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Development of a poly (ethylene glycol)-graphene oxide sol-gel coating for solid-phase microextraction of aromatic amines in water samples with gas chromatography-flame ionization detector

Ali Sarafraz-Yazdi*, Ali Yekkebashi

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Iran

*Corresponding author: Tel + 98 51 38432023; Fax + 98 51 38438032

E-mail addres: *asyazdi@ferdowsi.um.ac.ir*

Abstract

This study proposes a simple method for the preparation of graphene oxide (GO) nano-sheets modified solid-phase microextraction (SPME) fiber via a sol-gel technique. For the first time, the prepared polyethylene glycol-graphene oxide (PEG-GO) sol-gel coating was applied for the analysis of some aromatic amines in the aqueous samples as target compounds. Important parameters that influencing the extraction efficiency such as desorption temperature and time, extraction temperature, extraction time, stirring speed, saltting effect and pH were investigated and optimized in detail. Under optimized condition, the linearity for analytes was in the concentration range of 0.001 to 200 ng mL^{-1}. Limits of detection (S/N=3) was obtained between 0.0003 to 0.2 ng mL^{-1}. The relative standard deviation (RSD) values for one fiber (repeatability) (n=5) were from 4.2 to 6.6% and reproducibility between fibers (n=3) below 8%. The developed method was successfully applied to the real water samples while the relative recoveries obtained for the spiked water samples were from 92.6 to 107.4%.

Keywords: Solid-phase microextraction, Graphene oxide, Sol-gel technology, Aromatic amines.

1. Introduction

Aromatic amines are widely used as the intermediates materials in the dye, photographic, pharmaceutical, and pesticide industries.[1] During the production, use, and disposal of these compounds, emissions of aromatic amines may occur. The toxicological properties of aryl amines are mainly attributed to their ability to form DNA adducts.[2] They are recognized as carcinogenic to the human bladder, ureter, and renal pelvis, intestines, lung, liver, and prostate.[3] A number of aromatic amines have been classified by the International Agency for Research on Cancer (IARC) as known human carcinogens.[4] Due to their toxicity and potential carcinogenicity, the determination of aromatic amines in the environmental matrices is very important and need to be monitored regularly.

SPME was introduced by Pawliszyn et al. in the early 1990s.[5] SPME exhibits many advantages over conventional sample preparation methods by integrating sampling, extraction and introduction (generally to GC or HPLC) into a single step. It is based on the distribution of analytes between the sample and a fiber coated with a stationary phase. As the fiber coating plays a key role in SPME, development of fiber coating for highly efficient extraction of the analytes has attracted much attention. Commercial SPME fibers such as PDMS, polyacrylate (PA), carbowax/divinylbenzene (CW/DVB), poly-dimethylsiloxane/divinylbenzene (PDMS/DVB), divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and polydimethylsiloxane/carboxen (PDMS/CAR) are available.[6] Although SPME is very popular, commercial fiber coatings present some drawbacks such as low thermal and chemical stability, the stripping of coating and short lifetime.[7] Sol-gel

coating technology can overcome these problems by providing efficient incorporation of organic component into the inorganic polymeric structure in solution under extraordinarily mild thermal conditions.[8] The porous structure of the sol–gel coating offers a high surface area; allowing high extraction efficiency and the coating composition can be altered with a relative ease to give different selectivity characteristics. Strong adhesion of the coating onto the support due to chemical bonding is a very important characteristic which increases the coating stability towards organic solvents and high desorption temperatures.[7] Carbon materials have high adsorption capacity for organic compounds, and some of them, such as glassy carbon,[9,10] activated carbon,[11] single-walled carbon nanotubes[12] and multi-walled carbon nanotubes[13,14] have already been used as SPME coatings. Graphene (G), which is considered as the basic building block of all graphitic matetrials, is a single-atom-thick, two-dimensional honeycomb lattice.[15] Compared with other graphitic materials, G shows many outstanding advantages, such as its high specific surface area (2630 $m^2 g^{-1}$), remarkable thermal and chemical stability, ultra-high mechanical strength, low production cost.[16-18] As the large delocalized π-electron system of G can form a strong π-π stacking interaction with the benzene ring,[19] it might be also a good candidate as an adsorbent for the adsorption of benzenoid form compounds. The first report about the applications of the graphene-coated SPME fibers is related to the extraction of of pyrethroid pesticides from water samples by Chen and coworkers.[20] Lee et al.[21] prepared a graphene-based SPME coating via sol-gel approach for the extraction of PBDEs from water samples. However, the reports on the application of graphene-based SPME fibers to extract environmental pollutants is still very few in the literature and further investigation of the potential applications of the G-based SPME fibers is desirable.

The main purpose of the present work was the development of a novel SPME coatings based on GO as sorbent. The sol–gel coating technology was used to create a porous structure and enhance thermal stability of the coating. The prepared PEG-GO sol-gel coatings were then applied for the determination of aromatic amines in water samples with gas chromatography coupled to flame ionization detector (GC-FID).

