Talanta 120 (2014) 450–455

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of polar aromatic amines using newly synthesized sol–gel titanium (IV) butoxide cyanopropyltriethoxysilane as solid phase extraction sorbent

Mazidatulakmam Miskam [a,b,*], Nor Kartini Abu Bakar [a], Sharifah Mohamad [a]

[a] Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
[b] Department of Chemistry, Kulliyyah of Science, International Islamic University Malaysia, Bandar Indera Mahkota, 25200 Kuantan, Pahang, Malaysia

ARTICLE INFO

Article history:
Received 31 October 2013
Received in revised form
13 December 2013
Accepted 16 December 2013
Available online 22 December 2013

Keywords:
Solid phase extraction
Titanium(IV) butoxide-cyanopropyltriethoxysilane sorbent
Aromatic amines
Gas chromatograpy–flame ionization detector

ABSTRACT

A solid phase extraction (SPE) method has been developed using a newly synthesized titanium (IV) butoxide-cyanopropyltriethoxysilane (Ti-CNPrTEOS) sorbent for polar selective extraction of aromatic amines in river water sample. The effect of different parameters on the extraction recovery was studied using the SPE method. The applicability of the sorbents for the extraction of polar aromatic amines by the SPE was extensively studied and evaluated as a function of pH, conditioning solvent, sample loading volume, elution solvent and elution solvent volume. The optimum experimental conditions were sample at pH 7, dichloromethane as conditioning solvent, 10 mL sample loading volume and 5 mL of acetonitrile as the eluting solvent. Under the optimum conditions, the limit of detection (LOD) and limit of quantification (LOQ) for solid phase extraction using Ti-CNPrTEOS SPE sorbent (0.01–0.2; 0.03–0.61 μgL^{-1}) were lower compared with those achieved using Si-CN SPE sorbent (0.25–1.50; 1.96–3.59 μgL^{-1}) and C18 SPE sorbent (0.37–0.98; 1.87–2.87 μgL^{-1}) with higher selectivity towards the extraction of polar aromatic amines. The optimized procedure was successfully applied for the solid phase extraction method of selected aromatic amines in river water, waste water and tap water samples prior to the gas chromatography–flame ionization detector separation.

1. Introduction

Aromatic amines are generally identified as those chemical compounds having in their molecular structure one or more aromatic rings, bearing one or more amino substituents [1,2]. Even though aniline and its other substituted derivatives are consider as toxic aromatic amine, they are widely used to make dyes, synthetic polymers, pesticides, cosmetics, medicines and many other industrial chemicals. They may be released both from these manufacturing processes and power generators, such as coal-conversion waste facilities [3–5]. As the result, given their toxicity and biological activity, the residues have become problematic contaminants in environmental waters [6–8].

Given the increasing use of these compounds in various industries, aromatic amines have been extensively regulated and classified as priority pollutants by US Environmental Protection Agency (EPA) [9,10]. Therefore, in order to protect human health and the environment, it is significantly important to monitor their levels in environmental waters. This has increased the demand for the development of simple, reliable, sensitive and rapid analytical methods [11].

Liquid–liquid extraction (LLE) is not recommended as it is considered to be a time-consuming, tedious, multistage operation, where problems of emulsion formation obstruct automation. Moreover, low recoveries for some amines are sometimes found [2,12–14]. As solid phase extraction (SPE) available in a wide variety of sorbent materials [15–18] uses minimum amount of solvents compared to LLE, it is a good alternative to the LLE technique.

Sol–gel has been one of the emerging techniques to synthesis inorganic polymer which provides high stability to stationary phase and column efficiency in separation. The application of sol–gel technique to synthesis organic–inorganic sorbents have been proven to be quite successful in the extraction of solid phase microextraction (SPME) [19–24] and stir bar sorptive extraction (SBSE) [25–30]. However, the number of sol–gel sorbent materials reported were limited [4,19–30]. Thus, the quest for potential sol–gel sorbents to be used in analytical extraction can be explored using sol–gel technique since the reaction is easily carried out using various types of precursors under mild synthesis conditions.

Previously, a batch sorption extraction of aromatic amines based on newly synthesized hybrid titanium alkoxide metal with 3-cyanopropyltriethoxysilane (Ti-CNPrTEOS) sorbent has been

---

* Corresponding author at: Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia. Tel.: +60 379 674263.
E-mail address: mazidatul@gmail.com (M. Miskam).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.12.037

described in our laboratory and satisfactory recoveries (94–101%) were obtained [31]. Thus, it was the aim of this work to develop the polar selective solid phase extraction (SPE) method using Ti-CNPrTEOS sorbent for the determination of aromatic amines (aniline, *m*-toluidine, N,N-dimethylaniline, 4-ethylaniline, ethylaniline and N,N-diethylaniline). The selectivity feature is due to the ability of nitrile lone pair electrons from cyano moieties to form π–π interaction with polar aromatic amines.

