

Review

Application of polyurethane foam as a sorbent for trace metal pre-concentration — A review

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Abstract

The first publication on the use of polyurethane foam (PUF) for sorption processes dates back to 1970, and soon after the material was applied for separation processes. The application of PUF as a sorbent for solid phase extraction of inorganic analytes for separation and pre-concentration purposes is reviewed. The physical and chemical characteristics of PUF (polyether and polyester type) are discussed and an introduction to the characterization of these sorption processes using different types of isotherms is given. Separation and pre-concentration methods using unloaded and loaded PUF in batch and on-line procedures with continuous flow and flow injection systems are presented. Methods for the direct solid sampling analysis of the PUF after pre-concentration are discussed as well as approaches for speciation analysis. Thermodynamic properties of some extraction processes are evaluated and the interpretation of determined parameters, such as enthalpy, entropy and Gibbs free energy in light of the physico-chemical processes is explained.

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1. Introduction

Several of the conventional analytical techniques, such as flame atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry (ICP OES) are often not sensitive enough for the direct determination of inorganic analytes in environmental, geological, biological or food samples. Separation and pre-concentration techniques, such as liquid–liquid extraction [1], solid phase extraction [2–5], cloud point extraction [6] or co-precipitation [7], have therefore been widely used in analytical chemistry. Among these techniques, solid phase extraction (SPE) has been used most frequently because of the availability and easy recovery of the solid phase, the high pre-concentration factors that can be achieved, and the ease of separation and enrichment using continuous flow or flow injection systems that make possible a high degree of automation. Furthermore, SPE usually does not require organic solvents, many of which are toxic [8] and might complicate the final quantitation stage of the analysis.

2. Polyurethane foam in analytical chemistry — a historical overview

Polyurethane foam (PUF) is a good sorbent material in SPE, and it has been the subject of several review articles [9–11]. The first paper reporting sorption and recovery of some inorganic and organic compounds from aqueous solution using this sorbent was published in 1970 by Bowen [12]. One year later, Gesser et al. [13] proposed the use of untreated PUF for sorption of organic contaminants from water using a batch technique. Braun and Farag [14,15] published the first applications of PUF for chromatographic separation in 1972. These studies resulted in a number of papers, involving the use of unloaded and loaded PUF (polyether and polyester type) in separation and pre-concentration procedures for the determination of inorganic and organic species using different analytical techniques, as will be discussed in Sections 5 and 6.

The first on-line pre-concentration system using a mini-column filled with PUF and published in 1998 [16] described a method for the determination of zinc in biological samples using molecular absorption spectrophotometry. Soon after that, an on-line separation was described for the determination of nickel in silicates and alloys using the same technique [17]. Interferences from several metal ions were eliminated by their sorption as thiocyanate complexes on a PUF minicolumn. Later, this system was modified for use with FAAS [18]. Several other papers were published after that highlighting the use of minicolumns of PUF in on-line pre-concentration systems mainly with FAAS as the analytical technique. The combination of such a system with thermospray flame furnace AAS resulted in a method for the determination of cadmium, providing a

sensitivity comparable with that of electrothermal (ET) AAS [19].

3. Physical and chemical characteristics of polyurethane foams

Polyurethane foams can be defined as plastic materials in which a proportion of the solid phase is replaced by gas in the form of numerous small bubbles (cell) [20]. From the geometrical point of view, if the gas bubbles occupy a volume smaller than 76% they may be spherical. If they occupy a volume larger than 76%, they will be distorted into quasi-spherical polyhedra [21].

Polyurethane foams have been prepared in soft, flexible and rigid form using a variety of polyesters and polyethers. The two most important reactions in the preparation of urethane foams are those between isocyanate and hydroxyl compounds