2. Experimental

2.1 Reagents and standards

All chemicals were of analytical reagent grade and used without further purification. Graphite powder (< 50 μm), methyltrimethoxysilane (MTMOS, synthesis grade), trifluoroacetic acid (TFA, 99%), poly(ethylene glycol) (PEG, MW 6000), hydrochloric acid, nitric acid, and sodium hydroxide (98%) and sodium chloride were purchased from Merck (Darmestadt, Germany). Analytical grade standards of aromatic amines include aniline (AN, 99%) that was purchased from Fluka, *N*,*N*-dimethylaniline (DMA, 99%) was purchased from Merck, and 2-chloroaniline (2CA, 99%) and 3-chloroaniline (3CA, 99%) were purchased from Riedel-de Haen. Deionized water (18.2 MΩ/cm) was obtained from a water purification system (R.200.M, Absaz, Iran) and was used throughout the entire work.

2.2 Instrumentation

The separation of aromatic amines was carried out in a Chrompack CP9001 (Middelburg, the Netherlands) fitted with a split/splitless injector and flame ionization detector (FID). Helium (99.999%, Sabalan Co., Tehran, Iran) was used as the carrier gas at 1 mL min^{-1}. The separations were achieved with a CP-Sil 24 CB (50% phenyl, 50% dimethylsiloxane) capillary column, a WCOT Fused silica,

30 m × 0.25 mm i.d. with 0.25 µm stationary film thickness (Chrompack, Middelburg, the Netherlands). The column initial temperature was held at 80 °C for 5 min, increasing to 200 °C at a rate of 10 °C min^{-1}. The injection port temperature was set at 280 °C and desorption of analytes from the fiber surface was carried out in the splitless mode for 20 S, plus 5 additional minutes with the split valve on, to assure complete removal of analytes. The detector temperature was set at 250 °C. An ultrasonic bath (Branson 1510, Branson Ultrasonics Co., Danbury, CT) was employed at a frequency of 42 kHz to mix various solution ingredients in sol-gel process. Sample stirring and heating during the extraction step, was carried out with a VELP Scientifica heating magnetic stirrer, model ARE (Milano, Italy). The surface characteristics of the developed sol-gel coatings were studied by scanning electron microscopy (SEM) (LEO, model 1450VP, Germany). A home-made fiber holder was used for manual injection of the fibers.

2.3. Synthesis of GO nano-sheets

GO nano-sheets was prepared on the basis of the modified Hummer's[22] method as previously described in detail.[23] Briefly, aliquot of concentrated H_2SO_4 was added into a 250 mL flask filled with 0.5 g of graphite in ice bath, then 0.5 g of $NaNO_3$ added and stirred for 10 min. Then, during in 45 min 3 g of $KMnO_4$ was slowly added to the solution. The mixture was then stirred for another 2 h at 35 °C. Then, excess deionized water was slowly added to the above mixture while the temperature was kept below 65 °C. Finally, 3 mL of 30% H_2O_2 aqueous solution was added to the deep brown mixture to reduce the residual permanganate and manganese dioxide. The resulting suspension was filtered and washed with dilute HCl and deionized water to remove the acid. The resulting product was dried for 24 h under vacuum at 60 °C to obtain GO as a brown powder.

2.4. Preparation of PEG-GO sol-gel coating

Before sol-gel process, the commercially available fiber was cut with a cutter device in 3cm long. In order to remove the protective polyimide layer from a 1 cm segment of the fiber at one of a 3-cm-long fused silica fiber ends, this layer was burnt off using a naked flame. Then, the bare fiber segment was dipped into 1 M NaOH solution for 1h to expose the maximum number of silanol groups on the surface of the fiber and then rinsed with water. The fiber was placed into 0.1 M HCl solution for 30 min to neutralize the excess NaOH. Then it was cleaned again with water and dried.

The sol solution was prepared as follows: 10 mg GO and 100 mg PEG were added to 100 µL MTMOS, functioning as sol–gel precursor, in a micro-centrifuge tube and dissolved thoroughly by ultrasonic agitation for 5 min. PEG serves to enhance the sol–gel network. Finally 70 µL of TFA (acid catalyst, 95% water solution) was sequentially added to the solution and the mixture was sonicated for another next 5 min. The final mixture was then used for coating the fiber. The treated fused silica was dipped vertically into the sol solution for an optimized time of 30 min and gel coating was formed on the activated outer surface of the fused silica. For each fiber, this coating process was repeated several times using a freshly prepared sol solution until the desired thickness of the coating was obtained. The coated fiber was dried at room temperature for 24 h in a desiccator. The fiber was initially conditioned by placing it in a GC injection port under helium flow rate of 1 mL min^{-1} at 100 °C for 1 h, then 200 °C for 1 h, and finally 280 °C for 1 h.

