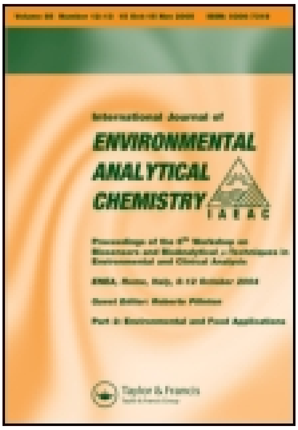

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Determination of heavy metal ions in environmental samples employing preconcentration on novel resins of polyurethane foam linked with o-Aminophenol or o-Hydroxyphenylazonaphthol

N. Burham [a], S.M. Abdel-Azeem [a] & M.F. El-Shahat [b]

[a] Chemistry Department, Faculty of Science, Fayoum University, Fayoum City, Egypt

[b] Chemistry Department, Faculty of Science, Ain-Shams University, Cairo, Egypt

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Determination of heavy metal ions in environmental samples employing preconcentration on novel resins of polyurethane foam linked with o-Aminophenol or o-Hydroxyphenylazonaphthol

N. Burham[a]*, S.M. Abdel-Azeem[a] and M.F. El-Shahat[b]

[a]*Chemistry Department, Faculty of Science, Fayoum University, Fayoum City, Egypt;*
[b]*Chemistry Department, Faculty of Science, Ain-Shams University, Cairo, Egypt*

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o-Aminophenol (AP) and its azo derivative with ß-Naphthol(Naph) is bonded to polyurethane foam (BPUF) and used as solid phase extractor of nickel, cadmium and zinc ions in aqueous solutions prior to their atomic absorption spectrometric determinations. The novel resins of polyurethane foam were characterised by density, elemental analysis, IR spectra and chemical stability. The parameters including pH, sample volume, matrix effects were investigated. The relative standard deviation (RSD) of the combined method of sample treatment, preconcentration and determination with atomic absorption spectrometry is generally lower than 10%. The limit of detection was found between 0.06 and 0.22 $\mu g\,L^{-1}$. The procedure was used for determination of analyte ions in natural water samples, apple leaves and fish liver.

Keywords: polyurethane foam; o-Aminophenol; ß-Naphthol; nickel; zinc; cadmium; preconcentration

1. Introduction

Trace levels of heavy metals are widely distributed in the environment due to industrial and agricultural processes [1]. The contamination by heavy metals from various environmental sources including natural waters is a great concern nowadays [2]. Thus, the determination of trace amounts of cadmium, zinc and nickel in water and food is very important in several fields, such as environmental analysis, food control and toxicology [3,4]. Determination of low levels of metals in complex matrices such as food generally is associated with preconcentration steps despite capability and sensitivity of analytical instrumentation having increased in recent years [5].

In these determinations, low concentration levels of the analytes and high levels of matrices are the main problems [6,7]. To solve these problems, solid phase extraction has been widely used as one of the important preconcentration methods for its simplicity, accuracy, repetitive use of sorbent and high preconcentration factor. Several enrichment procedures involving different analytical techniques have been developed for the determination of trace levels of elements in food samples such as table salt [8–10], flour [11] and leafy vegetables [12]. Great efforts have been contributed to develop new

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*Corresponding author. Email: n_burham@yahoo.com

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sorbents based on hydroxyapatite, activated carbons, biomass, silica gels, zeolites, clays and synthetic polymers [13–18].

Since Bowen [19] reported that flexible polyurethane foam (PUF) can be used as selective sorbent for a number of substances from dilute aqueous solutions, the application of polyurethane foam for extraction and separation of various inorganic and organic species has attracted considerable attention [20–22].

Loaded PUF extracts metal ions after complex formation. Organic and inorganic ligands can be used for this purpose. Several off-line and on-line procedures have been established in this way. In a batch method, for example, zinc, cadmium and mercury ions were quantitatively extracted with loaded or grafted PUF after formation of thiocyanate complexes [23]. Loaded PUF offers a wider range of applications than unloaded PUF. A multi-element procedure was proposed for simultaneous preconcentration and determination of cadmium, copper, nickel, lead and zinc in water using PUF loaded with piperidine dithiocarbamate [24].

Two main problems stand behind the preparation of organic reagents chemically bounded to PUF: lack of selectivity of the unloaded foams and leaching of reagents from the loaded ones.

Many studies have recently shown that the functional groups in polyurethane foam are highly reactive towards diazotisation by sodium nitrite and then azo coupling. The following were used as a coupling component in the reaction with PUF: 4-nitrophenyldiazonium tetrafluoroborate [25,26], 8-hydroxyquinoline [27], alizarin red s [28], resorcinol [29], 4-hydroxytoluene and 4-hydroxyacetophenone [30], α-Naphthol [31], ß-Naphthol [32] and acetylacetone [33].

