

Nickel(II) Determination by Spectrophotometry Coupled with Preconcentration Technique in Water and Alloy Samples

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A micro organism *Agrobacterium tumifaciens* as an immobilized cell on a solid support was presented as a new biosorbent in a simple and sensitive spectrophotometry determination of Ni(II) in various samples using 4-hydroxy benzaldehyde-4-bromophenyl hydrazone as a color developing agent (λ_{max} 497 nm) at pH 4.0 ± 0.2 . Beer's law was obeyed over the range of 0.01-0.1 $\mu\text{g L}^{-1}$. The molar absorptivity and Sandell's sensitivity were $1.285 \times 10^5 \text{ L mol}^{-1}\text{cm}^{-1}$ and $0.007245 \mu\text{g cm}^{-2}$ respectively. Under these conditions, the preconcentration factor obtained was 82, and the detection limit achieved was $0.05 \mu\text{g L}^{-1}$. The detailed study of various interfering ions made the method more sensitive and selective. The recovery of Ni(II) from various samples range from 97.75 to 99.35%. The present method was successfully applied for the determination of Ni(II) in spiked, natural water and alloy samples. The proposed method was compared with reported methods in terms of Student's 't'-test and Variance ratio 'f'-test which indicates that there is no significant difference between proposed and literature method at 95% confidence level.

Key Words : Nickel(II), 4-Hydroxy benzaldehyde-4-bromophenyl hydrazone (4-HBBPH), Solid phase extraction, Spectrophotometry, XAD-2010

Introduction

Nickel in nature is mainly available in the form of ores like Gernirite, Magnesium nickel silicate of variable composition. The important oxidation state of nickel is Ni(II). In olden days nickel is used as a coinage metal. Now days nickel becomes an important element, not only for industry, but also for biological systems. In rapidly expanding analytical fields, such as environmental, biological and material monitoring for trace metals. Nickel is used in ceramic industry, and also used in batteries which are in convincing to the environment. A dietary deficiency of nickel, leading to various pathological manifestations. Nickel is relatively non toxic element. The high concentration of the nickel does show serious health hazards. The high incident of respiratory track moplacia and dermatitis has been observed when exposed by nickel refineries. In views of this separation and determination of nickel from associated elements is indispensable. Therefore, it is very important to develop sensitive, rapid and economical method for quantitative determination of it's trace amount in various samples of environmental importance. Several analytical techniques have been monitored for the determination of trace level nickel(II), it includes atomic absorption spectrometry,¹⁻⁴ Inductive coupled plasma emission spectrometry⁵⁻⁷ and X-Fluoresces spectrometry^{8,9} were reviewed. A few reagents are available for the spectrophotometric¹⁰⁻¹⁸ determination of nickel(II) as shown in Table 1.

The above reported reagents suffer from several disadvantages such as, poor sensitivity, selectivity, required special conditions for the formation of complexes with the

reagents is less stable and few are commercial.

In this paper, biosorption of nickel by *Agrobacterium tumifaciens* has been investigated. A *tumifaciens* was selected because it is not a hazards bacterium for human. A *tumifaciens* is a Gram-Negative, non sporing motile, rod-shaped bacteria, closer related to *Rhizobium*, heich forms nitrogen-fixing nodules on clover and other leguminous plants and isolated from soil, stems and roots of plants.

Amberlite XAD-2010 is a member of Amberlite XAD adsorption resin family.¹⁹⁻²¹ It is poly(styrene-divinylbenzene) copolymer. It has high adsorption capacity like other members of this family.²² It has been used for the solid phase extraction of biomolecules and pharmaceuticals.^{19,22} Based on the literature survey, Amberlite XAD-2010 is not used for the solid phase extraction prior to spectrophotometric determination of metal ions.

In this investigation the novel, facile and sensitive sorbent, *Agrobacterium tumifaciens* was successfully anchored to Amberlite XAD-2010 resin for the preconcentration of Ni(II) in water and alloy samples. Optimum experimental conditions were investigated with respect to a standard solution of the same matrix, in order to examine the possibility to obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions. Under these conditions, the preconcentration factor obtained was 82, and the detection limit achieved was $0.05 \mu\text{g L}^{-1}$. The method was successfully applied for the spectrophotometric determination of Ni(II) in various water and alloy samples using newly synthesized analytical reagent 4-hydroxybenzaldehyde-4-bromophenyl hydrazone (4-HBBPH).

