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SOLID PHASE EXTRACTION AND PRECONCENTRATION OF Ni(II) USING 1-(2-PYRIDYLAZO)-2-NAPHTHOL) (PAN) MODIFIED *β*-CYCLODEXTRIN BUTANEDIOL DIGLYCIDYL ETHER POLYMER AS A SOLID PHASE EXTRACTANT

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A sensitive, simple and selective preconcentration method was developed for the preconcentration of trace amounts of Ni(II) ions using 1-(2-pyridylazo)-2-naphthol (PAN) modified *β*-cyclodextrin butanediol diglycidyl ether polymer as a solid phase extractant. Potential factors affecting the sorption of Ni(II) were investigated. Meanwhile, the optimum conditions were established. The sorbed Ni(II) was eluted using 5 ml of 2M HCl. The preconcentration factor was 70. The detection limit for Ni(II) was 1.18 ng/ml. The relative standard deviation (RSD %) was <1%. The developed method was successfully applied for the determination of trace Ni(II) in different water and potato chip samples as well as reference alloy samples.

Keywords: *β*-cyclodextrin polymer; Ni(II); preconcentration; 1-(2-pyridylazo)-2-naphthol

ЕКСТРАКЦИЈА И ПРЕКОНЦЕНТРАЦИЈА ВО ЦВРСТА ФАЗА НА Ni(II) СО МОДИФИЦИРАН ПОЛИМЕР НА *β*-ЦИКЛОДЕКСТРИН-БУТАНДИОЛ-ДИГЛИЦИДИЛ-ЕТЕР СО 1-(2-ПИРИДИЛАЗО)-2-НАФТОЛ) (PAN) КАКО ЕКСТРАКТОР ВО ЦВРСТАТА ФАЗА

Беше развиен едноставен селективен метод со преконцентрација на траги од јони на Ni(II) користејќи модифициран полимер на β-циклодекстрин-бутандиол-диглицидил етер со 1-(2-пиридилазо)-2-нафтол) (PAN) како екстрактор во цврста фаза. Беа испитувани потенцијалните фактори кои влијаат на сорпцијата на Ni(II). Во исто време се определени оптималните услови за екстракција. Сорбираниот Ni(II) беше изделен со 5 ml 2M HCl. Добиениот фактор на преконцентрација изнесува 70. Границата на детекција за Ni(II) е 1,18 ng/ml. Релативната стандардна девијација (RSD %) е <1%. Развиениот метод беше успешно применет за определување траги на Ni(II) во примероци вода и чипс од компир, како и во легури.

Клучни зборови: полимер на *β*-циклодекстрин; Ni(II); преконцентрација; 1-(2-пиридилазо)-2-нафтол

1. INTRODUCTION

Nickel is a siderophile element; its abundance in average crustal rocks is 75 mg g^{-1}. Nickel can be released into the atmosphere from several industrial processes, including oil- and coal-burning power plants, trash incinerators and the metallurgy industry. Although nickel is considered an essential element, which acts as an activator of several enzymes to enhance insulin activity, excessive nickel in the organism is very toxic, which can be manifested by effects on the activity of natural killer cells [1]. Preconcentration is commonly used if the concentration of trace elements in a sample is lower than the detection limit of an analytical technique. Furthermore, a number of interfering constituents can be removed using preconcentration procedures. The literature reports several preconcentration procedures such as liquid–liquid extraction [2], micellar mediated extraction [3], coprecipitation [4], cloud point extraction [5], electrochemical methods [6] and solid phase extraction [7]. Disadvantages such as significant chemical additives, solvent losses, complex equipments, considerable secondary waste, prefiltration problems and time-consuming procedures limit the application of most of these techniques. Solid phase extraction, however, solves this problem as it offers several advantages. These include: (1) high enrichment factors; (2) short extraction times; (3) minimal costs due to low consumption of reagents; (4) absence of emulsion; (5) ease of automation; (6) safety with respect to hazardous samples; and (7) high selectivity. This technique is also attractive as there is no need to use organic solvents, which may cause toxic effects. An actual tendency in the field of solid-phase preconcentration is related to the adoption of new sorbent materials with exceptional performance, such as high chemical resistance, selectivity, large surface area, and obviously, high sorption capacity. An important strategy for metal enrichment is the incorporation of complexing reagents in solid supports. 1-(2-Pyridylazo)-2-naphthol (PAN) is a versatile organic chromogenic reagent that forms complexes with a variety of transition metals in different pH ranges and with different adsorbents. There are many studies that have reported the use of PAN-modified solid supports in the preconcentration of metal ions [8–19]. The other advantage of PAN is the absence of its affinity for alkali and alkaline earth metal ions.

