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# **Synthesis of a New Sorbent Based on Grafted PUF for the Application in the Solid Phase Extraction of Cadmium and Lead**

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Rafael Vasconcelos Oliveira and Valfredo Azevedo Lemos

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## **1. Introduction**

The ability to determine trace elements in various types of samples is important in many areas of science including environmental, food, geochemical, forensic, and pharmaceutical. The amount of certain elements can indicate the level of contamination in a region, the nutritional value of a food and the quality of a manufactured product, among other things. However, the matrix of the samples can be chemically complex due to the large number of substances that are present. Some of these substances can hinder the determination of trace elements due to incompatibility with some detectors, especially those based on spectrometry. For example, substances can influence the viscosity of a solution that is introduced into the flame atomic absorption spectrometer (FAAS), interfering with the nebulization process (Teixeira et al., 2005). Additionally, some substances may interfere with the pyrolysis of a sample that is introduced into the graphite tube of an electrothermal atomization atomic absorption spectrometer (ETAAS) (Zambrzycka et al., 2011; Serafimovska, et al., 2011). Another common problem occurs when the content of the element is measured at a very low level in some matrices. In this case, the technique does not provide a detection limit sufficient to determine the element in the sample. These difficulties can be resolved or reduced by improving the selectivity and sensitivity of the analytical method or by including separation and preconcentration steps in the procedure. Separation is the removal of measurable constituents or interfering substances from the sample matrix. Preconcentration is a procedure based on the separation of a measured quantity of constituents for a medium volume that is smaller than the sample matrix.

Many procedures used for separation and preconcentration that involve different techniques are found in the literature, such as liquid-liquid extraction, coprecipitation, cloud-point extraction and solid phase extraction (Zeeb & Sadeghi, 2011; Tuzen et al., 2008; Lemos et al.,

2008; Oral et al., 2011). Among these techniques, solid phase extraction deserves special attention because of several advantages this technique offers. Among these advantages is the reduction or elimination of the use of toxic organic solvents, the achievement of high enrichment factors, a high versatility due to various types of sorbents that are low in cost, decreased operating time and ease of automation. Many substances are used as sorbents for solid phase extraction of trace elements, such as naphthalene, activated carbon, alumina, silica, biosorbents, such as hair, bagasse and peat, and polymeric sorbents, including polyurethane foam (PUF) and polystyrene-divinylbenzene (Beketov et al., 1996; Zhang et al., 2011; Jamshidi et al., 2011; Costa et al., 2011; Matos & Arruda, 2006; Gonzales et al., 2009).

Naphthalene is used in preconcentration procedures because of its ability to extract or form a complex with organic species (Fathi et al., 2011). This sorbent makes it possible to achieve high enrichment factors and is soluble in many solvents, which can facilitate the detection process. However, naphthalene is toxic and possibly carcinogenic, and its use is restricted to batch procedures.

Activated carbon is an excellent material for use in extraction procedures due to its large surface area and its strong interaction with organic species and trace elements (Zhang et al., 2011). The disadvantage of using activated carbon in extraction procedures is that the interaction with some species is so strong it can cause an irreversible sorption. In addition, activated carbon has a heterogeneous surface with active functional groups that often lead to low reproducibility. These sorbents are also very reactive and can act as catalysts of undesirable chemical reactions.

Silica gel is also widely used in solid phase preconcentration procedures due to its mechanical strength, resistance to swelling caused by solvent change and a high adsorption capacity of several species (Tzvetkova et al., 2010). The disadvantages of using this sorbent include a very low selectivity and hydrolysis at basic pH.

Biosorbents are materials of great interest for use in an extraction system because of their availability and versatility (Gonzales et al., 2009). However, some of these sorbents are difficult to recover and the mechanisms of sorption of trace species are not yet fully understood.

Macroporous hydrophobic resins are good supports for developing chelating sorbents. These materials are resins based on polystyrene-divinylbenzene with a high hydrophobic character and no ion-exchange capacity. Several reagents have been incorporated into polystyrene-divinylbenzene to form chelating resins for use in preconcentration procedures (Lemos et al., 2006a).

Among the sorbents used for the extraction of organic and inorganic species for separation and preconcentration, PUF is noteworthy due to the benefits achieved. This material was used for the extraction of aqueous species for the first time in the early 1970s (Braun and Farag, 1978). Since then, PUF has been used in several procedures for separation and preconcentration, and its use has been the subject of several books and reviews (Braun, 1983; Navratil et al., 1985; Lemos et al., 2007). PUF is low in cost, easy to purchase, and provides high enrichment factors. However, this sorbent may swell when treated with solvents (Braun, 1983; Navratil et al., 1985).

The polyurethane-based polymers are widely used for solid phase extraction, with or without treatment, due to their very low cost and simplicity of preparation (Moawed & El-Shahat, 2006; Saeed & Ahmed, 2005). Moreover, the sorbent is resistant to changes in pH and has a reasonable resistance to swelling in the presence of organic solvents. This material can also be used as a support for many reagents in separation and preconcentration. For example, the combination of PUF with chelating reagents has resulted in powerful sorbents for the extraction of metal ions. This association can be effected via impregnation, functionalization or grafting of chelating reagents in PUF. The use of this material to associate with organic reagents in the separation and preconcentration of trace species has many possible applications. However, the potential for grafted or functionalized foam in solid phase extraction has not been fully explored (El-Shahat et al., 2003; Lemos et al., 2006b).

Loading of chelating reagents in PUF is a fairly simple process. In this procedure, the chelating reagent is usually dissolved in an alcoholic solution and passed through a column that is packed with PUF. In batch procedures, the reagent solution is maintained in contact with the foam for a short period, while stirring. After sorption, the sorbent is washed with an alkaline solution to remove excess chelating reagents (El-Shahawi et al., 2011a; El-Shahawi et al., 2011b).

Chelating reagents may be directly introduced into PUF by chemical bonding. This procedure, sometimes called functionalization, produces a very stable sorbent. The binding is based on the participation of amino groups, which are constituents of terminal toluidine groups of PUF, in typical reactions of aromatic amines, such as diazotization or azo coupling reactions (Lemos et al., 2010)]. These reactions result in the incorporation of a ligand by an  $-N=N-$  or  $-N=C-$  spacer arm (Burhan, 2008; Azeem et al., 2010).

PUFs grafted with chelating reagents have shown excellent characteristics for use in systems of solid phase extraction, such as selectivity, high enrichment factors and stability. Grafted PUF is a material with two or more monomers polymerized through an addition reaction to provide a simple polymer containing different subunits. Grafted PUFs are considered excellent adsorbent materials that have good stability, high extraction capacity of inorganic and organic species, and good flexibility. Grafted PUF has been prepared by mixing PUF with an appropriate reagent prior to the addition of diisocyanate to form the foam material. Several substances, such as Nile blue A (Moawed & El-Shahat, 2006), methylene blue (Moawed et al., 2003; El-Shahat et al., 2007), rosaniline (Moawed, 2004), rhodamine B (El-Shahat et al., 2003) and brilliant green (El-Shahat et al., 2003), have been incorporated into PUF to obtain grafted sorbents. Table 1 summarizes the characteristics of various procedures that use grafted PUF for solid phase extraction of trace species.