2. Experimental

2.1. Chemicals and reagent

All chemicals and solvents used were of analytical and chromatographic grades, respectively. They were used as received. Standard polar and mid-polar aromatic amines namely aniline (A), m-toluidine (mT), N,N-dimethylaniline (DMA), 4-ethylaniline (4 EA), ethylaniline (EA) and non-polar N,N-diethylaniline (DEA) were purchased from Sigma-Aldrich (Steinheim, Germany). 3-cyanopropyltriethoxysilane (CNPrTEOS), ethanol, toluene and methanol also were purchased from Sigma-Aldrich (Steinheim, Germany). Titanium (IV) butoxide ($Ti(OBu)_4$), hydrochloric acids (HCl), dichloromethane (DCM) and n-hexane were from Fluka (Buchs, Switzerland). HPLC grade acetonitrile was purchased from Fisher Scientific (Leicestershire, UK). Si-CN sorbent and Chromabond C-18 sorbent were both purchased from Macherey-Nagel (Duren, Germany).

2.2. Instruments

Aromatic amines were analyzed using an Agilent 7890A GC system with an Agilent 5975C Series GC/FID from Agilent Technologies Inc. (Santa Clara, CA, USA). The GC column used was a HP-5MS column (30 m × 0.32 mm i.d. and 0.25 μm film thickness). Helium was used as carrier gas at a flow rate of 1.0 mL min^{-1}. The FTIR spectra of Ti-CNPrTEOS sorbent was obtained using the KBr pellet method on a 1600 Series Perkin-Elmer spectrophotometer (MA, USA) in the range of 400–4000 cm^{-1}. The surface area and pore size distribution of the sol–gel $Ti(OBu)_4$-CNPrTEOS were measured by nitrogen adsorption–desorption isotherms at 77 K on an Aurusorb Automated Gas Sorption analyzer (Quantachrome Corporation) using Brunauer–Emmett–Teller (BET) desorption methods.

2.3. Chromatographic conditions

The injection port and detector temperature were both set at 260 °C. Gas chromatography temperature profile was set at 60–220 °C, start at 60 °C (hold 1 min) ramp at 30 °C min^{-1}–220 °C (hold 2 min). Sample (1 μL) was injected manually into the injection port under splitless mode.

2.4. Preparation of Ti-CNPrTEOS sorbent

The preparation of Ti-CNPrTEOS sorbent was adopted from procedure as described in the literature [31]. The sorbent was prepared with the molar ratio $Ti(OBu)_4$:CNPrTEOS:THF:HCl:H_2O was 1:1:6:1:4. Initially, $Ti(OBu)_4$, CNPrTEOS and THF were mixed in a beaker and stirred for approximately 30 min at room temperature. Subsequently, water acidified with HCl was added drop wise to the beaker and stirred magnetically for 30 min. The clear and homogeneous wet gel obtained was aged in an oven (60 °C) for 24 h.

The dried gel was next ground into small pieces using mortar and pestle and washed with 3 × 10 mL acetone, followed by 3 × 10 mL deionized water. The product was finally dried at 100 °C for 24 h.

2.5. SPE procedure

The ground sol–gel material (100 mg) was packed manually into an empty 3 mL SPE polypropylene tube with frits. Then, the filled SPE cartridge was placed in a 12-port SPE vacuum manifold from Thermo Fischer Scientific (Waltham, MA, USA). The cartridges were conditioned by passing 10 mL dichloromethane. For optimization process, 10 mL of spiked (1 μg mL^{-1} of each aromatic amines prepared in hexane) was passed through the cartridge at a flow rate of 0.5 mL min^{-1}. The sorbent material in the cartridge was not allowed to dry at any moment. After the sample loading, the SPE cartridge was dried by passing air for 30 min. Retained aromatic amines were eluted from the sorbent with 5 mL acetonitrile and injected to GC–FID for analysis. Blank sample analysis was also performed for comparison purposes. For Si-CN SPE and C18 SPE, 3 mL cartridges were used for extraction and a similar procedure as the Ti-CNPrTEOS SPE was followed.

2.6. Real sample analysis

Water samples namely river water, waste water and tap water were used as real samples. River water was collected from river water nearby industrial area in Johor, Malaysia, waste water samples were collected from foods and beverages company waste water treatment plant in the industrial area in Selangor, Malaysia in Teflon bottles and tap water was obtained from the laboratory. The pre-cleaned bottles were covered with aluminum and stored in the dark at −4 °C until analysis. All water samples were used as received. To assess the matrix effect, 0.1 μg L^{-1} of aromatic amines was spiked to the river water sample, and its concentration was later determined by SPE using Ti-CNPrTEOS sorbent. For Si-CN SPE and C18 SPE, 10 μg L^{-1} was spiked to the river water sample.