The purpose of the present study was to assess the feasibility of using 1-(2-pyridylazo)-2-naphthol modified *β*-cyclodextrin butanediol diglycidyl ether polymer as a solid phase extractant for the preconcentration and determination of Ni(II) at ng/ml levels in different samples.

2. EXPERIMENTAL

2.1. *Materials and methods*

All reagents used were of analytical reagent grade. Double distilled water was used throughout the experiment. The Ni(II) solution was prepared by dissolving 0.237 g of nickel chloride hexahydrate [$NiCl_2 \cdot 6H_2O$] in 100 ml of distilled water to give a standard stock solution of 4×10^{-6} mol/l. The solution of the PAN reagent was prepared by dissolving an appropriate amount of PAN (Fluka Chemical Company) in N,N-dimethylformamide. 1,4-Butanediol diglycidyl ether was obtained from Sigma Aldrich (USA). β-Cyclodextrin was obtained from SD Fine Chemicals Ltd. (Mumbai, India). Buffer solutions were hydrochloric acid/sodium acetate for pH 2.0–3.5, sodium acetate/acetic acid for pH 4.0–6.5 and ammonia/ammonium chloride for pH 8–11. Glassware was washed with chromic acid and soaked in 5% nitric acid and rinsed with double distilled water before use.

2.2. *Apparatus*

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

2.3. *Sample collection and conditioning*

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

2.4. *Determination of Ni*(*II*) *in different potato chip samples*

Potato chips of selected brands that were available locally were purchased for further processing. Wet digestion of the chips was carried out by digesting 0.5 g of each sample with a mixture of $HNO_3 : H_2SO_4$ (8 : 4). This mixture was heated up to 130 ºC for 1 h. After cooling, 5 ml of distilled water was added to the sample and mixed. The residue was filtered. The sample was then diluted to 100 ml with distilled water. An aliquot of the above sample was taken and spiked with a known amount of Ni(II) and assayed using the general procedure.

2.5. *Determination of Ni*(*II*) *in standard alloys*

The accuracy of the proposed method was verified by the determination of ions in standard reference alloy samples. 0.1 g of the standard alloy was completely dissolved in 20 ml of hydrochloric acid 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 in a water bath. The solution was cooled, filtered and diluted to 100 ml with double distilled water. Further dilutions were made as required. An aliquot of this solution was taken and preconcentration was performed by the procedure described below.

2.6. *Procedure*

2.6.1. *Synthesis of β-cyclodextrin butanediol diglycidyl ether polymer* (*β-CDBP*)

β-CDBP was synthesized by a previously published method [20]. A brief procedure for the synthesis is mentioned here. 20 g of β-CD were dissolved in 50 ml of 20% NaOH. To this was added 20 ml of butanediol diglycidyl ether dropwise. The polymer was formed in 1.5 h and dried in a vacuum at 90ºC. The polymer was ground and sieved into <60, 60–80, 80–100 and >100 mesh fractions. The 80–100 mesh fraction was washed with double distilled water five to six times. Then, the polymer was dried again under vacuum at 90 ºC and kept at room temperature (25 ºC) in a dessicator.

