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Talanta 66 (2005) 664–669

Talanta

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Liquid–liquid–liquid phase microextraction of aromatic amines in water using crown ethers by high-performance liquid chromatography with monolithic column

Ali Sarafraz Yazdi[a,*], Zarrin Es'haghi[b]

[a] *Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Iran*
[b] *Department of Chemistry, Faculty of Sciences, Payam-e-Nour University, Iran*

Received 13 June 2004; received in revised form 16 September 2004; accepted 1 December 2004
Available online 15 January 2005

Abstract

Liquid–liquid–liquid phase microextraction (LLLME) coupled with high-performance liquid chromatography (HPLC) for the analysis of some aromatic amines is described. These compounds were extracted from 4.0 mL aqueous sample that adjusted to pH 13 with, NaOH–NaCl buffer solution (donor phase, P_1) into an organic phase (P_2) 150 μl benzyl alcohol and ethyl acetate (2:1) and then back extracted into a microdrop of aqueous acceptor phase (P_3), adjusted at pH 2, with Na_2HPO_4–H_3PO_4 buffer solution. The extraction time, T_1 (from P_1 to P_2) was 20 min and T_2 (from P_2 to P_3) was 1 min. Different crown ethers as complexing agents for amines were added to the acceptor phase to improve the extraction time. Factors such as organic solvents, extraction times, and addition of crown ethers to acceptor phase and stirring rate were optimised. The method was applied for determination of aromatic amines in wastewater samples. Enrichment factors ranged from 184.5 to 389.7. The linearity range was from 3 to 1000 ng/ml and the detection limits varied from 0.8 to 1.80 ng/ml. Relative standard deviations (%, $n = 5$) were found (at S/N 3) in the range of 1.9 to 10.1. All experiments were carried out at room temperature, $22 \pm 0.5\,^{\circ}C$.

Keywords: Liquid–liquid–liquid microextraction (LLLME); Aromatic amine; Crown ether; Water; HPLC; Monolithic column

1. Introduction

Aromatic amines are widely used in industry, in the production of dyes, cosmetics, pesticides, pharmaceuticals and as the intermediate in many chemical syntheses [1,2]. Despite their toxic and carcinogenic properties, aniline and their derivatives are important because of wide use in many industrial processes, therefore monitoring of their levels in environmental waters is important. These compounds have been included in the US environmental protection agency (EPA) list of priority pollutants [3,4]. Many of these amines are known to be highly mutagenic and carcinogenic and to from adducts with proteins and DNA [5].

Amines are present in the environment at low parts per billion or less. Therefore, a certain clean-up procedure for the complex sample matrix is necessary for the reliable and accurate analysis of amines. In order to remove co-eluting interferences and to pre-concentrate amines, the extraction and clean-up of the sample has been performed using a number of different purification techniques such as solid phase microextraction (SPME) [6–8] and liquid phase microextraction (LPME) [9–12].

The most popular techniques for the analysis of aromatic amines in environmental water are high-performance liquid chromatography [13]. These compounds are polar and thermally sensitive thus, HPLC seems to be a proper method for analysis and a preconcentration step is necessary. We prefer the use of liquid–liquid–liquid microextraction technique (LLLME) for study of these compounds. Recently three-phase microextraction was developed to extraction ionisable

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* Corresponding author. Tel.: +98 511 8432023; fax: +98 511 8438032.
E-mail address: asyazdi@ferdowsi.um.ac.ir (A.S. Yazdi).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.12.026

and chargeable compounds from different aqueous samples [14,15]. Ma and Cantwell, used an organic solvent to separate two aqueous phase, donor phase and acceptor phase. The pH of donor phase was adjusted to basic and the acceptor phase was acidic. An ionisable compound was extracted from the donor phase into the organic phase, then back extraction into the acceptor phase. Compared to the supported liquid membrane (SLM), the LLLME uses an unsupported liquid organic membrane. The thickness of the organic film is easier to control, and because this organic layer is changed for every extraction, no memory effects was observed together with long term instability in LLLME [16].