3. Results and discussions

3.1. Characterization of sol–gel Ti-CNPrTEOS

In FTIR spectra (Fig. 1), the appearance of characteristic vibration of Ti–O–Si (944.86 cm^{-1}) [31] confirming the polycondensation between sol–gel-active titania and silica precusors. The main band at the frequency between 1050 cm^{-1} and 1150 cm^{-1} was due to the silica networks. Absorption band at 2247 cm^{-1} confirmed the existence of cyano (-CN) which showed that cyano moieties were available to participate in the extraction process. The methyl stretching band (C–H) appeared at 2950 cm^{-1}.

The pore size and surface area of blank Ti and Ti-CNPrTEOS sorbent are shown in Table 1. As we can observe, with the addition of CNPrTEOS reduced the pore size and surface area of the synthesized sorbent. This may be due to the formation of a porous mesostructure contributed by the cross-linking and self-condensation reaction occurred during the process of CNPrTEOS chain bonded to the surface of $Ti(OBu)_4$ particles through Ti–O–Si combination.

3.2. SPE optimization

3.2.1. Sample pH

As the solubility of the acidic/basic target analytes is affected together with dissociation equilibrium, an adjustment of the pH can enhance the extraction [32]. In the present study, the extractions were performed under different pH conditions ranging from pH 4 to 9 (Fig. 2). An increase of extraction recovery was observed

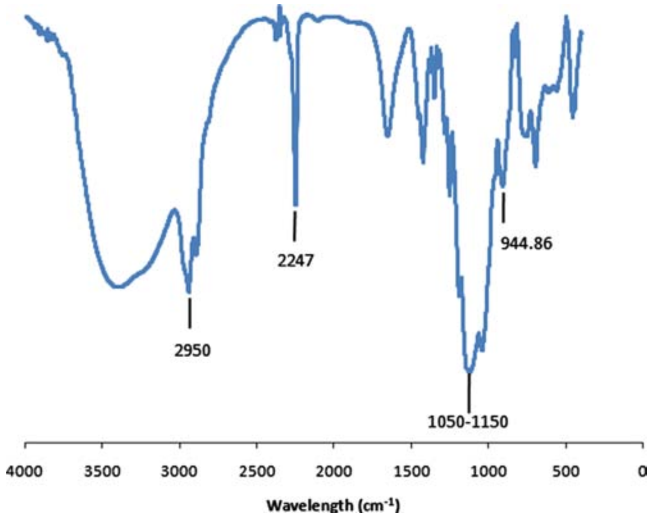

Fig. 1. FTIR spectra for Ti-CNPrTEOS sorbent.

Table 1
BET pore size and surface area.

Sample	Pore size (nm)	Surface area (m^2/g)
Blank Ti	47.1	22.28
Ti-CNPrTEOS	15.9	3.04

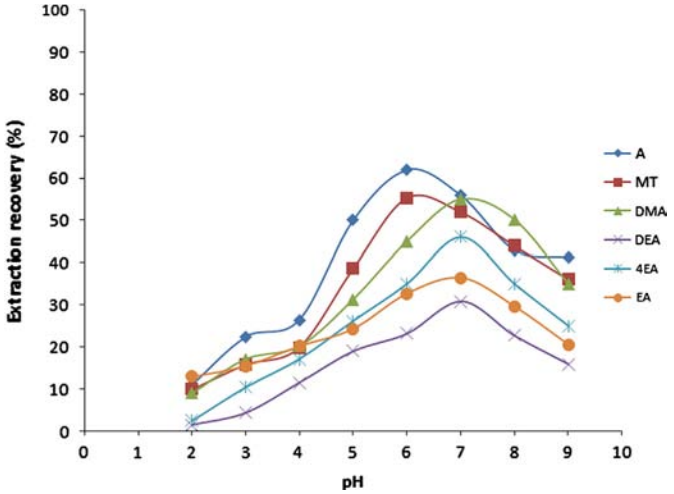

Fig. 2. Effect of pH of analytes mixture on the recovery of aromatic amines. Extraction conditions: toluene as conditioning solvent, 5 mL sample loading volume, 10 ml of acetonitrile as elution solvent.

when the pH was increased from 2 to 6 and the response remained constant or slightly decreased across pH range of 7–9.