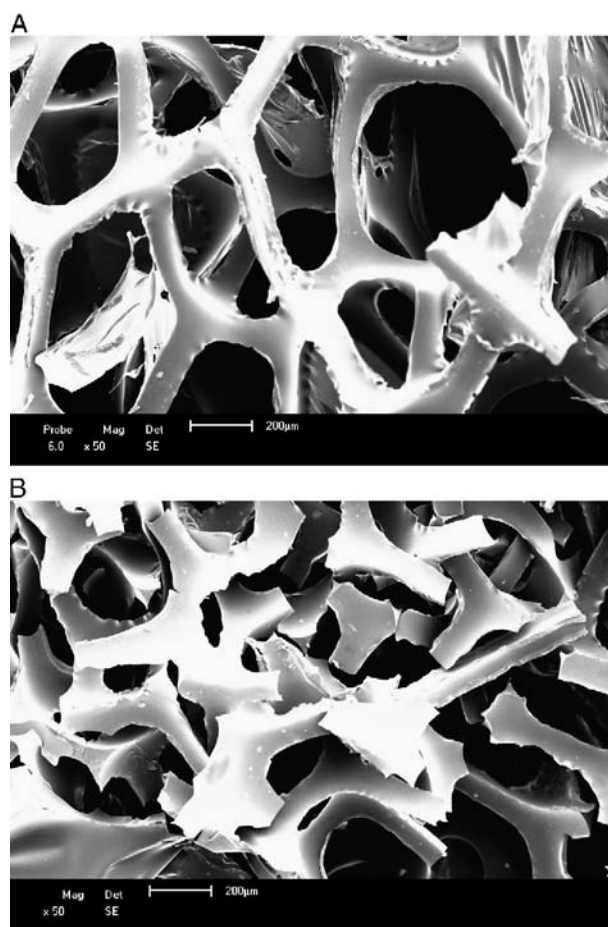


Fig. 1. Scanning electron micrographs of PUF; A) in its original untreated form; B) after grinding in a blender with ethanol (Shimadzu Superscan SS-550 scanning electron microscope).

(polyester or polyether polyols) and those between isocyanate and water [9]. The physical and chemical properties of PUF are a direct function of the preparation process. Fig. 1 shows the typical structure of PUF in its original form and after grinding in a blender with ethanol, i.e., in the form in which it is used for sorption purposes.

Unloaded PUF only adsorbs metal ions after complex formation. Organic and inorganic ligands can be used for this operation. Several batch and on-line procedures have been established this way. In a batch method, for example, molybdenum (VI) ions were quantitatively extracted with unloaded PUF after formation of thiocyanate complexes [22]. An on-line system was proposed for determination of zinc in biological matrices, where zinc (II) ions reacted on-line with thiocyanate ions and the complexes were adsorbed in a minicolumn packed with unloaded PUF [23].

Loaded PUF offers a wider field of applications than unloaded PUF. The loaded ligand can determine if an extraction process is selective or non-selective, i.e., multi-element. Loaded PUF can also be used in batch or on-line operation. PUF loaded with dimethylglyoxime was, for example, proposed for the selective extraction of nickel [24]. A multi-element procedure was proposed for simultaneous pre-concentration and determination of cadmium, cobalt, copper, manganese, nickel, lead and zinc in water using PUF loaded with piperidine dithiocarbamate [25]. Both procedures were based on batch operation. Several on-line systems have been proposed using a minicolumn of PUF loaded with organic ligands. Batch and on-line procedures are discussed in detail in Sections 5 and 6, respectively.

4. Characterization of the sorption process

The sorption process of metal ions by PUF can be evaluated and characterized by isotherms that are established according to Freundlich [26], Langmuir [27] or Dubinin and Radushkevich [28], and also by determination of the thermodynamic parameters [29].

The Langmuir isotherm is based on the assumption of monolayer sorption, i.e., sorption occurs on definite sites; all active sites are identical in energy and can accommodate only one molecule each. This isotherm allows two data (Langmuir constants) related to sorption capacity and sorption energy to be determined. It is written in the form: $C_{\text{ads}} = (QbC_e)/(1 + bC_e)$, where C_e is the equilibrium concentration of the metal ion in solution (mol L^{-1}), C_{ads} is the amount of metal ion sorbed onto the solid phase (mol g^{-1}) and Q and b are the Langmuir constants. Saeed determined the Langmuir constants for the sorption of Tm(III) ions onto PUF from a water–ethanol mixture containing 1-(2-pyridylazo)-2-naphthol. Results for the sorption capacity and sorption energy were $(2.5 \pm 0.7) \cdot 10^{-5} \text{ mol g}^{-1}$ and $(1.6 \pm 0.1) \cdot 10^4 \text{ mol L}^{-1}$, respectively [30].