In this work, we have synthesized a new sorbent material based on PUF grafted with the chelating reagent 2-[2'-(6-methyl-benzotiazolilazo)]-4-aminophenol (Me-BTAP). The material was characterized by IR spectroscopy and thermogravimetry. The sorbent was used in a solid phase extraction system for preconcentration and determination of cadmium and lead in water samples.

Reagent	Analyte	Limit of detection ( $\mu\text{g L}^{-1}$ )	Enrichment factor	Sample	Ref
Nile blue A	Zn(II)	-----	-----	Wastewater	(M.F. El-Shahat et al., 2003)
	Cd(II)				
	Hg(II)				
Methylene Blue	Cd(II)	<5,0	40	Wastewater	(Moawed et al., 2003)
	Hg(II)	<5,0	40		
	Ag(I)	<5,0	40		
Rosaniline	Cd(II)	-----	100	Wastewater	(Moawed, 2004)
	Hg(II)				
Methylene blue	U(VI)	-----	-----	Wastewater	(M.F. El-Shahat et al., 2007)
Rhodamine B					
Brilliant green					
Methylene blue	Penicillin G	12	14	Antibiotics	(M.F. El-Shahat et al., 2010)
	Amoxicillin	15	16		
	Ampicillin	19	11		

**Table 1.** Procedures involving grafted PUF applied in the preconcentration of chemical species by spectrophotometry.

## 2. Experimental

### 2.1. Apparatus

A Perkin Elmer (Norwalk, CT, USA) model AAnalyst 200 atomic absorption spectrometer equipped with a deuterium lamp for background correction was used for absorbance measurements. The wavelength value for the hollow cathode lamp for cadmium and lead was 228.8 nm and 283.3 nm, respectively. The flow rate of acetylene and air in the burner were 2.5 and 10.0 L min<sup>-1</sup>, respectively. The nebulizer flow rate was 8.0 mL min<sup>-1</sup>.

A Digimed (model DM 20, São Paulo, Brazil) pH meter was used to measure the pH of metal solutions. The preconcentration procedure was performed on a simple on-line system involving two steps: preconcentration and elution. The system consists of a Milan model 204 (Colombo, Brazil) four-channel peristaltic pump operated with silicone tubes and a six-port Rheodyne valve model 5041 (Cotati, USA). Teflon tubes were used in the construction of the system. Polyvinyl chloride (PVC) was used in the construction of the minicolumn (3.50 cm in length and an internal diameter of 4.0 mm). The minicolumn was filled with 400 mg of the synthesized sorbent.

The infrared spectrum was obtained using KBr pellets at 1.0% (w/w) in a Perkin Elmer Spectrum One FTIR spectrometer. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves were obtained in a Shimadzu TGA-50H apparatus in an aluminum cell under air or N<sub>2</sub> (50 mL min<sup>-1</sup>) and scanned between the temperature values of 0.0 to 800.0 °C at a heating rate of 20 °C min<sup>-1</sup>.

## 2.2. Reagents

Ultrapure water from an Elga Purelab Classic was used to prepare all solutions. Working solutions of cadmium and lead at the  $\mu\text{g L}^{-1}$  level were prepared daily by diluting a  $1000 \mu\text{g mL}^{-1}$  solution of each element (Merck). Hydrochloric acid solutions were prepared by direct dilution of the concentrated solution (Merck) with ultrapure water. Acetate buffer solutions (pH 4.0-6.0), borate (pH 7.0-8.5) and ammonia (pH 9.0-9.5) were used to adjust the pH. The reagents 2,4- toluene diisocyanate (Aldrich), tin(II) 2-ethylhexanoate (Aldrich), dimethylamino-1-propanol (Aldrich), polyethylene glycol (Aldrich) and silicone oil AP 100 (Aldrich) were used in the synthesis of the sorbent.

## 2.3. Synthesis of the reagent Me-BTAP

The synthesis of the reagent 2-[2'-(6-methyl-benzothiazolylazo)]-4-aminophenol (Me-BTAP) was performed as described previously (Lemos et al., 2006a). The production of the reagent has been completed in two steps: diazotization of 6-methyl-2-aminobenzothiazole followed by the coupling of the diazotized product with 4-aminophenol. The diazotization reaction was performed by dissolving 6-methyl-2-aminobenzothiazole (3.0 g) in 50 mL of a 6.0 M hydrochloric acid solution. Then, a solution of 2.0 g of sodium nitrite in 20 mL of water at  $0-5 \text{ }^{\circ}\text{C}$  was added dropwise, and the mixture was stirred at a constant temperature of  $0-5 \text{ }^{\circ}\text{C}$  for 1 h. The diazotate mixture was added dropwise to a solution of 3.0 g of 4-aminophenol in 20 mL of an 1.0 M sodium carbonate solution at  $0-5 \text{ }^{\circ}\text{C}$  under vigorous stirring. The system was allowed to stand overnight in a refrigerator at  $0-5 \text{ }^{\circ}\text{C}$ . The resulting dark-green precipitate was filtered and purified by recrystallization in ethanol. The proposed structure of Me-BTAP is shown in Figure 1.

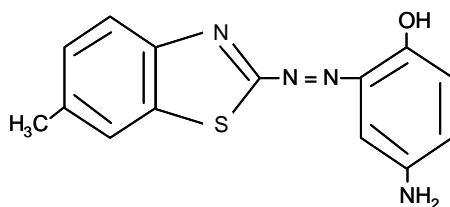


Figure 1. Proposed structure of Me-BTAP.

## 2.4. Synthesis of the sorbent

Preparation of the grafted sorbent was performed according to the following procedure (El-Shahat et al., 2003; Moawad, 2004): 20.00 g of polyethylene glycol and 0.04 g of dimethylamino-1-propanol were added to 1.0 g of distilled water under vigorous stirring. Next, silicone oil (0.05 g) and tin(II) 2-ethylhexanoate (0.04 g) were added to the mixture. The system was shaken to obtain a homogeneous mixture. The reagent Me-BTAP (0.02 g) was then added, and the mixture was stirred for ten minutes. Afterward, approximately 13.0 g of toluene diisocyanate was added gradually. The resulting polymer was cut into small pieces and washed with 1.0 M HCl, ethanol and water. After washing, the polymer was dried at room temperature.

