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Dispersive Micro-Solid-Phase Extraction using Graphene Oxide/Polydopamine-Polyacrylamide Nanocomposite Coupled with HPLC-UV for Determination of Phenobarbital in Plasma Samples

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Abstract

Graphene oxide/polydopamine-polyacrylamide nanocomposite was synthesized by a simple method and used as adsorbent for dispersive micro-solid-phase extraction of phenobarbital in plasma samples. The adsorbent was characterized by Fourier-transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy–energy dispersive spectroscopy and thermal gravimetric analysis. The results show that functionalization of graphene oxide by polymeric materials can enhance the sorption properties and thermal stability of the prepared adsorbent. Influential parameters on the extraction efficiency of Phenobarbital including adsorbent amount, elution solvent and its volume, sorption and desorption times and pH of sample solution were investigated and optimized. Under the optimized conditions, limits of detection and quantitation values were 1.4 and 5ng/mL, respectively. Relative recovery data for several real samples were obtained within the range of 84.0-98.0% with a relative standard deviation less than 7.2%. The proposed method was successfully applied to quantitative determination of phenobarbital in plasma samples.

Keywords: Graphene oxide, Polydopamine, Polyacrylamide, Phenobarbital, Plasma.

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Introduction

Phenobarbital belongs to barbiturate class that is widely used to control seizures.Also, it acts as a sedative hypnotic and an anticonvulsant in subhypnotic doses[1].Scheduled monitoring of drugs concentrations in biological samples increases their safety and efficacy. Also, the determination of drugs in biological samples is not only vital in therapeutic drug monitoring to consider poisoning but also important in new formulation development and forensic science. However, determination of target analyte concentrations at low amounts in biological samples, due to small sample sizes and matrix, without sample preparation is challenging. Hence, development of suitable sample preparation techniques as one of the main steps of analysis is essential. With the progress of extraction techniques, miniaturization and introduction of new extracting phases are important issues in sample preparation. Solid-phase extraction (SPE) is an effective sample preparation method used for extraction of a wide range of compounds with different polarities from a liquid matrix. The development of novel adsorbents and miniaturization of extraction method are two important issues which led to the expansion of SPE applications. Many miniaturized SPE techniques such as solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE), μ-SPE, microextraction in a packed syringe (MEPS), dispersive micro-solid phase extraction (d-μ-SPE) and matrix solid-phase dispersion (MSPD)were introduced as sample preparation methods for various analytes in different matrices [2-11]. Although in these techniques, the extraction principles and steps are different but the aim in all of them is to increase the contact between the adsorbent and the analyte as much as possible.

Literature reviews show that phenobarbital was determined by various sample preparation and analytical techniques in different matrices. These procedures, such as SBSE were coupled with high-performance liquid chromatography (HPLC) [12], and hollow-fiber liquid-phase microextraction (HF-LPME) was coupled with gas chromatography–mass spectrometry (GC-MS) [13]. Fluorescence sensors based on molecularly imprinted polymers (MIP) [14], solvent assisted-dispersive solid-phase microextraction (SA-DSPME) by GC-MS [15], electromembrane extraction were followed by HPLC-UV [16], colorimetric nano-platform procedure [17] and flat membrane-based liquid-phase microextraction (FM-LPME) followed by liquid chromatography-mass spectrometry (LC-MS) [18]. They all have advantages and disadvantages. As can be seen, most of these methods use analytical techniques such as LC-MS, electrochemical and luminescence for detection that are expensive devices and not routine in quality control laboratories.

