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Chelate Modified β -CDP as a Green and Economical Sorbent for Separation and Preconcentration of Co(II)

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ABSTRACT

A simple and sensitive method has been developed for the preconcentration and determination of trace level of Co(II) using UV-Vis spectrophotometry. β -Cyclodextrin polymer modified with 1-(2-pyridylazo)-2-naphthol (PAN) is used for the preconcentration of Co(II) from samples at pH 8.5. The polymer is synthesized and characterized using elemental analysis, FT-IR and SEM analysis. The factors affecting the recovery of Co(II) such as pH, adsorbent dose, contact time, sample volume, eluent concentration and volume are also optimized in order to achieve higher sensitivity. The recoveries of Co(II) are found to be \geq 95% and the relative standard deviation found by analyzing 3 replicates is \leq 2.9. The preconcentration factor is found to be 100. The limit of detection (LOD) determined as (3 σ) is found to be 4.2 ng/ml and limit of quantification (LOQ) determined as (10 σ) is found to be 14 ng/ml. The recoveries achieved by addition of Co(II) at known concentrations to samples and analysis results show that the described method has a good accuracy. The proposed method is applied to water, vegetable and alloy samples successfully.

KEYWORDS: Solid Phase Extraction; Preconcentration; Polymer.

1. INTRODUCTION

The problems of our ecosystem are increasing with the advancement of technology. Due to the negative effects of heavy metal ions for human health, heavy metal pollution is one of the important problems for human [1-2]. Toxic heavy metal release into the environment has been increasing continuously as a result of man's industrial activities and technological development. The release of these heavy metal poses a significant threat to the environment and public health because of their toxicity, bioaccumulation in the food chain and persistence in nature [3-4]. Co(II) is one of several metal ions that play an important role in the biological system. It is the core of vitamin B12 and possesses anti-anemic properties [5]. Drinking water, food and inhalation are common ways of cobalt contamination for living organisms. The deficiency of Co(II) in human and animal bodies lead to anemia [6]. While large amounts of Co(II) causes to toxic effects such as kidney and liver disorders, sinus tachycardia [7]. Consequently, it is of paramount importance and significant to enrich and determine Co(II) in various environmental samples. The direct determination of heavy metal ions at trace levels in real samples presents a challenge because of the low concentration and matrix effects. Therefore, preconcentration or separation of trace elements from the matrix is necessary. Different techniques are used for the separation and preconcentration of metals in the

solution. These include membrane filtration [8], ionexchange [9], cloud point extraction [10], Coprecipitation[11], solid-liquid extraction [12], liquidliquid extraction [13] and solid phase extraction. Disadvantages such as significant chemical additives, solvent losses, complex and expensive equipments, large secondary wastes, prefiltration problems, expert handling and time consuming procedures, limit the application of most of these techniques. Solid phase extraction, however, solves this problem as it offers several advantages such as high preconcentration factors, short extraction times, low cost, absence of emulsion, ease of use. This technique is also attractive as there is no need to use organic solvents, which may cause potential toxic effects. Several SPE sorbents as activated carbons [14], clay [15], polyurethane foam [16], Chromosorb-105 [17], amberlite XAD resin [18-20], cellulose [21], naphthalene [22], carbon nanotubes [23] and etc. have been employed to preconcentrate metal ions at trace level. Supramoleculer chemistry with β -Cyclodextrin has been a very active research field in the past few years [24-26]. β-Cyclodextrin (β-CD) is a very stable oligosaccharide that is composed of seven glucose units linked with each other by α -(1,4)-glycosidic linkage. It can form the Supramoleculer complexes with several organic compounds by incorporating them into their hydrophobic cavities. β-Cyclodextrin linked via cross linker is known as β -Cyclodextrin polymer. β -Cyclodextrin polymer has been used as SPE sorbents for preconcentrating several analytes [27-29]. There has not been any report of the use PAN modified β -Cyclodextrin Butanediol Diglycidyl Ether Polymer (β -CDBP) for the preconcentration of Co(II) till date. It was therefore, thought worthwhile to prepare a chelating resin by immobilizing PAN on β -CDBP and characterize it in a systematic manner for its use in the preconcentration of Co(II) and its determination by UV-Vis spectrophotometry.