2.6.2. *Inclusion of PAN in the β-CDBP cavity to form the β-CDBP-PAN modified polymer*

5.0 g of the synthesized polymer, *β*-CDBP (80–100 mesh size), was placed in a 250 ml stoppered conical flask. To this was added 10 ml of 9.0 pH buffer solution and the polymer was allowed to swell for 15 minutes. A fixed volume of 4×10^{-6} mol/l solution of PAN was added to the treated polymer and made up to 50 ml with distilled water. This was shaken for two hours. The colored polymer was washed with distilled water and vacuum dried at 100ºC. The modified polymer was stored in a dessicator until use.

2.6.3. *Batch extraction procedure*

At room temperature, i.e. 30 ºC, *β*-CDBP-PAN (500 mg) and 10.0 ml of buffer solution (pH 9.5) were added to a 100 ml stoppered conical flask. The mixture was allowed to stand for approximately 15 min so that β-CDBP-PAN could be swollen sufficiently. 100 ng/ml of Ni(II) was 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 a standard spectrophotometric method [21].

2.6.4. *Elution of Ni*(*II*)

Ni(II) retained on the *β*-CDBP-PAN polymer was eluted using 5 ml of 2 M HCl. Eluted Ni(II) was assessed using a standard spectrophotometric method [21].

2.6.5. *Regeneration of the polymer*

The polymer was regenerated by dipping it in 10.0% TX-100 (*w*/*v*) for 1 h and then washing with distilled water. *β*-CDBP was further treated with HNO_3 and was finally washed with distilled water to neutral conditions.

3. RESULTS AND DISCUSSION

3.1. Sorption of Ni(II) as a function of pH

For the solid phase extraction of heavy metal ions on different types of chelating resins, the pH of the aqueous solution is one of the foremost factors for quantitative recovery of the analyte [22]. Therefore, the effect of pH on the sorption of Ni(II) on the PAN-modified polymer was studied in the pH range of 4.5–10.5. For this purpose, 100 ng/ml of Ni(II) was spiked in 100 ml of the model solution and the pH of this solution was adjusted using different buffer solutions, then the general preconcentration procedure was followed. The correlation between the % sorption of Ni(II) on the resin and pH is presented in Fig. 1. The results of this study show that quantitative sorption (≥95%) of Ni(II) ions was achieved over the pH range of 8.5-10.5. Therefore, for subsequent experiments, pH 9.5 was selected as the working pH.