In the last decade, progress in the synthesis of nanomaterials and their use as adsorbents has had a significant effect on the growth of the SPE applications. Nanomaterials often show specific properties such as a surface effect and small size effect which leads to improvement in the

extraction efficiency by SPE method. Recently, reports show good adhesion and stability for polydopamine (PDA) and polyacrylamide (PAM) composites on various surfaces [19, 20]. For example, several PDA-based nano-sorbents including PDA@graphene, PDA@Fe_3O_4, PDA@multi-walled carbon nanotubes, graphene oxide (GO)/PAM membrane and PDA@GO/Fe_3O_4 have been synthesized and used for separation of various analytes from different matrices [21-28].Also, a flexible and scalable procedure was introduced for fabricating multi-layered GOFe_3O_4@PDA-PAM composites which are used for the anodes of lithium-ion batteries (LIBs)[29]. The aim of this study was to develop a graphene oxide/polydopamine-polyacrylamide (GO/PDA-PAM) composite as adsorbent for d-μ-SPE of phenobarbital from plasma samples. The prepared adsorbent was characterized by various analyzes and influence of important parameters on the extraction efficiency of phenobarbital using the D-μ-SPE procedure were investigated and optimized. Finally, performance of the proposed method was examined by real samples analysis and its analytical features for quantitative determination of phenobarbital were compared with the reported methods.

Experimental

Materials and methods

Phenobarbital, acrylamide (AM) and dopamine hydrochloride (DA) were obtained from Sigma-Aldrich (Missouri, USA). Ammonium persulfate (APS), N,N'-methylenebisacrylamide (MBAA), acetonitrile (ACN), methanol (MeOH), ethanol (EtOH), hydrochloric acid (HCl), phosphoric acid, trichloroacetic acid,disodium hydrogen phosphate, sodium dihydrogen phosphate and ammonia solution were purchased from Merck (Darmstadt,Germany).All solutions were prepared in deionized water which was supplied by a Milli-Q system (Millipore, USA).

Instrumentation

Separation and quantitation were performed using an HPLC system (Shimadzu Corp., Kyoto, Japan) with a quaternary pump (LC-10ATvp), a UV-Vis detector (SPD-M10Avp), a vacuum degasser, and a system controller (SCL-10Avp). A manual injector with a 10 μL sample loop was used for loading the sample and standard solutions. Class VP-LC workstation software was used to acquire and process chromatographic data. A reversed-phase Cyano (RP-CN) analytical column (150×4.6 mm, 5 μm, MZ-Analysentechnik GmbH, Germany) was employed. The elution was achieved by an isocratic mode. The mobile phase composition was water andmethanol (60/40, v/v). The mobile phase components were degassed separately by a Millipore vacuum pump prior to usage. The UV detector and flow rate were set at 210nm and 1.0 mL/min, respectively.

The crystal phase of prepared adsorbent was investigated using a X'PERT PRO X-ray diffractometer (XRD) (Panalytical, Netherlands). The functional groups of synthesized adsorbent were identified using a Fourier-transform infrared (FT-IR) spectrometer (IRPrestige-21, Shimadzu, Kyoto, Japan). The morphology of adsorbent surface was characterized by a field emission scanning electron microscope (FE-SEM) (Mighty-8 instrument, TSCAN Company, Prague). Scanning electron microscopy–energy dispersive spectroscopy (SEM–EDX) analyses were conducted using a Mighty-8 instrument (TSCAN Company, Prague).Thermal gravimetric analysis (TGA) and Brunauer-Emmett-Teller (BET) surface area analysis were performed by SDT Q600 (TA Instruments, USA) and BELSORP-mini II (LMS Instruments, Thailand), respectively.

Standard and sample preparation

Standard stock solution of phenobarbital was prepared by dissolving phenobarbital analytical standard in MeOH with concentration of 1000µg/mL. Working standard solutions at different concentrations were prepared freshly by mixing the appropriate volumes of the stock solution and diluting with deionized water. In order to prepare spiked plasma samples, healthy person plasma samples were treated with phenobarbital standard solution. Deprotenizeation of the prepared spiked samples were achieved using trichloroacetic acid and then subjected to D-µ-SPE procedure.