The Freundlich isotherm assumes surface heterogeneity of the sorbent, but never predicts saturation of the surface of the solid phase. Therefore, infinite surface coverage is predicted mathematically. The Freundlich isotherm is written as: $C_{\text{ads}} = K_F (C_e)^{1/n}$, where C_{ads} and C_e are the same parameters as described in the Langmuir isotherm, while K_F and $1/n$ are the

Freundlich constants, which define the sorption capacity and sorption intensity, respectively. In the same paper by Saeed [30], the data for sorption capacity and sorption intensity were determined as $(5.7 \pm 0.3) \cdot 10^{-3} \text{ mol g}^{-1}$ and $(0.66 \pm 0.02) \cdot 10^4 \text{ mol L}^{-1}$, respectively.

The Dubinin–Radushkevich (D–R) isotherm assumes that there are very small sub-regions of the sorption surface that are uniform in structure and energetically homogeneous as in the Freundlich isotherm in order to distinguish the physical or chemical nature of the adsorption. The equation of this isotherm is:

$$C_{\text{ads}} = X_m \exp(-\beta \varepsilon^2)$$

where X_m is the maximum sorption capacity of sorbent (mol L^{-1}), β is the net adsorbate–adsorbent affinity coefficient ($\text{kJ}^2 \text{ mol}^{-2}$) and ε is the Polanyi potential which is given by: $\varepsilon = RT \ln(1 + 1/C_e)$, where C_e is the equilibrium concentration of sorbate in solution (mol L^{-1}). The activity coefficient, β , of the D–R isotherm can be related to the free sorption energy (E) if the surface of the sorbent is heterogeneous in nature and an approximation to the Langmuir isotherm is chosen as a local isotherm for all the sites that are energetically equivalent. This isotherm has been used in order to distinguish if the adsorption process is physical or chemical in nature. The E value obtained directly determines the nature of the process. For E in the range of $1\text{--}8 \text{ kJ mol}^{-1}$, the adsorption process is physical and the chemical adsorption is characterized by E values from 9 to 16 kJ mol^{-1} . In the paper of Saeed [30], X_m is determined as $(1.7 \pm 0.2) \cdot 10^{-4} \text{ mol g}^{-1}$, β as $(-0.0052 \pm 0.0002) \text{ kJ}^2 \text{ mol}^{-2}$ and E is equal to 9.8 kJ mol^{-1} . This E value indicates that chemisorption phenomenon is predominant. The high sorption energy reflects strong bonding that might be due to the effective role played by PUF in chemisorption. An analysis of the results obtained by Saeed [30] demonstrates that the high value for the sorption capacity (K_F) obtained in the Freundlich isotherm is based on the assumption of a multilayer coverage of the sorbent, while the Langmuir and D–R isotherms are based on monolayer coverage of the sorbent, resulting in low values for the sorption capacity.

All these isotherms are graphically represented by linear curves. The value of the correlation coefficient reflects the fit of the data of the extraction process involved. Data for an extraction process that obey the Langmuir and Freundlich isotherm indicate that adsorption, rather than absorption, is involved. In the Saeed paper [30] the correlation coefficients were 0.9928 and 0.9906 for the isotherms of Langmuir and Freundlich, respectively.

5. Separation and pre-concentration using batch procedures

The first applications of PUF in analytical chemistry for the determination of inorganic as well as organic species were based on batch procedures, using analytical techniques such as molecular absorption spectrophotometry, FAAS, ET AAS and ICP OES. Methods for the direct analysis of the solid phase (PUF) have also been proposed using solid phase spectrometry,

diffuse reflectance spectrometry and wavelength dispersive X-ray fluorescence (WD-XRF), as will be discussed later.

