



## Spectrophotometric determination of Co(II) in various samples by Solid phase Extraction using Chemically Modified SiO<sub>2</sub>-PAN Nanoparticles

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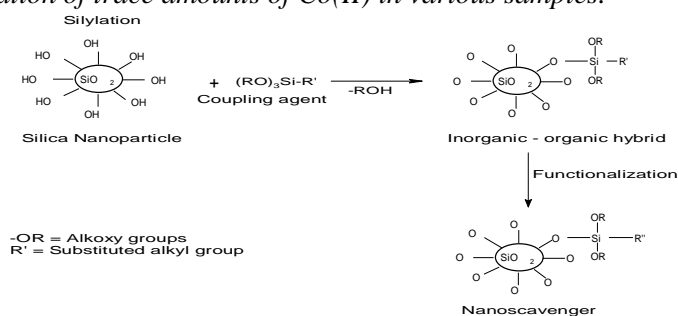
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Received on July 29<sup>th</sup> and finalized on 3<sup>rd</sup> September 2012

### ABSTRACT

The present paper reports on the application of modified silica Nanoparticles with PAN as a new, easily prepared and stable sorbent for the preconcentration of trace Co(II) metal ion. Factors influencing the sorption and desorption of Co(II) were investigated. The effects of experimental parameters, including the sample pH, sorbent amount, shaking time, sample volume of solution, adsorption capacity and preconcentration factor has been studied. The adsorption equilibrium of Co(II) on nanometer SiO<sub>2</sub>-PAN was achieved within 10min. Adsorbed Co(II) was easily eluted with 7mL of 5M hydrochloric acid. The maximum preconcentration factor has been found to be 50. The method was developed for the estimation of trace amounts of Co(II) in various samples.



**Keywords:** Nanoparticles, preconcentration, surface modifications, PAN {1-(2pyridylazo)-2-naphthol}.

## INTRODUCTION

Cobalt is an important element, not only for industry but also for biological systems. It is present in vitamin B<sub>12</sub> and is an essential micro nutrient for all living systems. However, in larger amounts it is toxic and causes pulmonary disorders, dermatitis, nausea and vomiting[1]. Over-exposure to cobalt causes irritation of the gastro-intestinal tract, nausea, diarrhea, and so on. At high concentrations, it inhibits heme-biosynthesis and enzyme activities. Moreover, the element is toxic, when taken directly. At high concentrations, it inhibits heme-biosynthesis and enzyme activities. Moreover, the element is toxic, when taken directly. Apart from the physiological utility of cobalt, it also finds extensive use in industry. Due to its strength and high resistance to corrosion in many media, it is widely used in high-speed steel tools, magnets and high temperature alloys. The metal finds wide applications in the manufacture of aircrafts, electromagnets, paints and ceramics. Cobalt is also used as a catalyst in industrial processes. Recent developments in the determination of cobalt have grown considerably, owing to its involvement in some essential metabolic and industrial processes, which are discussed above.

In the determination of trace cobalt, various methods including ICP-MS,[2] spectrofluorometry,[3] ICPAES,[4] differential pulse voltammetry,[5] anodic stripping voltammetry,[6] and GFAAS[7] have been used. Among these techniques, GFAAS, ICP-MS, and anodic stripping voltammetry can be directly applied to the determination of Co at the ng mL<sup>-1</sup> level. Among these, predominantly spectrophotometric methods are preferred, as they are less expensive and possess a greater sensitivity in comparison. However, some of these methods are time-consuming and require complicated and expensive instruments. They also have complex operational conditions, are not free from various types of interference, and have high maintenance costs. Therefore, other methods that can determine the low concentrations of cobalt conveniently in real samples were required.

Because of their extremely low concentration, a preliminary concentration step *i.e.* preconcentration is usually necessary prior to the determination of the metals. Nowadays, liquid- liquid extraction, [8-10] ion-exchange resins[11] and solid- phase extraction [12-13] are used for the preconcentration of different metal ions. Of all these methods, solid phase extraction has been widely used since it is simple, rapid and inexpensive, less polluting to the environment and can be easily automated. Many materials such as organic chelate resin, silica gel, activated carbon, activated alumina, zeolites and microcrystalline materials are commonly used as adsorbents.