2. EXPERIMENTAL

2.1. Materials and methods

All reagents used were of analytical reagent grade. Double distilled water was used throughout the experiment. Co(II) solution was prepared by dissolving of Copper sulphate pentahydrate 0.249 gm. [CuSO₄.5H₂O] in 100 mL of distilled water to give standard stock solution. 4×10^{-6} M solution of the PAN reagent was prepared by dissolving an appropriate amount of PAN (Fluka Chemical Company) in N,Ndimethylformamide solvent. 1,4-Butanediol diglycidyl ether was obtained from sigma Aldrich chemical company (U.S.A.). β-Cyclodextrin was obtained from SD fine chemical India private limited (Mumbai). Buffer solution used were hydrochloric acid/sodium acetate for pH 2.0-3.5, sodium acetate/acetic acid for pH 4.0-6.5, ammonia/ammonium chloride for pH 8-11. Glass wares were washed with chromic acid and soaked in 5% nitric acid and rinsed with double distilled water.

2.2. Apparatus

A Shimadzu UV-1800 spectrophotometer (Shimadzu Ltd., Japan) equipped with the matched 10-mm quartz cells was used to measure absorbance. All pH measurements were performed using Digital century pH-meter CP 901 (Ambala Cantt. India) with a combined glass electrode. A thermostatic shaking water bath (Perfit India Ltd.) was used to carry out all the inclusive procedures.

2.3. Sample Collection and Conditioning

Water samples were collected from the different parts of Patiala City. The water samples were immediately filtered through cellulose membrane filter (0.45 nm pore size) and stored in precleaned polyethylene bottles. After then, pH of the sample was adjusted to 9.5 and the preconcentration procedure as described above was applied.

2.4. Determination of Co(II) in vegetables

The established optimized conditions of extractive preconcentration method were applied to leafy vegetables, for the determination of Co(II) content. The leafy vegetables analyzed were brought from the local market during the month of January. The samples were cleaned and dried in open air, protecting them from mineral contamination and digested [30]. The dried

sample was pulverized in a mortar for the purpose of analysis, to a convenient size. 10 gm of leafy vegetable sample was transferred into a precleaned beaker and 50 ml of H_2SO_4 (3M) was added and heated on a hot plate for about an hour until white fumes ceases to evolve and the residue is completely evaporated to dryness, then the sample was dissolved in water, filtered and made up to mark in a standard measuring flask.

2.5. Determination of Co(II) in standard alloys

The proposed method has been applied for the determination of Co(II) in alloys to check the validity of the method. To dissolve the standard reference alloy, modified literature method was employed [31]. 0.1 gm of the standard alloy was completely dissolved in 20 mL of HCl by heating on a water bath; 2 mL of 30% hydrogen peroxide was added to the solution. The excess of peroxide was decomposed by heating the solution on a water bath. The solution was cooled, filtered and diluted to 100 mL with double distilled water. Further dilutions were made as and when required. An aliquot of this solution was taken and preconcentration was done by the developed procedure.

2.6. Synthesis of the β -Cyclodextrin polymer (β -CDP) and β -CDP-PAN modified polymer

β-CDP was synthesized by known method [32]. A brief procedure for the synthesis is mentioned here. 20 gm of β-CD was dissolved in 50 mL of 20% NaOH. To this was added 20 mL of 1,4-butanediol diglycidyl ether drop wise. The polymer was formed in 1.5 h and dried at 90 °C. The polymer was ground and sieved first into different mesh fractions. The 80-100 mesh fraction was washed with double distilled water 5-6 times. Then, the polymer was dried again at 90 °C and kept at room temperature (25 °C) in a dessicator. The scheme is depicted in Fig. 1.