The experimental variables that should be optimized in separation and pre-concentration procedures using PUF with batch techniques are pH, shaking time, sample volume, concentration of the complexing agent, type and amount of eluent and mass of PUF. All these variables are important and should be studied rigorously. The pH value can be of fundamental importance in a separation process. For the determination zinc in cadmium matrices, for example, the extraction of zinc should be conducted at a pH of 3.0 ± 0.5 because at pH higher than 5.0, cadmium (II) is also extracted by PUF as the

thiocyanate complex [31]. The choice of the eluent depends as well directly on the chemical system involved. Zinc(II) ions retained on PUF as thiocyanate complexes can be quantitatively eluted using water, ethanol, 0.10 mol L^{-1} nitric acid or 0.10 mol L^{-1} hydrochloric acid [23]. For the determination of zinc in cadmium matrices, the eluent of choice was water, mainly because the cadmium(II) thiocyanate complex is not extracted with water. This strategy makes possible an efficient separation of zinc from cadmium [23,31]. In a procedure for the determination of molybdenum in iron matrices by ICP OES, the elution of molybdenum(VI) retained on PUF (also as thiocyanate complex) required the use of concentrated nitric

Table 1
Separation and pre-concentration procedures for the determination of inorganic species using PUF as the sorbent in batch procedures

Analyte	Ligand	Conditions for sorption	Eluent	Sample	Shaking time of extraction/min	LOD/ $\mu\text{g L}^{-1}$	Analytical technique	Ref.
Th	EHPA	0.25 mol L^{-1} hydrochloric acid	*	Natural water	30	4.0	WD-XRF	[34]
Zn	Thiocyanate	pH 3.0	Water	Cd matrices	5	20	ST	[31]
Zn	Thiocyanate	pH 1.0–4.0	1.0% (m/v) nitric acid	Al matrices	10	–	ICP OES	[36]
Mo	Thiocyanate	1.0 mol L^{-1} hydrochloric acid	2.8 mol L^{-1} nitric acid	Iron matrices	10	0.90	ICP OES	[32]
Mo	Thiocyanate	6.0 mol L^{-1} hydrochloric acid	2.8 mol L^{-1} nitric acid	Sea water	16	1.5	ICP OES	[33]
Mo	Thiocyanate	$1.9\text{--}2.9 \text{ mol L}^{-1}$ hydrochloric acid	3.0 mol L^{-1} nitric acid	Water	**	0.08	ET AAS	[37]
Ge	Molybdate	pH 0.5–3.7	–	Water	–	70.0	WD-XRF	[38]
U	Salicylate	pH 3.5–4.0	*	Water	50	5.5	WD-XRF	[39]
As	Dithiocarbamate	$0.1\text{--}0.7 \text{ mol L}^{-1}$ hydrochloric acid	Methanol	Water	***	3.2	ICP OES	[40]
Bi	Dithiocarbamate	$0.1\text{--}0.7 \text{ mol L}^{-1}$ hydrochloric acid	Methanol	Water	***	8.0	ICP OES	[40]
Hg	Dithiocarbamate	$0.1\text{--}0.7 \text{ mol L}^{-1}$ hydrochloric acid	Methanol	Water	***	0.12	ICP OES	[40]
Sb	Dithiocarbamate	$0.1\text{--}0.7 \text{ mol L}^{-1}$ hydrochloric acid	Methanol	Water	***	2.0	ICP OES	[40]
Se	Dithiocarbamate	$0.1\text{--}0.7 \text{ mol L}^{-1}$ hydrochloric acid	Methanol	Water	***	3.0	ICP OES	[40]
Sn	Dithiocarbamate	pH 4.5	Methanol	Water	***	6.0	ICP OES	[40]
As	Dithiocarbamate	$0.1\text{--}0.7 \text{ mol L}^{-1}$ hydrochloric acid	IBMK	Water	***	0.06	ET AAS	[40]
Bi	Dithiocarbamate	$0.1\text{--}0.7 \text{ mol L}^{-1}$ hydrochloric acid	IBMK	Water	***	0.1	ET AAS	[40]
Hg	Dithiocarbamate	$0.1\text{--}0.7 \text{ mol L}^{-1}$ hydrochloric acid	IBMK	Water	***	0.3	ET AAS	[40]
Sb	Dithiocarbamate	$0.1\text{--}0.7 \text{ mol L}^{-1}$ hydrochloric acid	IBMK	Water	***	0.06	ET AAS	[40]
Se	Dithiocarbamate	$0.1\text{--}0.7 \text{ mol L}^{-1}$ hydrochloric acid	IBMK	Water	***	0.08	ET AAS	[40]
Sn	Dithiocarbamate	pH 4.5	IBMK	Water	***	0.1	ET AAS	[40]
Ru	HMN	pH 5–7	Ethanol	–	10	20.0	ST	[41]
Ga	Chloride	6.0 mol L^{-1} hydrochloric acid	*	Al matrices	60	60.0	WD-XRF	[42]
Tl	Molybdophosphate	–	Nitric acid	–	–	15.0	FAAS	[43]
Nitrite	–	–	–	Water	–	0.30	–	[44]
Hg	Iodide	pH 5.0	*	Cu ores	10	2.7	WD-XRF	[45]
Ca	TBP	0.5 mol L^{-1} sodium hydroxide	1.0 mol L^{-1} hydrochloric acid	Glass and ceramics	60	–	ST	[46]