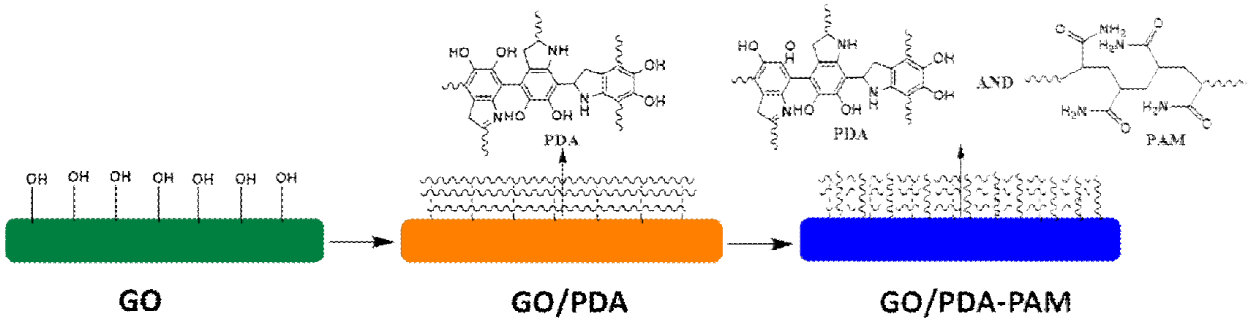
Synthesis of GO/PDA-PAM nanocomposites hydrogel

The GO/PDA-PAM nanocomposites hydrogel was synthesized by a simple three steps procedure. Firstly, DA was polymerized to PDA under the alkaline condition. Secondly, GO was added to the PDA solution and then the GO/PDA-PAM nanocomposites hydrogel was prepared by polymerization of AM in the presence of initiator and crosslinker agents [30]. Briefly, 1 g DA and 0.5 mL ammonia solution were added to 100 mL deionized water and stirred for 6 h. Then, 0.03 g GO was added to the PDA suspension and the mixture stirred for 2 h. Finally, 1 g AM, 0.3 g APS (initiator) and 0.3 g MBAA (crosslinker) were added to solution and the mixture was stirred for another 2 h. The final product was freeze-dried and named as GO/PDA-PAM nanocomposite. The synthesis process of the GO/PDA-PAM nanocomposite is shown graphically in Scheme 1.

D-µ-SPE procedure

In order to extract the phenobarbital from sample and standard solutions, 1 mL of the standard or sample solution was mixed with 4 mL of phosphate buffer (pH 8) and the mixture transferred into a centrifuge tube. The amount of 0.15 g of GO/PDA-PAM composite was added to the tube and the mixture vortexed for 5 min at room temperature. The suspension was centrifuged for 5 min at 6000

rpm and then the supernatant removed from the adsorbent. The adsorbent was washed with 2 mL of deionized water and then 2 mL of MeOH as elution solvent added to the adsorbent and sonicated for 5 min. The suspension was centrifuged for 5 min at 6000 rpm and the supernatant transferred to a test tube. Finally, 1 mL of the supernatant was filtered using 0.45 µm cellulose acetate membrane and 10 µL injected to HPLC system. The proposed adsorbent can be reused after each extraction by cleaning to remove possible residual phenobarbital. The used adsorbent was sonicated for 5 min with 4 mL of MeOH. The results show that adsorbent was reusable for up to 5 times without affecting the extraction efficiency.



Scheme 1. Synthesis of the GO/PDA-PAM adsorbent.

Results and discussion

The synthesized adsorbent was characterized using various analytical techniques such as FT-IR, XRD, SEM, EDX, TGA and BET. Then, the adsorbent was applied for extraction of phenobarbital from water and food samples by d-µ-SPE technique. Influential parameters on the extraction efficiency of phenobarbital using D-µ-SPE including adsorbent amount, elution solvent and its volume, sorption and desorption times and pH of sample solution were investigated and optimized.

