Talanta 130 (2014) 71–77

Contents lists available at ScienceDirect

Talanta

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

Graphene oxide-based dispersive micro-solid phase extraction for separation and preconcentration of nicotine from biological and environmental water samples followed by gas chromatography-flame ionization detection

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ARTICLE INFO

Article history:
Received 18 April 2014
Received in revised form
4 June 2014
Accepted 5 June 2014
Available online 30 June 2014

Keywords:
Graphene oxide
Nicotine
Dispersive micro-solid phase extraction
Water samples
Biological samples

ABSTRACT

Graphene oxide (GO) has showed great potential to use as an adsorbent in sample preparation procedures. In this research, GO was used as an effective adsorbent in a simple GO-based dispersive micro-solid phase extraction (GO-D-μ-SPE) method for isolation and preconcentration of nicotine prior to gas chromatography-flame ionization detection (GC-FID). The prepared GO was characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscope (SEM), thermogravimetric analysis/differential thermal analysis (TGA/DTA), and ultraviolet–visible (UV–vis) absorption spectroscopy techniques. Various experimental parameters affecting the extraction recovery, including the amount of GO, extraction time, pH of the sample solution, salt concentration, and desorption conditions were investigated and optimized. Under the optimized conditions, a linear response was obtained in the concentration range of 5–2000 ng mL^{-1} with a determination coefficient of 0.9987. The limit of detection (LOD) of the method at a signal to noise ratio of 3 was 1.5 ng mL^{-1}. The linearity was in the concentration range of 5–2000 ng mL^{-1} with a determination coefficient of 0.9987. Intraday and inter-day precisions were obtained equal to 2.7% and 5.2%, respectively. The method was successfully applied to the nicotine analysis in biological and water samples with the recoveries in the range of 88.7–109.7%.

1. Introduction

Nicotine, 3-(1-methyl-2-pyrrolidinyl) pyridine, is a highly toxic alkaloid with a lethal amount of 30–60 mg kg^{-1}. It is found naturally in high levels (2–8%) in tobacco leaves. Nicotine is the primary substance that causing addiction to smoking. It can be absorbed immediately in humans through the skin, mucosal lining of the mouth and nose or by inhalation in the lungs, which results in an increase in blood pressure and heart rate [1]. Furthermore, it is suspected to contribute to some damages such as cardiovascular disease, kidney disease and cancer [2,3].

Owing to high solubility in water, transfer of nicotine to surface waters through the wastewater system of different industries such as tobacco processing, cigarette manufacturing [4,5] and pharmaceutical industry [6–8] causes considerable environmental pollution. Besides, it has been used for a long time as a pesticide in agriculture due to its easy and low cost extraction from available natural resources such as tobacco leaves. In the European Union, all applications consisting of nicotine as a pesticide have been banned since 2009. However, it is still used in many developing countries to control pests [9–11]. Thus, the development of sensitive and specific analytical methods for the extraction and detection of trace amounts of nicotine in biological and environmental samples has become one of the major interest.

Trace analysis of analytes in various types of samples generally requires a pretreatment step to separate and enrich them before instrumental determination. Several sample pretreatment methods such as liquid–liquid extraction (LLE) [12–14], cloud point extraction (CPE) [15], pressurized liquid extraction (PLE) [16,17], liquid-phase microextraction (LPME) [18], solid phase extraction (SPE) [19–21], solid-phase microextraction (SPME) [22–24] and single drop microextraction (SDME) [25] have been reported for isolation and preconcentration of nicotine from different matrices prior to gas chromatography (GC) or liquid chromatography (LC) analyses. Among these methods, SPE is widely used due to its simplicity, reproducibility and availability. In a SPE procedure, the sorption of analyte(s) on an appropriate solid sorbent and the subsequent desorption using a suitable solvent, eliminate the potential interferences and preconcentrate analyte(s) of interest.

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http://dx.doi.org/10.1016/j.talanta.2014.06.004
0039-9140/

The sorbent materials used in SPE should provide the requirements for a good sample pretreatment (e.g. appropriate attraction, high sorption capacity, good recovery and enrichment factor) [26]. Therefore, great efforts are continuously being made to develop new materials for this purpose.

Nowadays, nanoscale carbon-based materials, such as fullerene, carbon nanotubes, graphene and graphene oxide have attracted considerable attention in SPE for the isolation or extraction of various compounds, due to their large surface area, chemical and thermal stability, ease of surface functionalization or modification and excellent adsorption capacity [27–32]. Graphene oxide (GO) is the oxidized derivative of graphene which is usually produced through the strong oxidation of graphite [33]. The GO sheets consist of a hexagonal ring-based carbon network that are covalently bonded with oxygen functional groups (such as hydroxyl, epoxy, and carboxyl). The oxygenated lattice of GO provides good solubility and dispersibility of this material in many solvents, particularly in water and non-covalent interaction with various compounds through electrostatic interaction and hydrogen bonding. Furthermore, the two dimensional plane structure and single-atom thickness of GO possesses an ultra-high specific surface area and high adsorption capacity [29,34]. These considerable properties, give GO great ability to use as a sorbent material in extraction/preconcentration techniques.