EF: enrichment factor; LOD: limit of detection; WD-XRF: wavelength dispersive X-ray fluorescence; ST: spectrophotometry; ET AAS: electrothermal atomic absorption spectrometry; ICP OES, inductively coupled plasma optical emission spectrometry; FAAS, flame atomic absorption spectrometry; EHPA: 2-ethylhexylphosphonic acid; IBMK: isobutyl methyl ketone; HMN: 3-hydroxy-2-methyl-1,4 naphthoquinone-4-oxime; *: metal determined directly in the solid-phase; **column method: 10 mL min^{-1} ; ***column method: 2 mL min^{-1} .

acid [32]. Under these conditions, the foam was partially destroyed, but the molybdenum(VI) was eluted quantitatively (>95%). The experimental conditions for determination of molybdenum in seawater by ICP OES using pre-concentration on PUF were optimized using multivariate techniques [33].

Unloaded PUF is generally used in batch procedures; first the complexes are formed by reaction between the metal ions and a complexing agent, and then PUF is added to promote the extraction. However, some methods using loaded PUF have also been described. For example, a method for the determination of thorium in natural water was proposed using PUF loaded with 2-ethylhexylphosphonic acid (EHPA) [34]. Another procedure used PUF loaded with dithiocarbamate (DTC) for the determination of antimony, arsenic, bismuth, mercury, selenium and tin by ICP OES [35]. The applicability of separation and pre-concentration methods using batch procedures is mainly determined by such analytical characteristics as linearity of the analytical curve, effect of other ions, and maximum sorption capacity of the PUF. The enrichment factor (EF), defined as the ratio between the analyte concentration in the solution after pre-concentration and that in the original sample, depends directly on the sample and eluent volumes. The limit of detection (LOD) also depends on the sample volume.

Table 1 summarizes separation and pre-concentration procedures for the determination of inorganic species with PUF as sorbent based on batch procedures.

6. On-line separation and pre-concentration procedures

On-line pre-concentration systems utilizing PUF have been introduced only recently; they are predominantly used with loaded PUF, although unloaded PUF has been applied as well. These systems have been coupled with analytical techniques such as molecular absorption spectrophotometry, FAAS and ICP OES.

With these procedures, the main experimental parameters that have been optimized are the pH, sampling flow rate, elution flow rate and type and concentration of eluent. The pH is studied because of the complexation reaction between the metal ions and ligands involved in the process. The sampling flow rate is determined by the sorption kinetics of the metal ions on the solid phase (PUF). Generally, a higher sampling flow rate implies a lower phase transfer factor. This, however, causes problems only if this factor is different for samples and standard solutions. The phase transfer factor quantifies the analyte mass that is transferred from the sample solution to the solid

