ISSN : 0974 - 7419 Volume 11 Issue 9,10

Analytical CHEMISTRY
An Indian Journal

Trade Science Inc.

Full Paper

ACAIJ, 11(9,10), 2012 [305-310]

Spectrophotometric method for the determination of nickel (II) using PAP on Amberlite XAD-16 in water and food samples

P.Yamini, K.Vijaya Kumar, R.Kishore Kumar V.Govinda, P.Venkateswarlu*
Enviro-Analytical Laboratories, Department of Chemistry, S.V.University, Tirupati - 517502 (INDIA)
E-mail: rayanuthalakishore@gmail.com

Received: 1st April, 2012 ; Accepted: 1st May, 2012

ABSTRACT

The very sensitive, fairly selective spectrophotometric method for the determination of trace amount of nickel with PAP has been developed. PAP reacts in basic media with Nickel (II) to give a blue chelate which has an absorption maximum at 445 nm. The stoichiometric composition of the chelate is 1:2 (Ni-PAP). The reaction is instantaneous and absorbance remains stable for 6days. A polystyrene divinylbenzene resin (Amberlite XAD-16) functionalized by PAP has been synthesized and its sorption properties have been investigated for preconcentration of Ni (II) in natural water and food samples. The analytical parameters including pH, sample volume etc. for the quantitative recoveries of the analyte ions using XAD-16-PAP resin was investigated. The effects of alkaline, earth alkaline ions and some anions on the sorption of analyte ions were also examined. The recovery values were greater than 95%.

KEYWORDS

Spectrophotometry;
Nickel determination;
PAP;
Water and biological samples.

INTRODUCTION

Nickel determination at trace levels is required in severalareas of the science, such as environmentalchemistry,toxicology,geology,biochemistry,etc. Preconcentration methods generally are associated with determination of this metals,because some conventional techniques, e.g. spectrophotometryand flame atomic absorption spectrometry (FAAS), have not adequate sensitivity for these analysis. The use of solid sorbents in preconcentration methods presents several advantagesover liquid–liquid extraction in terms of simplicity, reliability, and the ability to obtain a high enrichment factor[1].Furthermore, it reduces the use of organic solvents that could be toxic and expensive. Many procedures involving nickel preconcentration can be found in literature employing a varietyof materials, such as silica[2-4], activated carbon[5], fullerene[6], naphthalene[7] and Amberlite XAD-2[8,9].An important strategy for metal enrichment is the incorporation of complexing reagents in solid supports to adsorb and preconcentrate metal ions from solutions.The incorporation reduces problems of leaching of the ligand from the support. These supports include silica[10] polyurethane foam[11-13] and polymeric resins[14-17].Modified polymeric resins have been employed in preconcentration and separation methods. Ligands can be coupled on polymeric sorbent through several groups, such as an azo[18-21] or methylene group[22]. Immobilization via an azolinkage is the most commonly employed method. However, this synthetic procedure leaves residual amine groups on the polymer surface as a consequence of incomplete reaction[23,24]. Furthermore, several preconcentration methods employing other groups and ligands to produce powerful sorbents has been described[25]. The environmental pollution of heavy metals caused by industry,traffic, etc. is one of the most important human health problems[26,27]. Solid-phase extraction (SPE) has emerged as a powerful tool for the enrichment/separation of metal ions because of the various advantages it has over other methods, such as higher preconcentration factor, less waste generation, reduced interference of the matrix, consumption of low volume of solvents. Environmental friendly, and easier incorporation into automated analytical techniques easy regeneration and reusability of the solid phase[28-30]. In this respect, SPE has commonly been used as a selective technique for preconcentration/ separation of various inorganic and organic species and enhanced selectivity is achieved because of the discriminatory binding of the analyte to a solid support and accumulated analyte is subsequently eluted with a small volume of solvent.The adsorbents with high surface area are preferred in solidphase extraction of traces of heavy metals[31]. In the last decade, the use of synthetic polymers for this purpose has significantly increased. In this work, a new procedure is proposed for the preconcentration, separation and determination of Ni (II) ion was based on the sorption of analyte metal ions on Amberlite XAD-16 loaded by PAP. Solid phase extraction is an attractive technique because of its notable advantages. The present paper, based on the color reaction of PAP with nickel and the solid phase extraction of the colored chelate with Amberlite XAD-16 describes the development of a highly sensitive, selective and rapid method for the determination of nickel in water and food samples.

EXPERIMENTAL SECTION

Experimental apparatus

Shimadzu AUY 220 digital electronic balance was used for weighing the substances. The pH measurements were made using a pH meter Elico, Model LI-129, India in conjugation with a combined glass and calomel electrode A HITACHI U 2001 spectrophotometer with 1.0 cm matched quartz cells were used for all absorbance measurements.