According to Li et al., titanium represents anion-exchange properties at acidic pH and cation-exchange properties at alkaline pH [33]. Therefore, at acidic pH of 2–6, titanium presented as Ti^{4+}. The extraction recovery increased from 2 to 5. At pH 2, the extraction recovery was low as aromatic amines were protonated. The repulsion of Ti^{4+} and protonated aromatic amines lowered the extraction recovery. At pH greater than 2, aromatic amines began to formed neutral species [34]. At pH 6–7, the analytes showed a maximum extraction recovery. This may be because aromatic amines started to deprotonate and could be extracted by Ti-CNPrTEOS sorbent through π–π interactions and electrostatic interaction between negatively charged aromatic amines and positively charged titanium. At basic pH 8-9, titanium started to deprotonated. At this point, the repulsion of negatively charged analytes and Ti^{4-} caused the extraction recovery to decrease. Therefore, pH 7 was chosen for the subsequent analysis.

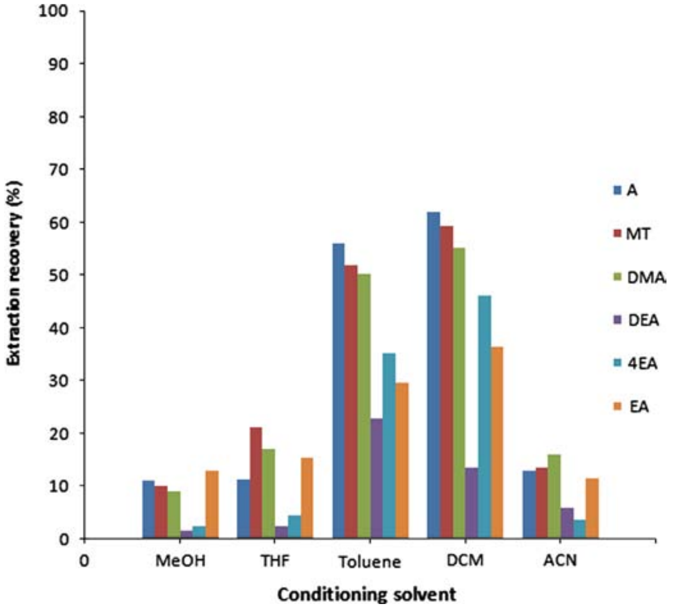

Fig. 3. Effect of conditioning solvent on the recovery of aromatic amines. Extraction conditions: sample at pH 7, 5 mL sample loading volume, dichloromethane as washing solvent, 10 ml of acetonitrile as elution solvent.

3.2.2. *Conditioning solvent*

The conditioning step is a critical factor in order to improve the reproducibility of the analytes retention and reduced sorbent impurities prior to extraction process [35]. The selection of organic solvent to enhance the wettability of sorbent was performed using methanol, acetonitrile, tetrahydrofuran, toluene, and dichloromethane (Fig. 3). It was found that conditioning the sorbent with non-immiscible solvents such toluene and dichloromethane gave higher extraction recoveries compared to other solvents. As the sample solvent was also non-immiscible (hexane), the results obtained were parallel as reported by Poole et al. where the same nature of sample solvent and conditioning solvent is the key for high recovery [35]. Dichloromethane showed the highest extraction recovery. Thus, dichloromethane was chosen as the optimum conditioning solvent.

3.2.3. *Sample loading volume*

In order to determine the loading capacity and overall time required to reach equilibrium (by the sorbent with analytes), sample loading volume plays an important role. To obtain highest sensitivity and sample enrichment, as large as possible sample volume is necessary. The sample size is governed by the breakthrough volume of the sorbent. Four different sample volumes (5–20 mL) were examined at a flow rate of 0.5 mL min^{-1}. Increasing sample volume increased the recovery of aromatic amines extracted. However, beyond 10 mL the recovery of aromatic amines extracted started to decrease significantly probably due to the sorbent breakthrough being exceeded. Thus, 10 mL was selected as the optimum sample volume.

3.2.4. *Washing solvents*

After the sample was loaded into the cartridges, the Ti-CNPrTEOS sorbent was rinsed with solvent to displace undesired matrices without displacing the analytes. The selection of the type of solvents

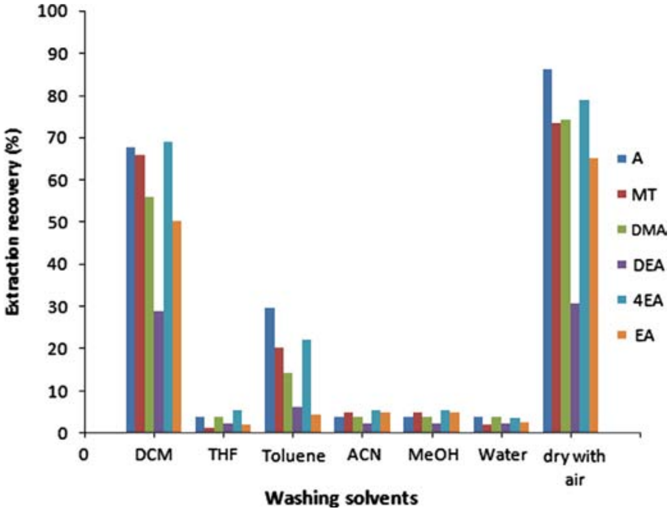

Fig. 4. Effect of washing solvent on the recovery of aromatic amines. Extraction conditions: sample at pH 7, dichloromethane as conditioning solvent, 10 ml of acetonitrile as elution solvent.