Nowadays, nanometer materials have become more important owing to its special physical and chemical properties. The field of nanocomposite materials has received the attention, imagination and close scrutiny of scientists and engineer in recent years. These particles fall within the colloidal range, exhibiting typical colloidal properties. The surface atoms are unsaturated and can therefore bind with other atoms, possess high chemical activity. Nanoparticles exhibit intrinsic surface reactivity and high surface areas and can strongly chemisorb many substances. The size, surface structure and interparticle interaction of nanomaterials determine their unique properties and the improved performances and make their potential application in many areas. Nanoparticles such as TiO<sub>2</sub>, [14] Al<sub>2</sub>O<sub>3</sub>, [15] ZrO<sub>2</sub>, [16] CeO<sub>2</sub>, [17] and modified silica nanoparticles have been used for the preconcentration of many metal ions and give promising results when used for trace element analysis of different samples. In present work, chemically grafted SiO<sub>2</sub>-PAN nanoparticles were prepared by sol-gel [18] method and characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR). These nanoparticles have been used for the preconcentration and separation of Co(II) prior to their determination by spectrophotometric method [19]. The main objective of studying its applications is to determine the trace amounts of cobalt(II) in pharmaceutical, Food and other water samples of significant importance.

## EXPERIMENTAL

**Apparatus :** Absorbance of Co(II) was measured with UV-Vis Shimadzu-1700 spectrophotometer. The pH values were controlled by century Cp901 digital pH meter.

**Reagents and standard solutions :** Unless otherwise stated, all reagents used were of analytical reagent grade and all solutions were prepared with double distilled water. The 3-aminopropyltriethoxysilane of GR grade was supplied by Acros Organics (USA). PAN was obtained from Merck (Mumbai). Nanometer  $\text{SiO}_2$  and modified  $\text{SiO}_2$ -PAN was synthesized according to the method reported [18].

**General procedure :** Aliquots of sample solution containing 0.48-4.56 $\mu\text{g}$  of Co(II) were taken in a flask and pH was adjusted to the desired value with 0.5M boric acid/disodium tetraborate buffer solution (20mL). Then, 35mg of  $\text{SiO}_2$ -PAN nanoscavengers were added, and the mixture was shaken vigorously for 10mins to facilitate adsorption of metal ion onto the adsorbent. Co(II) retained on the adsorbent and were filtered by cellulose nitrate membrane. Then, eluted with 7mL of 4.0M hydrochloric acid, and the elution was neutralized with 2M sodium hydroxide and were determined by standard spectrophotometric method[19].

## RESULTS AND DISCUSSION

**Scanning Electron microscopy:** The average diameter of the  $\text{SiO}_2$  nanoparticles,  $\text{SiO}_2$ -APTES nanoparticles and  $\text{SiO}_2$ -PAN nanoscavengers was 0.1 $\mu\text{m}$  (100nm), 1 $\mu\text{m}$  and 2 $\mu\text{m}$  confirmed by Scanning Electron Microscopy (Fig 1, 2, 3).

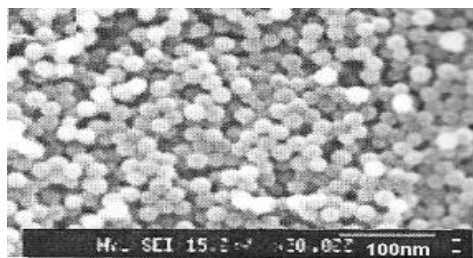


Fig. 1. SEM micrograph of  $\text{SiO}_2$  Nanoparticles.

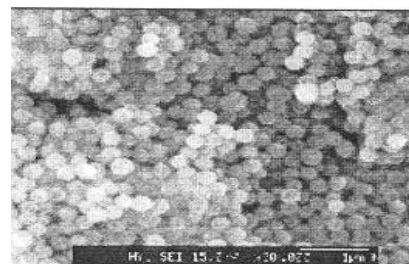


Fig. 2. SEM micrograph of  $\text{SiO}_2$ -APTES Nanoparticles

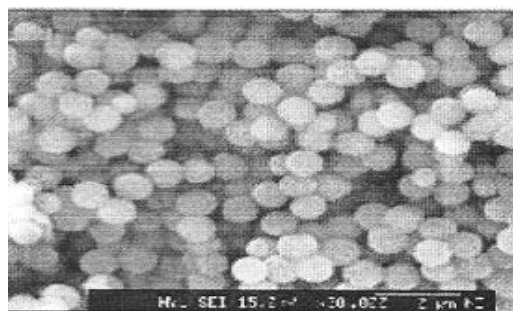


Fig. 3. SEM micrograph of  $\text{SiO}_2$ -PAN Nanoparticles.