In this work, a simple method for the analysis of nicotine in biological and environmental water samples was established based on the GO-dispersive micro-solid phase extraction (GO-D-μ-SPE) in which a dispersive system based on rapid injection of GO aqueous solution into the sample solution was applied. To the best of our knowledge, this may be the first report about the use of graphene oxide as a novel sorbent for the isolation and preconcentration of nicotine. The effects of the adsorption and desorption factors on the extraction recovery of the analyte were studied systematically.

2. Experimental

2.1. Reagents and materials

Sulfuric acid (99.8%), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl, 37%), quinoline, triethylamine (TEA), acetonitrile (ACN), ethyl acetate (EA), dichloromethane (CH_2Cl_2), sodium chloride (NaCl), sodium hydroxide and potassium permanganate ($KMnO_4$) with the purity higher than 99.9% were obtained from Merck Chemicals (Darmstadt, Germany). Methanol (MeOH), was obtained from Sigma Aldrich Ltd (St Louis, USA). Graphite powder was purchased from Samchun Pure Chemical Co Ltd (Pyeongtaek, Korea). Nicotine ($\geq$ 99%) was purchased from Acros Organics (New Jersey, USA). Nicotine and quinoline (internal standard) stock solutions were prepared in methanol at the concentration level of 10 mg mL^{-1} and stored at 4 °C before use. The working solutions were daily prepared by subsequent dilution of stock solution in deionized water.

2.2. Instrumentation

Gas chromatography. The GC analyses were carried out on a Shimadzu GC-17A (Tokyo, Japan) gas chromatograph equipped with a FID detection system and a split/splitless injector. The separations were performed with a CBP-5 capillary column (25 m, length; 0.25 mm internal diameter; 0.22 μm, film thickness; stationary phase, 5% phenyl–95% methyl polysiloxane). The carrier gas was helium with the purity of 99.999%. The injection port was set at 240 °C and used in the splitless mode at the splitless time of 0.30 min with the split ratio of 1:50. A Shimadzu OPGU-2200s hydrogen generator (Tokyo, Japan) was used to supply H_2 (g) for FID. The detector temperature was adjusted at 260 °C. The oven temperature was programmed as follows: initial temperature 100 °C (held for 1 min) raised to 260 °C at a rate of 30 °C min^{-1} (held for 5 min).

The pH values were measured using a WTW Inolab 720 pH meter (Weilheim, Germany). The centrifuges were performed with a Hermle centrifuge model Z 200 A (Wehingen, Germany). An Eurosonic 4D (Euronda, Montecchio Precalcino (Vincenza) Italy) ultrasonic water bath and a vortex mixer model ZX-Classic (Velp Scientifica, Milan, Italy) were employed for homogenization of solutions.

The infrared transmittance spectra were recorded using an Equinox 55 FT-IR spectrometer (Bruker, Bremen, Germany) in the range of 400–4000 cm^{-1}. The X-ray diffraction (XRD) patterns were collected on a X'Pert Pro MPD X-ray diffractometer (Almelo, Netherlands) with a Cu K_α radiation (λ=1.54178 Å). The morphology of GO was observed by scanning electron microscopy (SEM) with a Hitachi S-4160 machine (Tokyo, Japan) at an accelerating voltage of 20 KV.

2.3. Synthesis of graphene oxide

Graphene oxide was synthesized based on Hummers' method [35]. Firstly, 2.0 g graphite powder was added to 100 mL concentrated H_2SO_4 containing 1.5 g of $NaNO_3$ in a 500 mL flask. The mixture was allowed to react in an ice bath with constant stirring for 2 h. A portion of $KMnO_4$ (12 g) was then gradually added to the mixture under vigorous stirring. During this step, the temperature was carefully controlled to not exceeding 10 °C. The resulting suspension was stirred at 40 °C for 24 h, and then diluted slowly by 100 mL of deionized water (the temperature did not exceed 40 °C). Subsequently, it was heated to 95 °C and kept in this temperature for 15 min. Afterward, 300 mL deionized water was added to the mixture to stop the reaction. Successively, 20 mL of H_2O_2 was added dropwise to the mixture to reduce the residual $KMnO_4$. The resulting product was washed several times with 5% HCl aqueous solution (1000 mL) to remove impurities and sulfate ions, and then with distilled water to remove excess acid. Thereafter, the rinsed product was dispersed in deionized water using an ultrasonic bath for 30 min and finally air-dried under ambient conditions. The obtained GO was characterized and used in the following experiments.

2.4. Real sample collection and preparation

Urine and saliva samples were kindly collected from smoker and non-smoker volunteers in our laboratory and stored in polypropylene tubes at −20 °C. Prior to the sample preparation step, the samples were defrosted and centrifuged at 5000 rpm for 5 min to remove any particulate matter. Then, proteins were precipitated by addition of 1 mL ACN to 1 mL of sample solutions with subsequent vortexing for 5 min. The mixtures were maintained for 20 min at 4 °C and then centrifuged at 5000 rpm for 5 min. The upper phase was then separated and diluted to 10 mL with distilled water.