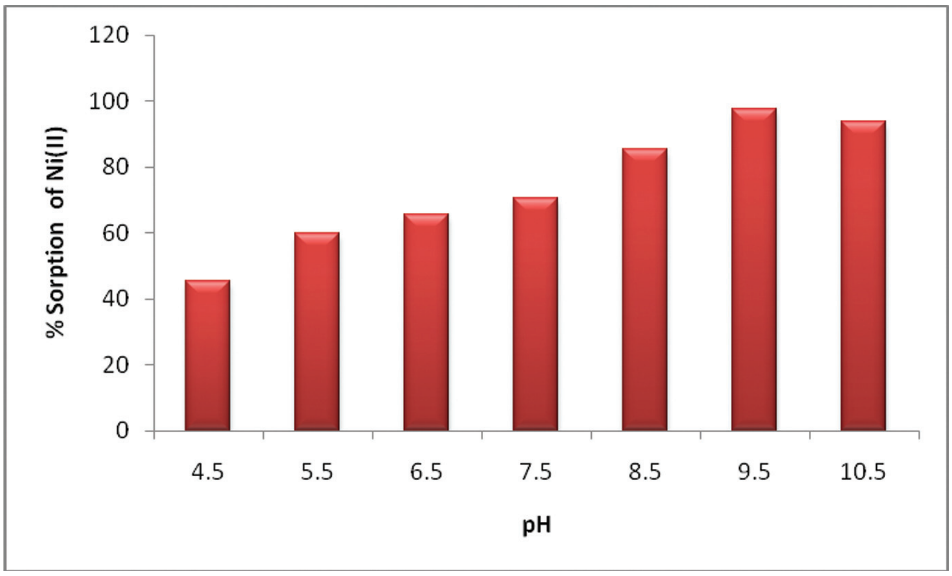

Fig. 1. Effect of pH on the sorption of Ni(II) on PAN-loaded *β*-CDBP polymer (100 ng/ml of Ni(II); 500 mg of the resin; 100 ml sample volume; temperature 25 ºC)

3.2. *Effect of the amount of adsorbent (bed height)*

The amount of solid phase extractant material is another imperative factor in sorption studies for the quantitative recovery of metal chelates [23]. Quantitative retention (≥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, 100, 200, 300, 400, 500, 600 and 700 mg of the resin were added to the same volume of the synthetic solution containing 100 ng/ml of Ni(II) and preconcentrated by the general procedure. Quantitative recoveries were obtained with 500 mg or more of resin (Figure 2). Therefore, 500 mg of the resin was used for subsequent experiments.

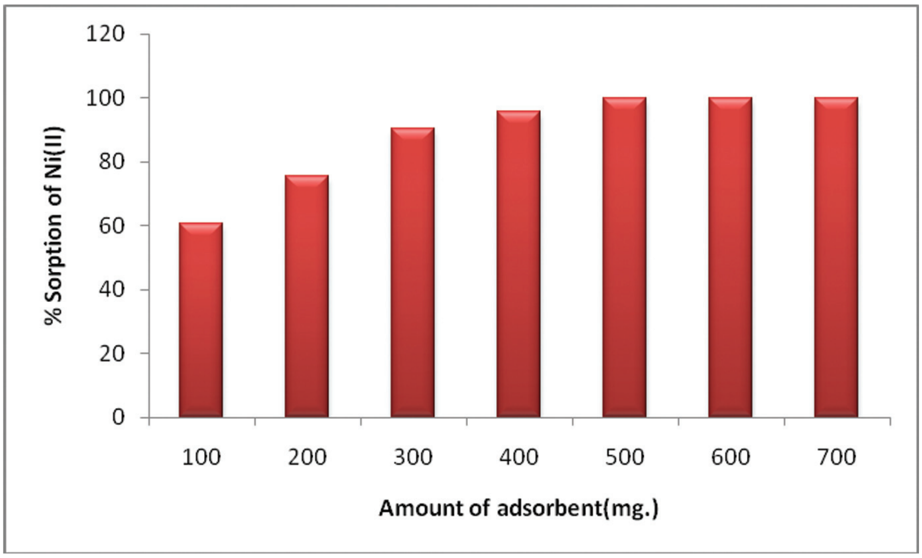

Fig. 2. Effect of the amount of the chelating resin on the sorption of Ni(II)
(100 ng/ml of Ni(II); pH 9.5; 100 ml sample volume; temperature 25 ºC)

3.3. *Kinetics of metal sorption*

The kinetics of metal sorption is an important factor in determining the possibility of application of the β-CDBP-PAN polymer for the selective uptake of Ni(II). 500 mg of the resin were shaken with 100 ml of the solution containing 100 ng/ml of Ni(II) at room temperature for different contact times ranging from 20 to 70 min. The loading half time ($t_{1/2}$) needed to reach 50% sorption of the total loading capacity (estimated from Figure 3) was found to be less than 20 min. The kinetics of the resin-metal interaction is sufficiently rapid for Ni(II) at the optimum pH. The faster uptake of Ni(II) on *β*-CDBP-PAN reflects a good accessibility of the chelating resin sites to metal ions. Therefore, contact time of 40 min was selected as the sorption equilibrium time.