## 2.5. Procedure for preconcentration

Solutions containing Cd and Pb were adjusted to pH 7.5 with borate buffer. These solutions were passed through the sorbent minicolumn that contained the PUF-Me-BTAP. At this stage, the elements are sorbed onto the solid phase. After preconcentration (120 s), the position of the six-port valve was changed, and an eluent flow was passed through the minicolumn. The eluent transported Cd (II) or Pb (II) to the nebulizer of the flame atomic absorption spectrometer. The analytical signal was then measured as the peak height (absorbance).

## 3. Results and discussion

### 3.1. Characterization of the sorbent

The spectrum in the infrared region of the material PUF-Me-BTAP (Figure 2) shows that the absorptions in the range of 3600-3300  $\text{cm}^{-1}$ , centered at 3448  $\text{cm}^{-1}$  and 3358  $\text{cm}^{-1}$ , can be attributed to the stretches of the -OH and -NH groups, respectively. The bands between 2970 and 2920  $\text{cm}^{-1}$  are characteristic of the aliphatic part (-CH<sub>2</sub> and CH<sub>3</sub>) of the sorbent structure. The peaks between 1500 and 1448  $\text{cm}^{-1}$  are characteristic vibrations of the -CS- group, related to the segment molecular organic reagent for the Me-BTAP. The absorption at 1708  $\text{cm}^{-1}$  was assigned to the axial deformation of the urethane carbonyl group conjugated by hydrogen bonding. There were no bands featuring free -NCO of urethane groups (1730-1720  $\text{cm}^{-1}$ ) (Radhakrishnan Nair, 2008). Solubility tests showed that the sorbent is insoluble in the following solvents: chloroform, methanol, ethanol, tetrahydrofuran, benzene, toluene, acetone, diethyl ether, isopropanol, dioxane and acetic acid. In the presence of pyridine and dimethyl sulfoxide, the material swelled. Briefly, the particles formed a gel with a volume greater than 3.2 times the initial volume.

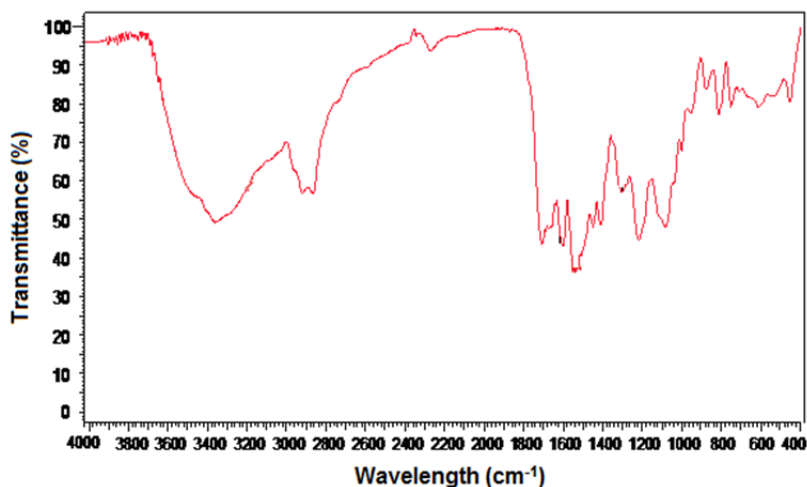
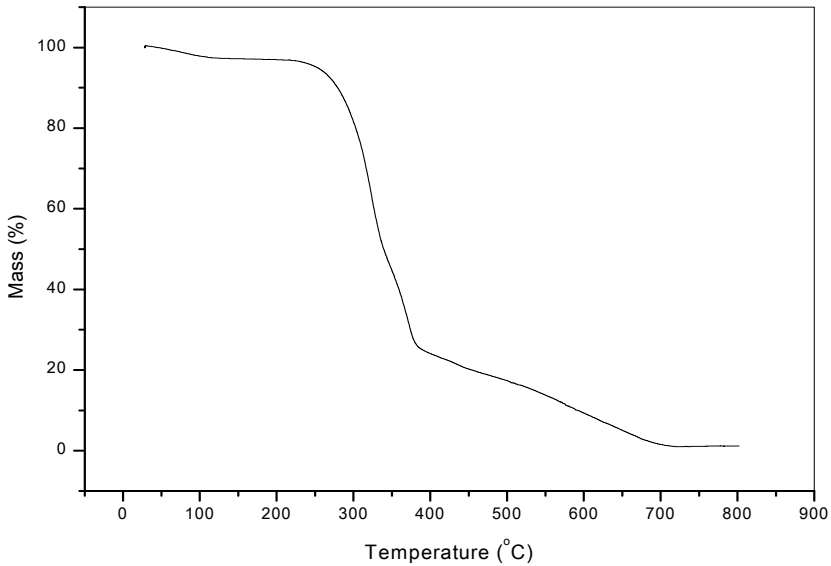
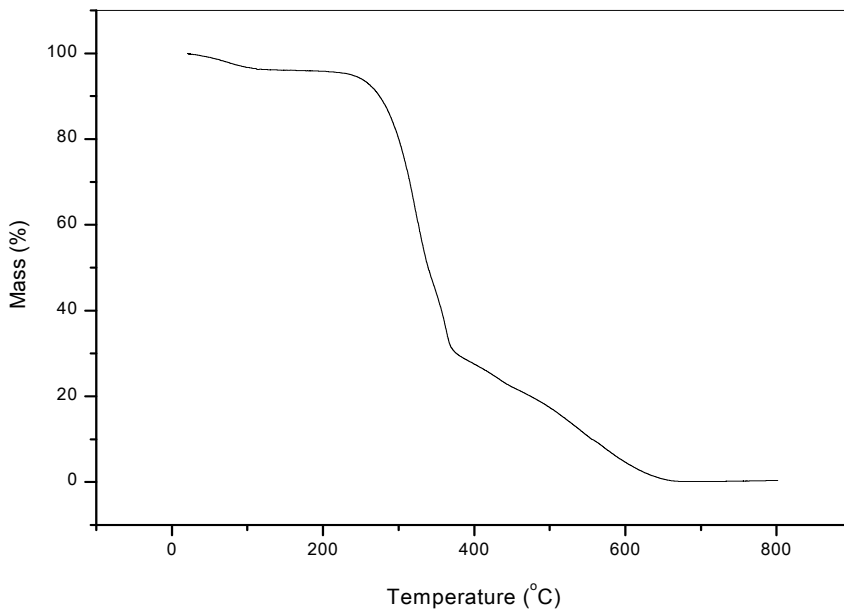


Figure 2. Infrared spectrum of PUF-Me-BTAP.

The graphs of TGA for Me-PUF BTAP in N<sub>2</sub> (Figure 3) and O<sub>2</sub> (Figure 4) show that there are no significant differences related to the atmosphere used during the degradation process for the amount of steps, temperature ranges and loss of mass.