**FT-IR spectrum analysis :** The main absorption peaks of nanometer  $\text{SiO}_2$  (3448.0, 1642.5, 1404, 1070.2, 964.2, 798.8 $\text{cm}^{-1}$ ) are in agreement with standard spectrum of  $\text{SiO}_2$ [20]. Many new peaks appeared in FT-IR spectrum of  $\text{SiO}_2$ -PAN which are assigned as follows: the peak at 1683.5  $\text{cm}^{-1}$  is due to N=N stretching vibration and 1590, 1540, 1500 and 695.9  $\text{cm}^{-1}$  peaks are due to C=C stretching vibration of the benzenoid and pyridyl unit in 1-(2-pyridylazo)-2-naphthol at, peak at 1381.6 $\text{cm}^{-1}$  due to  $\text{CH}_2$  shear deformation vibration, the peak at 1329.4 $\text{cm}^{-1}$  is due to C≡N stretching vibration for the benzenoid unit and the peak at 1098.1 $\text{cm}^{-1}$  is caused by C-O stretching vibration in 1-(2-pyridylazo)-2-naphthol.

It reveals that peak at 2907.2 $\text{cm}^{-1}$  is due to C-H stretching, peak at 1641.3 $\text{cm}^{-1}$  is due to N-H stretching and peak at 1093.5 $\text{cm}^{-1}$  C-O stretching in 3-aminopropyltriethoxysilane. The above experimental results suggest that nanometer  $\text{SiO}_2$  has been successfully modified by 1-(2-pyridylazo)-2-naphthol. (Fig. 4(a,b, c,d))