β-Naphthol has been used for the preconcentration of Ni^{2+}, Cu^{2+}, Ag^{+} and Hg^{2+} in our previous study [32]. This study involved the synthesis of a stable chelate foam matrix by covalently linking β-Naphthol to the foam in one step of diazotisation and coupling. The purpose of the present work is to anchor o-Aminophenol to the foam backbone followed by β-Naphthol in two steps diazotisation and coupling. An off-line preconcentration procedure is developed for the determination of Ni^{2+}, Zn^{2+} and Cd^{2+} in various environmental samples.

o-Aminophenol was chosen as a coupling agent in the first step in order to have a chelating amino group after the first coupling. This $–NH_2$ group is able to take part in reactions typical of aromatic amines such as diazotisation and azo coupling with β-Naphthol in the second step. The number of organic molecules immobilised on the support surface allows more removal of ions from the aqueous solution. It can coordinate with metal ions of different radii with high selectivity. Thus, anchoring of β-Naphthol to previously bonded AP on the foam surface through an azo spacer in the second step may result in chelating foam of long arm chelating centres with four nitrogen atoms, two of them adjacent to the two hydroxyl groups of the phenolic coupling component. The method is simple, selective, economical and sensitive.

2. Experimental

2.1 *Reagents and solutions*

Analytical grade-reagents were employed for the preparation of all solutions. Doubly distilled water (DDW) was used in all experiments. Standard metal ion solutions were diluted to obtain working solutions.

Stock solutions of Zn (II), Cd (II) and Ni (II) were prepared by taking appropriate amounts of analytical reagent zinc sulphate, $ZnSO_4 \cdot 7H_2O$ (Riedel-De Haén AG Seelze, Hannover, Germany), nickel (II) chloride, $NiCl_2 \cdot 6H_2O$ (Adwic, El-Nasser Chemicals, Cairo, Egypt), and cadmium nitrate, $Cd(NO_3)_2 \cdot 4H_2O$ (Panreac, Barcelona, Spain). o-Aminophenol was from Aldrich Milwaukee, USA and ß-Naphthol from Merck (Darmstadt, Germany). HCl and NaOH were from Adwic, El-Nasser Chemicals (Cairo, Egypt). Polyurethane foam (PUF), commercial open cell polyether type 31.60 kg m^{-3}, was supplied from an Egyptian company for foam production (Cairo, Egypt). All liquids were used without any further purification.

2.2 *Instrument*

The detection system used was an AAS5 FL flame atomic absorption spectrometer (Carl Zeiss Technology, Model 1995, Germany). The operating parameters for analytes measurements are depicted in Table 1. Atomic absorption measurements were conducted in air/acetylene flame.

Infrared (IR) spectra were recorded on a JASCO 420 FTIR spectrometer. The pH adjustment was carried out using the microprocessor pH meter (BT 500 BOECO, Germany) after calibration against standard buffer solutions. A mechanical shaker with up to 200 rpm (SL 350 Nüve San. Malz. Imal. Ve Tic. A.S., Akyurt, Ankara-Turkey) was used.

2.3 *Preparation of bonded polyurethane foams*

A portion of 20 g of small cubes of white PUF was washed with DDW, followed by acetone and allowed to dry at room temperature. The foam cubes were soaked in HCl 50% (v/v) with stirring at 0–3°C. To this mixture, 200 mL of 1 mol L^{-1} $NaNO_2$ solution was added drop by drop with continuous stirring until the PUF attained a yellow colour. One litre of 1 mol L^{-1} of o-Aminophenol solution was added to the PUF with stirring and kept in the refrigerator as previously reported [30,33]. The resulting brown-coloured aminophenol bonded PUF (AP-BPUF) material was filtered then washed with 0.1 mol L^{-1} HCl followed by DDW, and finally with acetone, then dried at room temperature.

Table 1. Operational measurement conditions for flame AAS.

	Metal ion		
Parameters	Zinc	Cadmium	Nickel
HC lamp current (mA)	4.0	2.0	6.0
Slit width (nm)	0.5	1.2	0.2
Wavelength (nm)	213.9	228.8	232.0

Notes: The linear equations along with regression (R^2) by using flame AAS determination are as follows: Zn(II), $A = 0.10919C + 0.00082$, $R^2 = 0.99202$; Cd(II), $A = 0.12272C + 0.0017$, $R^2 = 0.99995$. Ni(II), $A = 0.02688\mathrm{C} + 0.00079$, $R^2 = 0.99692$.

The previously prepared AP-BPUF was further diazotised by the method mentioned above then coupled to β-Naphthol (Naph) (14.4 g in 400 mL of 1 mol L^{-1} NaOH), and left for 24 h below 3°C. After that, the foam was washed repeatedly with DDW and dried in the air. o-Hydroxyphenylazo naphthol (HPANaph-BPUF) has a dark red colour.

2.4 *General procedures*

2.4.1 *Batch method*

2.4.1.1 *Effect of sample pH and shaking time.* To study the effect of pH and shaking time on the extraction of metal ions: In separate 100 mL stoppered flasks, 20 µg of the tested metal ions in 20 mL solution (1 µg/1 mL) adjusted at different pHs using NaOH or HCl to adjust only the beginning pH. The solutions were mixed with 0.1 g of the modified foam cubes. The pH of the metal ion solution was adjusted before equilibration with the foam over a range of pH 1–10. The flasks were then shaken for one hour in a mechanical shaker, at room temperature.