In the present work, a simple LLLME device was set-up to enrich some aniline derivatives from various water samples before HPLC analysis. Various aspects of the LLLME of these analytes including the effect of organic solvent, composition of acceptor and donor phase, extraction times in each step, the effect of crown ethers as extraction-enhancing additives and stirring rates were investigated. On the other hand, the case of the development of high-performance columns for HPLC, particles of smaller sizes were employed to obtain better column efficiency, based on the smaller eddy diffusion and shorter diffusion path length [14]. Silica particles with sizes of 1.5–2 μm have become available recently [15]. However, the limitation in the performance of a packed column is well recognized based on the pressure limit of a solvent delivery system, leading to the current compromise at about 3–5 μm particle size between the column efficiency and the pressure drop. One approach to overcome the problem of a high pressure drop associated with small particles is to fabricate a monolithic column made of one piece of a porous solid with small-sized skeletons and relatively large throughpores which could provide both high column efficiency and low pressure drop [30]. The monolithic silica columns were evaluated in reversed-phase HPLC. These showed lower plate heights and much lower pressure drops than the conventional columns packed with the 5 μm C_{18} silica particles. So, we used a Chromolith performance RP-18e column in this work.

2. Experimental

2.1. Chemicals and reagents

Analytical reagents grade *N*-ethylaniline (NEA), *N*,*N*-dimethylaniline (NNDMA), 3-chloroaniline (3CA), 3-bromoaniline(3BA), 4-bromoaniline (4BA), benzyl alcohol, ethyl acetate, *n*-hexane, iso-octane, cyclo-hexane, were purchased from Merck (Darmstadt, Germany). 2-Nitroaniline (2NA) and 4-nitroaniline (4NA) were obtained from Riedel-De Haenga (Hannover, Switzerland). Methanol and butyl acetate was purchased from Fluka (Buchs, Switzerland). These compounds were all HPLC grade. di-Natrium hydrogen phosphate 2-hydrate, natrum hydroxide and natrium chloride were from Merck. The 18-crown-6, 24-crown-8 and DB 24-crown-8 were bought from Fluka. Deionized water and lake water were purified in a Milli-Q purification system (Millipore). Lake water from Caspian lake, Iran and waters from the dye and plastic industries and wastewater of a research chemical institute, all of from Mashhad, Iran served as the environmental samples. Stock solutions of the analytes (2.0 mg/ml) were prepared separately in methanol and they were stored at 4 °C. A standard solution containing all aromatic amines at 2.5 μg/ml was prepared by diluting the stock solutions with a pH 2.0 buffer (Na_2HPO_4–H_3PO_4). Fresh mixtures containing each aromatic amine at different concentrations in a pH 13.0 buffer (NaOH–NaCl) were prepared from the stock solutions and used as working solutions.

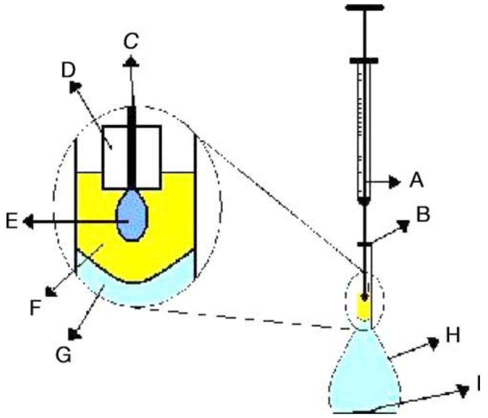

Fig. 1. Microextraction device, (A) 10-μl syringe, (B) aluminium foil, (C) microsyringe needle, (D) teflon washer, (E) microdrop (acceptor phase), (F) organic phase, (G) sample solution (donor Phase), (H) volumetric flask, (I) magnetic stirrer.

2.2. Instrumentation

2.2.1. Microextraction apparatus

The microextraction device is shown in Fig. 1. The sample solution was placed in a 5-ml volumetric flask (Durran, with DIN A, Germany). A stirring bar, measuring (5 and 3 mm) was used to facilitate the mass transfer process. A Ruhro (Retsch, Germany) R021 heater and magnetic stirrer was used to stir the extraction mixture. Aluminium foil was used to cover the flask during extraction to prevent the evaporation of the organic phase. A 25-μl flat-cut HPLC syringe was used to suspend the microdrop to receiving phase (P_3) during extraction and also for injection into the HPLC system after extraction.