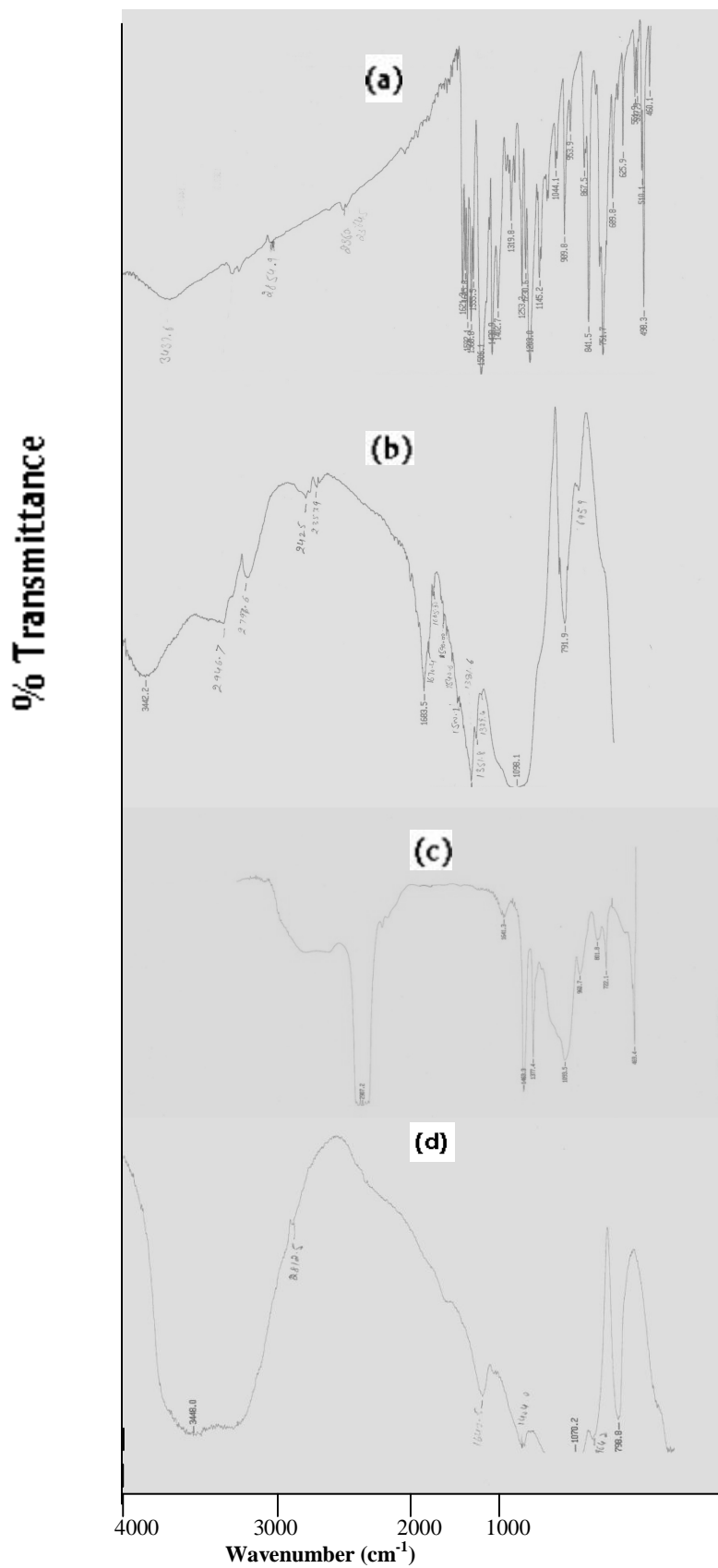


Fig. 4. FTIR spectra (a) PAN (b) nanometer  $\text{SiO}_2$ -PAN (c) nanometer  $\text{SiO}_2$  - APTES (d) nanometer  $\text{SiO}_2$ .

**Effect of pH on enrichment recovery :** The adsorption of Co(II) on SiO<sub>2</sub>-PAN nanoscavengers was studied at different pH value (1.87 -10.0) following the general procedure. It can be seen that a quantitative recoveries ( $\geq 95\%$ ) was found for Co(II) in the pH range of 8.0-10.0 and 9.2 pH was selected for further analysis. The results of effect of pH on the recoveries of Co(II) are shown in Fig. 5.

**Effect of eluent concentration and volume:** Elution of Co(II) from SiO<sub>2</sub>-PAN nanoscavengers as extractant was studied by using various concentrations of hydrochloric acid. It can be seen that quantitative recoveries ( $\geq 95\%$ ) of Co(II) can be obtained using 7mL of 5M hydrochloric acid as eluent. Therefore, 7mL of 5M was used as eluent in subsequent experiments. The results of effect of eluent concentration and volume are given in Table 1 and Table 2.

**Effect of amount of SiO<sub>2</sub>-PAN nanoscavengers:** To test the effect of amount of extractant on quantitative retention of analyte, different amounts (10-45mg) of nanometer SiO<sub>2</sub>-PAN were added into the solution following the general procedure. Quantitative extraction of the Co(II) ( $\geq 95\%$ ) was obtained in the range of 30-45mg of nanometer SiO<sub>2</sub>-PAN. 35mg of nanometer SiO<sub>2</sub>-PAN as extractant was found to be sufficient for further studies. The results are shown in Fig. 6.

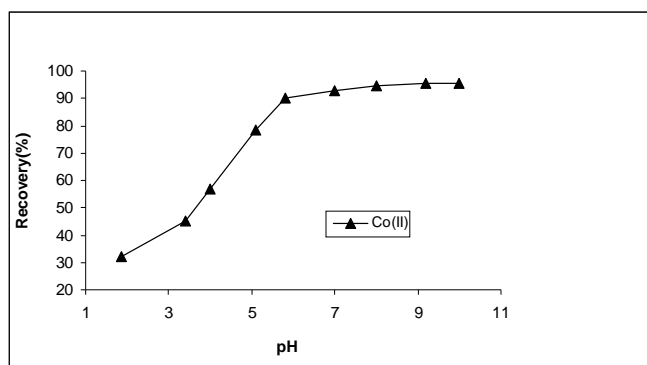


Fig.5. Effect of pH on recovery of Co(II).

**Table 1. Effect of concentration of hydrochloric acid solution on elution of Co(II) (n=3)\*.**

Concentration of eluent (molL <sup>-1</sup> )	Recovery(%)
0.5	34.42
1.0	70.40
2.0	80.50
3.0	88.75
4.0	95.25
5.0	95.67
6.0	74.59
7.0	54.70

\*n is the average of three replicate experiments.

**Table 2. Effect of volume acid solution on elution of Co(II) (n=3)\*.of hydrochloric**

Volume of eluent (mL)	Recovery (%)
2.0	37.10
4.0	65.41
5.0	75.36
6.0	83.01
7.0	96.02
8.0	80.05
10.0	71.53

\*n is the average of three replicate experiments.