The effect of shaking time on the extraction of the metal ions was studied: 0.1 g of the foam cubes were added to 20 mL (1 µg mL^{-1}) metal ion solution at the optimum pH. The samples were automatically shaken for different time intervals (5, 10, 20 , . . . , 120 min). The foam cubes were separated and the amount of metal ion remained in the aqueous solution was measured by FAAS procedure. The amount of metal ion extracted by the foam was calculated as concentration difference. If the metal ion concentration in aqueous solution before extraction is C_o and the concentration after equilibration with the foam is C. Then, the percentage extraction (%E) can be calculated by the equation:

$$\%E = [(C_o - C)/C_o] \times 100$$

2.4.1.2 *Effect of diverse ions.* The interference effect of some electrolytes, which may adversely affect the extraction of the studied metal ions, was investigated by testing the extraction percentage of 20 µg in 20 mL of the analyte ions at different concentrations of interfering ions. The tolerance limit was considered at ion concentration causing a relative error $\geq \pm 5\%$. The interfering ions considered are those normally present in water, e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Mn^{2+}, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-} and PO_4^{3-}.

2.4.1.3 *Reproducibility test.* The precision of the developed procedure was tested as the reproducibility of the experiment and it was carried out as follows: 10 sample solutions were prepared equally; 20 mL solution contains the studied metal ions (1 µg mL^{-1}) each adjusted to the optimum extraction conditions with 100 mg sorbent. The uptake was calculated for each sample by the concentration difference before and after extraction and the precision was calculated as RSD %.

2.4.2 *Column method*

2.4.2.1 *Breakthrough capacity.* To study the breakthrough capacity and the chromatographic behaviour of metal ions, a glass column (10 cm × 1 cm) packed with 1 g dry foam was used. Solutions (2 mg metal ion) were passed through the foam column at 3 mL min^{-1} flow rate. The flow rate was controlled by the column tap.

2.4.3 *Sample preparation*

2.4.3.1 *Analysis of certified sample.* Certified reference material NIST-SRM 1577b bovine liver was analysed: Decomposition of this material was carried out according to minor modification of the method [34]: Accurately weighed 0.4 g of material was treated with 4.0 ml of 1 : 1 (v/v) nitric acid solution and kept in a clean glass vessel. Afterwards, the vessel was closed and digested for 72 h. The thermal heating was carried out in a stove at 170°C for 16 h. After cooling at room temperature, the residue was diluted with DDW and adjusted to pH 7.0 with 10% (w/v) sodium hydroxide solution. Finally, the volume was made up to 25 ml by DDW.

2.4.3.2 *Water analysis.* Tap water sample (1500 mL) was collected from our research laboratory in Faculty of Science or Yussof River at Fayoum City, Egypt. The water samples were filtered through a filter paper to separate any suspended particles, adjusted to the optimum conditions, placed in glass container and passed through the modified foam columns at flow rate 3 mL min^{-1}. The columns were rinsed with doubly distilled water and 0.1 mol L^{-1} HCl eluted the metals. The concentration of each metal ion was determined by the recommended method. The experiment was triplicated and the RSD values were calculated.

2.4.3.3 *Analysis of apple leaves.* Fresh apple leaves were obtained from Fayoum City, Egypt, washed by DDW until dust free, then put in an oven between two aluminum foil sheets and dried at 105°C for 12 h. The dry leaves were ground in a porcelain mortar, dried again at 120°C for 6 h until constant weight, and then the procedure previously reported was followed [35]. An accurately weighed dried sample 4.013 g apple leaves were heated in 40.0 mL of concentrated (14.0 mol L^{-1}) HNO_3 until nearly dry and diluted to 1000 mL with DDW, removing cellulosic residues by filtration. Each 250 mL was adjusted to the optimum conditions and passed through the modified foam column. The retained metal ions in the column were eluted with 0.1 mol L^{-1} HCl and the metal ions were measured by flame AAS. The experiment was triplicated and the RSD values were calculated.

2.4.3.4 *Analysis of fish sample.* Fish sample (alive) was obtained from Qaroun farm for fish at Fayoum City, Egypt. The sample was cut and the liver was taken, cleaned well, washed several times with DDW then transferred into a clean and dry beaker and dried at 105°C for 24.0 h. After this, the fish liver sample was transferred into a clean and dry ignition crucible and ashed for 6.0 h in a muffle oven at 200°C then 400°C and finally at 600°C; the temperature was changed every 2.5 h. The sample was heated in 20 mL concentrated nitric acid (14.0 mol L^{-1}) till nearly dried then diluted up to 1000 mL with DDW and adjusted to the optimum conditions then passed into the column. The experiment was repeated three times and the extraction and RSD % values were found.

3. Foam characterisation

3.1 *Density*

For density measurement, the dry foam cubes (1 cm^3) were weighed. Density of the white foam and the bonded foam were measured. It was found that the density increases with increasing the number of coupling steps because the addition of the new chelating

Table 2. Elemental analysis of the modified foams.

