage recovery. EDTA was added to assess whether it masked the Ni(II) ion to form a complex with PAPT or not, but the excellent percentage recovery showed that it did not affect the complexation between Ni(II) and PAPT. Results of the analysis of the synthetic mixtures are shown in Table 4.

**Table 3.** Determination of nickel in water sample ( $\mu\text{g L}^{-1}$ , n = 3).

Samples	Sample source	Added	Ni	Recovery (%) $\pm$ SD
S1	Lake water	0.0	34.3	96 $\pm$ 5.3
		5.0	37.7	
S2	Tap water	0.0	0.0	104 $\pm$ 4.2
		5.0	5.2	

**Table 4.** Determination of nickel in synthetic mixture.

Sample	Composition of mixtures, mg L <sup>-1</sup> (20 mg L <sup>-1</sup> for all added metal ions)	Ni(II), mg L <sup>-1</sup>		Recovery (%)
		Added	Found	
A	Ni <sup>2+</sup>	0.50	0.49	98 ± 0.5
		0.80	0.80	100 ± 0.0
B	Ni <sup>2+</sup> + Ca <sup>2+</sup> + Na + K	0.50	0.5	100 ± 0.0
		1.00	0.98	98 ± 0.5
C	Ni <sup>2+</sup> + Ca <sup>2+</sup> + Na + K + Cr <sup>3+</sup> + Ba + Pb	0.50	0.49	98 ± 0.6
		1.00	1.00	100 ± 0.0
D	Ni <sup>2+</sup> + Ca <sup>2+</sup> + Na + K + Cr <sup>3+</sup> + Ba + Pb + Mg + AsO <sub>3</sub> <sup>3-</sup> + NO <sub>3</sub>	0.50	0.52	
		1.00	0.97	97 ± 1.8
E	Ni <sup>2+</sup> + Ca <sup>2+</sup> + Na + K + Cr <sup>3+</sup> + Ba + Pb + Mg + AsO <sub>3</sub> <sup>3-</sup> + NO <sub>3</sub> + Mo(VI) + Sn <sup>2+</sup> + EDTA (200)	0.50	0.51	100 ± 1.8
		1.00	0.95	100 ± 1.8

### Determination of Ni(II) in food samples

Nickel ions were analyzed in food samples such as chocolate, candy, soft drinks, and juices that were obtained from a local market in Hyderabad. The results of the analyses are summarized in Table 5. Nickel ion was successfully determined in all food samples by the proposed method with an acceptable standard deviation (0.02-0.35 mg L<sup>-1</sup>). The results obtained by the proposed method were compared to those obtained from atomic absorption analysis. The major source of Ni in chocolate may be the use of hydrogenated vegetable oil for its preparation.

**Table 5.** Determination of nickel in food samples.

Samples	Ni %RSD <sup>a</sup>	Ni (AAS) %RSD <sup>b</sup>
Juice and soft drink (mg L <sup>-1</sup> )		
S1	0.455 ± 0.058	0.383 ± 0.036
S2	0.102 ± 0.020	0.095 ± 0.011
S3	0.253 ± 0.120	0.192 ± 0.093
S4	0.145 ± 0.031	0.075 ± 0.007
Chocolate and candy (μg g <sup>-1</sup> )		
S1	5.12 ± 0.35	4.33 ± 0.25
S2	3.89 ± 0.25	3.55 ± 0.22
S3	2.02 ± 0.18	1.45 ± 0.13

%RSD: Relative standard deviation.

<sup>a</sup>Determined by proposed method (n = 3).

<sup>b</sup>Determined by atomic absorption spectrophotometry (n = 3).

Table 6 compares the analytical parameters for various reported spectrophotometric methods and the proposed method for the determination of Ni(II), showing the superiority of the present method over existing methods.

**Table 6.** Comparison of some spectrophotometric determination methods for nickel.

Reagent	Medium/ solvent	Interfering ions	$\lambda_{\max}$ nm	$\epsilon$ , $M^{-1} \text{ cm}^{-1}$	Linear range, $\mu\text{g mL}^{-1}$	Ref
5-Me-BTAMB	Aqueous, SDS	Cu(II), Co(II), Pd(II), Ag(I), Zn(II), Fe(II)	640	$13.2 \times 10^4$	0.0-0.4	27
6-Me-BTAMSB	Aqueous, SDS	Cu(II), Co(II), Ti(IV) Cu(II), Co(II),	620	$8.22 \times 10^4$	0.0-0.6	28
QADP	Chloroform	Cd(II), V(V) ) Zn(II), Fe(III)	574	$12.4 \times 10^4$	0.04-0.72	29
PANS	Chloroform	Cu(II), Co(II), Pd(II), Mn(II), Zn(II), Fe(III)	570	$5.6 \times 10^4$	0.1-1.0	30
QADEAA	Aqueous, SDS	Co(II), Ag(I)	595	$13.8 \times 10^4$	0.01-0.40	31
PAN	Aqueous, Tween 80	Co(II)	569	$4.62 \times 10^4$	0.03-1.80	21
PAPT	Chloroform	Co(II), Cd(II), V(V), Zn(II), Fe(III)	400	$2.7 \times 10^4$	0.8-2	13
PAPT	TX-100	No interference	430	$2.41 \times 10^5$	0.001-0.1	This work
				$5.79 \times 10^5$	0.1-1.0	

**5-Me-BTAMB:** 2-[2-(5-methylbenzothiazolyl)azo]-5-dimethylaminobenzoic acid

**6-Me-BTAMSB:** [2-(6-methylbenzothiazolyl)azo]-5-N-ethyl-N-sulfomethyl) aminobenzoic acid

**QADP:** 2-[2-(4-methylquinolyl)azo]-5-diethylaminophenol

**PANS:** 1-(2-pyridylazo)-2-naphthol-6-sulfonic acid

**QADEAA:** 2-(2-quinolylazo)-5-diethylaminoaniline

**PAN:** 1-(2-pyridylazo)-2-naphthol

**PAPT:** picolinaldehyde-4-phenyl-3-thiosemicarbazone

## Conclusion

A simple, economical, and environmentally friendly spectrophotometric method for the trace determination of nickel is described here; it is more sensitive than the existing spectral methods. The molar absorptivity for PAPT-Ni(II) in TX-100 was found to be  $2.41 \times 10^5$  and  $5.79 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$  for 0.001-0.1 and 0.1-1.0  $\text{mg L}^{-1}$ , respectively, as compared to  $3.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  in its absence. The use of aqueous TX-100

solution not only serves to remove the need for organic solvents but also enhances the analytical signal and consequently the sensitivity of method. With the use of a micellar system, less of the PAPT chelating reagent is required. The method is applicable to complex matrices and serves as a single-step, quick method that requires no clean-up process for interfering ions.

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