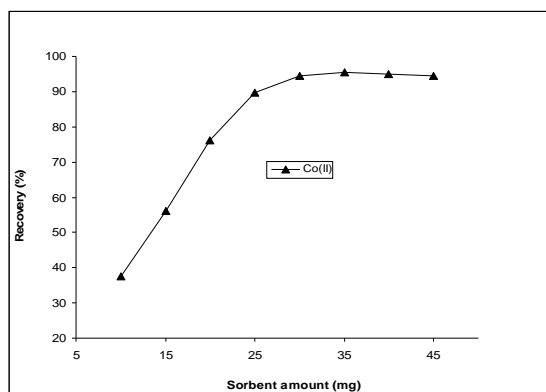


Fig. 6. Effect of sorbent amount on recovery.

**Effect of shaking time:** The adsorption of Co(II) on 35mg of nanometer SiO<sub>2</sub>-PAN was studied for different shaking times (2-25mins). The results indicated that within 10mins, the percentage quantitative recovery of Co(II) ( $\geq 95\%$ ) was achieved. The results are shown in Fig. 7.

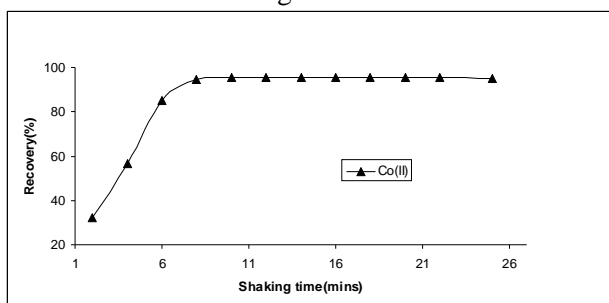
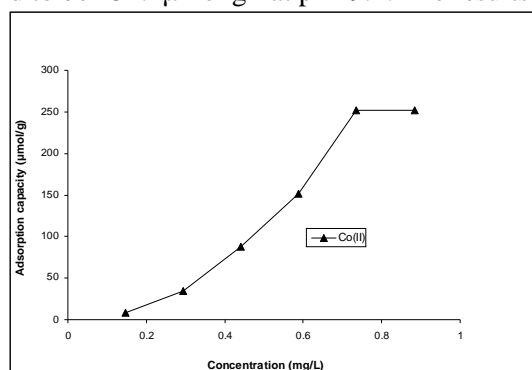


Fig. 7. Effect of shaking time on recovery.

**Adsorption capacity ( $Q_s$ ):** A breakthrough curve was obtained by plotting the concentration of Co(II) ( $\text{mg L}^{-1}$ ) vs. the  $\mu\text{mol}$  of Co(II) adsorbed per gram. From the breakthrough curve the adsorption capacity of SiO<sub>2</sub>-PAN for Co(II) was found to be  $252.1 \mu\text{mol g}^{-1}$  at pH 9.2. The results are shown in Fig. 8.

Fig. 8. Adsorption capacity of SiO<sub>2</sub>-PAN nanoscavengers for Co(II).

**Effect of sample volume :** In order to explore the possibility of concentrating low concentration of analytes from large volumes, the effect of sample volume on the retention of metal ions was also investigated. For this purpose 30, 50, 70, 100, 200, 250, 300, 350, 400 and 500mL of the sample solutions containing  $1.0 \mu\text{g}$  Co(II) was shaken, quantitative recoveries of Co(II) ( $>95\%$ ) were obtained for sample volume of  $\leq 350\text{mL}$ . The results are given in Fig. 9.

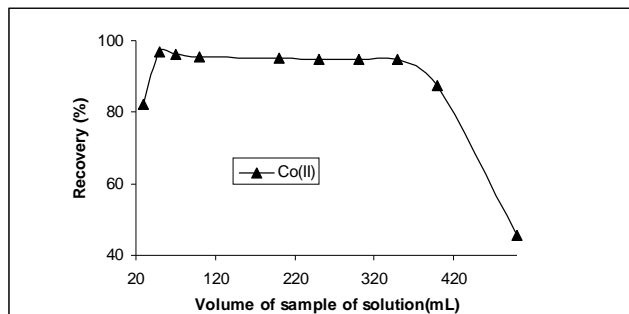


Fig. 9. Effect of sample volume on recovery.