Characterization of GO/PDA-PAM nanocomposites

The FT-IR spectra of GO, GO/PDA and GO/PDA-PAM nanocomposite are shown in Figure 1. The FT-IR spectrum of the GO indicates the characteristic bands at 1650 cm^{-1} and 3430 cm^{-1} which belong to C=C and OH groups, respectively. The band around 1750 cm^{-1} corresponds to C=O stretching vibrations from carbonyl and carboxylic groups[31]. The FT-IR spectrum of GO/PDA showsan absorption band at 3430 cm^{-1} corresponds to the characteristic starching frequency of hydroxyl groups which overlapped with a starching frequency band of N-H. Also, peaks at 1620 and 1280 $cm^{-1}$are correspond to bending vibration of N-H and C-O stretching, respectively [32].The FT-IR spectrum of GO/PDA-PAM indicates an absorption band at 3430 cm^{-1}which it is assigned to

the vibration corresponding to the NH groups. The peak at 2930 cm^{-1} is assigned to the asymmetric vibration of CH_2 groups in the macromolecular chains and crosslinking bridges. The absorptionband at 2850 cm^{-1} is attributed to the -N-CH_2- bonds from the crosslinking bridges. Stretching and deformation vibrations corresponding to the C=O and NH bonds were appeared at 1620 cm^{-1} and 1520 cm^{-1}, respectively [33]. XRD patterns of GO, GO/PDA and GO/PDA-PAM nanocomposite are shown in Fig. 2. Compared to GO, the XRD patterns of GO/PDA and GO/PDA-PAM nanocomposite show a series of sharp peaks that could be a reason for the crystalline structure of the prepared adsorbent.

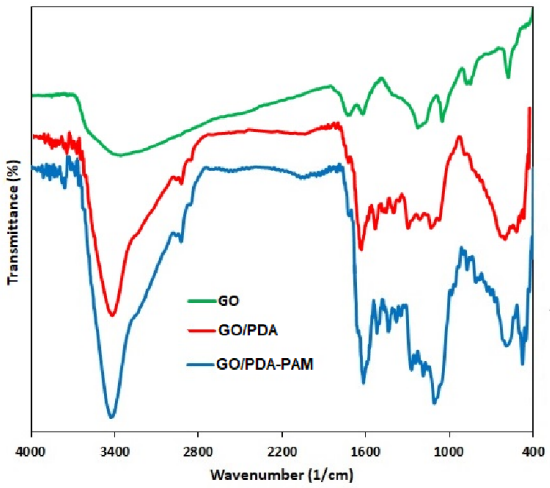


Figure 1.FT-IR spectra of GO, GO/PDA and GO/PDA-PAM nonocomposite.

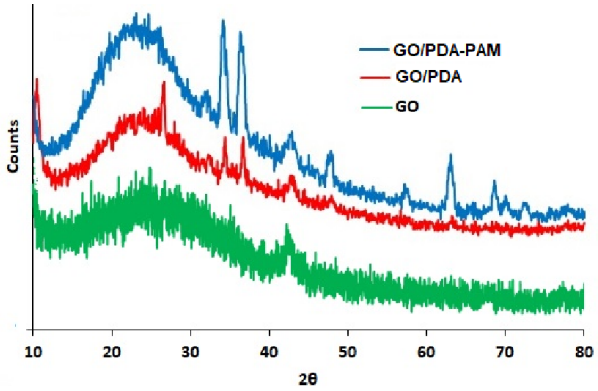


Figure 2. XRD patterns of GO, GO/PDA and GO/PDA-PAM nonocomposite.

Figure 3 shows SEM images of synthesized GO/PDA and GO/PDA-PAM nanocomposite. The morphology of GO/PDA in Figure 3b confirms the fiber structure of PDA. Also, the multi-layers structure of GO/PDA and GO/PDA-PAM composite are observed in Figures 3a and 3c, respectively.