Table 2
On-line pre-concentration methods using PUF as sorbent

Analyte	Ligand	Conditions for sorption	Eluent	Sample	PT/s	EF	LOD/ $\mu\text{g L}^{-1}$	Analytical technique	Ref.
Cd	BTAC	pH 9.0	0.1 mol L ⁻¹ hydrochloric acid	Environmental and biological samples	60	41	0.27	FAAS	[53]
Cu	APDC	1.0–3.0	IBMK	Natural waters and biological samples	60	170	0.2	FAAS	[54]
Pb	APDC	1.3–3.9	IBMK	Natural waters and biological samples	60	131	1.8	FAAS	[54]
Cr(VI)	APDC	0.8–1.6	IBMK	Natural waters and biological samples	60	28	2.0	FAAS	[54]
Cu	MeBTANC	7.0–8.5	0.01 mol L ⁻¹ hydrochloric acid	Food	90	–	1.2	ST	[55]
Pb	PAR	–	–	Drinking water and saline waste from oil refinery	–	51	0.4	FAAS	[56]
Pt	Thiocyanate	pH 2.0	10% (v/v) nitric acid	Water	60	100	0.28	ICP OES	[57]
Zn	PAR	pH 8.3	1.0 mol L ⁻¹ hydrochloric acid	Environmental samples	60	91	0.28	FAAS	[58]
Zn	Me-BTABr	pH 6.5–9.2	0.1 mol L ⁻¹ hydrochloric acid	Natural water	60	23	0.37	FAAS	[59]
Pb	TAM	pH 7.7	1.9 mol L ⁻¹ hydrochloric acid	Environmental samples	60	45	2.2	FAAS	[60]
Co	TAC	pH 10.5	2.0 mol L ⁻¹ hydrochloric acid	Water	120	37	3.2	FAAS	[61]
Co	TAC	pH 10.5	2.0 mol L ⁻¹ hydrochloric acid	Water	180	51	2.4	FAAS	[61]
Pb	BTAC	pH 7.0	0.1 mol L ⁻¹ hydrochloric acid	Sea water	60	26	0.13	FAAS	[52]
Ga	Chloride	–	IBMK	Aluminum alloys, natural water and urine	90	40	6	FAAS	[62]
Cd	DDTP	pH 2.0	80% (v/v) ethanol	Water	220	5.2	0.12	TS-FF-AAS	[19]
Pb	DDTP	pH 2.0	80% (v/v) ethanol	Water	220	6.4	1.5	TS-FF-AAS	[63]
Cd	PAR	8.2	1.0 mol L ⁻¹ hydrochloric acid	Drinking water	180	158	0.27	FAAS	[64]
Co	CA	8.0	0.50 mol L ⁻¹ hydrochloric acid	Lettuce samples	180	57	0.4	FAAS	[65]
Cd	Me-BTANC	7.5	1.0 mol L ⁻¹ hydrochloric acid	Black tea, spinach leaves and tap water	180	37	0.8	FAAS	[66]

EF: enrichment factor; LOD: limit of detection; PT: pre-concentration time; BTAC: 2-benzothiazolylazo-*p*-cresol; IBMK: isobutylmethylketone; APDC: ammonium pyrrolidine dithiocarbamate; Me-BTANC: 2-(6'-(methyl-2'-benzothiazolylazo) chromotropic acid; PAR: 4-(2-pyridylazo)-resorcinol; Me-BTABr: 2-[2'-(6-methyl-benzothiazolylazo)]-4-bromophenol; TAM: 2-(2-thiazolylazo)-5-dimethylaminophenol; TAC: 2-(2-thiazolylazo)-*p*-cresol (TAC); DDTP, *O,O*-diethyl-dithiophosphate TS-FF-AAS: thermospray flame-furnace atomic absorption spectrometry.

phase during the extraction process. In an on-line pre-concentration method for the determination of lead in saline effluents and drinking water using a minicolumn of PUF loaded with 4-(2-pyridylazo)-resorcinol (PAR), the sampling flow rate was optimized at 11 mL min^{-1} and the phase transfer factor was 73 [47]. The eluent flow rate was controlled by the aspiration rate of 5.0 mL min^{-1} for the spectrometer used for the quantitation. The choice of the eluent is made in the same way as in batch procedures; most procedures use hydrochloric acid in the concentration range $0.50\text{--}3.0 \text{ mol L}^{-1}$. Nitric acid has normally been avoided because it can destroy the PUF [48]. Methods using organic solvents as eluent have also been reported. Stratis and co-workers [49] used isobutylmethylketone (IBMK) for the determination of copper, lead and chromium(VI) in natural waters and biological samples by FAAS. Ascorbic acid was used as the eluent for iron(III) retained as thiocyanate complex on PUF in an on-line method for quantitation of iron in biological matrices [50].