Water samples were collected from the Darband and Darakeh Rivers in north of Tehran (capital of Iran). There were many hookah lounges alongside the rivers' banks where their wastes were directly introduced to the rivers and cause a huge amount of pollutants including nicotine. The collected water samples were filtered through a 0.45 μm membrane filter and stored in brown glass bottles at 4 °C until used for analysis.

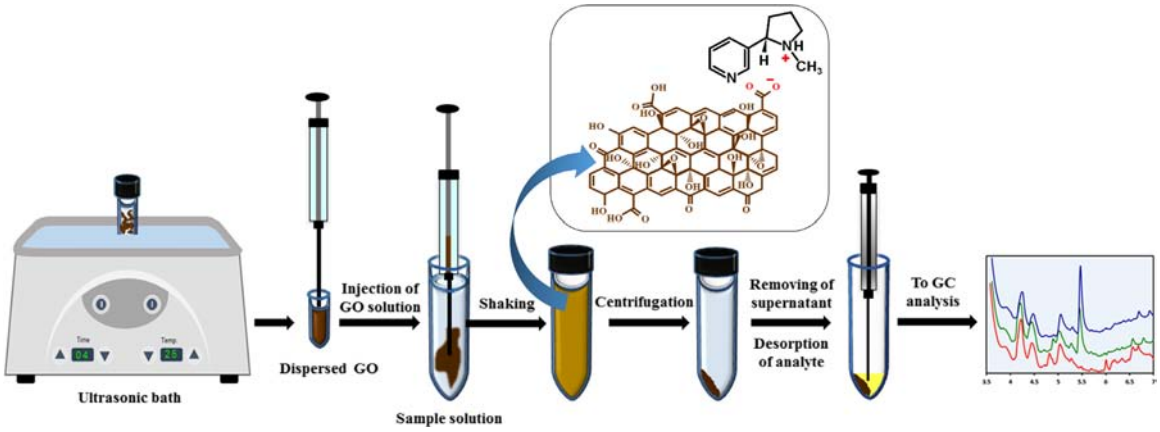

Fig. 1. Schematic of the graphene oxide-dispersive micro-solid phase extraction process.

2.5. The procedure

The general workflow of the procedure was depicted in Fig. 1. At first, 3 mg of graphene oxide was transferred into a glass test tube containing 1 mL of deionized water and sonicated for 5 min. Then, the dispersed GO solution was injected rapidly to 10 mL sample solution (containing 500 ng mL^{-1} nicotine and 100 ng mL^{-1} internal standard) with a 1 mL syringe. After adjusting the pH at 5.0, the solution was vortexed for 10 s. Subsequently, the GO nanosheets were isolated from the solution by centrifugation at 5000 rpm for 4 min and the upper phase was discarded. In order to eliminate the interferences, the sedimented sorbent was washed with 1 mL methanol and centrifuged at 5000 rpm for 4 min. After removing the methanol phase, 100 μL of desorption solvent (TEA/MeOH, 25% v/v) was added to GO and the mixture was vortexed for 2 min to speed up desorption of the analyte. Finally, the mixture was centrifuged at 5000 rpm for 4 min, and 1 μL of the supernatant was injected into the GC-FID system.

3. Results and discussion

3.1. Characterization of GO

The oxygen-containing functional groups on the surfaces of GO nanosheets were characterized by FT-IR analysis (Fig. 2a). The presence of a broad and intense peak at 3440 cm^{-1} can be attributed to the O-H stretching vibrations of the C–OH groups and water. The bands at 1220 and 1034 cm^{-1} are associated with C–O. The C=O stretching is located at 1734 cm^{-1}. The absorption band at 1622 cm^{-1} can be ascribed to aromatic C=C. These results confirm that a large amount of oxygen functional groups exist on GO nanosheets after the oxidation process.

The XRD patterns of graphite and GO are presented in Fig. 2b. Graphite shows a strong and sharp diffraction peak at $2\theta=25.8^{\circ}$ that corresponds to an interplanar spacing (002) of hexagonal layers of carbon atoms with $d=0.34$ nm. The pattern of GO, exhibits a broad and relatively weak diffraction peak at $2\theta=10.1^{\circ}$ ($d=0.85$ nm), which corresponds to the (002) plane, indicating an increase in d-spacing from 0.34 nm to 0.85 nm. This increased interlayer distance between the GO sheets may be due to the creation of oxygen functional groups on the surfaces of GO nanosheets.

Fig. 2c displays the typical SEM image of the synthesized GO that represent a layered and sheet-like structure with the large surface and wrinkled edge. These results indicate a good exfoliation of graphite during the oxidation process.

3.2. Optimization of the extraction method

In the present work, the main parameters affecting the adsorption and desorption processes including pH, extraction time, salt concentration, dosage of sorbent, type and volume of the desorption solvent, and desorption time were investigated to achieve the best extraction performance and recovery. The extraction recovery (ER) was calculated based on the following equation:

$$ER = \frac{C_{op} V_{ds}}{C_{aq} V_{aq}} 100 \quad (1)$$

where C_{op}, C_{aq}, V_{ds} and V_{aq} are the final concentration of analyte in the organic phase (desorption solvent), the initial concentration of analyte in the aqueous phase, the volume of desorption solvent, and volume of the aqueous phase, respectively. The C_{op} was calculated using a calibration curve obtained by direct injection of nicotine standard solutions in methanol. The experiments were performed in triplicate and the mean value was considered as the optimum point.