Table 1. Comparison of analytical parameters of the present methods with others spectrophotometric method for the determination of Ni(II)

Reagent	λ_{\max} (nm)	Σ ($\times 10^{-4}$) ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)	Remarks	Ref
5-(6-Bromo-2-benzothiozolyazo)-8-hydroxyquinoline	580	1.4	Many metal ions interfere and very poor sensitive	10
4-(5-nitro-2-thiozolyazo)resorcinol	540	1.0	Low sensitivity strong alkali medium, toxic KCN as masking agents	11
2-(5methyl-2-isoxazol)-3-azo-4chlorophenol	535	2.3	Low sensitivity and poor selective	12
3,5-dichloro-2-pyridylazo-2,4-diaminotoulene	270	1.3	Low sensitivity and high reagent consumption	13
p-azobenzene diammoazo benzene sulphonic acid	540	1.07	Many metals interfere and lack of sensitivity	14
2-carboxy-2-hydroxy-5-methylazobenzene	485	7.3	Poor selective and Many metal ions interfere	15
ATT	500	–	High reagent consumption and poor selectivity	16
Azocalix(4)arene	580	–	Very poor selectivity and less sensitivity	17
6-Me-BTAESB	406	–	Low sensitivity	18
4-Hydroxy benzaldihyde 4-bromo phenyl hydrazone	497	–	Sensitive, selective, facile, economical reagent, free from interference and contamination	Present work

Experimental Section

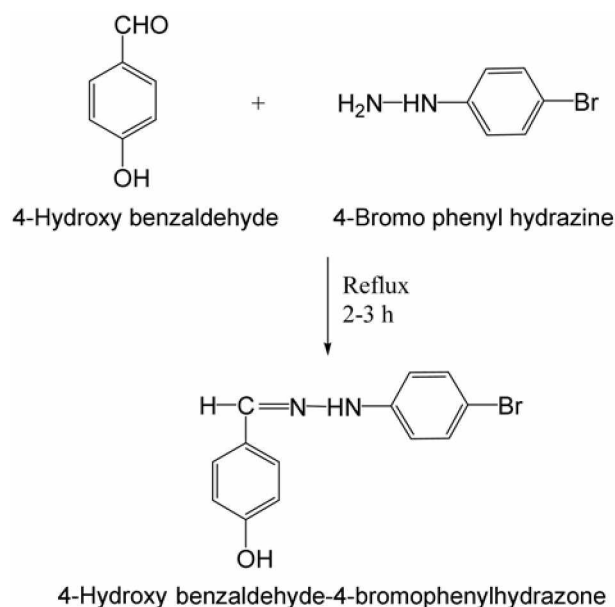
Reagents. All reagent used were of analytical reagent grade. Double distilled water was used throughout the experiment. Solutions containing 1.0 M of nitric acid (Merck, Mumbai, India) were used as eluent. A stock solution of Ni(II) (0.01 M) was prepared by dissolving 2.6288 g of Nickel sulfate (E-Merck, Germany) in double distilled water in 1000 mL standard flask. Nickel(II) working standard stock solutions were prepared freshly by appropriate dilution of the standard stock solution with double distilled water. 0.1 M of reagent solution was prepared by dissolving 0.346 g of reagent in 100 mL of 40% DMF. This solution is further diluted, when ever necessary with double distilled water. Amberlite XAD-2010 (specific surface area $660 \text{ m}^2 \text{ g}^{-1}$ and bead size, 20-60 mesh) and it was purchased from (E-Merck, Germany).

Acetate buffer was prepared by dissolving 8.2 g sodium acetate in 800 mL water. It was adjusted to pH 4.0 with high purity glacial acetic acid. It was stored in clean 1L (metal free) polyethylene bottle.

Apparatus. A HITACHI U 2001 spectrophotometer with 1.0 cm matched quartz cells were used for all absorbance measurements. An Elico Li-129 model pH meter with combined glass-calomel electrode was used for all pH measurements. Elemental analysis was carried out on Perkin-Elmer 240 elemental analyser.