The performance of C-18 immobilized on silica, activated carbon and PUF as sorbents, all loaded with *O,O*-diethyldithiophosphate (DDTP), was compared in a flow injection pre-concentration system for the determination of lead by FAAS. The best limit of detection of $0.3 \text{ } \mu\text{g L}^{-1}$ was obtained for the C-18, followed by $1.2 \text{ } \mu\text{g L}^{-1}$ for the PUF and $3 \text{ } \mu\text{g L}^{-1}$ for the activated carbon. The authors concluded that the C-18 has a much superior retention performance in comparison to the other two materials [51]. Lemos and Ferreira [52] compared the performance of two on-line pre-concentration systems for the determination of lead using a minicolumn of Amberlite XAD-2 loaded with 2-benzothiazolylazo-*p*-cresol (BTAC) and another one of PUF also loaded with BTAC. The minicolumn using PUF proved to be the pre-concentration system with higher sorption capacity, EF and better LOD. Table 2 gives an overview of on-line pre-concentration methods using PUF as the sorbent.

7. Application of PUF for speciation analysis

Braun et al. [67] established a procedure for the determination of phenylmercury, methylmercury and inorganic mercury in water using diethylammonium diethyldithiocarbamate (DDTC)-loaded PUF disks. The analytical technique used was radioisotope-induced X-ray-fluorescence. Elwakil et al. [68] proposed a specific procedure for the determination of chromium(VI) in natural water using PUF loaded with tributylphosphate (TBP) and molecular absorption spectrophotometry. Anthemidis et al. [49] also proposed an on-line pre-concentration system for the determination of chromium(VI) in environmental samples where the ammonium pyrrolidine dithiocarbamate (APDC) complex was sorbed on the unloaded PUF.

Lemos et al. [69] developed a method for the direct determination of free available lead(II) and total lead content in wine samples based on the chemical sorption of lead(II) from solutions buffered at pH 7 on a minicolumn of PUF loaded with BTAC. Lead was directly eluted into an air-acetylene flame with 0.1 mol L^{-1} hydrochloric acid and determined by FAAS. Free

available lead(II) was determined by direct on-line pre-concentration of the untreated sample, whereas total lead was determined after sample digestion with nitric acid and hydrogen peroxide.

8. Introduction of the PUF into the graphite furnace

Santelli and co-workers [70] developed an enrichment strategy for the determination of cobalt in water and biological materials with ET AAS, based on the direct introduction of the solid PUF, loaded with the cobalt–thiocyanate complex, into the graphite furnace. The results showed that PUF can be easily eliminated from the graphite tube using a pyrolysis temperature of $550 \text{ } ^\circ\text{C}$, and cobalt could be determined without a modifier. The same strategy was also used for the pre-concentration and determination of lead in biological samples [71]. The PUF was previously loaded with 2-(2-thiazolylazo)-*p*-cresol (TAC), the matrix was removed from the graphite tube by a pyrolysis at $600 \text{ } ^\circ\text{C}$, and lead could also be determined without using a modifier.

9. Other applications

The quantitative sorption of the heteropoly blue species of arsenomolybdic and phosphomolybdic acids by PUF has been used in a method for the determination of arsenate and phosphate using solid phase spectrophotometry [72]. PUF has also been used for enhancing the selectivity of analytical systems. Interferents were retained on PUF as thiocyanate complexes in a method for the determination of aluminum by flow injection spectrophotometry with methyl thymol blue [73]. Martinez and co-workers used PUF as a filter associated with ultrasonic nebulization for the determination of cadmium in commercial tea samples [74] and lead in *Ilex paraguariensis* samples [75] by ICP OES. A visual test has been developed for the determination of lead in soils using alkaline phosphatase immobilized in PUF. The procedure is based on the inhibitory effect of Pb ions towards the activity of the enzyme [76]. Ferreira and co-workers [36] proposed a separation procedure, using PUF as sorbent, to overcome the interference of aluminum in the determination of zinc in aluminum matrices by ICP OES. Zinc was retained on the solid phase as

Table 3
Thermodynamic characterization of ligand–PUF interactions

Metal ion	Ligand	$\Delta G/\text{kJ mol}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{JK}^{-1} \text{ mol}^{-1}$	$E/\text{kJ mol}^{-1}$	Ref.
Hg(II)	TAN	-5.1 ± 0.9	19.0 ± 0.9	80.73 ± 0.1	–	[78]
U(VI)	PAN	-10.6 ± 0.7	176 ± 5	626 ± 17	18.3 ± 0.3	[79]
Sb(V)	H2DZ	–13.8	–51.8	127.3	10.8	[80]
Zn(II)	Thiocyanate	6.67 ± 0.05	-77.5 ± 2.9	-5 ± 0.09	13.2 ± 0.5	[81]
Pd	Thiocyanate	–25.2	-48.9 ± 2.5	-127.3 ± 8.2	12.3 ± 0.35	[82]
Co(II)	Thiocyanate	–8.71	-64 ± 4.6	-92.6 ± 15.6	12.9 ± 0.4	[83]
Cd(II)	–	–12.7	-39.9 ± 5.9	-93 ± 19	13.8 ± 0.26	[84]
In	Iodide	–9.5	-50 ± 5	-140 ± 15	–	[85]