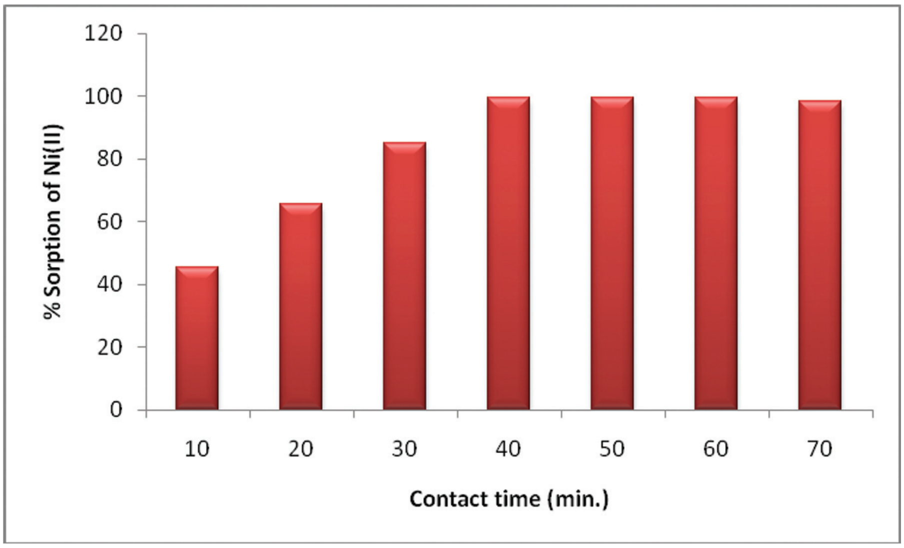

Fig. 3. Kinetics of Ni(II) sorption on PAN loaded β-CDBP polymer
(100 ng/ml of Ni(II); pH 9.5; 500 mg of resin; 100 ml sample volume; temperature 25 ºC)

3.4. *Effect of the sample volume*

In order to explore the possibility of enriching a low concentration of analyte from a large volume of solution, the effect of sample volume on the retention of Ni(II) ions was also investigated. For this purpose, 25, 50, 100, 150, 200, 250, 300, 350, 400 and 450 ml of sample solutions containing 100 ng/ml were assayed. Quantitative sorption (≥95%) was obtained for a sample volume less than 350 ml (Figure 4). Therefore, a sample volume of 100 ml was adopted for the preconcentration of the analyte from sample solutions.

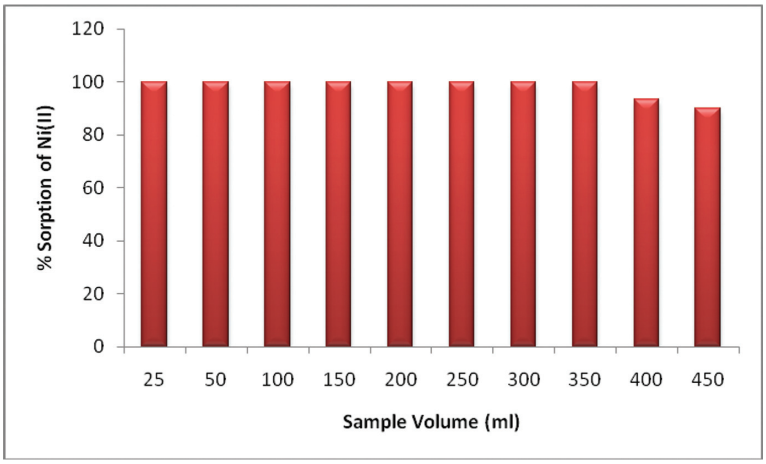

Fig. 4. Effect of the sample volume on the sorption of Ni(II) (100 ng/ml of Ni(II); pH 9.5; 500 mg of resin; contact time 40 min; temperature 25 ºC)