3.2.1. Influence of desorption solvent type and volume

The efficiency of desorption step is highly dependent on the type of desorption solvent. In order to obtain a good recovery, the solvents should be capable to dissolve nicotine and be compatible with gas chromatography conditions. Therefore, the solvent systems consisting of ACN, MeOH, EA/MeOH, CH_2Cl_2/MeOH, TEA/MeOH, and TEA/ACN were tested in accordance with the described procedure in Section 2.5. The experiments showed that only TEA/MeOH and TEA/ACN solvent mixtures were able to desorb nicotine from the GO surfaces. However, the other solvents did not show any peak at the retention time of nicotine. Thus, to find the best solvent system, TEA/MeOH and TEA/ACN with different volume ratio were investigated. The results in Fig. 3a demonstrate that the highest recovery was obtained using TEA/MeOH (25/75, v/v). Hence, it was chosen as desorption solvent system for further experiments.

The volume of desorption solvent has also a significant impact on the extraction capability. Accordingly, the effect of this parameter was investigated with different volumes of desorption solvent ranging from 50 to500 μL. According to the experiments, it was found that the maximum recovery of nicotine was obtained using 100 μL of the desorption solvent.

3.2.2. Effect of pH

The pH of the solution plays a key role in the adsorption of nicotine on the GO nanosheets surface. The surface chemistry of GO and the chemical structure of nicotine are both highly

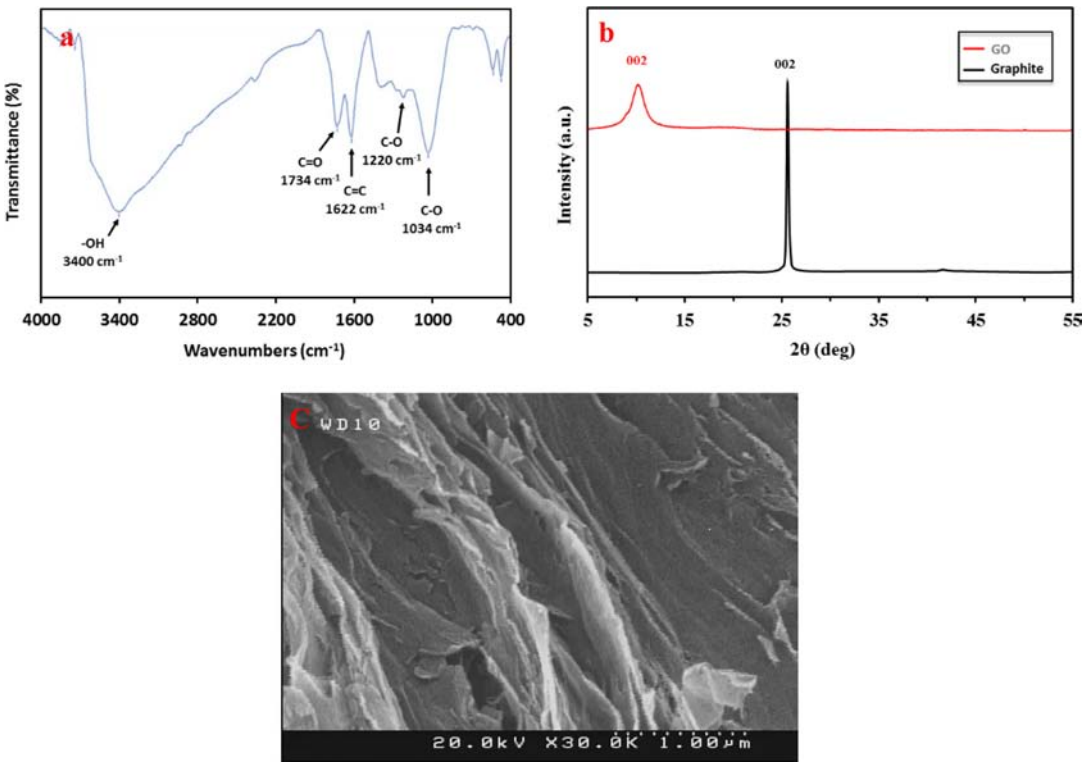

Fig. 2. Characterization of graphene oxide nanosheets: (a) FT-IR spectrum; (b) XRD patterns of graphite and GO; and (c) SEM image.