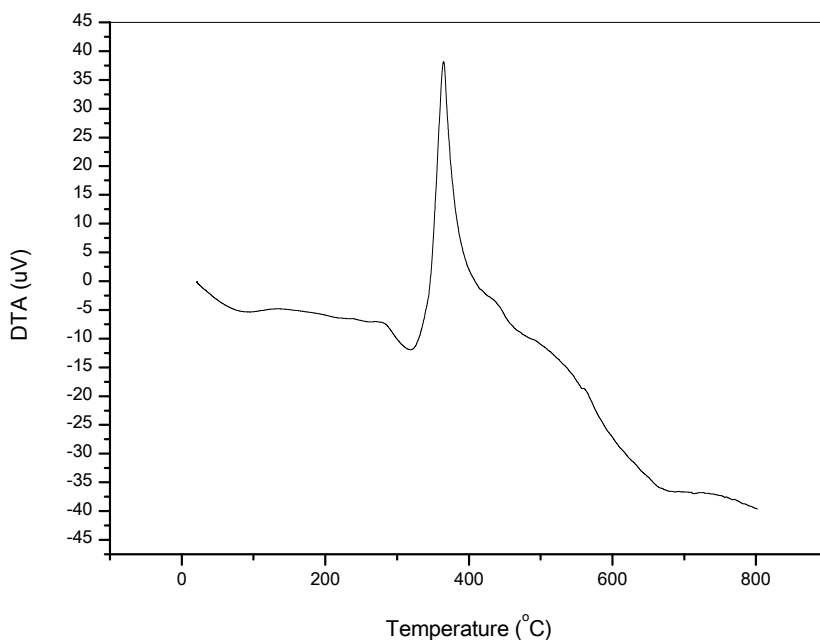


**Figure 3.** Thermogravimetric curve of the material PUF-Me BTAP under an N<sub>2</sub> environment.



**Figure 4.** Thermogravimetric curve of the material PUF-Me BTAP under an O<sub>2</sub> environment.

The degradation of the material occurs in two general stages. In Stage I, the degradation is mainly due to the decomposition of rigid segments and involves the dissociation of urethane and the original chain extender, which then form primary amines, alkenes and carbon dioxide. Stage I is influenced by the amount of rigid segments. In the subsequent stage II, depolymerization and degradation of the polyol occur. Therefore, this stage is affected by the content of flexible segments. According to Figure 5, there is a maximum of degradation, indicated by the first derivative curve of DTA at 364 °C in air (O<sub>2</sub>). The first stage of degradation occurred concomitantly with a phase transition, possibly because part of the polymer changed from a crystalline to an amorphous phase. An important observation is that the sorbent Me-BTAP-PUF has a high thermal stability at the final temperature for the first stage of degradation in air at 280 °C. The observed mass reduction, which occurred between 0 and 120 °C, was attributed to loss of water.

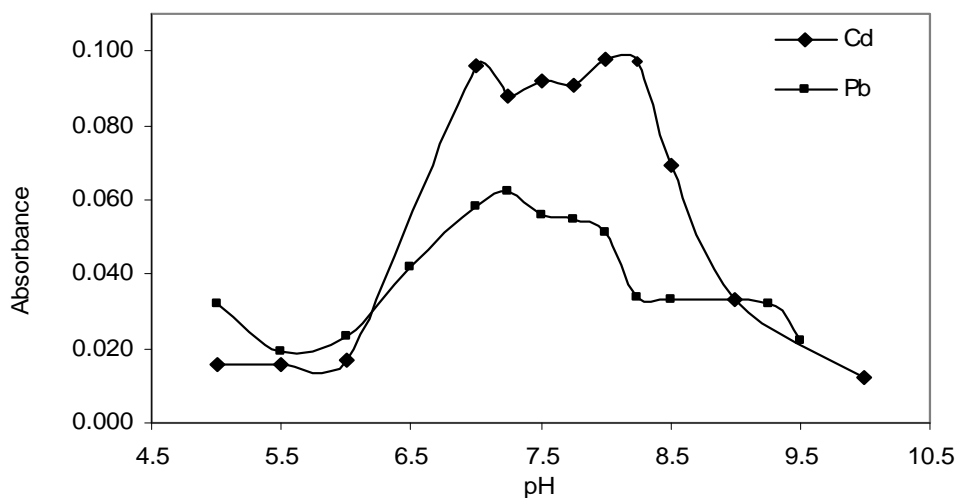


**Figure 5.** DTA curve of the material PUF-Me BTAP in an O<sub>2</sub> environment.

### 3.2. Effect of pH

Many complexing agents are Lewis bases (capable of donating electron pairs) and Brønsted bases (capable of receiving protons) and, as such, will be affected by changes in pH. The reaction for the formation of the chelate is influenced by pH because the chelating agent is not presented entirely in the form of a free ion. Thus, the effect of hydrogen concentration was studied to observe the pH range over which the cations cadmium and lead are absorbed by PUF-Me-BTAP. Figure 6 shows the influence of pH on the extraction of cadmium and lead by PUF-Me-BTAP.





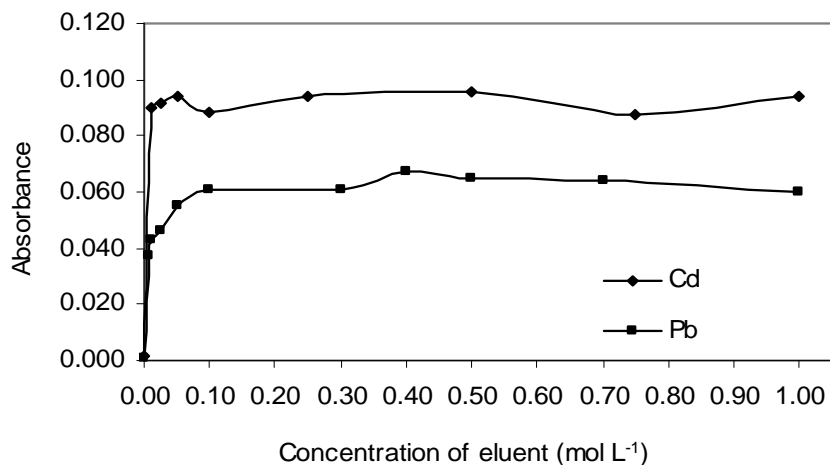
**Figure 6.** Influence of pH on the determination of Cd and Pb using solid phase extraction.

According to Figure 6, the best pH range for the extraction of cadmium is between 6.8 and 8.2. The extraction of lead is maximal when performed at pH values between 7.0 and 7.8. Thus, the extraction of both metals was performed at pH 7.5 in all subsequent experiments.