	Calculated (%)			Experimental (%)		
Sample name	C	H	N	C	H	N
Untreated PUF	62.07	8.8	4.64	62.09	8.9	4.65
AP-BPUF	62.01	8.64	5.35	62.12	8.62	4.80
HPANaph-BPUF	62.73	8.39	5.53	62.71	9.60	5.38

Table 3. Important IR bands.

	IR bands (wavenumber, cm^{-1})				
Sample designation	υ_{NCO}	υ_{OH}	υ_{CO}	υ_{NH2}	$\upsilon_{N=N}$
Untreated PUF	2100	3311–3509	1655	3111–3299	–
AP-BPUF	–	3329–3565	1661	2926–3297	1473
HPANaph – PUF	–	3300–3506	1653	–	1473

molecules to the backbone of the PUF leads to an increase in the weight of the foam. The bonded foam has more cross linking than white polyurethane foam due to the additional bonds between the reagents and other groups in the foam. These give indication about the difference in the chemical properties between white polyurethane foam and the new bonded foams.

3.2 *Elemental analysis*

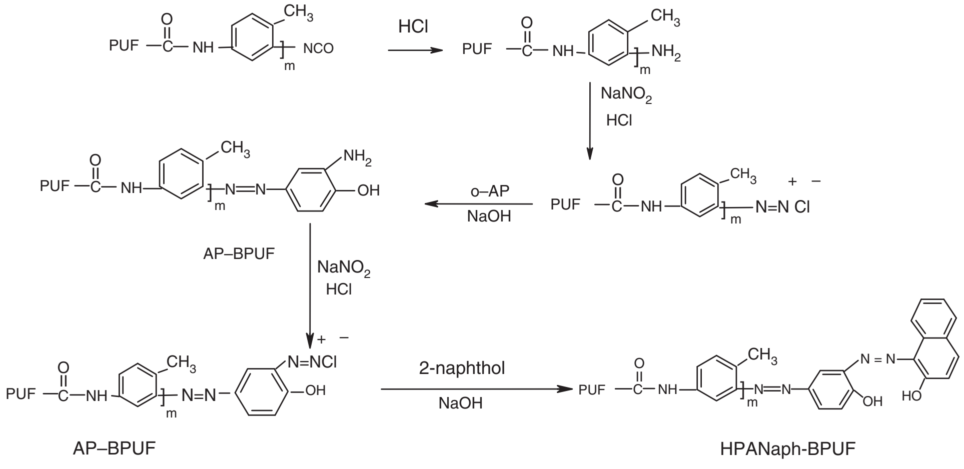
The results of the elemental analysis of AP-BPUF and HPANaph-BPUF are given in Table 2. These results show good agreement with the calculated carbon, hydrogen and nitrogen values from the proposed formula. It is obvious that the second coupling occurred by ratio (1 : 1) of AP-BPUF to HPANaph-BPUF. The elemental analysis is calculated as a relative ratio not as an absolute value to indicate the increase in nitrogen %, because PUF is a polymer and it is quite difficult to calculate the % of C, H and N.

3.3 *IR spectra*

Infrared spectra studies on the untreated and bonded polyurethane foams were made using potassium bromide technique. The characteristics groups of the bonded polyurethane foams are listed in Table 3. Scheme 1 shows the proposed reactions involved in the preparation of the novel bonded PUF.

3.4 *Stability of the bonded PUFs*

The chemical stability was investigated by measuring the change in the uptake capacity of the sorbents for the studied metal ions after soaking the modified foams for 12 hours in acids 1–6 mol L^{-1}HCl, 1–2 mol $L^{-1}H_2SO_4$, 1 mol $L^{-1}HNO_3$ and alkaline solutions of 1–2 mol L^{-1} NaOH and 1–2 mol L^{-1} NH_4OH, as well as organic solvents e.g. methanol,



Scheme 1. Proposed modification of PUF.

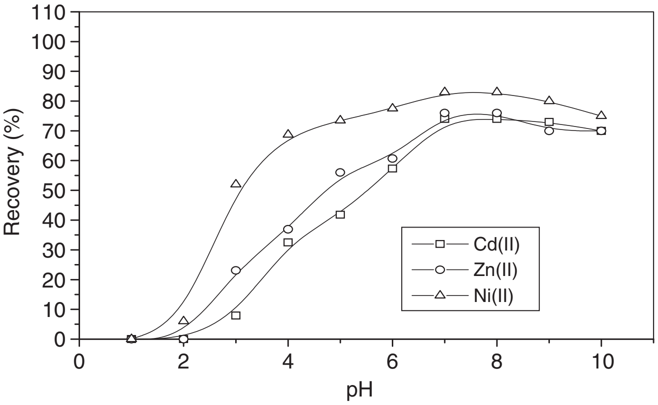


Figure 1. Effect of pH on the extraction of Cd(II), Zn(II) and Ni(II) with AP-BPUF. The experiment was triplicated.

ethanol, isopropanol, n-butanol, acetone, chloroform and carbontetrachloride. However, the decomposition is negligibly small and no significant decrease in the extraction capacity was observed, which indicates that AP-BPUF and HPANaph-BPUF extractors are believed to be sufficiently stable.