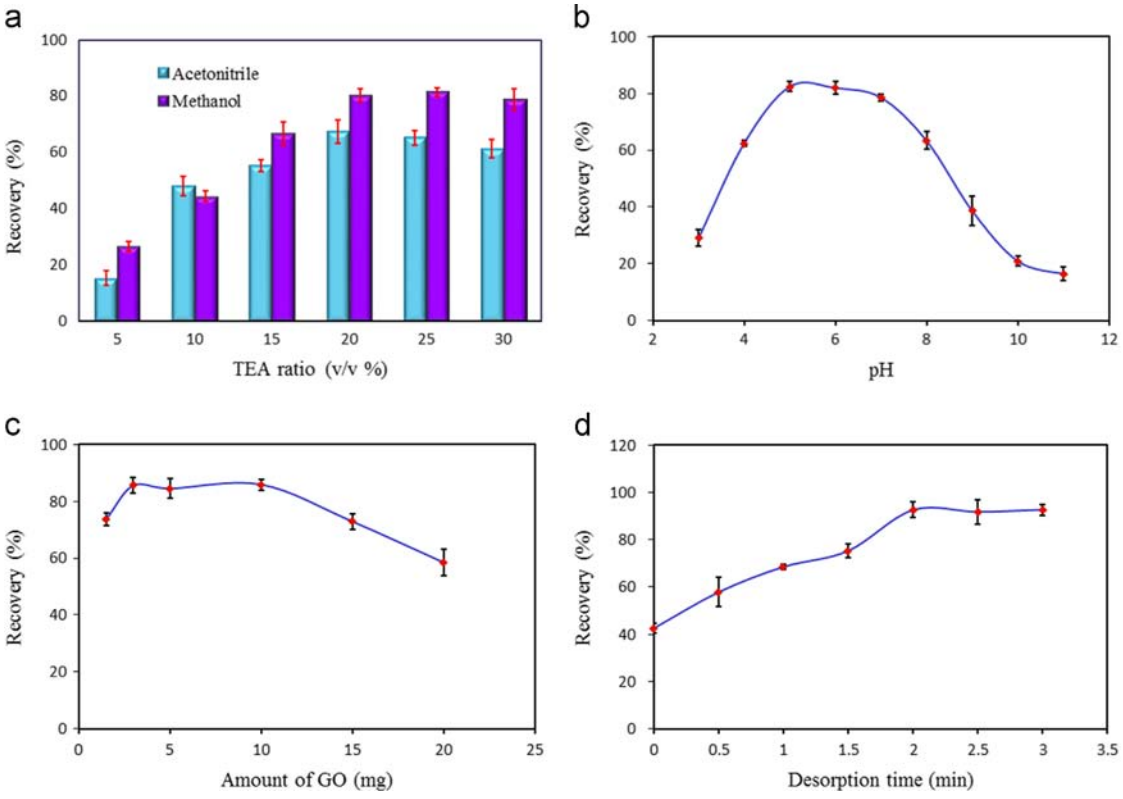

Fig. 3. Effect of (a) desorption solvent type; (b) pH; (c) sorbent amount; and (d) desorption time on the extraction recovery of nicotine.

dependent on the pH value of the sample solution. Therefore, this parameter has a great influence on the interaction between GO nanosheets and nicotine. The pH value of the solution would alter the protonation/deprotonation transition of the GO surface functional groups (–OH and –COOH), which is a primary factor that affects the adsorbing property of the surface. In the present study, the effect of pH on the extraction recovery of nicotine was studied in the range of 2–11. The pH value was adjusted by adding appropriate amounts of either HCl or NaOH solutions. As can be seen from Fig. 3b, the extraction recovery increased by increasing

Table 1
The determination of nicotine in biological and water samples.

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})	RSD% (n=3)	RR[a] %
Urine (nonsmoker)	–	n.d.[b]	–	–
	250	260.5	2.2	104.2
	500	512.2	5.1	102.4
Urine (smoker)	–	843.3[c]	3.3	–
	250	1065.1	4.9	88.7
	500	1392.0	5.2	109.7
Saliva (nonsmoker)	–	n.d.	–	–
	250	238.8	3.9	95.5
	500	468.5	3.6	93.7
Saliva (smoker)	–	1012.0[c]	2.4	–
	250	1243.8	4.6	92.7
	500	1518.1	2.8	101.2
Darakeh River	–	n.d.	–	–
	20	21.5	3.1	107.5
	50	47.3	4.7	94.6
Darband River	–	11.1	2.0	–
	20	29.6	3.9	92.5
	50	59.5	4.5	96.8

[a] Relative recovery.
[b] Not detected.
[c] Sampling after 2 h smoking three cigarettes.

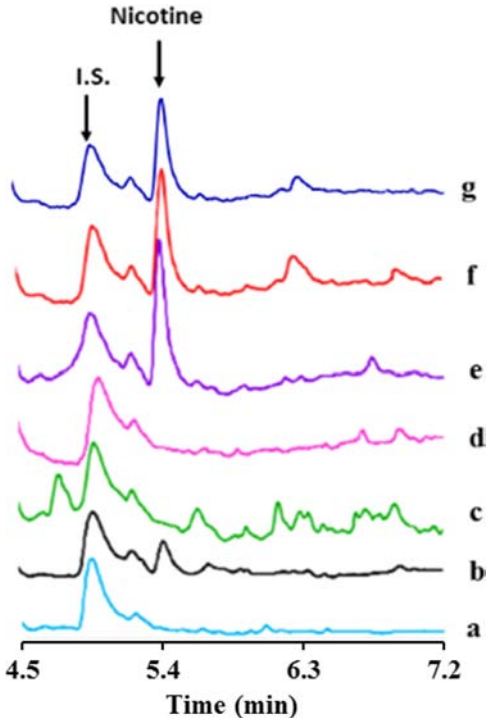

Fig. 4. Representative GC-FID chromatograms obtained using the method developed for (a) Darakeh water sample; (b) Darband water sample; (c) saliva (nonsmoker); (d) urine (nonsmoker); (e) standard solution (100 ng mL^{-1}); (f) saliva (smoker); and (g) urine (smoker).

the pH of medium up to 5 and then decreased with further increase in pH.