Fig. 1. Schematic presentation of structure and synthesis of β -cyclodextrin polymer

5.0 gm of the synthesized polymer, β -CDP (80-100) mesh size was taken in a 250 mL Stoppard conical flask. To this was added 10 mL of 9.5 pH buffer solution and polymer was allowed to swell for 15 minutes. A fixed volume of 4×10^{-6} M solution of the PAN was added to the treated polymer and made 50 mL with distilled water. It was shaken for two hours. The colored polymer so obtained was washed with distilled water and dried at 100 $^{\circ}$ C. The modified

polymer was stored in a dessicator at room temperature for future use.

2.7. Characterization of β -CDP and PAN- β -CDP

The synthesized polymers were characterized using elemental analysis, FT-IR and SEM micrographs. The synthesized polymers were subjected to elemental analysis. The analysis was carried out using Elementar Vario MICRO Cube CHNS instrument Hanau (Frankfurt) Germany at Instrumentation Laboratory, Department of Chemistry, Punjabi University, Patiala. The microanalysis results of β-cyclodextrin polymer (%C = 26.55, %H = 6.399, %N = 0, %S = 0) suggests that β -CD has been cross-linked by cross-linker. The final modified polymer resulting from modification of β -cyclodextrin polymer (β -CDP) with PAN [1-(2pyridylazo)-2-naphthol] also showed an increase in the percentage of carbon (C) and hydrogen (H) but at the same time the percentage of N was also observed (%C =36.51, %H = 8.941, %N = 6.46), which proves that β -CDP was modified with nitrogen containing chromogenic reagent.

The IR spectra for β -CD and β -CD polymer (β -CDP) were recorded with an FT-IR spectrophotometer (Perkin Elmer, Boston USA) instrument as KBr pellets in the range 4000-400 cm⁻¹ region at Department of Chemistry, Punjabi University, Patiala. From FT-IR (KBr) of β -CyD and β -CyD polymer as shown in Fig. 2, it can be seen that: for β -CD, 3600- 3000 ϑ (OH), 2900 ϑ (CH); while for β -CDP a sharp band at 3400 ϑ (OH) is obtained which indicates free OH group as shown in the structure above. A prominent band at 1120 ϑ (COC) ether linkage which is present in the linker and its absence in β -CyD spectra clearly indicates the polymerization process.



Fig. 2. IR spectrum of β -Cyclodextrin and β -Cyclodextrin polymer

SEM (Scanning Electron Microscopy) was utilized in order to determine and compare the surface features of the native β -CD, β -Cyclodextrin polymer (β -CDP) and β -CDP modified with PAN. SEM micrographs were taken at sophisticated instrumentation centre, Punjabi University, Patiala on a JEOL JSM-6510/LV SEM instrument at beam energy of 10Kv. The micrographs were taken at x3000 and x5000. From the micrograph it can be observed that the SEM micrograph of the native β -CD, β -Cyclodextrin polymer (β -CDP) and β -CDP modified with PAN are different, which proves that the polymer was synthesized and modified successfully. The SEM micrographs are provided as a supplementary file.

2.8. Batch extraction procedure

At room temperature i.e., 30° C β -CDP-PAN (0.4gm) and 10.0 mL of buffer solution (pH 9.5) were added to a 100-mL Stoppard conical flask. The mixture was allowed to stand for approximately 15 min so that β -CDP-PAN could be swollen sufficiently. 70 ng/mL of Co(II) were added and made up to 100 mL with double distilled water. After the mixture was shaken in the thermostatic shaking water bath for 40 min, 5.0 mL of the supernatant solution was transferred into a 10 mL volumetric flask and the absorbance was measured using standard spectrophotometric method [33]. Co(II) retained on β -CDP-PAN polymer was eluted using 4.0 mL of 2M HCl.