3.5. *Effect of the eluent concentration and its volume*

Various concentrations of hydrochloric acid were examined to obtain quantitative recovery values for Ni(II) from the chelating resin. The recovery values were not quantitative when the concentration of HCl was < 2 M > used as an eluent. Therefore, 2 M HCl was used for quantitative recovery of Ni(II) from the β-CDBP-PAN polymer in further studies. The volume of the eluent (2 M HCl) that can completely strip the retained Ni(II) from the solid phase is an important parameter for obtaining the maximum pre-

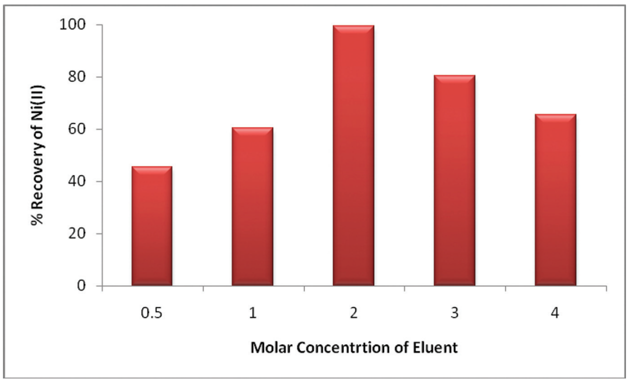

Fig. 5. Effect of the molar concentration HCl on the elution of Ni(II) (100 ng/ml of Ni(II); pH 9.5; 500 mg of resin; 100 ml sample volume; contact time 40 min; temperature 25 ºC)

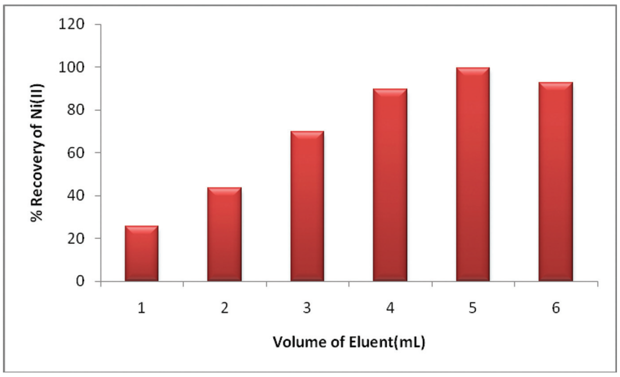

Fig. 6. Effect of the volume of HCl on the elution of Ni(II) (100 ng/ml of Ni(II); pH 9.5; 500 mg of resin; 100 ml sample volume; contact time 40 min; temperature 25 º)

concentration factor. Thus, some experiments were carried out in order to choose the proper eluent volume for stripping Ni(II) ions from the chelating resin (Figures 5 and 6). The recovery values for Ni(II) ions from the chelating resin were greater than 95% in the eluent volume range of 4–6 ml. Thus, an eluent volume of 5 ml was selected for further studies. The preconcentration factor was found to be 70 if the volume of eluent used was 5 ml.

3.6. *Matrix effects*

The preconcentration procedure for trace metals can be strongly affected by other constituents of the sample. For this reason, the reliability of the proposed method was examined in the presence of possible interfering ions. Interfering cations and anions were added to the model samples. Table 1 shows the tolerance limit of interfering ions to Ni(II).

Table 1

The effect of foreign ions on the determination of 100 ng/ml of Ni(II)

Foreign ions	Tolerance limit [WForeign ion/ WNi(II)]
NO_3^-, SO_4^{2-}, HPO_4^{2-}, SCN^-, NO_2^-, PO_4^{3-}	>1000
Na^+, K^+, Mg^{2+}, Ba^{2+}, Al^{3+}, Rb^+, Cs^+, Ag^+	1000
Sb^{3+}, Ca^{2+}, Zr^{4+}, Ti	500
Th^{4+}, Sn^{2+}, As^{3+}	100
[a]Fe^{3+}, [b]Cu^{2+}, [c]Co^{2+}	10
[d]Hg^{2+}, [d]Cd^{2+}, [e]Pb^{2+}, [f]Fe^{2+}, [g]Mn^{2+}	1
EDTA, Br^-, F^-, CN^-, citrate	1