### 3.3. Type and concentration of the eluent

Polyurethane may be dissolved by concentrated sulfuric acid or oxidized by concentrated nitric acid and potassium permanganate solutions. This material was resistant to solvents such as water, hydrochloric acid (up to 6 mol L<sup>-1</sup>), ethanol and glacial acetic acid (Navratil et al., 1985). Thus, HCl was chosen to prevent a reduction in the lifetime of the PUF that was grafted with Me-BTAP. PUF-Me-BTAP is resistant to ethanol. However, the use of this solvent in the elution of cadmium and lead presented pressure problems in the on-line system in this work. When ethanol was used as the eluent, there was a swelling of the sorbent, which caused backpressure on the minicolumn. This increase in pressure caused leaks throughout the system on-line. Thus, the use of this solvent was discontinued. Hydrochloric acid solutions were then used as the eluent in all further experiments.

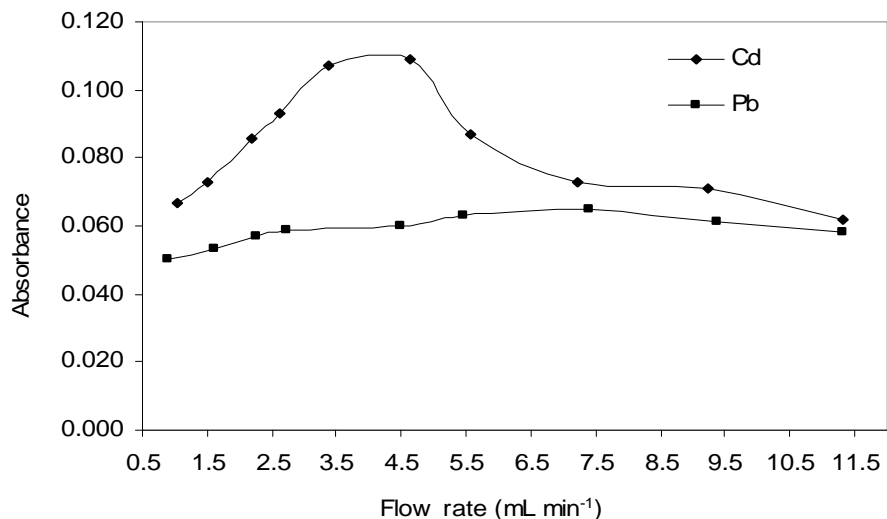
Figure 7 illustrates the phenomenon of desorption of cations from the solid phase when the concentration of HCl is varied. It was observed that the hydrochloric acid solutions that provided the highest analytical signals were those at concentrations ranging between 0.01 and 1.00 mol L<sup>-1</sup> (Cd) and 0.10 and 1.00 mol L<sup>-1</sup> (Pb). The use of low concentrations of acid is beneficial because it can increase the lifetime of the minicolumn. Moreover, in this work, we chose to use an eluent of identical concentration for both metals, with the aim of simplifying the operation of the on-line system. Therefore, a solution concentration of 0.10 mol L<sup>-1</sup> for the desorption of both chemical species was used in all subsequent experiments.



**Figure 7.** Influence of eluent concentration on the determination of Cd and Pb using solid phase extraction.

### 3.4. Flow rate of solutions

In on-line preconcentration systems, it is crucial to study the flow of the sample to meet the appropriate speed at which the ions pass through the minicolumn. The results of the influence of flow rate in on-line preconcentration systems of Cd (II), shown in Figure 8, show that the extraction is maximal when the flow rate ranges between 3.3 and 4.6 mL min<sup>-1</sup>. Values outside this range cause a decrease in the analytical signal.



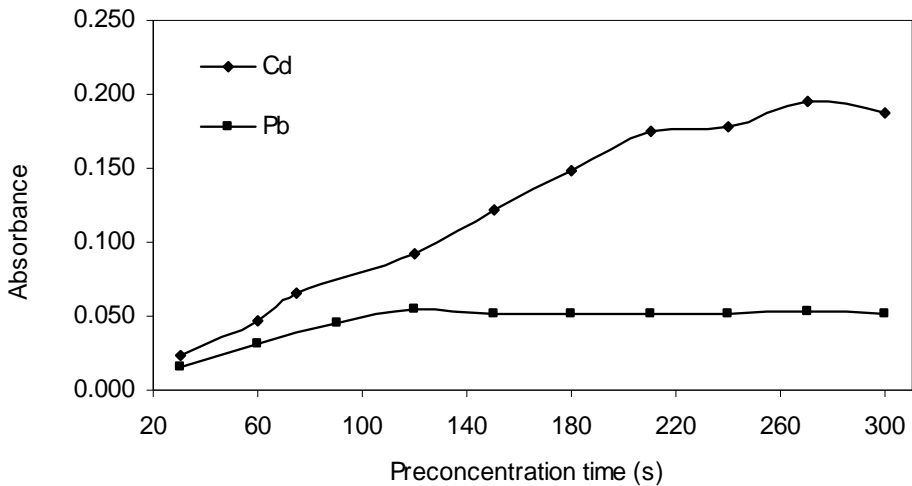
**Figure 8.** Influence of flow rate of the Cd and Pb solutions for the determination of elements using solid phase extraction.

If the flow rate of the metal solution is too high, there is a possibility that the metal ions can pass through the minicolumn at a speed so quickly that a portion of the analyte passes through without being sorbed. Conversely, an excessively low flow rate of the metal solution can also cause problems with the analytical signal. A solution that passes through the minicolumn with a very low flow rate can result in leaching of the complexed species and significantly increase the analysis time. Considering the curve that corresponds to the lead solution, we observed a similar behavior to that of cadmium. However, the decrease in the amount of extracted metal was smoother. The range of flow rate that produces the maximum extraction of lead was between 5.5 and 7.4 mL min<sup>-1</sup>. Based on these results, flow rates of 4.5 and 7.0 mL min<sup>-1</sup> were used in further experiments for solutions of cadmium and lead, respectively.

The inconsistency between the rate of aspiration of the nebulizer of the spectrometer and the flow rate of eluent of the on-line system could result in peak broadening of the analytical signal. This broadening will result in a decrease in the analytical signal (Lemos et al., 2007). Thus, the flow of the eluent for desorption of cadmium and lead ions was adjusted to 8.0 ml min<sup>-1</sup> to match the flow rates of elution and aspiration of the nebulizer of the spectrometer.

### 3.5. Preconcentration time

A linear relationship between preconcentration time and analytical signal is dependent on the flow of metal solution and the mass of sorbent. The graph in Figure 9 shows the variation of the analytical signal when the sample is inserted into the on-line preconcentration system at various time intervals. It is observed that the analytical signal is linear for preconcentration periods up to 210 and 120 seconds for cadmium and lead, respectively.



**Figure 9.** Influence of preconcentration time on the determination of Cd and Pb using solid phase extraction.

### 3.6. Lifetime of minicolumn

The life of the sorbent was investigated by monitoring the analytical signal corresponding to solutions of Pb (100.0 mg L<sup>-1</sup>) or Cd (10.0 mg L<sup>-1</sup>) at the end of a work day and by counting the number of runs. It was observed that the packed minicolumn did not provide a significant change in the extraction, even when used 350 times.