Synthesis of 4-hydroxy benzoldehyde-4-bromo phenyl hydrazone. Equimolar solution of 4-hydroxy benzaldehyde and 4-bromophenyl hydrazine in aqueous medium were refluxed for 2-3 h, and the contents were cooled to room temperature for separating the formed solid product. The solid was filtered, washed with water, dried and recrystallized from hot aqueous methanol (m.p. 163°C , 89% yield as shown in Scheme 1).

Elemental analysis calculated for $\text{C}_{14}\text{N}_2\text{H}_{13}\text{OBr}$. $\text{C}_{13}\text{N}_2\text{H}_{10}\text{Br}$. FAB-MS (m/z) -302.15 (C = 51.67%, N = 9.27%, H = 3.37%) was found to be C = 51.32%, N = 9.57%, H = 3.22%. The band at 1130.01 cm^{-1} is due to the -OH group and absorption bands at 1610.34 cm^{-1} , 1530.18 cm^{-1} and



Scheme 1

1445.83 cm^{-1} are due to the C=N group of reagent. The absorption band at 590.27 cm^{-1} is due to C-Br on benzene ring.

Preparation of bacterial biomass. A solid medium (nutrient agar) was prepared by mixing 10 g of meat extract, 10 g of peptone, 5 g of NaCl and 150 g of this nutrient agar (5 g) was dissolved with water and diluted to 200 mL. The mixture was sterilized in the previously sterilized Petri dish at $120 \pm 1^\circ \text{C}$ and leaved to become solid the bacterium. A tumifacients. was inoculated on the solid medium and stored at $28 \pm 2^\circ \text{C}$ in order to growth bacterium. Liquid medium was prepared by mixing the substances mentioned above expect agar and sterilized at $120 \pm 1^\circ \text{C}$ for about 30 min. Firstly, in order to prepare the starter culture, A tumifacient grown on the solid medium was impliated to 100 mL of liquid medium. Then, it is incubated for 48 h at $28 \pm 2^\circ \text{C}$ on a shaker (about 200 rpm) for preparing the experimental culture. 200 mL of liquid medium was prepared and

inoculated with 10 mL of the starter culture and incubated on shaker for 48 h at 28 ± 2 °C. Then, the bacterium grown in the experimental culture was separated from the media using centrifugation ($5000 \times g$ for 5 min) to isolate the biomass. In order to obtain the dead and dry bacteria, 10 mL of 0.1 mol/l HCl was added to the isolated biomass after 10 min, the mixture was centrifuged and the acid solution was discarded. This procedure was repeated three times and then followed by rinsing the acid washed biomass in distilled water. These rinsed bacteria were again centrifuged and the resulting biomass was lyophilized to yield a dry bacterial powder.

Immobilisation of bacteria onto Amberlite XAD-2010. Commercial available Amberlite XAD-2010 was prepared as substrate by washing successively with methanol, water, 1 mole of HNO_3 and water respectively, to remove organic and inorganic contaminants. Then the immobilization of the Amifaciants on the substrate was performed as follows. 150 mg of dry and bacteria powder was mixed with 1 g of Amberlite XAD-2010. The mixture was wetted with 2 mL of double distilled water and thoroughly mixed. After mixing, the paste was heated in an oven at 105 °C for 1 h to dry the mixture. The wetting and dry step was repeated to maximize the contact between a tumifacient and Amberlite XAD-2010, thereby improving the immobilization efficiency. Then the product obtained was ground to get original size (20-40 mesh) and used as an adsorbent.

General procedure. Agro bacterium tumifaciants (1.0 g) was first packed in a glass column (10 cm length \times 10 mm internal diameter) between frits, using the method recommended by the manufacturer. The column was treated with 1 M HNO_3 (25 mL) and washed with double distilled water until free from acid. A suitable aliquot of the sample solution containing Ni(II) in the concentration range of 0.01-0.1 $\mu\text{g L}^{-1}$ was passed through the column after adjusting its pH to the optimum range (acetate buffer of pH 4.0 ± 0.2) with a flow rate of 2.0-4.0 mL min^{-1} . The column was washed with double-distilled water to remove the free metal ion. The bound metal ion Ni(II) was stripped from the column with 1 M HNO_3 (8 to 10 mL) passed at a flow rate of 2.0-4.0 mL min^{-1} . The eluent was then mixed with 0.1 M 4-hydroxy-benzaldehyde-4-bromophenyl hydrazine to form a red colored product, which was measured spectrophotometrically at wavelength 497 nm against reagent blank as shown in Figure 1.