2.2.2. HPLC system

The HPLC system used in this work was a Waters (Millipore co., Milford, MA, USA) and consisted of a Waters (488) tuneable absorbance detector and a Waters (746) integrator, a Chromolith performance RP-18e column (4.6 mm diameter, 100 mm length, 2-μm macropore size and 13-nm mesopore size) from Merck (Darmstadt Germany), was used for separation. A RP-18 guard column was fitted upstream of the analytical column.

The mobile phase was methanol–water optimized on (45:55, v/v) was delivered by a Waters LC-600 HPLC pump. The flow rate of the mobile phase was: 3 ml/min and the UV detection wavelength were set at 254 nm.

3. Results and discussion

3.1. Theoretical considerations

Liquid–liquid–liquid microextraction technique involves three phases: the donor phase (P_1), containing aqueous amines solution adjusted at pH 13; organic phase (P_2) and acceptor phase (P_3) or a microdrop of aqueous phase pH 2.0, so that the aromatic amine compounds were deionized in the P_1 and their solubilites in the sample solutions were reduced.

The aromatic amines were extracted into the organic phase because of their affinities to the organic solvents, and then aromatic amines in these strong acidic phases were protonated and these protonated species have very small affinity for the organic phase, and then they enter rapidly into the receiving phase. For one of these analytes, for example A, the extraction process is:

$$A_{P_1} \leftrightarrow A_{P_2} \leftrightarrow A_{P_3} \qquad (1)$$

At equilibrium, the distribution ratios for the analyte A, in this system are:

$$K_1 = [A]_{P_2,eq}/[A]_{P_1,eq}$$

and $K_2 = [A]_{P_2,eq}/[A]_{P_3,eq}$, thus

$$[A]_{P_1,initial} = [(K_2[A]_{P_3,eq}/K_1) + (K_2[A]_{P_3,eq} \times V_{P_2}/V_{P_1}) + ([A]_{P_3,eq} \times V_{P_3}/V_{P_1})] \qquad (2)$$

where $[A]_{P_3,initial}$ is the initial concentration of A in the donor phase P_1; $[A]_{P_3,eq}$ is the equilibrium concentration of A in the acceptor phase P_3; V_{P_2} is the volume of the organic phase; V_{P_3} is the volume of the acceptor phase. The EF (enrichment factor), defined as the ratio $[A]_{P_3,eq}/[A]_{P_1,initial}$ can be calculated.

$$\mathrm{EF} = \frac{1}{(K_2/K_1) + (K_2 V_{P_2}/V_{P_1}) + (V_{P_3}/V_{P_1})} \qquad (3)$$

since V_{P_2} is very small (150 μl), Eq. (3) is simplified in to

$$\mathrm{EF} = \frac{1}{(1/K) + (V_{P_3}/V_{P_1})} \qquad (4)$$

where

$$K = \frac{K_1}{K_2} = \frac{[A]_{P_3,eq}}{[A]_{P_1,eq}} \qquad (5)$$

To have a large K, the concentration of analaytes should be increased in the acceptor phase by such reactions as protonation, complexation, etc. These reactions must prevent the reverse extraction from the acceptor phase to the donor phase. Therefore, in this work we used both protonation and complexation to obtain larger K and to prevent the reverse extraction forces [16,17].

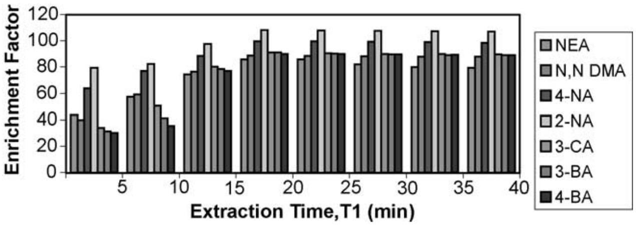

Fig. 2. The effect of extraction time for the initial two phases of P_1 and P_2.

The extraction recovery (R) for LPME was expressed as the percentage of total analyte amount ($n_{P_1,initial}$ number of mole of analyte originally present in the sample), which was transferred to the acceptor phase at the end of the extraction ($n_{P_3,final}$, number of mole finally collected in the acceptor phase):

$$R = (n_{P_3,final}/n_{P_1,initial}) \times 100\% = \frac{100 \times K V_{P_3}}{K V_{P_3} + K_2/K_1 V_{P_2} + V_{P_1}} \qquad (6)$$

3.2. Optimization method

Parameters and practical considerations affecting the LLLME procedure are as follow.