Chemicals and reagents

All chemicals, regents, and standard individual metal ion stock solutions used in the process of resin synthesis and subsequent metal extractive studies were of analytical grade. Macroporous Amberlite XAD-16 resin beads (divinylpolystyrene, 20–50 mesh, surface area 825m^2 g –1, bead size 0.3–1.2 mm)were procured from Fluka Chemicals. The resin beads were purified by successive washing with4 mol L^{-1} HCl, 2 mol L^{-1} NaOH, and finally with plenty of water. The purified resin was filtered and vacuum-dried prior to usage.

PAP (1.0x10^{-2} *M*) (p-amino phenol)

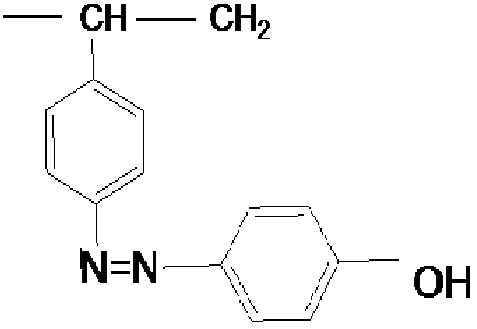
Prepared by dissolving the requisite (0.0109g in 100 mL) amount of PAP (p-amino phenol) (Merck Darmastadt, Germany) in a known volume of methanol. More dilute solutions of the reagent were prepared as required.

Standard solution Ni (II)

A stock standard solution of nickel (0.0262 g of nickel suphate) was dissolved in 100 mL.

Chelating resin and column preparation

Amberlite XAD-16 resin was treated with 1 M nitric acid and 1 M NaOH solutions, and then washed with distilled water until pH of supernatant was neutral. The resin was dried in an oven at 110^{o}C. 0.5 g of the resin was saturated for 2 h with 10 mL of 0.1% (w/v) HCl solution by stirring in a beaker. The chelating resin was filtered, washed with water and dried in an oven at 110^{o}C. Prepared resin was slurried in water and poured into glass column (1 cm in diameter × 10 cm in length) in which the column contains a small amount of glass wool on the disc. The impregnated resin was rinsed with distilled water and conditioned with 10 -15 mL of pH 10 buffer solution prior to passage of the sample solution. The chealating scheme represented in Figure 1.



Scheme 1 : The proposed structure of the AXAD-16 with PAP

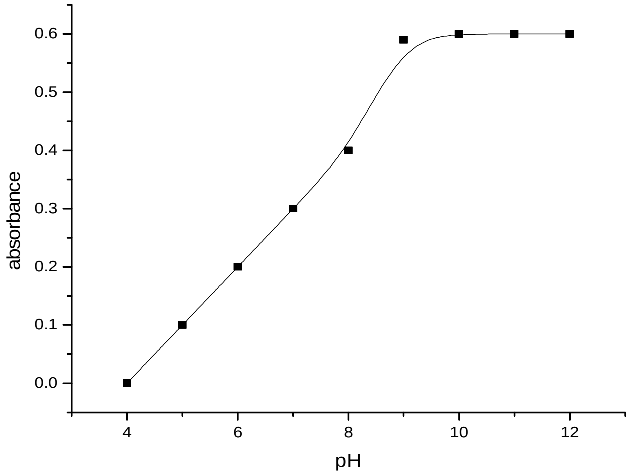


Figure 1 : Effect of pH on the absorbance of Ni (II) ion.

Preconcentration procedure

The glass column (10 cm I .d., length of 15 cm) was fitted with 1.0 g of Amberlite XAD-16 resin coated with PAP. In the lower part of the column, the resin was held by glass ball and a fine layer of glass wool. In the upper part, another layer of glass wool was placed. The sample solution (10-200 ml) containing NI (II) in the concentration range 10-200 mg l^{-1} was taken in 250 ml beaker.. Then the solution was allowed to pass through the column at a flow rate of 2.0ml min^{-1}. Then the sample solution was passed through the column at flow rate of 2.0 ml min^{-1}. After passing this solution the column was washed by 10 ml of distilled water. Thereafter, the metal ions sorbed on the resin were eluted with 10 ml of acetone at a flow rate of 2.0 ml min^{-1} and determined by Spectrophtometry.