2.5. Preparation of sample solutions

A mixed standard solution (1000 µg mL^{-1}) containing the aromatic amines of aniline, *N*,*N*-dimethylaniline, 2-chloroaniline, and 3-chloroaniline was prepared in methanol and stored in the dark at 4 °C. Standard working solutions were prepared daily from the refrigerated stock solution by dilution in deionized water. Genuine water samples (tap water, well water and wastewater) were collected from

Mashhad, Razavi Khorasan Province, Iran and stored in amber-glass bottles without headspace and maintained in the dark at 4 °C before analysis.

2.6. HS-SPME procedure

Every day before sampling, the fiber was cleaned in the injection port at 280 °C for 5 min to eliminate any carry-over of analytes from the previous extraction. Afterward a blank run was performed to verify that no contaminants were desorbed from the fiber. HS sampling mode are used to prevent damage to the fiber and elimination of the matrix effect on the fiber. For this purpose, 10 mL of the water sample at pH 13 was placed in a 15 mL glass vial with a magnetic stir bar. The vial was sealed with rubber septa and para-film to prevent sample evaporation during extraction. Extractions were performed in the water bath provided with a temperature control system in order to control the extraction temperature. During extraction, the fiber was exposed to the headspace above the sample under the optimal conditions. After the optimal extraction period, the fiber was withdrawn into the needle, removed from the vial, and then immediately inserted into the hot GC injection port at 280 °C for desorption. Each sampling was performed in triplicate.

3. Results and discussion

3.1. Preparation of PEG-GO sol-gel coatings

The sol-gel chemistry is based on the hydrolysis and simultaneous condensation of metal alkoxides. The major reactions that occur during the sol-gel approach are: (1) hydrolysis of the precursor by TFA; (2) condensation of the hydrolyzed products with PEG and GO; (3) polycondensation of the condensation products into a three-dimensional sol–gel network and (4) chemical anchoring of the evolving sol–gel polymer to the surface of the fiber to create a surface-bonded polymeric coating. The sol solution was prepared by mixing appropriate amounts of MTMOS (a sol–gel precursor), PEG (a sol–gel active organic polymer), GO (a sorbent of stationary

phase) and TFA containing 5% water (a sol–gel catalyst). PEG was used to lengthen the sol–gel network and to help uniformly spread the stationary phase on the fiber.

3.2. Surface structure of the coating

Scanning electron microscopy (SEM) under different magnifications was employed to study the surface characteristics of the PEG-GO sol-gel coatings (Fig. 1). SEM images showed that the coating was distributed homogeneously on the entire surface of the fiber. GO nanosheets were observed on the surface of the PEG-GO sol–gel coating at high magnification. It is also evident that the coating possessed a porous and wrinkled network (Figs. 1c and 1d). The wrinkled nature of GO was highly beneficial in maintaining a high effective surface on the coating, thus enhancing extraction efficiency. The porous structure also increases the speed of extraction and desorption.