4. Results and discussion

4.1 *Effect of solution pH on the retentions of metal ions*

The effects of pH on preconcentration of metal ions on AP-BPUF and HPANaph-BPUF were examined in the range of pH 1–10 before sorption as a beginning pH. The results are presented in Figures 1 and 2. The extraction depended on the pH of the sample solution, which was nearly constant in the range of pH 7–8 for all the metal ions. In all, subsequent studies were performed at pH 7. At low pH values ($pH < 3$) the chelating

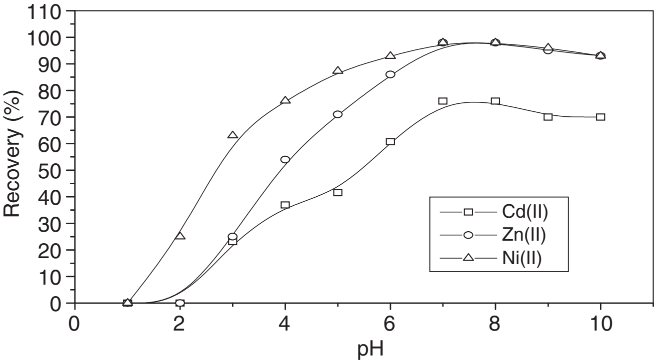


Figure 2. Effect of pH on the extraction of Cd(II), Zn(II) and Ni(II) with HPANaph-BPUF. The experiment was triplicated.

Table 4. Effect of pH on the separation factor (α) and the selectivity for the analyt ions on HPANaph-BPUF.

	Separation factor (α)					
pH	Zn/Cd	Cd/Zn	Cd/Ni	Ni/Cd	Zn/Ni	Ni/Zn
4	0.87	1.14	0.81	1.23	0.71	1.40
5	0.98	1.00	0.83	1.21	0.81	1.23
6	1.08	0.93	0.86	1.16	0.93	1.08
7	1.04	0.96	0.96	1.04	1.00	1.00
8	1.04	0.96	0.96	1.04	1.00	1.00
9	1.09	0.92	0.94	1.06	0.99	1.01
10	1.10	0.94	0.90	1.10	1.00	1.00

groups –N=N– and OH in the sorbent is believed to be protonated by H^+ which reduce the affinity of the sorbent towards the positively charged metal ions and reach zero uptake with Zn, Cd and Ni at pH 1.

The greater affinity of metal ions with the two steps coupled foam is confirmed through the stable complexes formed between the metal ion and the free electron pairs on the nitrogen atoms of the azo group and the two oxygen atoms of the two hydroxyl groups. Values of the separation factors (α) for the analyte ions on HPANaph-BPUF are in Table 4. The separation factor is the degree of resolution, or the efficiency of the method to separate a specific pair of ions under specific pH value. It is a measure of the ability of the system to separate two solutes.

From Table 4 it is clear that, Ni > Zn, Cd > Zn and Ni > Cd in the pH range of 4–6, 4–5 and 4–6, respectively and Ni $\approx$ Cd, Zn $\approx$ Cd, Ni $\approx$ Zn in the pH range of 7–9, 7–8 and 7–10, respectively. Thus, the separation factor is ≈ 1 indicating no possibility of separation of the two metal ions in these pH ranges. These results show that controlling the pH can play an important role in enhancing the selectivity of the studied metal ion separation with the HPANaph-BPUF.

Thus, the new modified foam is a promising material to be applied for metal ions removal from aqueous solutions.

Table 5. Optimum conditions for the proposed procedure.

Sorbent	Procedure	Property	Metal ion Zn(II)	Cd(II)	Ni(II)
AP-BPUF	Batch method	pH range	7–8	7–8	7–8
		Loading half time($t_{1/2}$), min	15.0	12.0	20.0
		Capacity (μ mol g^{-1})	7.2	5.9	6.8
		RSD (%)[a]	3.0	3.5	2.7
	Column method	Breakthrough capacity (μ mol g^{-1})	4.2	1.7	3.1
HPANaph-BPUF	Batch method	pH range	7–8.5	7–8	7–8.5
		Loading half time($t_{1/2}$), min	7.0	10.0	12.0
		Capacity (μ mol g^{-1})	13.3	7.9	10.5
		RSD (%)[a]	3.6	3.0	2.3
	Column method	Breakthrough capacity (μ mol g^{-1})	8.2	4.7	7.1

Note:[a]RSD = Relative standard deviation for 10 replica for the uptake.

Table 6. Kinetic data from Lagergren plots with the new PUF sorbents at 25°C.

PUF type	Parameter	Zn	Cd	Ni
AP-BPUF	K, min^{-1}	0.032	0.049	0.043
	$t_{1/2}$, min	21.6	14.1	16.1
HPANaph-BPUF	K, min^{-1}	0.099	0.334	0.133
	$t_{1/2}$, min	7.0	2.1	5.2

4.2 *Effect of shaking time on the extraction*

The percentage of extraction of Ni(II), Cd(II) and Zn(II) on the new bonded foams has been measured by the static extraction technique in separate experiments. The results obtained indicated that equilibrium extraction was obtained after 20–25 mins of shaking. The loading half-time $t_{1/2}$ is the time needed to reach 50% uptake of the total foam capacity. The results are summarised in Table 5.