Procedure for the determination of Ni(II) in spiked water samples. The extraction efficiency was studied using spiked water samples for the recovery of nickel. Doubly distilled water was spiked with known amounts of metal standards (20-80 ng L^{-1}) and allowed to stand overnight. The concentration of nickel in spiked water samples was determined and results were summarized in Table 2.

Procedure for the determination of Ni(II) in natural water samples. Different water samples (river water and Tap water) were collected from various places in and around Tirupati, A.P., India. The samples (150 mL) were stored at 0-5 °C in metal free polyethylene bottles. Water samples were filtered through Whatman filter paper no. 41 and clean

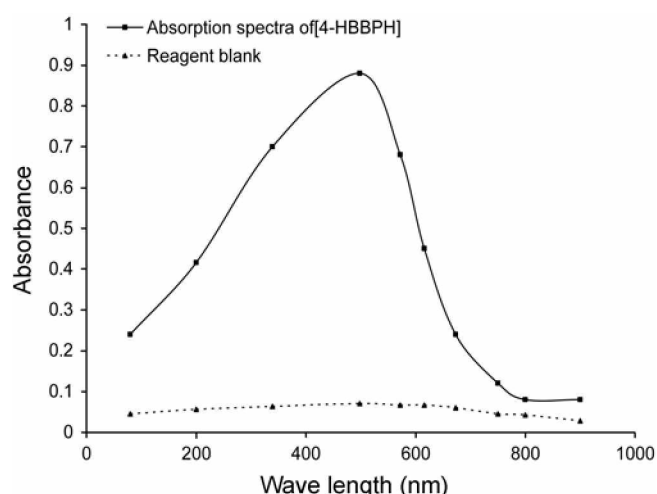


Figure 1. Absorption spectra of [Ni(II)-4-Hydroxy benzaldehyde 4-bromo phenyl hydrazone] complex system.

Table 2. Recovery of nickel from various concentrations of spiked water samples using Preconcentration spectrophotometric method

	Concentration of nickel added (ng L^{-1})	
	Proposed Method	Reported Method ²³
20		
Found (ng L^{-1})	19.55	19.78
Recovery (%)	97.75	98.90
S.D ^o (%)	± 0.045	± 2.54
t&f-test	0.872, 0.069	
40		
Found (ng L^{-1})	39.62	39.72
Recovery (%)	99.02	99.30
S.D ^o (%)	± 0.048	± 2.54
t&f-test	0.359, 0.019	
60		
Found (ng L^{-1})	59.66	59.78
Recovery (%)	99.35	99.63
S.D ^o (%)	± 0.129	± 2.54
t&f-test	0.119, 0.221	
80		
Found (ng L^{-1})	79.85	79.91
Recovery (%)	98.12	99.88
S.D ^o (%)	± 0.146	± 2.54
t&f-test	0.129, 0.009	

^oRecovery (%) and Standard deviation for ten determinations.

Table 3. Determination of Nickel in natural water samples

samples	Proposed method		Reported method ¹⁶	f-test	t-test
	Found	Recovery ^o	Recovery ^o		
River water	62.8	99 ± 1.8	98 ± 1.8	1.0	0.14
Tap water	20.2	98 ± 1.8	96 ± 2.2	0.75	0.80

^oRecovery(%), \pm Standard deviation for Ten determinations (n = 10)

solution was collected into 250 mL beaker. The contents were diluted up to the mark with double distilled water. 15 mL of this solution was further diluted to get working solution for

Table 4. Determination of Nickel in a certified standard alloy samples

Samples	Proposed method
Steel(GBW01329) ^a	0.175 ± 0.009
Steel(GBW08532) ^b	0.420 ± 0.006

^aC(0.188), Si(0.305), Mn(1.44), P(0.013), S(0.046), Cr(0.389), Ni(0.166), Cu(0.277), V(0.158), Ti(0.285), Al(0.112), B(0.023), ^bC(0.506), Si(1.96), Mn(0.755), P(0.034), S(0.012), Cr(0.102), Ni(0.314), Cu(0.126), V(0.241), Ti(-), Al(0.201), B(0.019). ^cMean ± Standard deviation (n = 10)