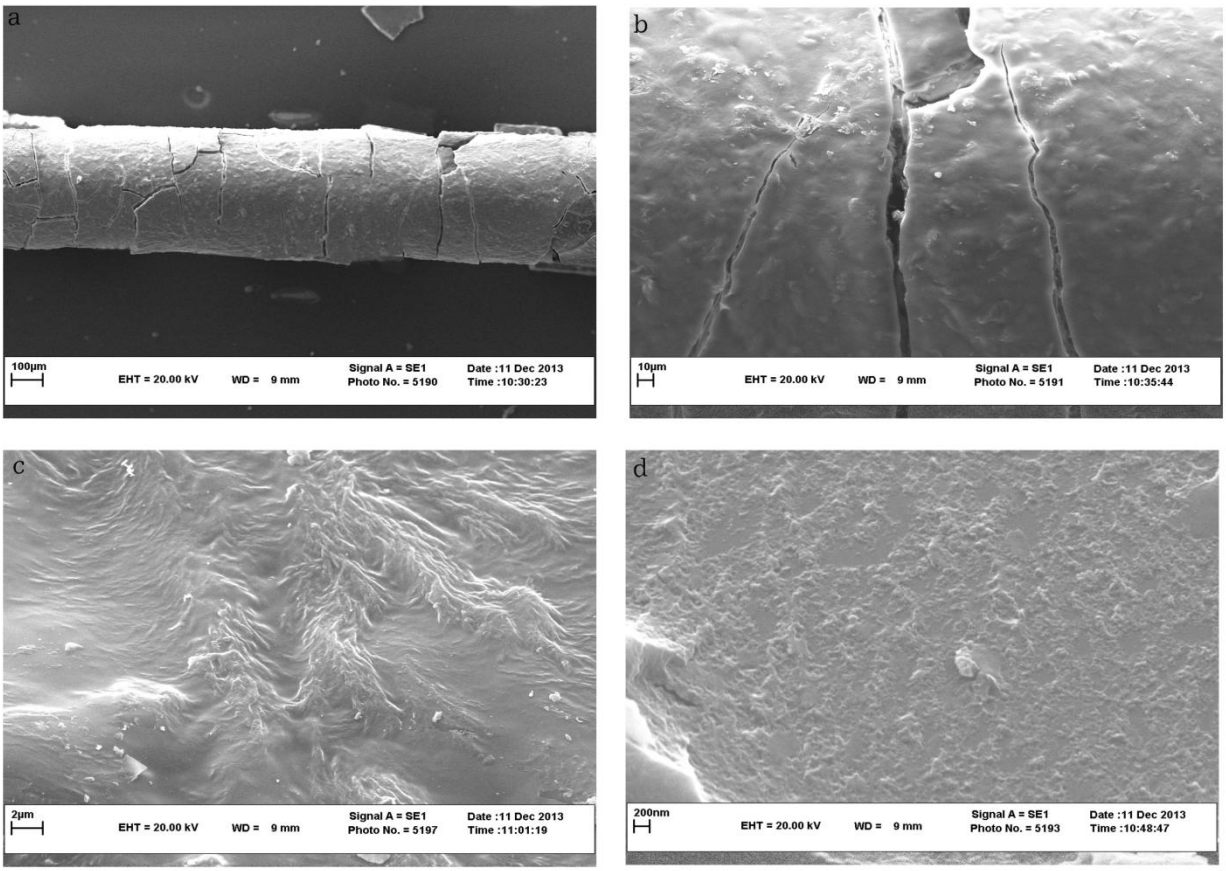

Fig. 1. Scanning electron micrograph images of the PEG-GO SPME fiber; surface view at a magnification of (a) 200-fold, (b) 1,000-fold, (c) 10,000-fold and (d) 50,000-fold.

3.3. Operational stability of the coating

The coating is damaged mainly by its exposure to high temperatures, organic solvents, strong acidic and basic solutions.[24] Thermal stability of the coating is a substantial parameter in the SPME application, because it allows us to use higher temperatures for complete desorption of the analytes from the fiber surface without carry-over effects especially for low volatile compounds. The GO-based sol–gel fiber's thermal stability was investigated by performing extraction after it had been conditioned in the GC injector for 1 h at 250, 280 and 300 °C, respectively. The results indicated (data not shown) that GO-based sol–gel coating can withstand a temperature of up to 300 °C without loss of extraction efficiency. Such high operating temperatures are due to the thermal stability of GO and the strong

chemical bonding of coating to the silica fiber surface provided by sol–gel technology. The fiber lifetime was studied by monitoring the change of extraction peak areas during its use and no obvious decline was observed after it had been used for about 200 runs. This long life span is because of the thinness of the coating and the heat-resistant properties due to strong chemical bonding between the sol–gel generated organic–inorganic composite coating and silica fiber surface.

3.5. Optimization of HS-SPME procedures

HS-SPME method is based on the multiphase equilibration principle which equilibrium of analytes take place between the aqueous phase and the headspace and between headspace and coating of fiber. In order to study the extraction behavior of the new coating towards aromatic hydrocarbons, factors affecting the extraction efficiency including desorption time and temperature, extraction time and temperature, the stirring speed and the salt addition were investigated and optimized. Water samples used for the optimization were prepared containing 50 ng mL^{-1} of each analyte.

3.5.1. Desorption temperature and time

The complete desorption of extracted analytes from the fiber surface into the GC injection port is affected by desorption time and temperature. Increasing the desorption temperature led to decrease in the partition coefficient of the analyte between the coating and the gaseous phase; therefore, desorption time and carry-over is minimized.[25] However, increasing desorption temperature may damage the coating. In order to investigation of desorption temperature, temperatures between 150 and 300 °C were tested (data not shown). The appropriate temperature for desorption of analytes from the fiber without damaging its coating was obtained at 280 °C. At this temperature, desorption times were investigated from 10 to 60 s and 20 s was selected. Despite increasing peak area, tangible broadening of peak was observed at times more than 20 s. In addition, fibers were held for 5 min in the

GC injection system in the split mode to eliminate any possible carry over effects of analytes from the previous extraction.

3.5.2. Extraction temperature

The extraction temperature is a critical parameter in the HS-SPME procedure because it has two conflicting effects on the extraction process. Increasing the extraction temperature could increase the partition coefficient of analytes between headspace and sample solution leading to enhancement of the extraction rate. On the other hand, due to the exothermic nature of the sorption process at higher temperatures the coating/headspace partition coefficient decreases. Therefore, the extraction efficiency decreases.[26] The effect of temperature on the extraction was investigated at temperatures ranging from 25 to 50 °C. As shown in Fig. 2, the extraction efficiency increased up to 40 °C and decreased at higher temperature. Therefore, the temperature of 40 °C was selected as the optimal extraction temperature.