[a] Masked with 1.0 ml of 5.0% ammonium oxalate solution;
[b] Masked with 1.0 ml of 3.0% sodium thiosulphate;
[c] masked with 1.0 ml of 10.0% α-benzilmonoxime;
[d] masked with 5.0 ml of 2.0% sodium thioglycollate solution;
[e] masked with 2.0 ml 0f 1.0% sodium sulfate solution;
[f] masked with 1.0 ml of 2.0% 1,10-phenenthroline;
[g] masked with 2.0 ml 3.0% sodium hexametaphosphate solution;
masked with 1.0 ml of 10.0% sodium citrate solution.

3.7. *Total sorption capacity*

The capacity of the resin determined according to [24] was found to be of 29.05 µg/g of dry *β*-CDBP-PAN resin.

Table 2

Various parameters studied for the preconcentration of Ni(II) using β-CDBP-PAN modified polymer as the sold phase extractant

Parameters	Ni(II)
pH	9.5
Shaking time	40 min
Sample volume	100 ml
Adsorbent dose	500 mg
Mesh size of the polymer	80-100
Eluent used	HCl
Eluent concentration	2 M
Volume of eluent used for elution	5 ml
Preconcentration factor	70
Sorption capacity	29.05 µg/g of resin
Limit of detection	1.18 ng/ml
Relative standard deviation	< 1%
Limit of quantification	3.7 ng/ml

4. APPLICATIONS OF THE METHOD

The method was applied to the determination of Ni(II) in water, potato chip samples and certified alloy samples. The results are shown in Tables 3, 4 and 5, respectively.

Table 3

Determination of Ni(II) in different water samples

Water samples	Spiked (ng/ml) Ni(II)	Found (ng/ml) Ni(II)[a]	Relative error %	Recovery %
Tap water	0.0	11.6	--	--
	70.0	83.7 ± 0.36	–3.00	103.0
	55.5	68.8 ± 0.21	–3.06	103.0
Rose water	0.0	N.D.	--	--
	60.0	62.1 ± 0.26	–3.5	103.5
	50.0	51.7 ± 0.21	–3.4	103.4
Bore water	0.0	15.7	--	--
	60.0	77.3 ± 0.17	–2.7	102.6
	70.0	85.7 ± 0.17	–2.0	102.0

[a] Mean ± standard deviation

Table 4

Determination of Ni(II) in potato chip samples

Sample	Spiked (ng/ml) Ni(II)	Found (ng/ml) Ni(II)[a]	Relative error %	Recovery %
American sour cream and onion flavor	75.0	74.5 ± 0.25	0.66	99.33
	80.0	79.4 ± 0.17	0.75	99.25
	60.0	59.5 ± 0.16	0.83	99.16
Classic salted	35.0	34.4 ± 0.21	1.714	98.28
	40.0	39.5 ± 0.10	1.250	98.75
	50.0	49.6 ± 0.15	0.80	99.20

[a] Mean ± standard deviation

Table 5

Determination of Ni(II) in certified alloy samples

Alloy sample	Certified composition	Present (ng/ml) Ni(II)	Found (ng/ml) Ni(II)a	Relative error %	Recovery %
Constantan	Cu 60, Ni 40	80.0	79.80 ± 0.05	0.25	99.75
		40.0	39.81 ± 0.10	0.47	99.52
		100.0	99.70 ± 0.05	0.30	99.70
Monel wire	Ni 60, Cu 33, Fe 6.5	48.0	47.76 ± 0.10	0.50	99.51
		32.0	31.85 ± 0.05	0.46	99.53
		120.0	119.7 ± 0.07	0.25	99.75

[a] Mean ± standard deviation

5. ACCURACY OF THE METHOD

The accuracy of the described preconcentration method was tested in recovery studies by adding known amounts of Ni(II) to water samples and potato chip samples and also by the analysis of certified alloys containing Ni. The results obtained from the analysis of different samples are depicted in the tables and the recovery values were satisfactory. These results confirm the validity of the proposed method.