was crucial as strong solvent will wash the analytes together with the solvents meanwhile weak solvent will not displacing the matrix components. Several solvents (methanol, acetonitrile, tetrahydrofuran, water, dichloromethane and toluene) with different strengths have been chosen in this study to assess the effect of washing solvent on SPE. As shown in Fig. 4, when polar solvents (methanol, acetonitrile, water and tetrahydrofuran) were used to wash the sorbent, low extraction recoveries were obtained. This may be because with the solvent strength between 0.48 and 0.73 ε°, the aromatic amines retained during sample loading were displaced by the solvents. When weaker solvent such as toluene and dichloromethane (elution strength of 0.22 and 0.32 ε° respectively) was used, the extraction recoveries increased.

As the study showed that a weak solvent could sufficiently wash the sorbent, this indicated that the matrix components did not interfered the extraction [36]. Thus, drying step was introduced prior to the elution step to replace the washing solvent. Drying step reduces the volume of solvent retained in the sorbent after the sample loading step. During this step, the sorbent was flowed with air for 30 min which considerably sufficient to remove all sample solvent that was trapped in the sorbent pores. As expected, the extraction recoveries obtained were much higher compared washing the sorbent with solvents. Thus, the drying step was used throughout the subsequent analysis.

3.2.5. Elution solvent

Elution step is crucial to elute analytes that have been retained in the sorbent. Six eluting solvents of different polarities namely acetonitrile, tetrahydrofuran, methanol, toluene, hexane and dichloromethane were investigated to determine the best eluting solvent. The solvents used should be a strong solvent that able to displace all analytes from the sorbent in a small volume [35]. In that case, polar solvents (methanol, acetonitrile and tetrahydrofuran) were the best candidates as the solvent strengths are higher compared to non-polar solvents (toluene, hexane and dichloromethane).

The results indicated that acetonitrile was the most effective eluting solvent and thus selected as it gave the highest recovery for polar the aromatic amines studied (Fig. 5).

3.2.6. Elution solvent volume

To ensure all retained analytes were eluted from the sorbent with a minimum yet sufficient volume, elution solvent volume from 1 to 15 mL was investigated. As the elution solvent volume increased, from 1 mL to 5 mL, the recovery of aromatic amines extracted increased. The highest recoveries for the aromatic amines were obtained when 5 mL of eluting solvent were used. Thus, 5 mL acetonitrile was selected as the optimum eluent volume.

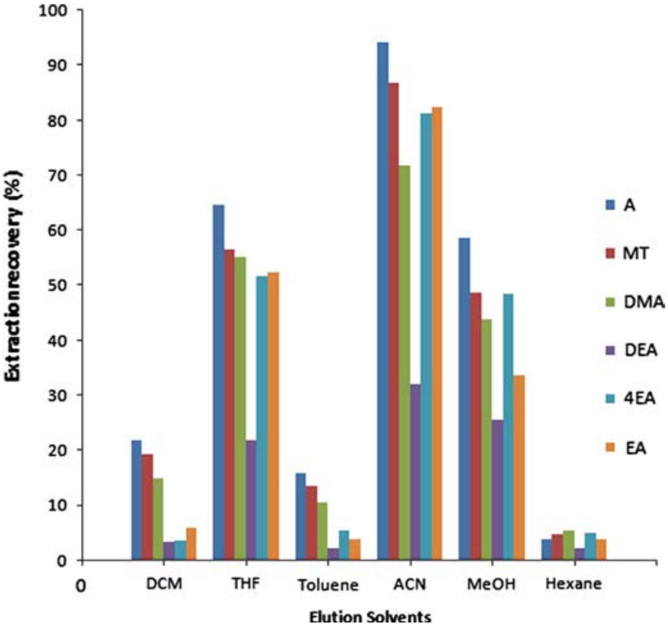

Fig. 5. Effect of eluting solvent on the recovery of aromatic amines. Extraction conditions: sample at pH 7, dichloromethane as conditioning solvent, 10 mL sample loading volume, 30 min of drying and 10 mL of elution solvent.