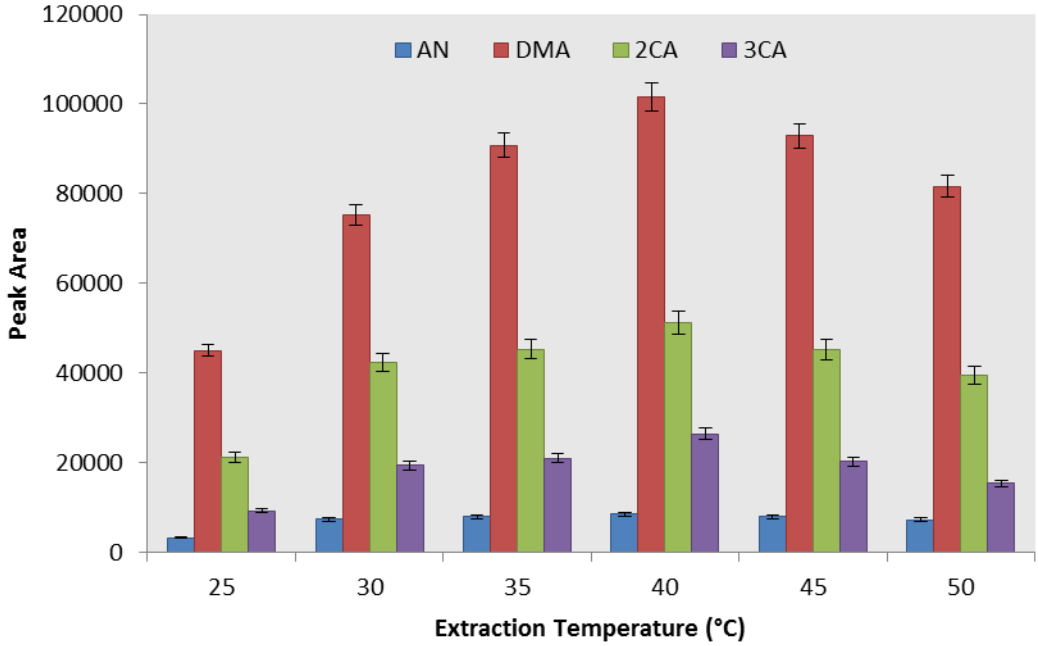

Fig. 2. Effect of temperature on extraction efficiency. Extractions were performed for 30 min from a 10 mL aqueous sample solution, no salt addition and spiked with each aromatic amine at

50 ng mL^{-1}. Stirring was performed at 1000 rpm and thermal desorption was performed for 5 min at 280 °C.

3.5.3. Extraction time

SPME is an equilibrium–based extraction process and analytes are not completely extracted.[27] The extraction time profiles were studied by varying the exposure time of the fiber to the headspace of aqueous sample in the range of 10–50 min. It was observed (data not shown), that approximately the equilibrium was achieved at 30 min sampling time. After this time, the extraction efficiency was not changed significantly for most of the analytes. Thus the time of 30 min was chosen as the optimum value to shorten the analysis time.

3.5.4. Stirring speed

In SPME, agitation of sample solution increases the extraction efficiency and reduces the time required to reach thermodynamic equilibrium. The effect of the stirring speed on the responses of the target compounds was investigated in detail at the stirring speeds ranging from 200 to 1000 rpm. The results showed (data not shown) that the peak area of analytes increased by increasing the stirring rate. Therefore, the stirring speed of 1000 rpm was used as the optimal value in further extractions.

3.5.5. Effect of pH

Aromatic amines are weak organic bases and exist in two un-dissociated and dissociated forms in aqueous solutions. They must be predominantly in the un-dissociated form for partitioning. According to Henderson-Hassel Balch equation, to make sure that at least 99% of the basic compound is in the neutral form, the pH should be at least two units larger than the pK_b of the analyte. Subsequently, all sampling solutions were adjusted to a pH greater than 13 by the addition of strong

bases.[28] As shown in Fig. 3, the amount of analytes extracted onto the fiber increased with increasing NaOH concentration.