2.9. Regeneration of the β -CDP

Regeneration of β -CDP was examined following the reported method [34]. Polymer was regenerated by dipping the polymer in the 10.0% TX-100 (w/v) for 1 h and then washing with distilled water; β -CDP was further treated with HNO₃ and was finally washed with distilled water to neutral conditions. Following treatment polymer was filtered off and dried at 90 °C. The results for the removal of Co(II) using regenerated β -CDP are summarized in Fig. 3. Polymer about 96% of its original tendency to remove Co(II) even after using seven times because the conditions used for the regeneration of the polymer were extremely milder.



Fig. 3. Uptake of Co(II) from the sample solution with the regenerated β -CDP adsorbent: Each adsorption experiment was carried out by placing (0.4g) of adsorbent and sample solution containing 70 ng/mL of Co(II) in 100 mL of solution in a 500 mL of flask and shaking it at room temp. at 100 (r.p.m.) for 40 minutes.

3. RESULTS AND DISSCUTIONS

3.1. Effect of pH

The sorption of an analyte on the chelating resin is dependent on the pH of sample solution due to the competitive reaction between chelate forming groups and hydrogen ions in the solutions. An excess of Co(II) 70 ng/mL were spiked to a 100 mL of the sample solution containing 0.4 g of resin and shaken for 40 min. The pH of this solution was adjusted in the range of 3.5 to 10.5 using different buffer system and then the preconcentration procedure as described was applied. As it can be seen in (Fig. 4), quantitative uptake ($\geq 95\%$) was obtained at pH 7.5-10.5 ± 0.01. The nitrogen of the heterocyclic ring of PAN gets protonated at lower pH while the phenolic OH group dissociates in the alkaline medium. Due to which reagent reacts with the Co(II) under slightly alkaline medium to form stable complexes. PAN acts as the tridentate ligand complexing with metal ion through the ortho-hydroxyl group, the azonitrogen nearest the phenolic ring and the heterocyclic nitrogen atom, giving two five membered chelate rings. Therefore, the working pH was chosen as 9.5 for the subsequent experiments. The addition of more than 10 mL of buffer solution to adjust the pH did not affect the sorption of Co(II).



Fig. 4. Effect of pH on the % uptake of Co(II) using β -CDP-PAN polymer {Co(II) 70 ng/mL, sample volume, 100 mL, shaking time 40 min, adsorbent dose 0.4 gm, particle size 100 mesh}

3.2. Effect of the amount of adsorbent (Bed Height)

The amount of the resin is another important parameter that affects the uptake of an analyte. A quantitative retention (\geq 95%) cannot be achieved when the resin is less than the optimum amount. On the other hand, an excess amount of resin prevents the quantitative elution of the retained metal chelate by a small volume of the eluent. In order to optimize the smallest amount of extractant 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 gm of the resin were added to the 100 mL of the sample solution containing 70 ng/mL of Co(II) and preconcentrated by the general procedure. The quantitative recoveries were obtained for and above 0.4gm of resin (Fig. 5). Therefore, 0.4 gm of the resin has been used for subsequent experiments.

3.3. Kinetics of sorption

Shaking time is an important factor in determining the possibility of application of the β -CDBP-PAN polymer for the uptake of Co(II). For studying the effect of shaking time on the % uptake, a 0.4 g amount of resin was stirred with 100 mL of solution containing 70 ng/mL of Co(II) for different shaking time (ranging from 10 to 50 minutes) with an interval of 10 minutes at optimum pH. The results of % uptake of Co(II) vs. the shaking time show that the percentage uptake reached maximum (above 95%) at 40 min (Fig. 6). Therefore, the shaking time of 40 min. was selected as the adsorption equilibrium time.