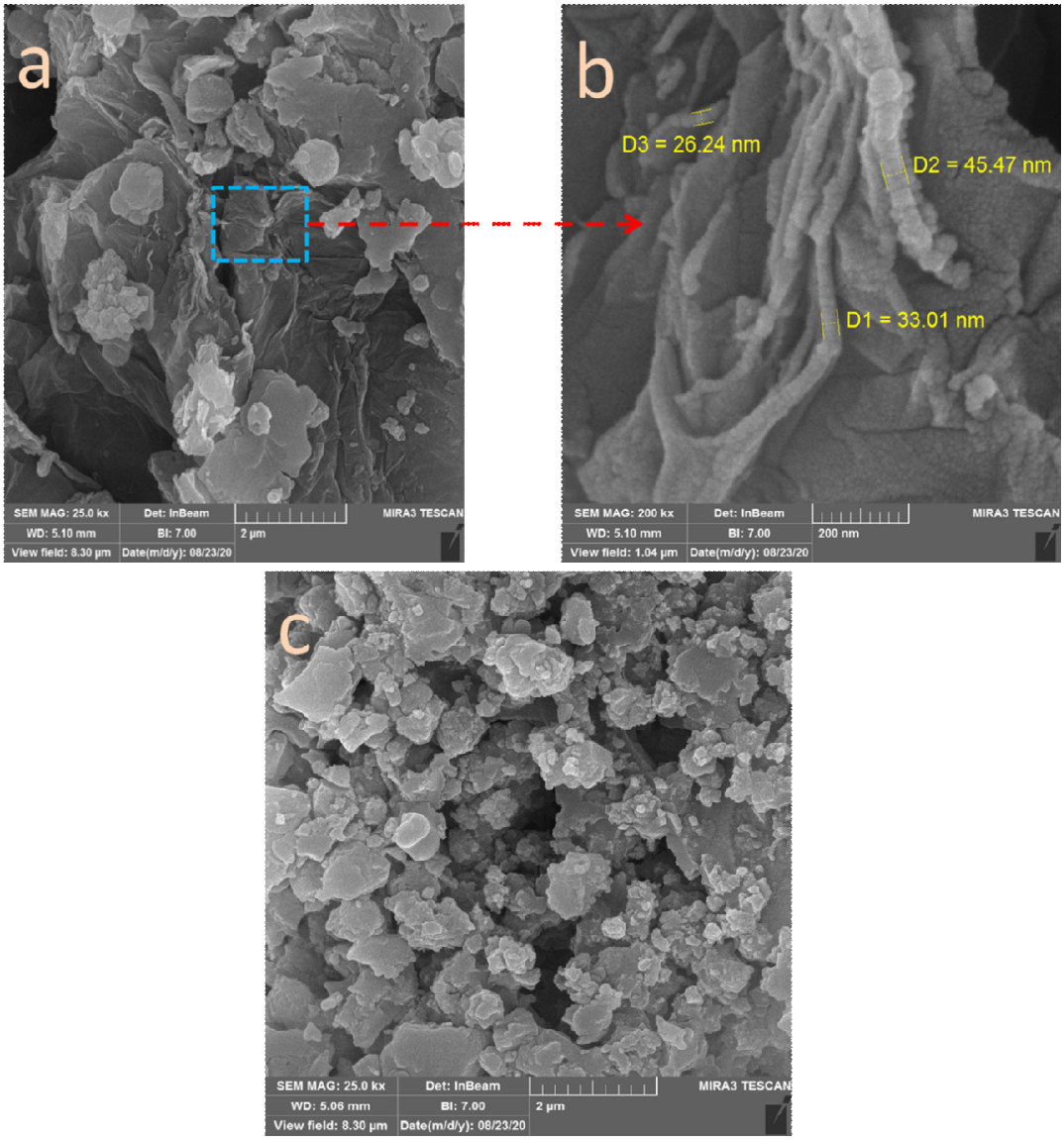


Figure 3.SEM images of (a, b) GO/PDA and (c) GO/PDA-PAM nonocomposite.