The faster uptake of the analyte ions with AP-BPUF or HPANaph-BPUF sorbents probably reflects the better accessibility of the analyte ions on the chelating sites in the bonded foams and strong bond formation with the built AP or Naph sites.

Lagergren plot is a very useful mathematical method to calculate the half-time for reactions. The time dependence is given by the Lagergren equation $\log(q_e - q_t) = \log q_e - Kt/2.303$, where q_e and q_t are the amount of metal ion ($\mu g\, g^{-1}$) sorbed by 100 mg bonded PUF after reaching the equlibrium at any time t (min), respectively, and K is the rate constant (min^{-1}). A plot of $\log(q_e - q_t)$ against t resulted in a straight line relationship which indicates that the process is first-order with regard to the concentration of the sorbed metal ions. The calculated values for K and $t_{1/2}$ are recorded in Table 6, where $t_{1/2} = 0.693/K$.

4.3 *Desorption studies*

Since metal extraction occurred at neutral or weakly basic conditions, consequently the desorption of Zn, Cd and Ni should be performed in acidic media. Really, extraction of metal ions on HPANaph-BPUF in batch or minicolumn is negligible under acidic conditions ($\text{pH} < 2$). Therefore, elution studies were performed with hydrochloric acid solution. The acid concentrations were tested in the range of $0.05\text{–}1.5\,\text{mol}\,\text{L}^{-1}$ for the desorption ability of $20\,\mu\text{g}$ of the studied ions. Complete desorption was achieved at acid concentrations $\geq 0.1\,\text{mol}\,\text{L}^{-1}$ HCl for the analyte ions.

4.4 *Sorption capacity*

The sorption capacity of the HPANaph-BPUF for the retention of zinc, cadmium and nickel was also determined by batch procedure under the optimum conditions. The results demonstrated that the HPANaph-BPUF has a sorption capacity of 13.3, 7.9 and $10.5\,\mu\text{mol}\,\text{g}^{-1}$ for zinc, cadmium and nickel, respectively, as shown in Table 5.

The new chelating foams have hard donor atoms thus; it could form stable complexes with small ionic radii metal ions such as Al, Cr, Mn, Co, Ni, Fe, Cu, Zn., etc. However, the new foam has good affinity for large size Cd ions. This means that the donating centres are accessible for complex formation process with metal ions of different atomic radii.

Furthermore the number of chelating centres should be theoretically equal for the two modified foams, but the second coupling has led to the formation of new chelating sites with greater number of chelating groups (two OH groups and one azo group) which provides higher chelating stability. In addition the second coupling has led to longer spacer arm chelating groups which reduce the steric hindrance. Finally, the overall metal uptake is enhanced.

4.5 *Effect of the foreign ions*

The interference effect is one of the main problems that influence the efficiency of separation and determination in the trace level. The matrix effect in highly saline samples such as seawater is an important factor.

These interferences due to co-existing ions were studied systematically by the proposed procedure. The criterion used for interference was a ±5% relative error of the extraction. As shown in Table 7, it is clear that the presence of the most investigated species have no significant effect on the preconcentration of zinc, cadmium and nickel by HPANaph-BPUF.

4.6 *Breakthrough capacity*

The breakthrough capacities are more significant and useful than batch capacities in the foam chromatographic applications. From the Figures 3 and 4, it is clear that the steep curves at breakthrough point for all metal ions suggest the ability of HPANaph modified foam for separation and preconcentration of these metal ions. From Table 5 the capacities of HPANaph-BPUF for the metal ions can be seen to be quite high in comparison to the AP-BPUF bonded foam. Although the removal capacity of the new bonded HPANaph is generally low, it can be used to remove metal ions from dilute solution with lower detection limit and higher preconcentration factor.

Table 7. Interference effect of foreign ions.

Foreign ions	Conc. of foreign ions mg L^{-1}	Recovery % *HPANaph-BPUF*			Recovery % *AP-BPUF*		
		Zn(II)	Ni(II)	Cd(II)	Zn(II)	Ni(II)	Cd(II)
Non	–	98.0	98.0	96.0	76.0	83.0	74.0
NaCl	15000	94.5	98.0	97.7	70.0	80.7	70.3
KCl	1000	97.6	96.0	95.4	69.8	81.0	72.0
$Ca(NO_3)_2$	50	96.7	97.4	96.4	75.7	83.3	73.3
$Mg(NO_3)_2$	50	96.2	95.0	98.1	75.9	82.7	72.8
NH_4Cl	1500	100.0	100.0	96.1	71.6	81.0	71.3
NaBr	100	98.8	98.7	97.0	74.5	80.0	71.0
NaI	100	97.0	98.2	97.0	75.3	78.0	71.0
Na_2SO_4	500	97.6	95.0	95.0	72.4	82.8	73.3
$NaNO_3$	1000	97.7	98.7	97.1	71.6	82.1	74.0
Na_3PO_4	150	96.4	96.0	98.0	72.4	81.3	68.4
$FeCl_3$	0.10	97.3	96.6	98.1	76.2	83.7	73.1
$MnCl_2$	0.10	95.0	94.1	99.2	76.0	82.4	74.0

Notes: Tolerance limits ±5% for the studied ions 20 μg in 20 mL.
Based on three replicate measurements.