3.2.1. Extraction time of initial two phases (T_1)

The extraction of the aromatic amines from the water sample (P_1) into the organic phase by LLLME is a slow equilibrium process [18]. Because solute molecules need time to pass through interface between donor phase and organic phase, and this LLLME process depends on liquid–liquid equilibrium. Therefore, extraction time was that one of the most important factors influencing the extraction efficiency that was considered. The range of extraction times investigated was between 5 and 40 min. As shown in Fig. 2, the enrichment factors increased with increasing extraction time (T_1) from 5 to 20 min and reached a maximum when the initial two phases were stirred for 20 min (with stirring rate, 800 rev/min) but after 20 min, the efficiency showed a soft decline because of the loss of the ethyl acetate due to its evaporation and solvation in water. The optimized extraction time (T_1) for the first equilibrium was 20 min.

3.2.2. Back extraction time (T_2)

Single drop LLLME is not an exhaustive extraction technique. Although maximum sensitivity is attained at equilibrium, complete equilibrium need not be attained for accurate and precise analysis. Life time of the drop cannot be too long due to drop dissolution and loss, therefore, extraction time of the back extraction (T_2) from the organic solvent to the aqueous receiving phase (P_3) should not be

Table 1
Characteristics of organic solvents [16]

Solvents	Polarity index	Solubility in water (g/100 ml)	Surface tension (dyne/cm)	Viscosity cp (30 c)
n-Hexane	0.0	0.2	18.4	0.372
iso-Octane	0.0	Insoluble	21.80	0.706
cyclo-Hexane	0.2	Insoluble	24.99	0.98
Buthyl acetate	4.0	0.83	24.8	0.63
Ethyl acetate	4.4	10	23.6	0.428
Benzyl alcohol	>4.0	3.5	39.0	4.43

too long. It took only 1 min for the back extraction to attain equilibrium and the EF did not increase significantly after 1 min.

3.2.3. *Organic solvent*

Selection of an organic solvent is one of the critical steps in LPME. The organic phase serves to separate the aqueous acceptor phase from the aqueous donor phase. The organic phase must, therefore, be immiscible with both the acceptor and the donor phase. The solubility of the analytes should be higher in the organic phase than the donor phase to promote the extraction of the analytes. On the other hand, the solubility of the analytes should be lower in the organic phase compared to the acceptor phase, in order to achieve a high degree of recovery of analytes in the acceptor phase. Six different organic solvents were investigated namely: *n*-hexane, iso-octane, cyclo-hexane, butyl acetate, ethyl acetate and benzyl alcohol. The characterizations of these solvents are shown in Table 1. iso-Octane, *n*-hexane and cyclo-hexane only extract 3-chloroaniline, 3-bromoaniline and 4-bromoaniline, but butyl acetate, ethyl acetate and benzyl alcohol extract all analytes and transfer them into the aqueous receiving phase. In the case of ethyl acetate in spite of reported work [16], ethyl acetate was not a suitable solvent here by itself due to high water solubility and the unstability of the drop in large time. But it solved 4NA and 2NA better than benzyl alcohol and thus benzyl alcohol; ethyl acetate (2:1, v/v) was optimized as the most suitable organic solvent. Generally, it was recognized that organic solvents with higher polarity and lower solubility in water are more suitable than non-polar and water soluble solvents for extraction of the aromatic amines.

3.2.4. *Stirring speed*

Agitation of the sample is routinely applied to accelerate the extraction kinetics. Increasing the stirring speed of the donor phase enhances extraction as the diffusion of analytes through the organic phase is facilitated and improves the repeatability of the extraction method [19]. Sample agitation by using either vibration or magnetic stirring dramatically increased extraction but the liquid drop (acceptor phase) at the end of the needle, to be lost under great agitation. Therefore as showed in Fig. 3, the stirring speed was selected 800 rev/min.

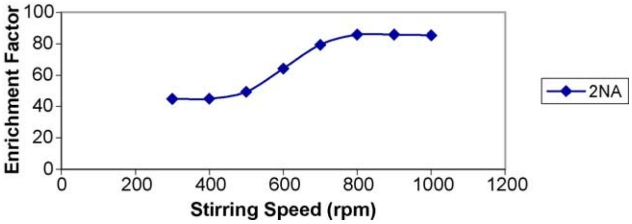

Fig. 3. The effect of stirring speed on the extraction of 2-nitroaniline.