ΔH : enthalpy; ΔG : Gibbs free energy; ΔS : entropy; E : mean free energy; TAN: 1-(2-thiazolylazo)-2-naphthol; PAN: 1-(2-pyridylazo)-2-naphthol; H2DZ: diphenylthiocarbazone.

thiocyanate complex. Several papers also describe the direct analysis in the solid phase (PUF) using WD-XRF. Details of these methods are summarized in Table 1.

10. Thermodynamic properties of the PUF extraction process

Studies of sorption of metal ions with variation of temperature were conducted for the determination of thermodynamic parameters established during the process. These parameters are calculated employing the following equations:

$$\text{Log}K_c = (-\Delta H/2.303RT + \Delta S/2.303R)$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -RT\ln K_c$$

$$K_c = F_e/(1-F_e)$$

where ΔH , ΔS , ΔG and T are the enthalpy, entropy, Gibbs free energy and temperature in K, respectively, R is the gas constant ($8.3143 \text{ J mol}^{-1}$) and K_c is the equilibrium constant depending on the fractional attainment (F_e) at equilibrium. The plot of $\log K_c$ vs. $1/T$ gives the numerical values of ΔH and ΔS from the slope and the intercept, respectively.

Several authors have studied the physico-chemical phenomena involved in sorption processes of metal complexes on PUF. Saeed and co-workers [78–84] determined the thermodynamic parameters of extraction processes of several metal complexes on PUF. These data are reported in Table 3. Santelli and co-workers [77] undertook thermodynamic characterization of the extraction process of the cadmium-diethyldithiocarbamate complex by PUF. Another paper [85] studied the extraction process of indium(III)–iodide complex on PUF. The thermodynamic parameters have been determined and are summarized in Table 3. An evaluation of this table shows that most of the extraction processes using PUF can be considered as exothermic chemisorption due the negative values of the enthalpy (ΔH). The negative values for Gibbs free energy (ΔG) characterize the spontaneous nature of the sorption process. The negative values for the entropy (ΔS) indicate also that several processes occur with faster adsorption of the metal ion complexes onto active sites of the PUF. The fact that all E values (mean free energy computed by D–R isotherm) are higher than 9 kJ mol^{-1} demonstrates also that chemisorption is dominant in all the processes (refer to Section 4).

11. Conclusion

PUF is a sorbent that has been used quite frequently in recent years for the determination of trace metals. It has been used unloaded and also loaded with complexing reagents. The unloaded system has been used mainly for adsorption of anionic complexes such as iodide, thiocyanate and chloride. The loaded forms depend directly on the complexing reagent. A multi-

element pre-concentration procedure can be proposed using a complexing reagent with multi-element characteristics or a specific procedure can be performed using a selective reagent.

The structural form allows the easy use of this sorbent in automatic and on-line pre-concentration systems. In this context, it has advantages over other sorbents, such as active carbon, alumina and silica. The use of PUF and classical complexing agents also makes possible several procedures for speciation analysis. The application of PUF for pre-concentration and determination of metals by ET AAS has been investigated in only two papers [71]. The results reported there, however, propose that this could be another interesting field of application.

A comparison between PUF and other sorbents reveals that this solid phase has obvious advantages and limitations. PUF cannot adsorb metal ions without prior complexation, whereas, for example, activated carbon and alumina can. The sorption capacity of PUF is generally lower than that of activated carbon; however, for on-line systems this property is actually a disadvantage. Analyte elution from activated carbon as a consequence requires drastic conditions, including the use of concentrated acids. The great advantage of PUF is in on-line systems, as the backpressure presented by minicolumn is very low compared with other sorbents, such as activated carbon, silica or alumina.

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