Fig. 5. Effect of the amount of adsorbent on the % uptake of Co(II) using β -CDP-PAN polymer {Co(II) 70 ng/mL, sample volume, 100 mL, shaking time 40 min, pH 9.5, particle size 100 mesh}



Fig. 6. Effect of the contact time on the % uptake of Co(II) using β -CDP-PAN polymer {Co(II) 70 ng/mL, sample volume, 100 mL, pH 9.5, resin amount 0.4 gm, particle size 100 mesh}

3.4. Effect of the sample volume

In order to explore the possibility of enriching low concentration of analytes from large volume of sample, the effect of sample volume on the retention of Co(II) was also investigated. 50, 100, 150, 200, 250, 300, 350, 400, 450 mL of sample solutions containing a fixed amount of Co(II), 0.4 gm of resin at optimum pH and shaken for 40 min. Quantitative uptakes (\geq 95%) were obtained for sample volume of \leq 400 mL (Fig. 7). Therefore, 100 mL of sample solution was adopted for the preconcentration of analyte from sample solutions. The preconcentration factor is calculated by the ratio of the highest sample volume (400 mL) and the lowest eluent volume (4 mL). Therefore, the preconcentration factor was 100.



Fig. 7. Effect of the sample volume on the % uptake of Co(II) using β -CDP-PAN polymer {Co(II) conc. fixed, shaking time 40 min, pH 9.5, resin amount 0.4 gm, particle size 100 mesh}

3.5. Effect of HCl concentration on elution

The effect of HCl concentration and volume on elution of Co(II) on β -CDP-PAN polymer was studied by carrying out the elution with (0.5-4) M HCl. The results indicate that the highest recoveries for Co(II) were obtained when HCl concentration was 2M or more. Hence 2M was chosen as eluent for further experimental conditions.

3.6. Effect of eluent volume

In order to obtain the quantitative recovery of retained Co(II) metal ion on β -CDP-PAN polymer was studied by carrying out the elution with (1-6 ml) of 2MHCl (Fig. 8). During these studies, 100 ml aliquots of the sample solutions containing 70 ng/ml of Co(II) were used at pH 9.5. Quantitative recovery values were obtained by using 4 ml of eluent.



Fig. 8. Effect of the eluent volume on the % recovery of Co(II) using β -CDP-PAN polymer {Co(II) 70 ng/ml, shaking time 40 min, pH 9.5, resin amount 0.4 gm, particle size 100 mesh}

3.7. Effect of coexisting ions

The effect of various coexisting ions on the % recovery of a solution containing 70 ng/mL of Co(II) was studied. An ion was considered to interfere when its presence produced a variation in the absorbance of the sample $\pm 5\%$. Among the anions examined CO₃²⁻, SO₃², SO₄²⁻, NO₃⁻, IO₃⁻, NO₂⁻ did not interfere at concentrations 1000 times more than those of the analyte. The complexation between Co(II) and PAN was completely masked by EDTA (ethylenediamine tetraacetate ion) and cyanate even at lower concentration. Alkali and alkaline earth metal ions did not interfere. The results are shown in Table 1.

3.8. Analytical figure of merits

The standard addition technique was applied to the real water and vegetable samples and the recoveries obtained revealed that the proposed method has good accuracy. The analytical procedure was also validated by determining Co(II) in certified reference alloy material. The results revealed good agreement between the observed values and the certified values. The limit of detection (LOD) was calculated as three times the standard deviation (3σ) of 3 replicate measurements with the proposed preconcentration procedure. The precision of the method was evaluated as the RSD,

obtained after analyzing a series of three replicates with the preconcentration step; it is found to be ≤ 2.9 for Co(II).

Table 1. Tolerance lin	nit of foreign	ions in t	he determina	tion
	of Co(II)			

Ion	Tolerance Limit
	$W_{foreign ion}/W_{Co(II)}$
NO ₃ ⁻ , SO ₄ ⁻ , HPO ₄ ² ⁻ , SCN ⁻ , NO ₂ ⁻ ,	>1000
PO4 ³⁻ , ClO3 ⁻ , IO3 ⁻ , Cl ⁻ , I ⁻ , Br ⁻ ,	
$CH_{3}COO^{-}, C_{2}O_{4}^{2}$	
Na(I), K(I), Mg(II), Ba(II), Al(III),	1000
Rb(I), Cs(I), Ag(I)	
Sb(III), Ca(II), Zr(IV), Ti(IV)	500
Th(IV), Sn(II), As(III)	100
^a Fe(III), ^b Ni(II)	10
^c Zn(II), ^d Pb(II), ^e Fe(II), ^e Mn(II), ^f Hg(II),	1
^f Cd(II)	
EDTA, CN ⁻ , F ⁻ , S ₂ O ₃ ²⁻	1