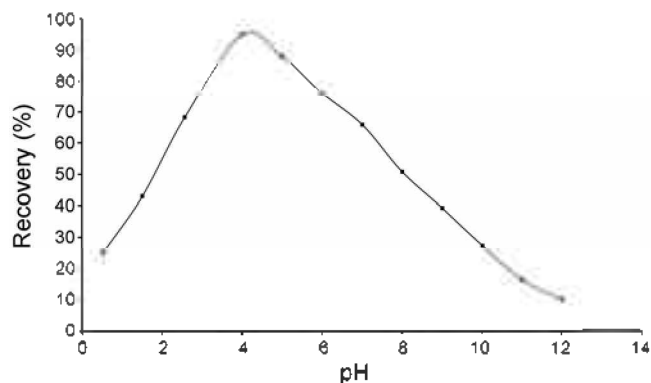
determination of Ni(II) as described in above procedure and compared with the reported method²³ with statistical validation. The results were summarized in Table 3.

Procedure for the determination of Ni(II) in alloy samples. 1 g of alloy sample was dissolved in a 10 mL of aqua regia, and evaporated to minimum volume, extracted with 10 mL of 2 M HNO₃ and then diluted with double distilled water to a suitable volume (10 mL) it serves as stock solution, the experimental solution was prepared by pipetting out 10 mL of the stock solution in to the 100 mL standard flask and the solution was made up to the mark with distilled water. A known volume of this solution was placed in a 10 mL standard flask and made up to the mark and analysed as per general procedure mentioned earlier. The results were shown in Table 4.

Results and Discussion

Effect of pH. The effect of pH on the peak height of Ni(II) at different concentrations was investigated with a fixed 0.1 M 4-hydroxybenzaldehyde-4-bromophenyl hydrazone concentration. The pH of acetate buffer was taken in the range of 3.0-7.0 and the peak height wave measured for each concentration level of Ni(II). At all concentration levels of Ni(II) maximum peak height were found between 3.5 to 4.5. Therefore, a pH 4.0 ± 0.2 of acetate buffer system was chosen throughout in the study as represented graphically in Figure 2.

Analytical parameters. Beer's law was obeyed in the concentration range 0.01 to 0.1 μg L⁻¹ of Ni(II). The molar absorptivity and Sandell's sensitivity of complex at pH 4.0 was calculated as 1.285 × 10⁵ M and 0.007245 μg cm⁻² respectively. The correlation coefficient (r) for the experimental data is 0.9996 as shown in Table 5.

**Figure 2.** Effect of pH on the complexation of [Ni(II)-4-Hydroxy benzaldehyde 4-bromo phenyl hydrazone].**Table 5.** Optical characteristics and precision data

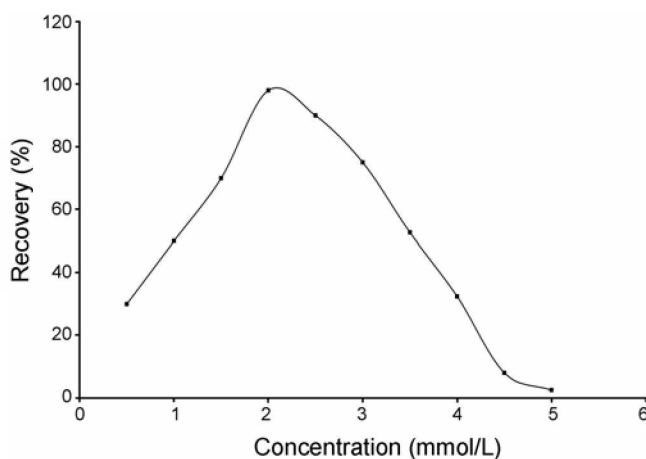
Parameters	(Ni(II)-HBBPH)
Color	Red
λ_{max} [nm]	497
Stability	36 h
Beer's law range [μg mL ⁻¹]	0.01-0.1
Molar absorptivity [L mol ⁻¹ cm ⁻¹]	1.285 × 10 ⁵
Sandell's sensitivity [μg cm ⁻²]	0.007245
Regression equation (Y) ^b	
Slope ^a	0.023
Intercept ^b	0.0167
Correlation coefficient ^c	0.9996
Relative Standard deviation [%] ^c	0.2981
Detection Limit, μ (μg mL ⁻¹)	0.035
% error	0.023