### 3.7. Analytical characteristics

The analytical characteristics of the method were calculated under the optimized conditions for preconcentration. Table 2 summarizes the analytical characteristics of the method. The analytical curves were constructed using solutions of cadmium and lead ranging from 1.0 to 10.0 and from 10.0 to 100.0 mg L<sup>-1</sup>, respectively.

Regression curves without preconcentration resulted in the following equations:  $A = 3.97 \times 10^{-4} C + 6.40 \times 10^{-3}$  for Cd and  $A = 1.98 \times 10^{-5} C + 2.38 \times 10^{-4}$  for Pb, where A is the absorbance and C is the metal concentration in solution, in  $\mu\text{g L}^{-1}$ . These equations were obtained under optimum conditions of the spectrometer. Enrichment factors (EF) were calculated as the ratio of the slopes of the linear section in the calibration graphs for preconcentration and direct aspiration (Fang et al., 1992). The term concentration efficiency (CE) is defined as the product of EF and the number of samples analyzed per minute (Fang et al., 1992). Therefore, if f is the sampling frequency expressed in samples analyzed per hour,  $CE = EF \times (f/60)$ .

Element	Cadmium	Lead
Preconcentration time, s	120	120
Enrichment factor	30	35
Concentration efficiency, min <sup>-1</sup>	13	15
Transfer phase factor	0.91	0.86
Sample volume, mL	9.00	14.0
Consumptive index, mL	0.30	0.40
Sample frequency, h <sup>-1</sup>	26	26
Limit of detection, $\mu\text{g L}^{-1}$	0.8	1.0
Limit of quantification, $\mu\text{g L}^{-1}$	2.7	3.3
Precision, %	4.1	4.8
Calibration function	$A = 3.20 \times 10^{-3} + 1.19 \times 10^{-2} C$	$A = 7.78 \times 10^{-4} + 6.93 \times 10^{-4} C$

**Table 2.** Features of the preconcentration system for the determination of cadmium and lead (A, absorbance and C, metal concentration,  $\mu\text{g L}^{-1}$ ).

The transfer phase factor is defined as the ratio between the analyte mass in the original sample and that in the concentrate. Consumptive index (CI) quantifies the efficiency of an FI on-line column preconcentration system in terms of the sample volume consumed to achieve a defined EF. The term CI is defined as the sample volume (V), in mL, consumed to achieve a unit EF, expressed by the equation  $CI = V/EF$  (Fang et al., 1992).

The limits of quantification and detection of the method were also calculated. The detection limit was calculated using the following equation:  $3s_b/b$ , where  $s_b$  is the standard deviation for eleven measurements of the blank, and  $b$  is the slope of the analytical curve for each metal. The limit of quantification was calculated as  $10s_b/b$ .

The accuracy of the proposed procedure was evaluated by determining the amounts of Cd and Pb in a certified reference material. The following material was analyzed: BCR-713, Wastewater (effluent) from the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium). The results were  $4.8 \pm 0.5 \mu\text{g L}^{-1}$  for cadmium and  $45 \pm 4 \mu\text{g L}^{-1}$  for lead. According to the results, no significant difference was found between the results that were obtained and the certified values of the reference material ( $5.1 \pm 0.6 \mu\text{g L}^{-1}$  and  $47 \pm 4 \mu\text{g L}^{-1}$  for cadmium and lead, respectively).

### 3.8. Application of the proposed procedure

The preconcentration procedure was applied to determine the metal content in water samples. These real samples were collected at Jequié, Bahia, Brazil. Known concentrations of Cd and Pb were added to the samples to minimize the change in the matrix of the original sample. Recoveries of the spiked samples ( $2.0$  and  $30.0 \mu\text{g L}^{-1}$  for cadmium and lead, respectively) were determined. The results shown in Table 3 demonstrate the applicability of the method. Recoveries (R) were calculated as follows:  $R (\%) = \{(C_m - C_o)/m\} \times 100$ , where  $C_m$  is the concentration of metal in a spiked sample,  $C_o$  is the concentration of metal in a sample and  $m$  is the amount of metal spiked. The described procedure can be successfully applied to these matrices for the preconcentration and determination of cadmium and lead.

Amostra	Amount of Cd ( $\mu\text{g L}^{-1}$ )		R (%)	Amount of Cd ( $\mu\text{g L}^{-1}$ )		R (%)
	Added	Found		Added	Found	
Tapwater Sample 1	0.0	< LOQ	93.5	0.0	< LOQ	95.7
	2.0	$1.87 \pm 0.05$		30.0	$28.70 \pm 0.98$	
Tapwater Sample 2	0.0	< LOQ	101.5	0.0	$15.23 \pm 0.98$	96.8
	2.0	$2.03 \pm 0.06$		30.0	$44.57 \pm 2.59$	

**Table 3.** Results for the determination of Cd and Pb using the proposed procedure. LOQ: limit of quantification, R: recovery.

The results obtained from this procedure are comparable to those of other preconcentration methods for Cd and Pb determination. Table 4 summarizes some of these methods and their characteristics.

Element	Process of extraction	Enrichment factor	Limit of detection ( $\mu\text{g L}^{-1}$ )	Sample volume (mL)	Reference
Cd	Solid phase extraction	30	0.8	9.0	This work
Pb		35	1.0	14.0	
Pb	Ionic liquid dispersive liquid-liquid microextraction	40	1.5	20.0	(Soylak & Yilmaz, 2011)
Pb	Solid phase extraction		2.1	-----	(Yalcinkaya et al, 2011)
Cd	Dispersive liquid-liquid microextraction	55	0.4	-----	(Rojas et al., 2011)
Cd	Solid phase extraction	19	0.77	-----	(Tang & Hu, 2011)
Cd	Ion-flotation Separation	45	1.2	-----	(Tavallali et al., 2011)
Cd	Cloud point extraction	29	0.1*	-----	(Moghimi & Tajodini, 2010)
Pb	Cloud point extraction	56 and 42	1.14	-----	(Shah <i>et al.</i> , 2011)
Pb	Solid phase extraction	50	0.65	-----	(Melek et al., 2006)

**Table 4.** Analytical characteristics of various procedures for the determination of Cd and Pb by FAAS, \*  $\mu\text{g g}^{-1}$ .

#### 4. Conclusion

The PUF grafted with Me-BTAP was successfully applied to the preconcentration of cadmium and lead. The sorbent showed characteristics that are desirable for materials used in solid phase extraction systems, such as resistance to swelling and changes in pH, low resistance to flow passage and simplicity in preparation. Moreover, when applied to the preconcentration system, the solid phase provided a simple and sensitive method for the determination of cadmium and lead by FAAS. The synthesized material is a good alternative for the determination of these elements. The extraction of other elements will be tested using this sorbent, and further work in this area is currently being conducted in our laboratory.