3.3. Method validation

Based on the results, the optimized parameters obtained for the extraction of aromatic amines using sol–gel Ti-CNPrTEOS were sample at pH 7, dichloromethane as conditioning solvent, 10 mL sample loading volume, acetonitrile as the eluting solvent and 5 mL of elution solvent used. The optimized results were used for SPE with Si-CN sorbent. Optimum SPE conditions for the C18 SPE sorbent are 10 mL sample loading and 5 mL acetonitrile as the eluting solvent.

The applicability of the proposed SPE method was validated using the sol–gel Ti-CNPrTEOS sorbent, linearity, limit of detection (LOD) and limit of quantification (LOQ) for Ti-CNPrTEOS SPE sorbent, Si-CN SPE sorbent and commercial C18 SPE sorbent were assessed using the optimum extraction conditions. The linearity of the extraction technique was studied at five different concentration levels of aromatic amines in the range for Ti-CNPrTEOS SPE sorbent (0.01–10 $\mu g L^{-1}$), Si-CN SPE sorbent (0.5–50 $\mu g L^{-1}$), C18 SPE sorbent (0.5–50 $\mu g L^{-1}$). Different ranges were used for each sorbent depending on their sensitivity towards aromatic amines.

Table 2 shows that good linearities were obtained for both SPE extractions using all three sorbents with coefficient of determination, $r^2 > 0.9992$. The LOD and LOQ achieved by sol–gel Ti-CNPrTEOS sorbent were lower compared to the LOD and LOQ for Si-CN and C18 sorbent (Table 2).

3.4. Real sample analysis

The proposed method using the sol–gel Ti-CNPrTEOS SPE sorbent was applied to the analysis of river water and waste water samples. None of the target analytes were detected in these water samples under the experimental conditions described. In order to

Table 2
Analytical figures of merits of sol–gel Ti-CNPrTEOS SPE, Si-CN SPE and C18 SPE: linearity, repeatability (%RSD, $n=5$), limit of detection and limit of quantification of aromatic amines.

Analytes	Ti-CNPrTEOS SPE				Si-CN SPE				C18 SPE			
	Correlation coefficient (r^2)	RSD %	LOD (μgL^{-1})	LOQ (μgL^{-1})	Correlation coefficient (r^2)	RSD %	LOD (μgL^{-1})	LOQ (μgL^{-1})	Correlation coefficient (r^2)	RSD %	LOD (μgL^{-1})	LOQ (μgL^{-1})
Aniline	0.9996	2.6	0.01	0.03	0.9997	4.3	0.33	1.56	0.9995	3.5	0.98	1.96
m-toluidine	0.9995	2.5	0.02	0.05	0.9994	3.5	0.49	1.68	0.9993	4.4	0.59	1.87
Dimethylamine	0.9993	3.6	0.02	0.05	0.9992	4.4	0.38	1.97	0.9997	4.3	0.49	1.93
Diethylamine	0.9997	3.1	0.20	0.61	0.9995	3.1	1.50	2.36	0.9996	3.8	0.37	2.56
4-ethylamine	0.9996	2.6	0.01	0.02	0.9997	4.6	0.61	1.96	0.9993	2.8	0.50	2.73
Ethylamine	0.9995	3.5	0.10	0.21	0.9998	3.6	0.25	3.59	0.9999	4.1	0.41	2.87

[a] Linearity ranges: Ti-CNPrTEOS (0.01–10 μgL^{-1}), Si-CN (0.5–50 μgL^{-1}), C18 (0.5–50 μgL^{-1}).
[b] LOD: $S/n=3$.
[c] LOQ: $S/n=10$.

Table 3
Percentage recovery and % RSD ($n=5$) for spiked aromatic amines from river water, waste water and tap water samples using developed sol–gel Ti-CNPrTEOS SPE, Si-CN SPE and C18 SPE method with GC–FID analysis.

Aromatic amines	Ti-CNPrTEOS SPE recovery (± RSD%, $n=5$)			Si-CN SPE recovery (± RSD%, $n=5$)			C18 SPE recovery (± RSD%, $n=5$)		
	River water	Waste water	Tap water	River water	Waste water	Tap water	River water	Waste water	Tap water
Aniline	99 (4)	98(4)	98(2)	92 (6)	91(7)	95(6)	89 (7)	88(8)	90(7)
m-toluidine	97 (3)	96(4)	97(2)	94 (7)	94(6)	96(6)	88 (8)	88(7)	91(7)
Dimethylamine	96 (3)	95(3)	98(2)	92 (6)	95(6)	94(5)	90 (6)	91(7)	90(5)
Diethylamine	67 (4)	57(4)	69(1)	60 (7)	55(8)	70(6)	86 (8)	87(8)	89(7)
4-ethylamine	98 (4)	97(3)	96(2)	93 (6)	95(6)	97(5)	88 (7)	86(7)	90(6)
Ethylamine	98 (1)	96(1)	99(2)	93 (4)	92(5)	96(5)	88 (4)	83(6)	92(6)

[a] Spiking level of: Ti-CNPrTEOS (0.1 μgL^{-1}), Si-CN (10 μgL^{-1}), C18 (10 μgL^{-1}).