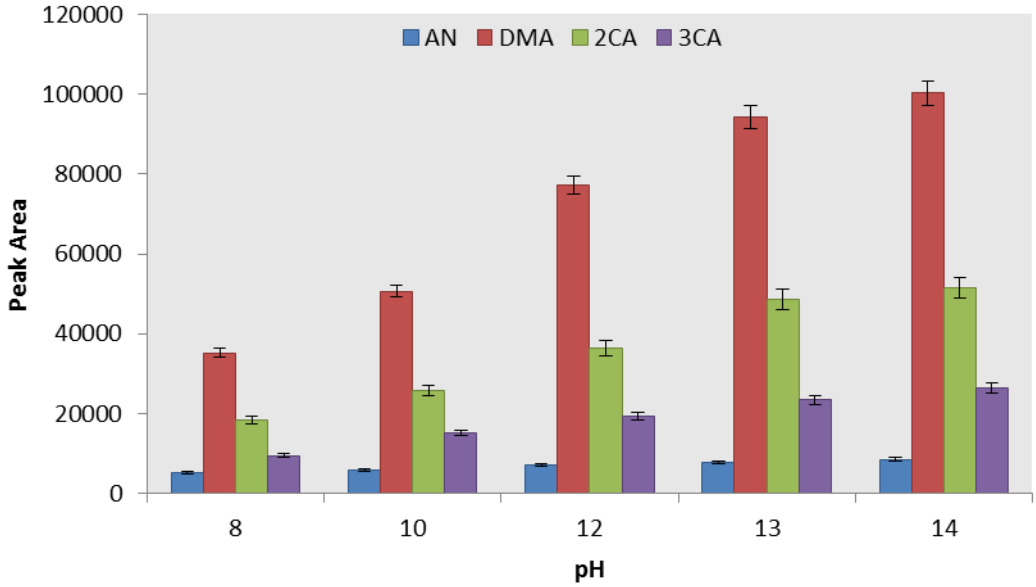

Fig. 3. Effect of pH on extraction efficiency. Extractions were performed for 30 min from a 10 mL aqueous sample solution, no salt addition and spiked with each aromatic amine at 50 ng mL^{-1}. Stirring was performed at 1000 rpm and thermal desorption was performed for 5 min at 280 °C.

3.5.6. Salt addition

The influence of salt addition on the extraction efficiency was also investigated. Usually, the addition of salt increases the ionic strength of the sample solution and would affect the solubility of organic solutes. This effect leads to varying the partition coefficient of analytes between fiber coating and solution hence the extraction efficiency may be changed. Nevertheless, it could increase the viscosity and density of the aqueous phase and thus negatively affect the kinetics of the process and, consequently, the extraction efficiency. In summary, the addition of salt might be favorable from a thermodynamic point of view but unfavorable from a kinetic point of view.[21] In this experiment, sodium chloride concentration of 0.0 to 40% w/v was tested while the extraction temperature and time were kept constant at 40 °C and 30 min, respectively. As shown in Fig. 4, the extraction

efficiencies of aromatic amines were increased with the salt addition in the tested range, and maximum extraction efficiency was observed in the saturated salt concentration. Therefore, 40% (w/v) of NaCl was used as the optimum quantity for subsequent studies.

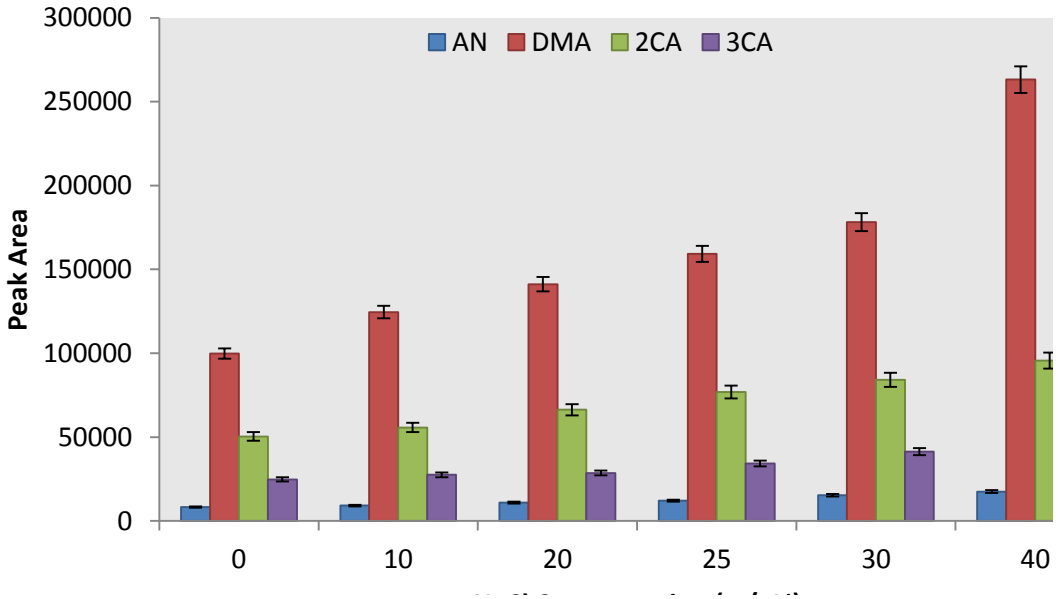

Fig.4. Effect of salt addition on extraction efficiency. Extractions were performed for 30 min from a 10 mL aqueous sample solution spiked with each aromatic amine at 50 ng mL^{-1} at pH 13. Stirring was performed at 1000 rpm and thermal desorption was performed for 5 min at 280 °C.