**Effect of coexisting ions :** The effect of common coexisting ions on the sorption of Co(II) was investigated. In these experiments, an aliquot of Co(II) that contains the added interfering ion was preconcentrated according to the general procedure. Amount of interferent causing changes in recovery of Co(II) not greater than  $\pm 5\%$  was taken as tolerance limit. The results are given in Table 3 and Table 4.

**Analytical precision and detection limit :** Under optimized conditions, three portions of Co(II) standard solutions was enriched and analyzed simultaneously by the general procedure. The relative standard deviation (RSD) and the detection limit of this method were 3.2% and  $0.65\mu\text{gL}^{-1}$  respectively.

Table 3. Effect of diverse anions on the preconcentration Co(II).

Ion/ Salt	Tolerance ( $\text{mgmL}^{-1}$ )
$\text{PO}_4^{2-}$	50
$\text{NO}_3^-$	30
$\text{SO}_4^{2-}$	50
$\text{S}_2\text{O}_3^{2-}$	45
$\text{Cl}^-$	40
$\text{F}^-$	30
$\text{Br}^-$	46
$\text{I}^-$	50
$\text{CH}_3\text{COO}^-$	30
$\text{C}_6\text{H}_5\text{O}_7^{3-}$	42
$\text{SCN}^-$	4
$\text{S}_2\text{O}_5^{2-}$	10
EDTA	Interfered strongly

**Determination of Cobalt(II) in food Samples :** The food samples like carrot (*Daucus carota*) and potato (*Solanum tubersum*) were analyzed for Co(II). Sample (10g) is transferred into a pre- cleaned porcelain dish and 50mL of sulfuric acid (3M) was added and gently heated on a water bath for about 30mins and retransferred on to a hot plate, continuing until white fumes cease to evolve, and the residue is completely evaporated to dryness. The dish is then placed on a hot plate and reheated up to  $100^\circ\text{C}$  for 5mins. The contents were transferred quantitatively into a 25mL calibrated flask, by washing the dish with double distilled water to ensure homogeneity and Co(II) pre concentrated by general procedure. Results are given in Table 5.

**Determination of Co(II) in Pharmaceutical Samples :** The proposed method is applied for the determination of Co(II) in pharmaceutical samples like Sineurjon (Albert David, India), Neurobion (Merck, India), Vitneurion (Glaxo, India), Polybion (Merck, India). To 10mL of the inject able solution, concentrated sulfuric acid and nitric acid are added and evaporated until nearly dryness. It is then treated

with 5mL of 30 % (v/v) hydrogen peroxide each time, until the solution becomes colorless. Finally, it was treated with dilute hydrochloric acid and the solution was evaporated, till nearly dry and each residue was dissolved in double distilled water and made upto 25mL in a volumetric flask and Co(II) were pre concentrated by general procedure. The results of analysis are given in Table 6.

**Table 4. Effect of diverse cations on the preconcentration Co(II).**

Ion/Salt	Tolerance ( $\mu\text{g mL}^{-1}$ )
Ni(II) <sup>a</sup>	30
Cu(II) <sup>a</sup>	50
Cd(II) <sup>b</sup>	60
Hg(II) <sup>b</sup>	60
Sb(III)	80
Pb(II) <sup>b</sup>	100
Mn(II) <sup>d</sup>	30
Fe(III) <sup>b</sup>	100
Fe(II) <sup>b</sup>	100
Zn(II) <sup>c</sup>	50
Bi(III) <sup>c</sup>	80
Th(IV) <sup>c</sup>	65
Mo(VI) <sup>d</sup>	50
Na(I)	30
K(I)	40
Ca(II)	30
Mg(II)	40

<sup>a</sup>masked with 2mL of 0.01% potassium thiocyanide, <sup>b</sup>masked with 1mL of 5% sodium fluoride, <sup>c</sup>2mL of 0.1% sodium citrate, <sup>d</sup> masked with 1.5mL of 5% potassium bromide, <sup>e</sup>2mL of 5mL sodium nitrate.

**Table 5. Preconcentration of Co(II) in food samples(n=3)\*.**

Sample	Added( $\mu\text{g g}^{-1}$ )	Found( $\mu\text{g g}^{-1}$ )	Recovery(%)
Carrot ( <i>Daucus carota</i> )	---	0.50	---
	0.5	0.98	98.0
	1.0	1.47	98.0
Potato ( <i>Solanum tubersum</i> )	---	0.30	---
	1.0	1.25	96.15
	2.0	2.22	96.52

\*n is the average of three replicate experiments.