6. *Comparison with other solid phase extraction methods*

Table 6

Comparison of the described method with some solid phase extraction methods for Ni(II) determination

Impregnated resin	Eluent	Detection technique	Adsorbent dose (mg)	PF[a]	pH	Sample	RSD(%) / DL[b]	Ref.
2-Aminothiazole immobilized on silica gel	2 M HCl	FAAS	500	10	--	Hydrated fuel ethanol samples	3 / 2.3	25
Chromosorb-107 resin	2.5 ml of 4.5 M HNO_3	ETAAS	300	10	≥/6	Apple leaves and sea water samples	± 2 / --	26
Chitosan functionalized with 3,4-dihydroxy-benzoic acid	0.5 ml of 2 M HNO_3	FI-ICP-AES	--	11.8	5.5	River and sea water samples	-- / 0.09	27
Pyrocatechol violet immobilized amberlite XAD-2	7.5 ml of 4 M HCl/ HNO_3	FAAS	1000	18	3.0	Well water samples	≤ 9 / --	28
Chemically modified silica gel with amino thio-amido anthraquinone	5 ml of 1% HNO_3	FAAS	60	20	≥ 4	Various water samples	≤9 / 2.9	29
Amberlite XAD-2 functionalized with 5-palmitoyl-8-hydroxyquinoline	20 ml of 2M HNO_3	FAAS	1000	50	4.5–6.0	Water samples	5.2 / 4.0	30
1-(2-Pyridylazo)-2-naphthol modified SiO_2 nanoparticles	5 ml of 6 M HCl	UV-VIS	30	60	9.2	Water samples	4.1 / 0.43	31
TiO_2 nanotubes using 8-hydroxy quinoline	3 ml HNO_3	FAAS	200	66.7	8.0	Water samples	2.6 / 1	32
1-(2-Pyridylazo)-2-naphthol immobilized on amberlite XAD-1180	20 ml of 2M HNO_3	FAAS	400	100	9.0	Water samples	≤8.5 / 1.2	33
Activated carbon	2.5 ml of 1.5 M HNO_3	FAAS	125	100	4.5	Natural water samples	9 / 0.6	34
Silica gel modified with 3-aminopropyltriethoxy silane	5 ml of 2 M HCl	GFAAS	500	--	≥ 5	Sea water samples	± 2 / 0.5	35
1-(2-Pyridylazo)-2-naphthol immobilized on β-cyclodextrin butanediol diglycidyl ether polymer	5 ml of 2 M HCl	UV-VIS	500	70	9.5	Water and alloy samples	<1 /1.18	This work

[a]PF–Preconcentration factor; [b]DL–Detection limit (ng/ml or μg/l)

7. CONCLUSION

The proposed preconcentration method consists of a simple and low-cost procedure which permits the quantitative recovery of Ni(II) from water and certified alloy samples. Based on the high affinity of the modified polymer for Ni(II), the selective determination of Ni(II) is possible. The preparation of the polymer is easy and the method has good accuracy, sensitivity and repeatability. The modified polymer was used in all the experiments performed for this study. It has a unique stability, is very economical and can be used repeatedly without a loss of sorption capacity. The resin is also durable against strong acids and concentrated bases. A resin used 10 times or more in succession did not lose its sorption efficiency. The relative standard deviation (RSD %) of the method was <1.0%. The recoveries were ≥ 95% in all cases. The method provided a preconcentration factor of 70, which is higher than in most studies in the literature. The limit of quantification was 3.7 ng/ml.

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