3.6. Method validation

Table 1 lists the analytical characteristics of the proposed method such as the linear range, limits of detection (LODs), limits of quantification (LOQs), repeatability and reproducibility using GO based sol-gel fiber. Under the optimal conditions, the linearity of the method was tested by preparing the calibration graphs for each analyte at different concentrations with eight points. For each point three replicates were performed. The obtained calibration graph was linear in the concentration range of 0.001 to 200 ng mL^{-1}. The regression coefficient for all the analytes was rather satisfactory ($r^2 > 0.991$). The values of LODs and LOQs based on signal-to-noise ratio (S/N) of 3:1 and 10:1, were determined experimentally. LODs and

LOQs were obtained in the range of 0.0003 to 0.2 and 0.001 to 0.5 ng mL^{-1}, respectively. Repeatability of the proposed method was obtained with five replicate determinations using a single fiber at three different concentrations. Moreover, reproducibility between three different fibers (fiber-to-fiber or batch to batch) prepared under the same conditions was investigated. The obtained RSD values are shown in Table 2.

3.7. Application to real samples

The proposed method was applied for the determination of trace aromatic amines in environmental water samples. The quantitative results of this water samples are listed in Table 3. Peak identification was accomplished by comparing the retention time with that of an authentic standard. Some analytes were detected in these water samples but some of their concentrations were lower than LOQs. To evaluate the accuracy of the method, the relative recovery test was performed by spiking aromatic amine standards into water samples at 1 ng mL^{-1} of 3-chloroaniline and 0.1 ng mL^{-1} of other compounds. Results of relative recoveries and RSDs in triplicate are listed in Table 3. The results demonstrate that the relative recoveries ranged from 92.6% to 107.4%. The RSDs of target compounds were less than 9.3%, that showing good repeatability. Fig. 4 shows a typical chromatogram obtained for aromatic amines in real wastewater sample with the proposed coating (PEG-GO sol-gel coating).

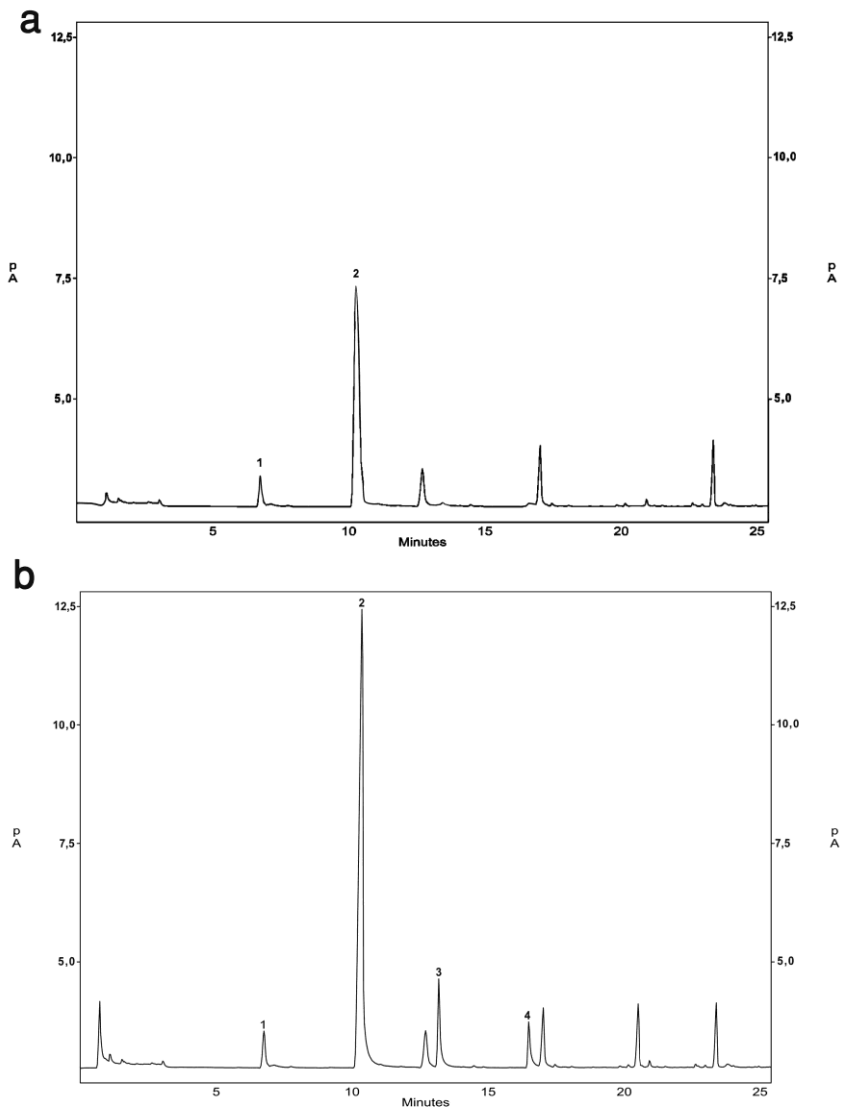

Fig. 5. Typical chromatogram of aromatic amines in: (a) a real wastewater and (b) a real wastewater spiked with 0.7 ng mL^{-1} of each analyte using proposed fiber. Peak numbers correspond to (1) aniline, (2) *N*,*N*-dimethlaniline, (3) 2-chloroaniline and (4) 3-chloroaniline.