^aExperiments performed under optimized conditions (see text) with 5 mL of 0.01 M NiSO₄ 6H₂O solution. ^bY = ax + b, where x is the concentration of Ni(II) in mg mL⁻¹. ^cn = 10

Efficiency of elution. The choice of selecting an eluent was a difficult problem. In addition to an eluent should not destroy the solid support in the column. Hence, for the determination of the preconcentrated Ni(II) by spectrophotometry, the elution was performed with 0.5-3.0 M HNO₃ and is dependent on the concentration of HNO₃ as shown in Figure 3, quantitatively Ni(II) was achieved for 4 mL of 1 M HNO₃. Hence, 4 mL of 1 M HNO₃ was chosen the optimum eluent for the Ni(II) determination and recoveries were higher than 99% and the results are shown in Figure 3.

Effect of volume of a sample on elution. The effect of the sample volume on the extraction of Ni(II) was studied by taking different volumes of water samples in the range of 100, 200, 300, 400, 500 and 600 mL. As the volume of sample increases, the recovery of metal ion increases gradually upto 500 ml to obtain higher than 99%. Hence, the 500 mL of water sample was chosen for the present study.

Effect of the reagent concentration. The effect of concentration of 4-hydroxybenzaldehyde-4-bromophenyl hydrazone on the peak height was investigated at pH 4.0 ± 0.2 by using 2.0 and 3.5 μg L⁻¹ Ni(II) solutions. The concentration

**Figure 3.** Concentration HNO₃ on elution of Ni(II).

of 4-hydroxybenzaldehyde-4-bromophenyl hydrazone was varied in the range 0.01 M-1.0 M. Maximum peak height was obtained at a concentration of 0.1 M of 4 mL 4-hydroxybenzaldehyde-4-bromophenyl hydrazone as color developing reagent for lower concentration level of Ni(II) solution.

Effect of volume of an eluent on percentage of elution of Ni(II). The effect of volume of an eluent on elution of Ni(II) for various water and alloy samples on Agro bacterium tumefaciens measured at 30-35 °C. It can be observed that the percentage of recovery increases with the increase in the volume of eluent to some extent. After increasing the volume of an eluent, the elution percentage slightly decreases. Thus 4.0 mL of 1 M HNO₃ was chosen for 100% recovery of Ni(II) ion.

Ringbom's plot for (Ni(II), 4-HBBPH) Complex. Ringbom's plot is the established standard adopted to know the optimum range of concentration for a system that obeys Beer's law. The plot is drawn between log C of Ni(II) and (1-T) (Where T is the transmittance). The plot has sigmoid shape with a linear segment intermediate absorbance values (0.2 to 0.8) and concentration values (2.0 to 8.0 µg mL⁻¹). The slope of the Ringbom plot from Figure 4 is 0.0833. Hence, the ratio between the relative error in concentration and photometric error 0.1 for concentration of 0.1 M for 1.0% photometric error.

Precision and accuracy. The precision and accuracy of the proposed method was evaluated by the good results which obtained by the reported method. The results were shown in Tables 2 to 4. It reveals that the good correlation between the two methods indicate that the present method is more sensitive than the reported method in literature

Detection limit. Under optimum conditions the detection limits for the determination of Ni(II) in various environmental samples was found 5.0 µg mL⁻¹ for a 500 mL volume Ni(II) in solution.

Calibration graph. The extraction of a typical calibration is $p = 5031c + 4.93$ $r^2 = 0.9998$ (p. peak height; c. concentration). The calibration graph was obtained at the optimum working conditions: 4-hydroxy benzaldehyde-4-bromophenyl hydrazone concentration 0.01 M, sample volume 500 mL; eluent concentration 1 M HNO₃ and volume of eluent 4.0

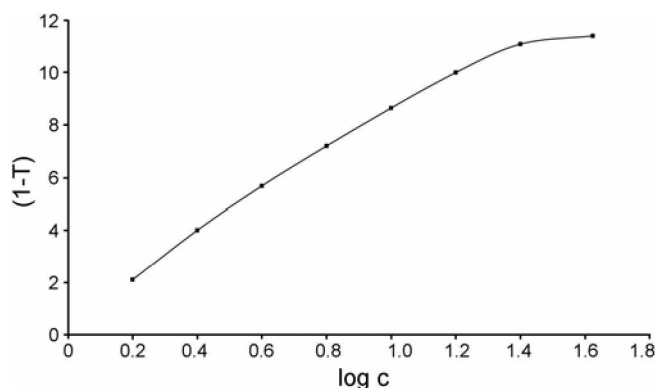


Figure 4. Ringbom's plot of [Ni(II)-4-Hydroxy benzaldehyde 4-bromo phenyl hydrazone] complex.