#### Author details

Rafael Vasconcelos Oliveira and Valfredo Azevedo Lemos  
*Universidade Estadual do Sudoeste da Bahia,*  
*Laboratório de Química Analítica (LQA), Campus de Jequié, Jequié, Bahia, Brazil*

## 5. References

- Azeem, S. M. A., Arafa, W. A. A. & El-Shahat, M. F. (2010). Synthesis and application of alizarin complexone functionalized polyurethane foam: Preconcentration/separation of metal ions from tap water and human urine. *Journal of Hazardous Materials*, Vol.182, No.1-3, p.p.286-294.
- Beketov, V. I., Parchinskii, V. Z. & Zorov, N. B. (1996). Effects of high-frequency electromagnetic treatment on the solid-phase extraction of aqueous benzene, naphthalene and phenol. *Journal of Chromatography a*, Vol.731, No.1-2, p.p.65-73.
- Braun, T. & Farag, A. B. (1978). Polyurethane foams and microspheres in analytical-chemistry - improved liquid-solid, gas-solid and liquid-liquid contact via a new geometry of solid-phase. *Analytica Chimica Acta*, Vol.99, No.1, p.p.1-36.
- Braun, T. (1983) Trends in using resilient polyurethane foams as sorbents in analytical chemistry, *Fresenius' Journal of Analytical Chemistry*, Vol. 314, No. 7, p.p. 652-656.
- Burham, N. (2008). Uses of 5-Methylresorcin-Bonded Polyurethan Foam as a New Solid Phase Extractor for the Selective Separation of Mercury Ions from Natural Water Samples. *Central European Journal of Chemistry*, Vol.6, No.4, p.p.641-650.
- Costa, L. M., Ribeiro, E. S., Segatelli, M. G., Do Nascimento, D. R., De Oliveira, F. M. & Tarley, C. R. T. (2011). Adsorption studies of Cd(II) onto Al<sub>2</sub>O<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub> mixed oxide dispersed on silica matrix and its on-line preconcentration and determination by flame atomic absorption spectrometry. *Spectrochimica Acta Part B-Atomic Spectroscopy*, Vol.66, No.5, p.p.329-337.
- El-Shahat, M. E., Moawed, E. A. & Farag, A. B. (2007). Chemical enrichment and separation of uranyl ions in aqueous media using novel polyurethane foam chemically grafted with different basic dyestuff sorbents. *Talanta*, Vol.71, No.1, p.p.236-241.
- El-Shahat, M. F., Moawed, E. A. & Zaid, M. A. A. (2003). Preconcentration and separation of iron, zinc, cadmium and mercury, from waste water using Nile blue a grafted polyurethane foam. *Talanta*, Vol.59, No.5, p.p.851-866.
- El-Shahawi, M. S., Bashammakh, A. S. & Abdelmageed, M. (2011a). Chemical Speciation of Chromium(III) and (VI) Using Phosphonium Cation Impregnated Polyurethane Foams Prior to Their Spectrometric Determination. *Analytical Sciences*, Vol.27, No.7, p.p.757-763.
- El-Shahawi, M. S., Hamza, A., Al-Sibaai, A. A. & Al-Saidi, H. M. (2011b). Fast and selective removal of trace concentrations of bismuth (III) from water onto procaine hydrochloride loaded polyurethane foams sorbent: Kinetics and thermodynamics of bismuth (III) study. *Chemical Engineering Journal*, Vol.173, No.1, p.p.29-35.
- Fang Z., Dong L. P. & Xu S. K., (1992). Critical Evaluation of the Efficiency and Synergistic Effects of Flow Injection Techniques for Sensitivity Enhancement in Flame Atomic Absorption Spectrometry. *Anal. Atom. Spectrom.* Vol.7 pp. 293-299.
- Fathi, M. R., Pourreza, N. & Ardan, Z. (2011). Determination of aluminum in food samples after preconcentration as aluminon complex on microcrystalline naphthalene by spectrophotometry. *Quimica Nova*, Vol.34, No.3, p.p.404-407.

- Gonzales, A. P. S., Firmino, M. A., Nomura, C. S., Rocha, F. R. P., Oliveira, P. V. & Gaubeur, I. (2009). Peat as a natural solid-phase for copper preconcentration and determination in a multicommuted flow system coupled to flame atomic absorption spectrometry. *Analytica Chimica Acta*, Vol.636, No.2, p.p.198-204.
- Jamshidi, M., Ghaedi, M., Mortazavi, K., Biareh, M. N. & Soylak, M. (2011). Determination of some metal ions by flame-AAS after their preconcentration using sodium dodecyl sulfate coated alumina modified with 2-hydroxy-(3-((1-H-indol 3-yle)phenyl) methyl) 1-H-indol (2-HIYPMI). *Food and Chemical Toxicology*, Vol.49, No.6, p.p.1229-1234.
- Lemos, V. A., Baliza, P. X., De Carvalho, A. L., Oliveira, R. V., Teixeira, L. S. G. & Bezerra, M. A. (2008). Development of a new sequential injection in-line cloud point extraction system for flame atomic absorption spectrometric determination of manganese in food samples. *Talanta*, Vol.77, No.1, p.p.388-393.
- Lemos, V. A., David, G. T. & Santos, L. N. (2006a). Synthesis and application of XAD-2/Me-BTAP resin for on-line solid phase extraction and determination of trace metals in biological samples by FAAS. *Journal of the Brazilian Chemical Society*, Vol.17, No.4, p.p.697-704.
- Lemos, V. A., Santos E. S. & Gama, E. M. (2007). A comparative study of two sorbents for copper in a flow injection preconcentration system. *Separation and Purification Technology*, Vol.56, No.2, pp.212-219.
- Lemos, V. A., Santos L. N., Alves, A. P. O. & David, G. T. (2006b). Chromotropic acid-functionalized polyurethane foam: A new sorbent for on-line preconcentration and determination of cobalt and nickel in lettuce samples. *Journal of Separation Science*, Vol.29, No.9, pp.1197-1204
- Lemos, V. A., Santos, L. N. & Bezerra, M. A. (2010). Determination of cobalt and manganese in food seasonings by flame atomic absorption spectrometry after preconcentration with 2-hydroxyacetophenone-functionalized polyurethane foam. *Journal of Food Composition and Analysis*, Vol.23, No.3, p.p.277-281.
- Lemos, V. A., Santos, M. S., Santos, E. S., Santos, M. J. S., Dos Santos, W. N. L., Souza, A. S., De Jesus, D. S., Das Virgens, C. F., Carvalho, M. S., Oleszczuk, N., Vale, M. G. R., Welz, B. & Ferreira, S. L. C. (2007). Application of polyurethane foam as a sorbent for trace metal pre-concentration - A review. *Spectrochimica Acta Part B-Atomic Spectroscopy*, Vol.62, No.1, p.p.4-12.
- Matos, G. D. & Arruda, M. A. Z. (2006). Online preconcentration/determination of cadmium using grape bagasse in a flow system coupled to thermospray flame furnace atomic absorption spectrometry. *Spectroscopy Letters*, Vol.39, No.6, p.p.755-768.
- Melek, E., Tuzen, M. & Soylak, M. (2006). Flame atomic absorption spectrometric determination of cadmium(II) and lead(II) after their solid phase extraction as dibenzylidithiocarbamate chelates on Dowex Optipore V-493. *Analytica Chimica Acta*, Vol.578, No.2, p.p.213-219.
- Moawed E. A. & El-Shahat M. F. (2006). Preparation, characterization and application of polyurethane foam functionalized with  $\alpha$ -naphthol for preconcentration and determination of trace amounts of nickel and copper in cast iron and granite. *Reactive & Functional Polymers*, Vol. 66, No.7, pp. 720-727.