3.8. Comparison with other related SPME methods

The extraction efficiency of proposed fiber was compared with the other reported SPME fibers in literature for analysis of aromatic amines. Some statistical data related to each fiber are presented in Table 4. The results showed that the proposed fiber is more sensitive compared to other commercial fibers and has lower LOD than those of the other reported works. It can be seen that RSD values of the

proposed method using sol-gel PEG-GO fiber were comparable with the other ones. This might be due to the fact that the PEG-GO sol–gel coatings possess porous structures which should significantly increase the surface area availability on the fibers. Furthermore, GO nano-sheets with high surface area as a sorbent will also be able to provide the enhanced adsorption efficiency for the target analyte.

4. Conclusions

In this work, for the first time, sol–gel PEG modified to GO coating was proposed as a new SPME fiber for detection of aromatic amines in environmental water samples. Due to the adsorptive and inherent advantageous of GO nanosheets and also the performance of the sol–gel coating technology, this innovative fiber exhibited porous surface structure, good precision and accuracy, high selectivity and sensitivity, longer life span (over 200 times) and high thermal stability. The wrinkled structure of sol–gel coating increases the surface area on the fiber, the speed of extraction and desorption steps and sample capacity. An excellent thermal stability of at least 300 °C was obtained for the fiber coating, suggesting chemical bonding between the substrate and the polymeric coating, which will allow these fibers to be applied to a wider range of volatile compounds, especially less volatile compounds. Based on these features, in this article, a rapid and facile method for routine ultra-trace analysis of aromatic amines in real water samples was introduced. Therefore, it could be expected to have a potential use in the other complex matrix samples. On the other hand, there are still some areas of research left to modify G with other functional groups to increase coating fiber selectivity for highly complex samples.

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Table 1

Some analytical figures of merit of the proposed method using PEG-GO sol-gel coating.

Analyte	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	Linear range (ng mL^{-1})	Correlation coefficient (r^2)
Aniline	0.004	0.01	0.01-100	0.994
N,*N*-Dimethylaniline	0.0003	0.001	0.001-100	0.991
2-Chloroaniline	0.02	0.05	0.05-100	0.993
3-Chloroaniline	0.2	0.5	0.5-200	0.992

436 **Table 2**

437 The repeatability and reproducibility of the proposed method using PEG-GO sol-
438 gel coating for the analysis of monocyclic aromatic amines.

Analyte	RSD (%) one fiber (repeatability) (n = 5) at three concentrations (ng mL^{-1})			RSD (%) batch to batch (reproducibility) (n = 3) at three concentrations (ng mL^{-1})		
	0.1	1	50	0.1	1	50
Aniline	7.3	5.6	5.1	8.7	6.2	6.2
N,*N*-Dimethylaniline	6.4	5.9	5.8	8.1	6.4	7.5
2-Chloroaniline	8.6	7.2	5.5	8.4	7.3	6.8
3-Chloroaniline	-	7.6	4.7	-	6.6	6.5

439

Table 3

Amount of aromatic amines in real water samples and the accuracy of the proposed method using the sol–gel PEG-GO fiber.

Analyte	Tap water			Well water			Wastewater		
	Mean (ng mL^{-1})[a]	RSD (%)	Relative recovery (%)[b]	Mean (ng mL^{-1})[a]	RSD (%)	Relative recovery (%)[b]	Mean (ng mL^{-1})[a]	RSD (%)	Relative recovery (%)[b]
Aniline	NQ	5.84	101.25	0.31	6.75	95.28	7.26	8.87	103.55
N,*N*-Dimethylaniline	NQ	4.27	92.24	0.64	7.22	92.69	2.15	9.33	107.37
2-Chloroaniline	NQ	6.55	97.31	NQ	6.25	105.65	NQ	7.57	92.64
3-Chloroaniline	NQ	6.12	106.11	0.56	5.43	99.22	NQ	8.09	102.76

NQ, not quantified.

[a] Founded concentration.

[b] Relative recovery (%) = (the amount found in the spiked sample − the amount found in the sample/the amount added) × 100.

448 **Table 4**

449 Comparison of the proposed method with other reported methods for aromatic
450 amines determination in the literature.

Fiber type	Detection system	Linear range (ng mL^{-1})	LOD (ng mL^{-1})	RSD (%)	Reference
PDMS/DVB	GC-MS	–	0.88–3.17	4.7–6.5	28
PANI	GC-FID	5.1–27,500	0.02-1.06	4.03–6	29
PDMS/DVB	HPLC-UV	5–5000	1–2.2	1.5–9.8	30
DVB/CAR/PDMS	GC-MS	0.05–100	0.006–0.025	2.1–3.4	31
Crown ether	GC-FID	110–29,000	0.17–0.98	3.23–6.20	32
Calix[4]arene	GC-FID	20–20,000	0.041	3.4	33
PEG/CNT	GC-FID	0.001–200	0.0005–0.05	5.1–9.1	34
PEG/GO	GC-FID	0.001–200	0.0003–0.2	4.2–6.6	This work

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