Table 6. Tolerance limits for the determination of 5 µg of Ni(II) with (4-HBBPH)

Ions	Tolerance limits (µg mL ⁻¹)
NO ₃ ⁻ , K ⁺ , borate, Mg ²⁺	200 ^a
Li ²⁺ , Al ²⁺ , PO ₄ ³⁻ , NO ₂ ⁻ , SO ₄ ²⁻ , ClO ₄ ⁻	20
Ca ²⁺ , Sr ⁺ , IO ₃ ⁻ , BrO ₃ ⁻ , B(III), ClO ₃ ⁻	10 ^b
Mn ²⁺ , Ce(IV), Fe ³⁺ , Mo(VI), Br ⁻	5
Ti(IV), Bi(III), V(V), Cr(VI), Ba ²⁺ , W(VI), U(IV)	1
Cd ²⁺ , Pd ²⁺ , Cr ³⁺ , La ³⁺ -Cl ⁻ , Zn ²⁺ , Cu ²⁺ , Zr(IV)	0.5
Bi(III), Pb ²⁺ , Hg ²⁺ , Sb ³⁺ , Th(IV), Sn(IV), Pd ²⁺	0.2
Se(IV), Te(IV), Au ³⁺ , Ag ⁻	0.1
Co ²⁺	0.03 ^c

^aMasking with 20 µg mL⁻¹ of 0.5% EDTA

mL.

Effect of column performance. In order to examine the long term stability of the support, it was subjected to successive adsorption and desorption cycles (6 runs in a day and the next 6 runs another day, and so on, total 30 runs) by 500 mL of metal solutions through the column. The stability and potential recycle ability of the column containing support was assessed by monitoring the change in the recoveries of the analyte. After 15 runs, the recoveries of the analyte slightly decreased to < 95%.

Effect of foreign species. Various salts and metal ions were added individually to a solution containing 20.0 µg of Nickel and the general procedure was applied. The tolerance limit was set as the amount ion required to cause ± 2% error in Nickel(II) determination. The proposed method is selective and can be used for Nickel(II) determination in various water samples and alloy samples with out any prior separation. The results obtained were given in Table 6.

Applications of the extractive spectrophotometric method for the determination of nickel(II) with reported method. To evaluate the applicability of the proposed preconcentration spectrophotometric method was applied to the determination of Nickel(II) in spiked water, natural water samples were compared with reported method and results were shown in Table 2 and 3. The determination of Ni(II) in alloy samples was compared with SRM values and results were shown in the Table 4. The analytical data summarized in Tables 2 to 4 suggest that the percentage of recovery of Nickel(II) from water and alloys samples ranges from 97.75 to 99.35% which is more reliable and sensitive than the methods reported in literature.

Conclusions

The proposed preconcentration spectrophotometric method is simple, highly sensitive and selective for the determination of Ni(II) in Water and alloy samples. The limit of detection of the proposed method is superior when compared to reported method. The method has additional advantage over reported method owing to it's.

i. Complexing reagent employed in the present method *i.e.* 4-hydroxy benzaldehyde-4-bromophenyl hydrazone was

economical and easy to prepare in an ordinary laboratories.

ii. Proposed method is highly sensitive due to the stabilization of colored complex for more than 36 h formed by interactions of the metal ion with newly synthesized reagent.

iii. Low reagent consumption, elimination of the analytical error, less interference and statistical analysis which made the method to be more sensitive and selective.

iv. *Agrobacterium tumifaciens* used as a biological adsorbent is highly selective with respect to Ni(II) determination.

v. The performance of the column are simple and sensitive to Ni(II) determination by using ecofriendly biological material (*Agrobacterium tumifaciens*).

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