The pH_{pzc} (point of zero charge) value of GO is about 3.9 [36–39], therefore at the pH values lower than pH_{pzc}, the surface charge of GO is positive because of the protonation reaction. In addition, nicotine molecule contains two basic functional groups, a tertiary amine with pK_a=8.2 and a pyridine with pK_a=3.1. Therefore, it is mostly protonated in the range of pH 3.1–8.2 and double protonated below pH 3.1. As a result, the doubly protonated nicotine (below pH 4) cannot bind well to the positively charged surface of the GO nanosheets due to the electrostatic repulsion. However, at pH values higher than the pH_{pzc}, the surface charge of GO becomes negative because of deprotonation reaction. Accordingly, with increasing the pH, the electrostatic interactions between the GO nanosheets and the protonated nicotine become stronger, and thus the adsorption of nicotine on the GO nanosheets increases. At pH values greater than 5, the recovery of nicotine was decreased. This can be ascribed to the fact that more oxygen containing groups on the GO surface are deprotonated (carrying negative charge) at the higher pH values. Thereby, more water molecules are adsorbed at these sites and prevent the adsorption of nicotine on the surface of GO nanosheets. Furthermore, at pH values higher than 8, nicotine exists mostly in its molecular form, while the GO nanosheets are still negatively charged. Therefore, the electrostatic interactions between nicotine and the GO surface are significantly reduced which leads to lower adsorption of nicotine. Based on the above explanations it can be concluded that, pH 5 is the most suitable value for achieving the maximum adsorption of nicotine on the GO nanosheets.

3.2.3. *Effect of extraction time*

The extraction time, is the time necessary for a quantitative adsorption of analyte on the sorbent surface. The influence of this parameter on the recovery of nicotine was investigated by vortexing sample solution in the range of 0–5 min. The results indicated that the vortex time did not have a significant effect on the recovery. This may be due to the very large contact surface area between the GO nanosheets and the sample solution. Therefore, the mass transfer of analyte from the aqueous phase to the sorbent surface is so fast that the equilibrium is achieved very rapidly. However, in order to obtain a well dispersed mixture of GO and sample solution, it was vortexed for 10 s.

3.2.4. *Effect of salinity*

To evaluate the effect of salt concentration on the extraction recovery of nicotine, NaCl was added to the sample solution in the concentration range of 0–10% (w/v). According to the obtained results, with the increase of salt content, the recovery of nicotine decreased. At high ionic strengths the electrostatic repulsion between GO nanosheets decreases and as a direct consequence, the probability of the nanosheets aggregation increases. This condition may reduce the available sites to bind nicotine on the GO surfaces or hinder the effective desorption of it. Therefore, further studies were performed in the absence of salt.

3.2.5. *Effect of the sorbent amount*

The effect of GO dosage on the extraction recovery of nicotine was studied in the range of 1–20 mg. The tests were performed with the procedure in Section 2.5. The results presented in Fig. 3c indicate that the maximum recovery was achieved using 3 mg of GO for extraction from 10 mL of sample solution. This may be due to the chemical structure and high surface area of GO that increases the adsorption capacity drastically. Further increasing the amount of GO gave no improvement in the nicotine extraction recovery. Thus, 3 mg of GO was used in the subsequent studies as the optimum amount of GO.

3.2.6. *Effect of the desorption time*

The desorption time is another main factor that affect the recovery of analyte. Hence, it was studied by changing the vortex time from 0 to 3 min. As shown in Fig. 3d, the recovery reached a maximum at 2 min and then remained constant. Therefore, desorption time of 2 min was selected for further experiments.

Table 2
Comparison of the proposed method with other previously reported methods for determination of nicotine.

Methods	Sample	LDR (ng mL^{-1})	LOD (ng mL^{-1})	RSD%	Recovery (%)	Ref.
SPME/LC–MS[a]	Urine, saliva	0.5–20	0.03	3.8, 7.1	83.0–95.2	[24]
SDME/GC-FID	Urine, saliva	0.5–25 mg L^{-1}	0.37, 0.33 mg L^{-1}	5.2–9.2	73.5–100.9	[25]
SPE/GC–MS/MS	Saliva	0.5–1000	0.5	10 and 12	89.4–98.1	[40]
SPE/HPLC-PDA	Urine	0.5–10 μg mL^{-1}	5	4 and 9	79.0–97.0	[41]
SPE/LC/APCI[b]-MS	Plasma	2.5–500	1	15	108.2–110.8	[42]
HF-LPME/HPLC-UV	Saliva	0.1–50 mg L^{-1}	0.05 mg L^{-1}	5	96.3–102.2	[43]
GO-D-μ-SPE/GC-FID	Urine, saliva, water	5–2000	1.5	2.7 and 5.2	88.7–109.7	This work

[a] Liquid chromatography–mass spectrometry.
[b] Atmospheric pressure chemical ionization.