Procedure for the determination of Ni (II) in water samples

Different water samples (river water,tap water,, Lake water) were collected from various places in and around Tirupati, A.P., and India. The samples (150 mL) were stored at 0-5 ^{0}C in metal free polyethylene bottles. Water samples were filtered through Whatman filter paper no.41 and clean solution is collected into 250 mL beaker. The contents are diluted up to the mark with double distilled water. 15 mL of this solution is further diluted to get working solution for determination of Ni (II) as described in above procedure. The results were summarized in TABLE 1.

TABLE 1 : Determination of nickel in the water sample.

Samples	Reference method	Found *	RSD %	Recovery (%) (n=5) (µg/L) (Add 1.0 µg nickel)
River water	46.7	48.2	2.5	96
Lake water	22.8	23.2	2.4	102
Tap water	14.9	15.6	2.7	96

Procedure for the determination of Ni (II) in food samples

Natural food samples obtained from supermarkets of Tiruapti. The samples were homogenized and dried overnight at 110^{0}C, and were kept in dry ambient. For the nickel determination in food samples, an alternative dry-ashing sample preparation was carried out for a sample mass of 1.0 g decomposed at 500^0 C for 60 min, followed by a treatment with few drops of concentrated nitric acid or 30% (v/v) hydrogen peroxide and a second step of heating for 45 min as recommended by the ASTM[32]. The analytical data was represented in TABLE 2.

TABLE 2 : Results obtained for the certified reference materials analyzed (*n* = 3)a.

Sample	Nickel found by the methodology proposed (µgg−1)	Certified values (µgg−1)
Rice flour (NIES 10)	0.21 ± 0.04	0.19 ± 0.03
Spinach leaves (NIST 1570)	2.15± 0.12	2.14 ± 0.10
Orchard leaves (NIST 1571)	1.26 ± 0.15	1.3 ± 0.2
Peach leaves (NIST 1547)	0.71 ± 0.04	0.69 ± 0.09

RESULTS AND DISCUSSION

Ni (II) reacts with PAP on amberlite XAD-16 to form a blue colored complex in buffer of pH 10. The organic extract shows a maximum absorption at 445 nm. The complex is stable for more than 6 days the conditions for effective are improved by studying the effect of various factors such as pH, reagent concentration, choice of solvent and salting out agent,influence of diverse ions in order to enhance the sensitive and rapid extraction spectrophotometric method for the determination of Ni (II) in µg level. The complex formation reaction between Ni (II) with PAP has been studied in detailed.

Absorption spectra

Under experimental condition, the absorption spectra of the PAP and Ni (II) -PAP complex were scanned against the reagent blank. Similarly, the absorption spectrum of the reagent is recorded against the solvent as blank. The absorption spectra of both the reagent and the complex are shown in Figure 2. The spectra obtained reveal that the [Ni (II)- PAP] complex gave an absorbances at 445 nm respectively.

Composition of the absorbance

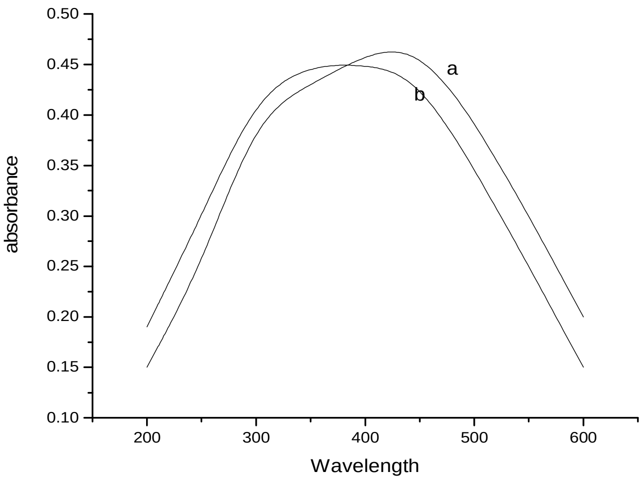


Figure 2 : Absorption spectra of PAP and its Ni (II) complex blank against water (b) PAP Ni (II)- complex against reagent blank.

Job's method of continuous variation and the molar-ratio method were applied to ascertain the stoichiometric composition of the complex. A Ni (II) (1:2) complex was indicated by both methods

Analytical parameters

Beer's law was obeyed in the concentration range 0.1 to 5.0 µg mL^{-1} of Cu (II). The molar absorptivity and Sandell's sensitivity of complex at pH 10.0 was calculated as 1.34×10^4 L mol^{-1}cm^{-1} and 1.49×10^5 µg cm^{-2} respectively.

Effect of reagent concentration

To a series of 25 mL separating funnels, each containing 2 mL of Ni (II) solution (0.01 M), 2 mL of buffer solution (pH -10) were added different volume of the reagent solution to obtain the maximum color formation. The absorbance of each solution was measured at 445 nm against a reagent blank. From the experimental observation it was found that beyond a ten-fold excess of the reagent, the absorbance remained almost constant. Hence, for further studies, 2 mL of the reagent was recommended for complete color development. Comparison studies is represented in TABLE 3.