Elemental composition of the synthesized adsorbent was determined by EDX analysis. Quantitative results of EDX analysis were shown in Table 1. Results confirm the synthesis of GO/PDA and GO/PDA-PAM through the interactions between GO, PDA, and PAM. As can be expected, N content of GO/PDA-PAM composite was increased than GO/PDA.

The results of BET analysis for GO/PDA and GO/PDA-PAM composite are shown in Table 1. As can be seen, after treatment of GO/PDA with AM and produce of GO/PDA-PAM composite, specific surface area of GO/PDA-PAM composite is reduced which demonstrated the polymerization process.

Table 1. The results ofBET and EDX analysis of GO/PDA and GO/PDA-PAM composite.

BET			EDX		
Parameter	GO/PDA	GO/PDA-PAM	Element	GO/PDA	GO/PDA-PAM
Specific surface area (m^2/g)	5.55	2.25	C	51.88	50.65
Total pore volume (cm^3/g)	0.041	0.042	N	15.97	25.85
Mean pore diameter (nm)	29.71	74.54	O	32.15	23.50

Figure 4 shows the TGA graphs of GO, GO/PDA and GO/PDA-PAM composite. As can be seen, coating the surface of GO with PDA and PAMleads to a reduction in the rate of weight loss and thus increases the thermal stability ofGO/PDA and GO/PDA-PAM composite. However, at temperatures below 200 □Cin the GO/PDA-PAM composite, due to the presence of crosslinked structure, the thermal stability is higher than GO/PDA.

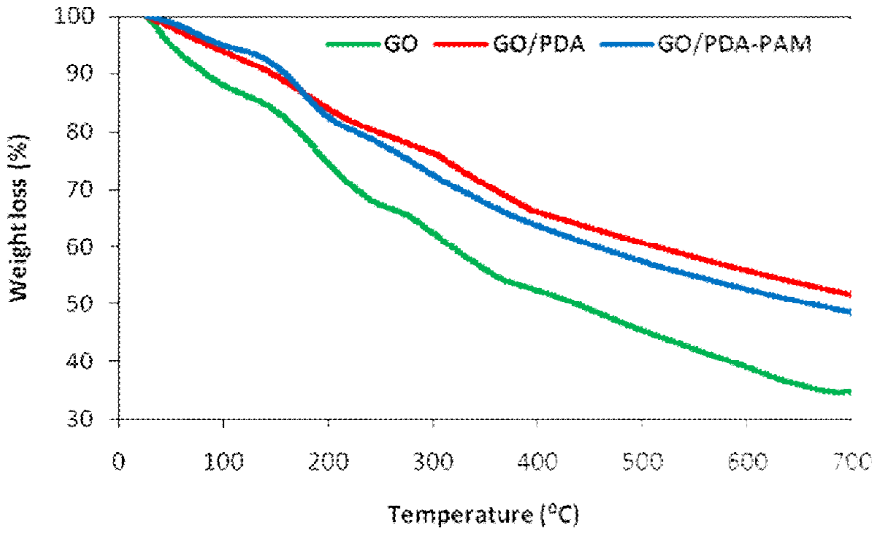


Figure 4. TGA thermograms of GO, GO/PDA and GO/PDA-PAM nonocomposite.

Adsorbent amount

The effect of adsorbent amount on the extraction efficiency of phenobarbital was investigated in the range of 0.05-0.25 g (Figure 5a). The results show that with increasing the amount of adsorbent the extraction efficiency increases up to 0.15 g and then remains constant. In other words, there is no analyte for sorption at higher amounts of adsorbent (0.15 g). Therefore, 0.15 g was selected as the optimum adsorbent amount for further investigations.

Elution solvent and its volume

The influence of elution solvent on the Phenobarbital desorption from the adsorbent surface was considered by three common organic solvents including ACN, MeOH and EtOH. Figure 5b shows MeOH has the maximum elution power than other solvents. Thus, MeOH was chosen as elution solvent for subsequent experiments.