3.3. Reusability of GO

In order to investigate the possibility of regeneration and reusability of the GO as an adsorbent, after desorption of nicotine from the GO sorbent, it was washed with 2.0 mL methanol and 2.0 mL double-distilled water, respectively. Then, the washed GO was reused for the next analysis run. The results showed that the GO sorbent can be reused at least 5 times without a significant loss of the sorption capacity and desorbed amount of nicotine.

3.4. Validation of the method

Under the optimum experimental conditions, the proposed method was validated by figures of merit such as linear dynamic range (LDR), limit of detection (LOD), limit of quantification (LOQ), precision and accuracy. A series of standard solutions containing nicotine in the concentration range of 5–2000 ng mL^{-1} were prepared for the establishment of the calibration curve. Calibration was made by plotting the ratio of the peak areas of nicotine to that of the internal standard as a function of the nicotine concentration of the standards. Good linearity was observed over a wide concentration range of 5–2000 ng mL^{-1} with a determination coefficient (R^2) of 0.9987. The LOD and LOQ values based on a signal to noise ratio of 3 ($S/N=3$) and 10 ($S/N=10$), were found to be 1.5 and 5.0 ng mL^{-1}, respectively. The enhancement factor (EF=93) was calculated as the ratio of the final concentration of nicotine in the organic phase after desorption, to the initial concentration of nicotine in the aqueous solution.

To evaluate the precision of the method, five similar experiments were carried out for the spiked samples at the concentrations of 500 ng mL^{-1} nicotine on the same day and the three consecutive days. The relative standard deviations (RSD%) of the intraday precision (2.7%) and interday precision (5.2%) showed good reproducibility and precision for this method.

3.5. Real samples analysis

In order to investigate the applicability of the proposed method, the procedure was applied for determination of nicotine in real biological and environmental water samples. The results summarized in Table 1 show that the recoveries for nicotine are within the acceptable range of 88.7–109.7%. Representative chromatograms of the real samples and the standard solution (100 ng mL^{-1}) are shown in Fig. 4. No significant interfering peaks were observed at the retention position of analyte.

3.6. Comparison of the GO-D-μ-SPE method with other methods

The important features of the proposed method with those of other reported researches in the literature [24,25,40–43] are given in Table 2. The comparative analysis shows that the developed method has the merit of a very wide dynamic linear range, which can be attributed to the GO large surface area. Moreover, the proposed method represents a good recovery and reproducible results. Furthermore, the detection limit of this work is comparable with and in some cases better than that of the other methods. Overall, these results indicate that GO based dispersive micro-SPE combined with GC-FID is a sensitive and reproducible method for the preconcentration and determination of nicotine in various matrices.

4. Conclusions

In this research, the GO was successfully prepared, characterized and then applied in a dispersive micro-solid phase extraction (D-μ-SPE) method as a highly efficient sorbent for isolation and enrichment of nicotine from water and biological samples. The adsorption process using a very small amount of sorbent (3 mg for 10 mL sample solution of nicotine) needed only a few seconds to be completed. This can be attributed to the rapid mass transfer of the analyte to the GO nanosheets. In addition, the nicotine molecules were desorbed from the surface of GO using low volume of organic solvents (100 μL). The results indicated that the GO can be used as a potential adsorbent for the separation and enrichment of nicotine in different real samples. Compared with conventional extraction methods, GO-D-μ-SPE is a simple, rapid, cost-effective and environment-friendly method with a wide LDR for the extraction of nicotine.

References

[1] M.P. Pellegrini, D.E. Newby, S. Maxwell, D.J. Webb, Cardiovasc. Res. 52 (2001) 321–327.
[2] G. Jain, E.A. Jaimes, Biochem. Pharmacol. 86 (2013) 1215–1223.
[3] H. Ashton, Adverse Drug React. Bull. 150 (1991) 560–566.
[4] R.M. Maduro, M. Aznar, Fluid Phase Equilib. 259 (2007) 83–88.
[5] N.D. Grozdanic, V. Najdanovic-Visak, M.L. Kijevcanin, S.P. Serbanovic, M. Nunes da Ponte, Z.P. Visak, Fluid Phase Equilib. 310 (2011) 198–206.
[6] Y. Zuo, L. Zhang, J. Wu, J.W. Fritz, S. Medeiros, C. Rego, Anal. Chim. Acta 526 (2004) 35–39.
[7] A.K. Dash, S.-T. Wong, J. Chromatogr. A 749 (1996) 81–85.
[8] B. Sellergren, Å. Zander, T. Renner, A. Swietlow, J. Chromatogr. A 829 (1998) 143–152.
[9] A. Lozano, M.A. Martínez-Uroz, M.J. Gómez-Ramos, M.M. Gómez-Ramos, M. Mezcua, A.R. Fernández-Alba, Anal. Bioanal. Chem. 402 (2012) 935–943.
[10] C. Müller, F. Bracher, F. Plössl, Chromatographia 73 (2011) 807–811.
[11] S. Guleria, A.K. Tiku, Botanicals in pest management: current status and future perspectives, in: R. Peshin, A.K. Dhawan (Eds.), Integrated Pest Management: Innovation-Development Process, Springer, Dordrecht, The Netherlands, 2009, pp. 317–329.
[12] M. Yasuda, T. Ota, A. Morikawa, K. Mawatari, T. Fukuuchi, N. Yamaoka, K. Kanekob, K. Nakagomi, J. Chromatogr. B 934 (2013) 41–45.
[13] C.N. Man, S. Ismail, G.L. Harn, R. Lajis, R. Awang, J. Chromatogr. B 877 (2009) 339–342.
[14] B. Siegmund, E. Leitner, W. Pfannhauser, J. Agric. Food Chem. 47 (1999) 3113–3120.
[15] J. Shen, X. Shao, Anal. Chim. Acta 561 (2006) 83–87.
[16] N. Ramírez, M.Z. Özel, A.C. Lewis, R.M. Marcé, F. Borrull, J.F. Hamilton, J. Chromatogr. A 1219 (2012) 180–187.