TABLE 3 : Tolerance limits for the determination of 2 µg of Ni (II)with PAP (relative error}5%.

Ion added	Tolerate (mg)
$NO^{3-,}$ K^+, borate, Mg^{2+}	50
Li^+, $Al^{3+,}$ $PO4^{3-,}$ $NO^{2-,}$ $SO_4^{2-,}$ ClO_4^-	5
$Ca^{2+,}$ $Sr^{2+,}$ $IO^{3-,}$ BrO_3^-, B (III), ClO_3^-	2
$Mn^{2+,}$ Ce (IV) , $Fe^{3+,}$ Mo (VI), Br^-	1
Ti (IV), Bi (III), V (V), Cr (VI), Cr (VI), Ba^{2+} W (WI)	0.3
$Cd^{2+,}$ $Pd^{2+,}$ $Cr^{3+,}$ $La^{3+,}$ Cl^-, $Zn^{2+,}$ $Cu^{2+,}$ Zr (IV)	0.1
Bi (III), $Pb^{2+,}$ Hg $^{2+,}$ Th (IV), Ag^+, Sn (IV)	0.05
Se (IV), Te (IV), Au^{3+}	0.03
Co2+	0.02

Effect of pH

The buffer solution of pH 10 is recommended to control pH, as the use of 8-15 mL buffer solution (pH 10.0) per 200 mL of final solution was found to give a maximum and constant absorbance. The use of 10 mL of buffer solution is recommended. The buffer solution containing a 12.78 g of sodium borate in 100 ml of water followed by addition of 6.18 g of boric acid and wasdiluted 1000 mL can increase the selectivity of this system. It is represented in Figure 1.

Effect of eluents type and volume

The nature and concentration of eluting agents were found to have a significant effect on the elution process of the retained ions from the solid phase. The type and concentration of eluent is also important for the performance of the solid-phase preconcentration system. Among the solvents studied, especially the acetone solution provided higher recovery efficiency compared to the acids in aqueous or alcoholic solutions and the highest recoveries were obtained for acetone. Finally, 4 mol L^{-1} acetone was taken as the eluent for desorption of metal ions chelates from loaded Amberlite XAD-16 and was used for the optimization of the other parameters. The effects of 4 $molL^{-1}$ acetone solutions in the volume range between 2 and10 mL were investigated and quantitative recoveries were obtained for 6 mL or more of the eluent. The optimum eluent volume is specified as 6-10 mL for the subsequent studies.

Interference

The selectivity of the proposed method was investigated by the determination of Ni (II) in the presence of various ions within a relative error of ± 5%. See TABLE 4.

CONCLUSIONS

The proposed spectrophotometric method is simple, highly sensitive and selective for the determination of Ni (II) in water and food samples. The limit of detection of the proposed method is superior to other methods. The method has additional advantage over method owing to it's.

i. Proposed method is highly sensitive due to the stabilization of colored complex for more than 6 days formed by interactions of the metal ion with newly procured reagent.
ii. Low reagent consumption, elimination of the analytical error and statistical analysis which made the method to be more sensitive and selective.
iii. The application of the procedure proposed showed that nickel can be effectively separated/preconcentrated from different types of water samples on Amberlite XAD-16 columns. The method may be used for the preconcentration of traces of heavymetals from other matrices, such as natural water samplesand biological materials etc.

TABLE 4 : Comparison of the present method with other spectrophotometric methods for the determination of Nickel (II).

Reagent	λ_{Max}/nm	Optimum pH range	Beer's law validity range,ppm	Molar absorptivity/$lmol^{-1}cm^{-1}$	Remarks	Ref
2-(2-Quinolylazo)-5-dimethylaminoaniline	590	7-9	1.32×10^5	0.01-0.6	Less sensitive	[33]
2-(2-Quinolylazo)-5-diethylaminoaniline	590	6.0	0.03-0.05	0.02-0.7	High cost	[35]
Salicylaldehyde 3-oxobutanoylhydrazone	410	5–10	1	0.5-0.3	expensive	[35]
PAP with XAD-16	540	6	0.01–0.37	3.11×10^5	High detection	[36]
	445	10	0.01-0.05	$1.34x10^4$	Sensitive,easily available,low cost	(Present Method)

ACKNOWLEDGEMENT

The authors are grateful to the Department of Biotechnology, S.V.University, and Tirupati for providing instrumental facility.

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