3.2.5. *Phase volume*

Generally in the three-phase LLLME systems, sensitivity of the method can be increased by decreasing the volume ratio of the acceptor to the donor phase [20,21]. However, the volume of the acceptor solution used for extraction may also be adjusted depending on the analytical technique coupled to LLLME. For example, in contrast to GC, sample volumes in the range from 10 to 25 μl are easily injected into a HPLC instrument, so the whole acceptor phase may be analysed, potentially providing lower detection limits [22]. In this manner, the use of a large drop results in an increase of the analytical response. However, larger drops are difficult to manipulate and are less [23]. Additionally, larger injection volumes result in band broadening [25]. Thus, in this investigation we used 4.0-ml donor phase (P_1), 150-μl organic phase (P_2) and 2-μl acceptor phase (P_3).

3.2.6. *Addition of crown ethers to acceptor phase*

Crown ethers can form stable complexes with ammonium salts selectively [24,25]. This phenomenon helps to enhance the affinity of the acceptor phase for these amines. Thus in this work, some crown ethers were added into the aqueous receiving phase to increase the efficiency of the extraction from the organic phase into the aqueous drop (P_3). These compounds facilitate the back extraction and stabilizing the analytes in the aqueous acceptor phase (P_3). Different crown ethers with different concentrations were used. As is shown in Fig. 4, the effect of DB 24-crown-8 on enrichment factors of the aromatic amines are greater than 24-crown-8 and 18-crown-6. Probably, first case is the larger cavity of DB24C8 with respect to 18C6, in which case less steric hindrance

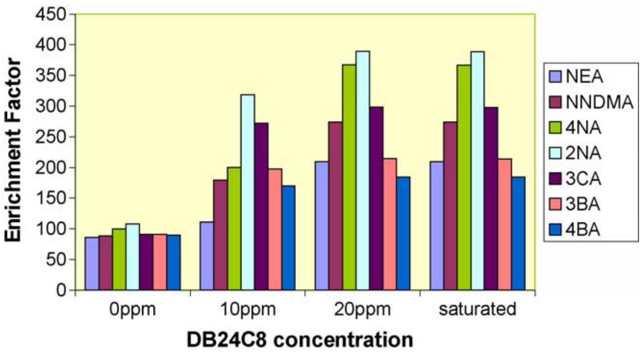

Fig. 4. The effect of DB24C8 concentration in the aqueous accepting phase on the extraction efficiency.

Table 2
Performance of the method

Compound	Enrichment factor	R.S.D.%	Linear range (ng/ml)	LOD (ng/ml, $n = 7$)	Recovery (%)	
					5^a ng/ml	10^a ng/ml
NEA	209.5	10.1	4–1000	1.80	74.7	86.5
NNDMA	274.2	7.2	4.5–1000	1.75	76.5	89.4
4NA	367.4	2.1	3.5–1000	0.90	88.5	98.9
2NA	389.7	1.9	3–1000	0.80	87.1	99.5
3CA	298.2	5.5	4–1000	1.60	77.7	91.5
3BA	214.8	6.8	3.5–1000	1.60	77.5	91.3
4BA	184.5	6.83	4–1000	1.65	75.6	90.9

LLLME conditions: P_1, 4-ml aqueous sample with NaOH–NaCl (2.5 μg/ml), pH 13; P_2, 150-μl organic phase, benzyl alcohol–ethyl acetate (2:1); P_3, 2-μl aqueous drop with Na_2HPO_4–H_3PO_4 (50 mM), pH 2 and DB24C8 (20 μg/ml); $T_1 = 20$ min; $T_2 = 1$ min; stirring speed 800 rev/min. Original sample concentrations: 2 and 1 mg/ml; 10, 5 and 1 μg/ml; 10, 5 and 1 ng/ml.

[a] Final concentration of each analyte after spiking in water.

than 18C6. Furthermore, obviously interaction between two aromatic rings of crown ether and aniline derivatives helped to the stability of the complexes that are formed between these two compounds and thus, this structure indicate that certain conformations are available which allow a close, parallel alignment of the mean planes of the two aromatic rings of crown ether such that a cationic aromatic amine could be completely enveloped, and rationalized this in terms of a favourite molecular geometry for complexation [28,29]. Moreover, the enrichment factors were increased with the concentration of crown ethers up to the optimum value (20 ppm) after while decreasing of the EF was observed. These results may be due to the adsorption of surface-active species at the liquid–liquid interface that can produce an interfacial resistance, which reduces the mass transfer rates of other compounds across the interface [26,27].