The volume of elution solvent plays an important role in extraction efficiency. The effect of elution solvent volume was investigated in the range of 1.5-4.0 mL.As can be seen from Figure 5c, the maximum peak area was obtained using 2.0 mL MeOH. Therefore, 2.0 mL was selected as the optimum elution solvent volume.

Sample pH

The effect of solution pH on the extraction efficiency was evaluated in the range of 2-12. Figure 5d shows with increasing pH the peak area of phenobarbital increases up to 8and then remains constant. Phenobarbital is a weak acid (pK_a=7.3) that is sparingly soluble in water (1mg/ml) [34].Therefore, it is nonionized at acidic pHs and ionized at basic pHs. At higher pHs (>8), phenobarbital becomes completely ionic and its solubility in water increases. For this reason, its tendency to extract and transfer from the aqueous phase to the adsorbent surface decreases. Therefore, pH 2 was chosen as the optimum pH for further experiments.

Extraction and desorption times

In d-μ-SPE procedure extraction time depends on the equilibrium process involving the transfer of the analytes from the sample bulk to the adsorbent surface. This parameter was evaluated in the range of 1-15 min. Vertex was used to accelerate the mass transfer from the solution bulk to the adsorbent surface.Fig.5e shows that the extraction efficiency increases with increasing of vortex time up to 5 min and then gradually decreases. Consequently, 5 min was selected as the optimum extraction time.

After extraction analyte from sample matrix by adsorbent particles, the mixture was centrifuged for separation of the adsorbent particles from sample solution. Then, elution solvent was added to the adsorbent and mixture was sonicated for various times in the range of 1 to 10 min.Sonication helps to complete desorption of analyte from the adsorbent surface. The results (Fig. 5f) indicate the maximum desorption was obtained by 5 min sonication. Therefore, 5 min was selected as the optimum sonication time for further tests.