- Moawed, E. A. (2004). Separation and preconcentration of trace amounts of cadmium(II) and mercury(II) ions on rosaniline-grafted polyurethane foam. *Acta Chromatographica*, Vol.14, p.p.198-214.
- Moawed, E. A., Zaid M. A. A. & El-Shahat, M. E. (2003). Methylene blue-grafted polyurethane foam using as a chelating resin for preconcentration and separation of cadmium(II), mercury(II), and silver(I) from waste water. *Analytical Letters*, Vol.36, No.2, pp.405-422.
- Moghimi, A. & Tajodini, N. (2010). Extraction of Cadmium(II) Using Cloud-Point Method and Determination by FAAS. *Asian Journal of Chemistry*, Vol.22, No.7, p.p.5025-5033.
- Nair, M. N. R. & Nair, M. R. G. (2008). Synthesis and characterisation of soluble block copolymers from NR and TDI based polyurethanes. *Journal of Materials Science*, Vol.43, No.2, p.p.738-747.
- Navratil, J. D., Braun, T. & Farag, A. B. (1985). *Polyurethane foam sorbents in separation science* (first edition), CRC Press, Inc, 0-8493-6597-x, Boca Raton, Florida
- Oral, E. V., Dolak, I., Temel, H. & Ziyadanogullari, B. (2011). Preconcentration and determination of copper and cadmium ions with 1,6-bis(2-carboxy aldehyde phenoxy)butane functionalized Amberlite XAD-16 by flame atomic absorption spectrometry. *Journal of Hazardous Materials*, Vol.186, No.1, p.p.724-730.
- Rojas, F. S., Ojeda, C. B. & Pavon, J. M. C. (2011). Dispersive liquid-liquid microextraction combined with flame atomic absorption spectrometry for determination of cadmium in environmental, water and food samples. *Analytical Methods*, Vol.3, No.7, p.p.1652-1655.
- Saeed M. M. & Ahmed R. (2005). Adsorption modeling and thermodynamic characteristics of uranium(VI) ions onto 1-(2-pyridylazo)-2-naphthol (PAN) supported polyurethane foam. *Radiochimica Acta*, Vol. 93, No. 6, pp. 333-339.
- Serafimovska, J. M., Arpadjan, S. & Stafilov, T. (2011). Speciation of dissolved inorganic antimony in natural waters using liquid phase semi-microextraction combined with electrothermal atomic absorption spectrometry. *Microchemical Journal*, Vol.99, No.1, p.p.46-50.
- Shah, F., Kazi, T. G., Afridi, H. I., Naeemullah, Arain, M. B. & Baig, J. A. (2011). Cloud point extraction for determination of lead in blood samples of children, using different ligands prior to analysis by flame atomic absorption spectrometry: A multivariate study. *Journal of Hazardous Materials*, Vol.192, No.3, p.p.1132-1139.
- Soylak, M. & Yilmaz, E. (2011). Ionic liquid dispersive liquid-liquid microextraction of lead as pyrrolidinedithiocarbamate chelate prior to its flame atomic absorption spectrometric determination. *Desalination*, Vol.275, No.1-3, p.p.297-301.
- Tang, A. N. & Hu, Y. F. (2011). Determination of trace cadmium by flow injection on-line microcolumn preconcentration coupled with flame atomic absorption spectrometry using human hair as a sorbent. *Instrumentation Science & Technology*, Vol.39, No.1, p.p.110-120.
- Tavallali, H., Lalehparvar, S., Nekoei, A. R. & Niknam, K. (2011). Ion-flotation Separation of Cd(II), Co(II) and Pb(II) Traces Using a New Ligand before Their Flame Atomic Absorption Spectrometric Determinations in Colored Hair and Dryer Agents of Paint. *Journal of the Chinese Chemical Society*, Vol.58, No.2, p.p.199-206.

- Teixeira, L. S. G., Bezerra, M. D., Lemos, V. A., Dos Santos, H. C., De Jesus, D. S. & Costa, A. C. S. (2005). Determination of copper, iron, nickel, and zinc in ethanol fuel by flame atomic absorption spectrometry using on-line preconcentration system. *Separation Science and Technology*, Vol.40, No.12, p.p.2555-2565.
- Tuzen, M., Citak, D. & Soylak, M. (2008). 5-Chloro-2-hydroxyaniline-copper(II) coprecipitation system for preconcentration and separation of lead(II) and chromium(III) at trace levels. *Journal of Hazardous Materials*, Vol.158, No.1, p.p.137-141.
- Tzvetkova, P., Vassileva, P. & Nickolov, R. (2010). Modified silica gel with 5-amino-1,3,4-thiadiazole-2-thiol for heavy metal ions removal. *Journal of Porous Materials*, Vol.17, No.4, p.p.459-463.
- Yalcinkaya, O., Kalfa, O. M. & Turker, A. R. (2011). Preconcentration of Trace Copper, Cobalt and Lead from Various Samples by Hybrid Nano Sorbent and Determination by FAAS. *Current Analytical Chemistry*, Vol.7, No.3, p.p.225-234.
- Zambrzycka, E., Roszko, D., Lesniewska, B., Wilczewska, A. Z. & Godlewska-Zylkiewicz, B. (2011). Studies of ion-imprinted polymers for solid-phase extraction of ruthenium from environmental samples before its determination by electrothermal atomic absorption spectrometry. *Spectrochimica Acta Part B-Atomic Spectroscopy*, Vol.66, No.7, p.p.508-516.
- Zeeb, M. & Sadeghi, M. (2011). Modified ionic liquid cold-induced aggregation dispersive liquid-liquid microextraction followed by atomic absorption spectrometry for trace determination of zinc in water and food samples. *Microchimica Acta*, Vol.175, No.1-2, p.p.159-165.
- Zhang, L., Li, Z. H., Du, X. H. & Chang, X. J. (2011). Activated carbon functionalized with 1-amino-2-naphthol-4-sulfonate as a selective solid-phase sorbent for the extraction of gold(III). *Microchimica Acta*, Vol.174, No.3-4, p.p.391-398.