3.3. Quantitative aspects

Enrichment factors, linear range, precision (R.S.D.) and detection limits (LOD) are given in Table 2. The linearity of this method for analyzing standard solution has been investigated over the ranges 3–1000 ng/ml, in the case of DB 24-crown-8. The precision of method was studied for a set of five replicates. The R.S.D. ranged from 1.9 to 10.1%. LODs were calculated as three time the standard deviation of blank for seven replicate runs and were calculated in the range from 0.80 to 1.80 ng/ml.

3.4. Real water analysis

Caspian lake water samples, spiked with all of the aromatic amines were extracted using LLLME under optimal conditions. The results of which were shown in Fig. 5. Because of the matrix effect on the pH adjustment, more concentrated NaOH (6 M) was needed to adjust the pH of sample at 13.0, we used a spiked sampled to test because no aromatic amines were detected in real water samples. The recoveries of the analytes from this real sample were higher than 86% compared with that of spiked pure water. This indicates that the matrix effect did not have a significant role on the extraction efficiency.

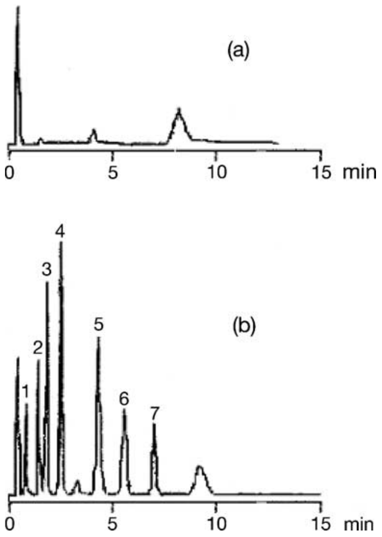

Fig. 5. Chromatograms obtained from (a) lake water sample and (b) the same sample spiked with 2 ng/ml of aromatic amines under optimum condition. Peaks (1) *N*-ethylaniline (NEA), (2) *N*,*N*-dimethylaniline (NNDMA), (3) 4-nitroaniline (4NA), (4) 2-nitroaniline (2NA), (5) 3-chloroaniline (3CA), (6) 3-bromoaniline (3BA), (7) 4-bromoaniline (4BA).

The performance of this method was also tested by analyzing real waters from the dye and plastic industries and wastewater of a research chemical institute, all of from Mashhad, Iran. As shown in Table 3, 2NA, 4NA and 3CA were the contaminations and found in low concentration levels.

Table 3
Concentration (μg/l) of aromatic amines detected in real waters using LLLME–HPLC

Analytes	Dye plant	Plastic industries	Wastewater
2NA	0.002	0.007	0.022
4NA	0.014	0.009	0.029
3CA	Trace	0.067	0.013

4. Conclusion

The present work has demonstrated that LPME may be utilized for the extraction of hydrophobic basic compounds and drugs from environmental and biological samples. LLLME coupled with HPLC was successfully applied to the analysis of aromatic amines in water samples. Compared to most conventional procedures and according to the obtained results, this extraction technique requires very little aqueous sample solution, organic solvent and acceptor solvent. Low detection limits and high enrichment factors are readily achievable. DB 24-crown-8 ether was added to the aqueous receiving phase to increase the extraction performance and enabling high enrichment factors ranging from 184.5 to 389.7. The method is recommended for determination of these aromatic amines in natural water and consequently, this procedure can be applied for determination of trace residue of aromatic amines or many other drugs in foods, water and biological fluids. This technique is simple, economical, rapid and applicable to the biological and environmental samples. With this method the analytes were extracted from water sample quantitatively, these method provided extracts with highly enriched analytes and excellent clean-up of some environmental pollutants. Good linearity and relative recoveries were also obtained. Work is in progress to further enhancements.

Acknowledgements

The authors wish to thank the Ferdowsi university of Mashhad, Iran (A.S. Yazdi) and Payame noor University, Iran (Z. Es'haghi) for financial support of this work.

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