^amasked with 1.0 mL of 5.0% ammonium oxalate; ^bmasked with 1.0 mL of 2.0% dimethylglyoxime; ^cMasked with 1.0 mL of 10.0% sodium citrate solution; ^dmasked with 2.0 mL of 1% sodium sulphate; ^emasked with 2.0 mL of 3.0% sodium hexametaphosphate solution; ^fmasked with mixed masking agent solution of 1.0 mL of 5.0% potassium pyrophosphate, 1.0 mL of 25.0% citric acid and 1.0 mL of 10.0% thiourea solution.

3.9. Applications of the proposed procedure

The developed method was applied with satisfactory results on water, vegetable and alloy samples. The results are depicted in Tables 2, 3 and 4, respectively.

 Table 2. Determination of Co(II) in different water samples;

 mean±RSD(%) (for n=3)

Sample	Spiked	Found	%Relative	%Recovery				
	(ng/ml)	(ng/ml)	Error	±RSD(%)				
Тар	0.0	25.5						
Water								
	50.0	74.0	3.0	97.0±1.6				
	45.0	69.1	2.9	97.1±2.9				
R.O.	0.0	N.D.						
Water								
	60.0	58.5	2.5	97.5±1.7				
	55.0	53.4	2.9	97.1±2.4				
BMW	0.0	N.D.						
	150.0	68.3	2.4	97.6±1.3				
	30.0	29.2	2.7	97.3±2.0				
NTD (1 () 1)							

N.D. (not detected)

Table 3. Determination of Co(II) in leafy vegetable samples;
$mean \pm RSD(\%)$ (for n=3)

Sample	Spiked	Found	%Relative	%Recovery				
_	(ng/ml)	(ng/ml)	Error	$\pm RSD(\%)$				
Carrot	0.0	N.D.						
	45.0	43.7	2.9	97.1±2.2				
	75.0	72.9	1.9	97.2±1.9				
Spinach	0.0	N.D.						
	20.0	19.4	3.0	97.0±2.1				
	40.0	38.9	2.8	97.2±2.2				

N.D. (not detected)

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TADIC 7. Determination of $CO(11)$ in contined and y samples. Anneo J , incan-RSD(J 0) (1

Alloy Sample	Composition (%)	Present (ng/ml)	Found (ng/ml)	% Relative Error	% Recovery±RSD(%)
Alnico 9	Al 7 Ni 15	35.0	34.0	2.8	97.1±1.5
	Co 35 Cu 4	70.0	68.7	1.8	98.1±1.7
	Ti 5	47.0	45.4	3.4	96.6±1.5