**Table 6. Preconcentration of Co(II) in pharmaceuticals samples (n=3)\*.**

Sample	Certified amount of Co(II)( $\mu\text{g mL}^{-1}$ )	Found amount of Co(II) ( $\mu\text{g mL}^{-1}$ )	Recovery(%)
Sinearion	1.44	1.43	99.31
Neurobion	1.44	1.40	97.22
Vitueurion	1.44	1.41	97.92
Polybion	1.44	1.41	97.92

\*n is the average of three replicate experiments

**Preconcentration of Co(II) in water and food samples :** The developed procedure has been applied for the determination of trace amounts of Co(II) in tap water, mineral water samples. Results are given in Table 7.

**Table 7. Preconcentration and recovery yields of Co(II) in spiked water samples(n=3)\*.**

Sample	Added( $\mu\text{g mL}^{-1}$ )	Found( $\mu\text{g mL}^{-1}$ )	Recovery(%)
Tap water	0.0	----	----
	5.0	4.87	97.40
	10.0	9.7	97.0
Mineral water	0.0	----	----
	5.0	4.9	98.0
	10.0	9.8	98.0

\*n is the average of three replicate experiments.

For food samples, the mixture of nitric acid and hydrochloric acid in ratio (2:1) was used for digestion of samples of potato chips(0.2g)/biscuits(0.2g) and the method of digestion was repeated for 2-3 times and then the sample was dissolved in water, filtered and made up to level in a standard flask. Then, Co(II) were preconcentrated by general procedure. The results are given in Table 8.

**Table 8. Preconcentration and determination of heavy metal ions concentration ( $\mu\text{g g}^{-1}$ ) in different brands of potato chips (PC-1to PC-2) and biscuits (BC-1 to BC-2) available in Patiala city, Punjab, India(n=3)\*.**

S. No.	Sample	Properties	Co(II)
1	PC-1	Salted	0.41
2.	PC-2	Tomato tango	0.99
3.	BC-1	Sweet	1.0
4.	BC-2	Milk sweet	1.25

\*n is the average of three replicate experiments.

## APPLICATIONS

The application of the method is the modified silica Nanoparticles with PAN can be used as a new stable sorbent for the preconcentration of trace Co(II) metal ion in pharmaceutical, food and water samples.

## CONCLUSIONS

1-(2-pyridylazo)-2-naphthol- anchored silica Nanoparticles were prepared and used as solid sorbent for preconcentration and separation of trace Co(II) prior to their determination. These analytes can be easily screened at  $\mu\text{g mL}^{-1}$  level with preconcentration times of 10mins and preconcentration factor of 50 for Co(II).

The method can be used as screening to estimate the total concentration of Co(II) present in a large number of samples and thus avoiding the continuous use of expensive instrumentation in routine analysis. The 1-(2-pyridylazo)-2-naphthol- anchored silica nanoparticles have been found to be much selective for preconcentration of these analytes and showed great capacity, and rapidness. The proposed method has been used for the determination of these metal ions in various water and synthetic samples. The results of determination have been found to be accurate and reproducible. Comparative information from some studies on preconcentration of Co(II) by various methods for figure of merits is given in Table 9. The proposed method developed using  $\text{SiO}_2$ -PAN nanoparticle had a relatively high preconcentration factor compared to other methods reported in Table 9.

**Table 9. Comparison of preconcentration factor of some sorbents used for the separation and preconcentration of Co(II).**

Support	Reagent	Preconcentration factor	References
Silica gel	DPTH <sup>a</sup>	25	21
Silica gel	MPSP <sup>b</sup>	40	22
knotted reactor	PMBP <sup>c</sup>	28	23
microcrystalline naphthalene	5-BPADAP <sup>d</sup>	30	24
Polyurethane foam	Pyrocatechol	42	25
MCNTs	-----	19.10	26
$\text{SiO}_2$ -PAN	nanoscavengers	50	this work

<sup>a</sup>DPTH: 1,5-bis(di-2-pyridyl)methylene thiocarbonylhydrazide

<sup>b</sup>MPSP: 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone

<sup>c</sup>PMBP: 1-phenyl-3-methyl-4-benzoylpyrazol-5-one

<sup>d</sup>BPADAP: (2-(5-bromo-2-pyridylazo)-5-dimethylaminophenol

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