[17] S.G. Sant'anna, C.D.R. Oliveira, E.M.D.A. Diniz, M. Yonamine, J. Anal. Toxicol. 36 (2012) 19–24.
[18] K. Shrivas, D. Kumar, Food Chem. 122 (2010) 314–318.
[19] K. De Cremer, I. Van Overmeire, J. Van Loco, J. Pharm. Biomed. Anal. 76 (2013) 126–133.
[20] W. Liu, R. Zhao, B. Li, G. Wu, Y. Xue, Food Anal. Methods 6 (2012) 643–647.
[21] J.E. Jablonski, J.E. Schlesser, P. Mariappagoudar, J. Agric. Food Chem. 54 (2006) 7460–7465.
[22] I. Brčić Karačonji, L. Zimić, N. Brajenović, L. Skender, J. Sep. Sci. 34 (2011) 2726–2731.
[23] M. Bao, P. Joza, W.S. Rickert, J.H. Lauterbach, Anal. Chim. Acta 663 (2010) 49–54.
[24] H. Kataoka, R. Inoue, K. Yagi, K. Saito, J. Pharm. Biomed. Anal. 49 (2009) 108–114.
[25] F. Kardani, A. Daneshfar, R. Sahrai, J. Chromatogr. B 878 (2010) 2857–2862.
[26] X. Chen, L. Hu, J. Liu, S. Chen, J. Wang, Trends Anal. Chem. 48 (2013) 30–39.
[27] X. Luo, F. Zhang, S. Ji, B. Yang, X. Liang, Talanta 120 (2014) 71–75.
[28] B. Pérez-López, A. Merkoçi, Microchim. Acta 179 (2012) 1–16.
[29] R. Sitko, B. Zawisza, E. Malicka, Trends Anal. Chem. 51 (2013) 33–43.
[30] Q. Shen, L. Gong, J.T. Baibado, W. Dong, Y. Wang, Z. Dai, Talanta 116 (2013) 770–775.
[31] B.T. Zhang, X. Zheng, H.F. Li, J.M. Lin, Anal. Chim. Acta 784 (2013) 1–17.
[32] S. Su, B. Chen, M. He, B. Hu, Z. Xiao, Talanta 119 (2014) 458–466.
[33] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Adv. Mater. 22 (2010) 3906–3942.
[34] D. Chen, H. Feng, J. Li, Chem. Rev. 112 (2012) 6027–6053.
[35] W.S. Hummers, R.E. Offeman, J. Am. Chem. Soc. 80 (1958) 1339.
[36] H. Cheng, K. Zeng, J. Yu, J. Radioanal. Nucl. Chem. 298 (2013) 599–603.
[37] G. Zhao, T. Wen, X. Yang, S. Yang, J. Liao, J. Hu, D. Shao, X. Wang, Dalton Trans. 41 (2012) 6182–6188.
[38] G. Zhao, X. Ren, X. Gao, X. Tan, J. Li, C. Chen, Y. Huang, X. Wang, Dalton Trans. 40 (2011) 10945–10952.
[39] G. Zhao, J. Li, X. Ren, C. Chen, X. Wang, Environ. Sci. Technol. 45 (2011) 10454–10462.
[40] B.M. da Fonseca, I.E.D. Moreno, A.R. Magalhães, M. Barroso, J.A. Queiroz, S. Ravara, J. Calheirosa,c, E. Gallardo, J. Chromatogr. B 889–890 (2012) 116–122.
[41] P.B. Doctor, V.N. Gokani, P.K. Kulkarni, J.R. Parikh, H.N. Saiyed, J. Chromatogr. B 802 (2004) 323–328.
[42] I. Kim, M.A. Huestis, J. Mass Spectrom. 41 (2006) 815–821.
[43] Y. Xin-Lei, L. Ming-Biao, D. Jian-hua, Chin. J. Anal. Chem. 35 (2007) 171–175.