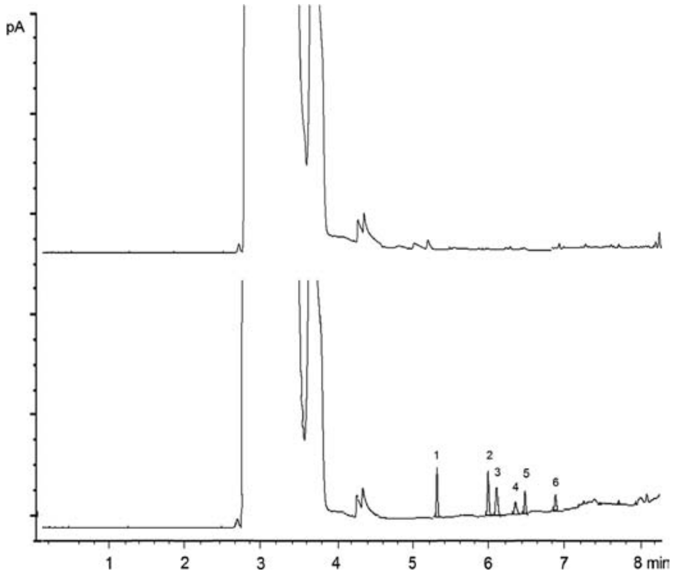

Fig. 6. Chromatograms of river water analysis; (a) unspiked river water, and (b) spiked aromatic amines (0.1 $\mu g\,L^{-1}$). Peaks: (1) aniline; (2) m-toluidine; (3) N, N-dimethylaniline; (4) N,N-diethylaniline; (5) 4-ethylaniline; and (6) ethylaniline.

assess the matrix effect, all the water samples were spiked with 0.1 μgL^{-1} for Ti-CNPrTEOS SPE sorbent and 10 μgL^{-1} for Si-CN and C18 sorbents to assess recovery (accuracy of the proposed method). Analyses of a blank sample were performed for comparison purposes.

Table 3 shows the comparison of recovery and precision (repeatabilities and reproducibilities) obtained using sol–gel Ti-CNPrTEOS SPE sorbent, Si-CN SPE sorbent and C18-SPE sorbent, respectively for river water sample. The recoveries and repeatability obtained from water samples using the sol–gel Ti-CNPrTEOS SPE sorbent were 57–99% and RSDs 1–4%, $n=5$, Si-CN SPE sorbent were 55–97% and RSDs 4–8% while the recoveries and repeatability for the C18 SPE sorbent were 86–92%, and 4–8%, $n=5$, respectively. The lowest recovery of non-polar DEA using Ti-CNPrTEOS SPE sorbent indicated that the sorbent was very selective towards the extraction of polar aromatic amines. Fig. 6(A) and (B) shows the chromatogram of blank analysis and spiked river water respectively using Ti-CNPrTEOS SPE sorbent.

4. Conclusion

Ti-CNPrTEOS has been successfully prepared via sol–gel technique and used as SPE sorbent prior to the analysis of GC–FID for determination selected aromatic amines. The SPE parameters affecting the extraction recovery have been optimized as follow: sample at pH 7, dichloromethane as conditioning solvent, 10 mL sample loading volume, acetonitrile as the eluting solvent and 5 mL volume used. The limit of detection (LOD) and limit of quantification (LOQ) for solid phase extraction using Ti-CNPrTEOS SPE sorbent (0.01–0.2; 0.03–0.61 μgL^{-1}) were lower compared with those achieved using Si-CN SPE sorbent (0.25–1.50; 1.96–3.59 μgL^{-1}) and C18 SPE sorbent (0.37–0.97; 1.87–2.73 μgL^{-1}) with higher selectivity towards the extraction of polar aromatic amines. Due to the polar selectivity via π–π interaction between polar aromatic amines with cyano moieties and electrostatic interaction of Ti-CNPrTEOS sorbent demonstrated higher extraction capability than that of commercial Si-CN sorbent, especially to the polar aromatic amines. The application of the Ti-CNPrTEOS SPE sorbent was successfully carried out by the analysis of aromatic amines in river water, waste water and tap water samples.

Acknowledgments

The authors are grateful to University of Malaya for the facilitations and financial support (Grant PV 096-2011A) and International Islamic University Malaysia and the Ministry of Higher Education (MOHE) Malaysia for fellowship for Mazidatulakmam Miskam.