Table 5. Comparison of the preconcentration factors of the various solid supports used for the preconcentration of Co(II)											
Modification Mode	Adsorbent	Modifier	pH/SD	PF	LOD/ RSD (%)	Detection	Preconcen. Mode	Eluent	Applications	%Rec.	Ref.
Im- mobilization (Physically modified)	Diaion HP- 2MG	Aspergillus fumigatus	8/500	50	0.72/<7	FAAS	Off-line	10 mL of 1M HCl	Water, tomato paste, black tea & dust	≤98	35
Chemically modified	Silica gel	SPIMP	5/800	83	2.0/2.3	FAAS	Off-line	6.0 mL of 4.0M HNO ₃	Rice, fish, biscuit & vegetables	97.8	36
Im- mobilization (Physically modified)	Silica gel	Salicyl- aldoxime	4.2/800	50	1.5/	AAS	Off-line	20.0 mL of 0.5M HNO ₃	Pharma samples	93	37
Im- pregnation (Physically modified)	Naphthalene	ΤΜΤΑ	4.5/210	250	0.51/2.31	FAAS	Off-line	2.0 mL of 1.0M HCl	Orange juice & Vitamin B ₁₂ capsules	>97	38
Chemically modified	XAD-4	O-Amino benzoic acid	6/3500	150	/3.5	FAAS	Off-line	20.0 mL of 1.0M HNO ₃	Synthetic metal mixture solution	98	39
Chemically modified	Silica gel	Aminothio- amidoanthra -quinone	4.5/60	20	0.95/<9	FAAS	Off-line	5.0 mL of 1% HNO3	Different water samples	97	40
Chemically modified	Cellulose	8-Hydroxy- quinoline	5.3/500	100	/3.2	FAAS	Off-line	20.0 mL of 1.0M HNO ₃	Water & Pharma samples	97.5	41
Im- pregnation (Physically modified)	Amberlite- XAD-1180	PAR	9.5/	50	3.3/3.5	FAAS	Off-line	20.0 mL of 3.0M HNO ₃	Buffalo river sediment and water samples	95±3	42
Im- pregnation (Physically modified)	Amberlite XAD-7	BPMBDA	7.0/500	200	0.24/1.8	FAAS	Off-line	5.0 mL of 2M HNO ₃ in ethanol	Different water samples	98.4	43
Im- pregnation (Physically modified)	Ambersorb 563	PAN	9.0/500	125	0.21/<10	FAAS	Off-line	10.0 mL of 1M HNO ₃ in acetone	Natural water samples & sediment ref. material	>95	44
Chemically modified	XAD-2	Pyro- catechol	8.0/100	40	0.59/4.7	FAAS	On-Line	80 μL 0.5M HCl	Black tea & rice flour	≥97	45
Embedded	Styrene- EGDMA	5,7-DCQ	7.0/40	200	2.0/2.5	FAAS	Off-line	5.0 mL of 2.0M HCl	Soil & sediments	>99	46
Chemically modified	Silica gel	FCPASA	9.0/20	100	14.0/3.1	FAAS	On-Line	1M HNO3	Different water samples	91	47
Inclusion	β-CDP	PAN	9.5/400	100	4.2/<2.9	UV-VIS	Off-line	4.0 mL of 2.0M HCl	Water, food & alloy samples	≥95	This work

SD: Sorbent dose; PF: Preconcentration factor; LOD: limit of detection (ng/ml); Rec: Recovery; FAAS: Flame atomic absorption spectrometry; AAS: atomic absorption spectrometry; UV-Vis: Ultra violet-visible spectrophotometry; SPIMP: 2-[-(3-silylpropylimino) methyl]phenol; TMTA: 2,4,6-trimorpholino-1,3,5-triazin; BPMBDA: N,N'-bis(pyridine-2-yl-methyl0benzene-1,4-diamine; 5,7-DCQ: 5,7-dichloroquinone-8-ol; PAR: 4-(-2-pyridylazo)-resorcinol; FCPASA: 5-formyl-3-(1'-carboxyphanylazo) salicylic acid; PAN: 1-(2-pyridylazo)-2-naphthol

4. CONCLUSION

The developed SPE procedure allowed the determination of Co(II) ions to be carried out at ng/ml. Due to preconcentration step, it was possible to obtain low limit of detection for Co(II). The adsorbent is ecofriendly, recyclable and a very small amount of it is consumed per analysis making it highly economical. The advantages of the proposed method are simple, time saving, convenient, rapid and low cost. A compareson of the proposed method with other preconcentration procedures is presented in Table 5. Some parameters obtained were compared to those presented by other methods described in the literature. As can be seen from the data in Table 5, the proposed method developed by using β-cyclodextrin polymer modified PAN system has a relatively high preconcentration factor and a low LOD when compared to other methods reported in literature.

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