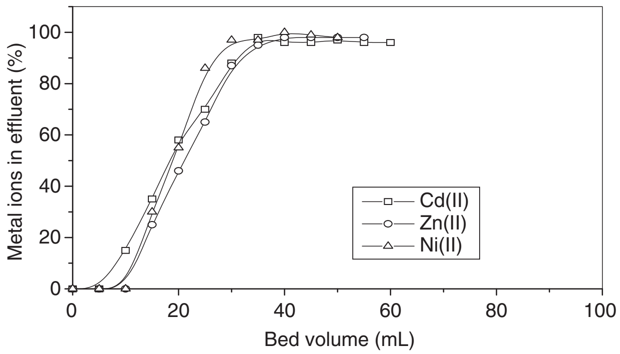


Figure 3. Breakthrough capacity of Cd(II), Zn(II) and Ni(II) with Ap-BPU at 3 mL min^{-1} and 10u μg mL^{-1}soulutions. The experiment was triplicated.

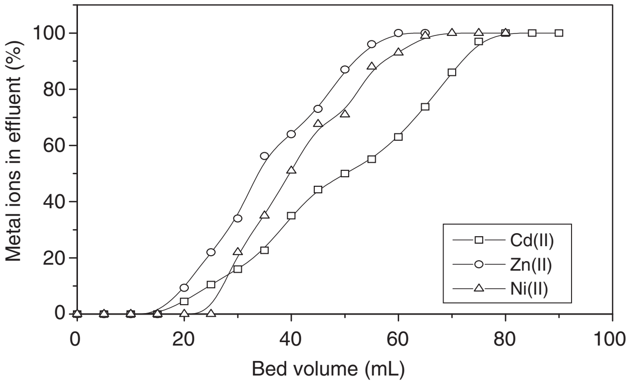


Figure 4. Breakthrough capacity of Cd(II), Zn(II) and Ni(II) with HPAN-BPU at 3 mL min^{-1} and 10u μg mL^{-1}soulutions. The experiment was triplicated.

Table 8. Preconcentration factor (CF) of Zn(II), Cd(II) and Ni(II) with the new sorbents.

Foam Type	Metal ion	Initial Volume mL	Desorption Volume ml	Recovery%	CF	RSD%
AP-BPUF	Zn(II)	1500	12	94	125	2.7
	Cd(II)	1500	12	98	125	3.0
	Ni(II)	1500	12	96	125	2.8
HPANaph-BPUF	Zn(II)	1500	3.5	96	429	3.5
	Cd(II)	1500	3.5	98	429	3.6
	Ni(II)	1500	3.0	97	500	1.1

Notes: Initial metal ion concentration 13 µg $L^{-1.}$
Based on three replicate measurements in the same loaded column.

4.7 *Effect of the sample flow rate*

The extraction of Ni, Zn and Cd on the HPANaph-BPUF column was studied at different solution flow rates with a fixed sample volume (50 mL, 1 µg mL^{-1}). For each metal ion, a set of solutions were passed through the HPANaph-BPUF column at a flow rate varying from 1 to 12 mL min^{-1}. The metal ions could be eluted by 10 mL of 0.1 mol L^{-1} HCl and determined by flame AAS. It was found that the optimum flow rate was 3 mL min^{-1}. The percentage uptake decreased from 97 to 90% by increasing the flow rate from 3 to 10 mL min^{-1}; the sampling was volume based.

4.8 *Preconcentration of metal ions from different solution volumes*

The effect of the ratio of sample to the elution volume (preconcentration factor) on the percentage uptake was studied by column procedure; the results obtained are shown in Table 8. Elution of Ni, Zn and Cd in 1500 mL sample from the new bonded PUF columns was achieved with recoveries ranging from 94–98% and RSD varies within 1.1–3.6% by 12 mL and 3–3.5 mL in the case of AP-BPUF and HPANaph-BPUF, respectively. Eluent volumes were obtained from the study of desorption breakthrough. The results show that the tested metal ions can be effectively concentrated from large volumes of dilute aqueous solutions using HPANaph-BPUF columns. Preconcentration factors of 500, 429 and 429 were achieved for Ni, Cd and Zn, respectively. The value of preconcentration factor for Ni is superior to that reported [32].

4.9 *Detection limits*

Limits of detection (LOD) were calculated as three times the standard deviation (σ) of blank of seven replicate measurements by applying 1500 mL blank solution using the proposed method. Also, the limit of quantification LOQ was calculated from blank concentration + 10σ. The LOD recorded in Table 9 was found to be 0.06, 0.06 and 0.22 µg L^{-1} for Ni, Cd and Zn, respectively. The values of LOD are comparable with those obtained using Amberlite XAD-2 [36–39].

4.10 *Validation of the method*

Certified reference material NIST-SRM 1577b (bovine liver) was analysed by the proposed method. The obtained data are listed in Table 10. It is obvious from the extraction

Table 9. Limits of detection and quantification of Zn, Cd and Ni with the modified sorbents.