References

[1] L. Muller, E. Fattore, E. Benfenati, J. Chromatogr. A 791 (1997) 221.
[2] B. Jurado-Sanchez, E. Ballesteros, M. Gallego, Talanta 79 (2009) 613–620.
[3] A. Sarafraz-Yazdi, F. Mofazzeli, Z. Es′hanghi, Talanta 174 (2010) 592–597.
[4] H. Kataoka, J. Chromatogr. A 733 (1996) 19.
[5] K. Reedy-Noone, A. Jain, K.K. Verma, Talanta 73 (2007) 684–691.
[6] R.D. Voyksner, R. Straub, J.T. Keever, H.S. Freeman, W.W. Hsu, Environ. Sci. Technol. 27 (1993) 1665.
[7] C.T. Yan, T.S. Shih, J.F. Jen, Talanta 64 (2004) 650–654.
[8] M. Saaid, B. Saad, I.A.B. Rahman, A.S. Mohamed Ali, M.I. Saleh, Talanta 80 (2010) 1183–1190.
[9] EPA Method 1625, Fed. Reg. US Government Print Office, Washington, DC, September 1994.
[10] EPA Method 8270B, Fed. Reg. US Government Print Office, Washington, DC, September 1994.
[11] Z. Lin, J. Zhang, H. Cui, L. Zhang, G. Chen, J. Chromatogr. A 963 (2000) 231–237.
[12] N. Garcia-Villar, J. Saurina, S. Hernandez-Cassou, Anal. Chim. Acta 575 (2006) 97.
[13] C. Molins-Legua, P. Campins-Falco, Anal. Chim. Acta 546 (2005) 206.
[14] B. Jurado-Sanchez, E. Ballesteros, M. Gallego, J. Agric. Food Chem. 59 (2011) 7519–7526.
[15] W. Bi, J. Zhou, K.H. Row, Talanta 83 (2011) 974–979.
[16] M. Mulugeta, G. Wibetoe, C.J. Engelsen, W. Lund, Talanta 82 (2010) 158–163.
[17] S. Kose, G. Hall, Food Res. Int. 33 (2000) 839.
[18] J. Hernandez-Borges, G. D′Orazio, Z. Aturki, S. Fanali, J. Chromatogr. A 1147 (2007) 192.
[19] S. Segro, A. Malik, J. Chromatogr. A 1216 (2009) 7677.
[20] W.A. Wan Ibrahim, H. Farhani, M.M. Sanagi, Hassan Y. Aboul-Enein, J. Chromatogr. A 1217 (2010) 4890.
[21] A. Sarafraz-Yazdi, H. Vatani, J. Chromatogr. A 1300 (2013) 104–111.
[22] Z. Gao, Y. Deng, X. Hu, S. Yang, C. Sun, H. He, J. Chromatogr. A 1300 (2013) 20–26.
[23] A. Rajabi Khorrami, A. Rashidpur, Anal. Chem. Acta 727 (2012) 20–25.
[24] M. Saraji, B. Rezaei, M.K. Boroujeni, A.A.H. Bidgoli, J. Chromatogr. A 1279 (2013) 20–26.
[25] W. Liu, Y. Hu, J. Zhao, Y. Xu, Y. Guan, J. Chromatogr. A 1095 (2005) 1.
[26] W. Liu, H. Wang, Y. Guan, J. Chromatogr. A 1045 (2004) 15.
[27] W.A. Wan Ibrahim, W.N. Wan Ismail, A.S. Abdul Keyon, M.M. Sanagi, J. Sol–Gel Sci. Technol. 58 (2011) 602.
[28] W.A. Wan Ibrahim, A.S. Abdul Keyon, N. Prastomo, A. Matsuda, J. Sol–Gel Sci. Technol. 59 (2011) 128.
[29] S. Vo Duy, P.B. Fayad, B. Barbeau, M. Prevost, S. Sauve, Talanta 101 (2012) 337–345.
[30] X. Mao, B. Hu, M. He, B. Chen, J. Chromatogr. A 1256 (2012) 32–39.
[31] M. Miskam, N.K. Abu Bakar, S. Mohammad, J. Sol–Gel Sci. Technol. 67 (2013) 121–129.
[32] H.H. See, M.M. Sanagi, W.A. Wan Ibrahim, A.A. Naim, J. Chromatogr. A 1217 (2010) 1767–1772.
[33] X. Li, J. Gao, Z. Zheng, Anal. Chim. Acta 590 (2007) 26–33.
[34] J.C. Yu, Z.T. Jiang, H.Y. Liu, J. Yu, L. Zhang, Anal. Chim. Acta 477 (2003) 93–101.
[35] C.F. Poole, A.D. Gunatilleka, J. Chromatogr. A 885 (2000) 17–39.
[36] W.A. Wan Ibrahim, K.V. Veloo, M.M. Sanagi, J. Chromatogr. A 1229 (2012) 55–62.