Foam type	Metal ion	LOD μg L^{-1}	LOQ μg L^{-1}
AP-BPUF	Zn(II)	0.385	0.910
	Cd(II)	0.034	0.111
	Ni(II)	0.071	0.197
HPANaph-BPUF	Zn(II)	0.223	0.370
	Cd(II)	0.061	0.200
	Ni(II)	0.056	0.147

Table 10. Determination of zinc and cadmium in a certified sample.

Sorbent	Element	Certified values μg g^{-1}	Found by the present method μg g^{-1}	Recovery (%)	RSD (%)
AP-PUF	Zn	127.0	115.5	91	6.8
	Ni	–	–	–	–
	Cd	0.50	0.44	89	5.0
HPANaph-PUF	Zn	127.0	124.1	98	3.0
	Ni	–	–	–	–
	Cd	0.50	0.521	104	3.7

percentage and the RSD % values for three measurements that these sorbents are extensively efficient for analytical determination of the studied ions. Good agreement was obtained between the estimated content by the proposed method and the certified values. This also indicates that the developed preconcentration method is not affected by potential interferences from the major biological matrix.

4.11 *Reusability of the bonded PUFs*

The metal ions were sorbed and desorbed on 100 mg of AP-BPUF or HPANaph-BPUF several times. It was found that the extraction capacity of the foam after more than 20 cycles of its equilibration with the studied ions, changes less than 3.7%. Therefore, repeated use of the bonded PUF is feasible.

5. Analytical application

The suitability of the proposed method for the analysis of natural water samples was checked by spiking samples of Yussof River and tap water with 20 μg of the studied ions. The results are given in Table 11. Good agreement was obtained between the added and analyte recovered content using the experimental procedure. The recovered values calculated by the standard additions for the investigated analyte ions were always higher

Table 11. Application of the proposed method in real water samples.

Sorbent	Sample	Metal ion	Added or spiked	Found $\mu g\,L^{-1}$	Recovery (%)	RSD* (%)
HPANaph -BPUF	Yussof River	Zn(II)	20.0	20.3	101.5	1.5
		Cd(II)	20.0	20.5	102.5	6.6
		Ni(II)	20.0	20.4	102.0	5.2
	Tap water	Zn(II)	20.0	19.9	99.5	1.4
		Cd(II)	20.0	20.1	100.5	3.4
		Ni(II)	20.0	20.2	101.0	2.9

Note: *Based on three replicate measurements in the same loaded column.

Table 12. Determination of Zn, Cd and Ni in apple leaves and fish liver.

Sorbent	Sample	Metal ion	Found $\mu g\,g^{-1}$	RSD*%
HPANaph -BPUF	Apple leaves	Zn(II)	8.4	2.8
		Cd(II)	7.0	7.1
		Ni(II)	81.0	5.7
	Fish liver	Zn(II)	8.8	2.8
		Cd(II)	7.3	7.1
		Ni(II)	73.5	5.7

Note: *Based on three replicate measurements in the same loaded column.

than 95%, thus confirming the accuracy of the procedure and the lower interference by matrix.

The accuracy and applicability of the proposed method has been applied to the determination of Zn, Ni and Cd in fish liver and apple leaves samples. The results that are given in Table 12 indicate the successful applicability of the proposed method for the determination of these cations in real samples.

6. Comparison with other methods

The new PUF sorbents exhibits highest preconcentration factor for Zn, Ni and Cd (429, 500 and 429) compared to Polyurethane foam/Acetylacetone [33], Polyurethane foam/2-(6-Methyl-2-benzothiazolylazo) chromotropic acid [40], Poly (hydroxyethylmethacrylate)/Cibacron blue F3-GA [41], Amberlite XAD-7/Xylenol orange [42], Sepabeads SP70/α-Benzoin oxime [43], Amberlite XAD-2/2-[2-(6-Methyl-benzothiazolylazo)]-4-aminophenol [44], Amberlite XAD-2/2,3-Dihydroxypyridine [45], Amberlite XAD-4/o-Aminobenzoic acid [46] and C_{18} membrane disk/methyltrioctylammonium chloride [47]. Generally, the present method requires lower acid concentration and less volume for efficient analyte elution, and gives better precision. Finally, the detection limit is comparable to those reported in the literature.

7. Conclusion

The outcomes of this work clearly demonstrate the utility offered by the proposed method. Solid-phase extraction of trace amounts of Cd, Zn and Ni using laboratory-prepared

HPANaph-PUF and their determination in natural samples by flame atomic absorption spectrometry were successfully performed. The off-line procedure developed in this study is precise and accurate alternative to conventional methods for determining cadmium, zinc and nickel in real samples. In addition, the proposed method is very simple, sensitive and inexpensive and it shows low tolerance to interfering ions. Due to its good analytical characteristics such as detection limit, preconcentration factor and precision, the proposed procedure has been recognised to be applicable for trace element analysis. Functionalised sorbents, based on polyurethane foams, are very promising materials for application in off-line and on-line preconcentration systems.

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