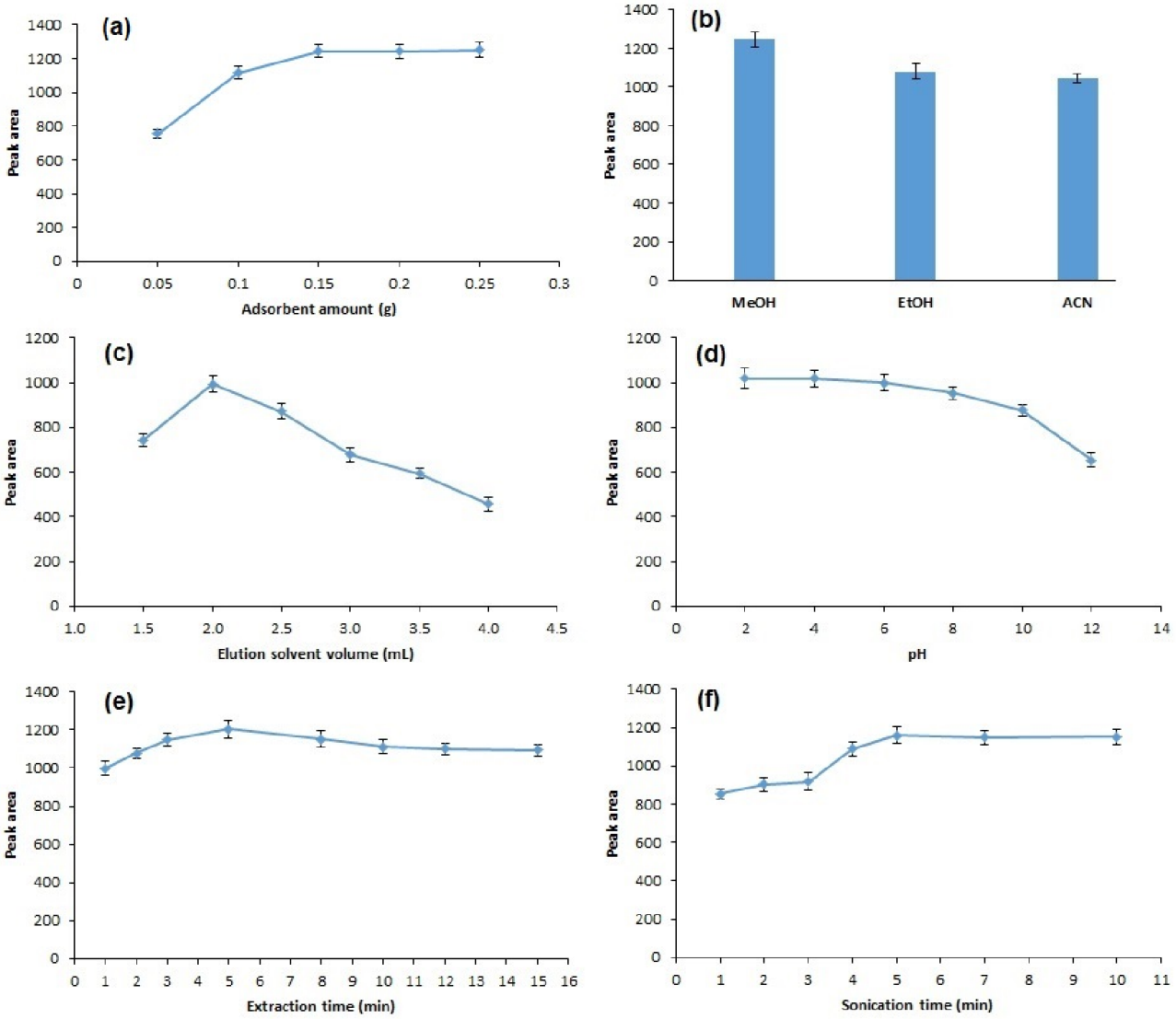


Figure 5. Optimization of (a) adsorbent amount, (b) elution solvent, (c) elution solvent volume, (d) sample pH, (e) extraction time and (f) sonication time on the extraction efficiency of phenobarbital. The initial conditions for optimization of adsorbent amount were: elution solvent, MeOH; volume of elution solvent, 2 mL; sample pH, 2; extraction time, 5 min and sonication time, 5 min. For other parameters, the optimum values of the previous steps were applied.

Method validation

The aim of analytical method validation is to prove that it is suitable forits intended purpose. Typical validation parameters such as linear range, accuracy, precision, limits of detection and quantitation were considered. The calibration curve for the proposed method was constructed by spiked plasma samples with different concentrations of phenobarbital. The results show that the proposed method is linear in the range of 5-1000 ng/mL with an R-squared of 0.9934. Under the optimized conditions, limit of detection based on signal to noise ratio equal to 3 and limit of quantitation based on signal to noise ratio equal to 10 were 1.4 and 5 ng/mL, respectively.

Intra- and inter-day precisions were calculated by analysis of replica samples under the optimized conditions using the proposed method. The results in Table 2 show that relative standard deviation (RSD) values were less than 7.2%. Also, the obtained recoveries for spiked plasma samples at different concentration levels were indicated the method accuracy is satisfactory.

Typical chromatograms of phenobarbital standard solution before and after extraction by the proposed method were presented in Figure 6.

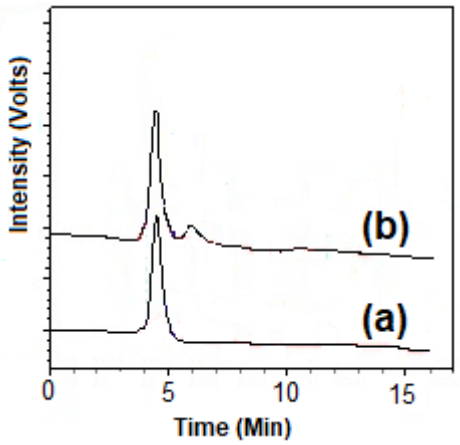


Figure 6. Typical chromatograms of standard solution of phenobarbital before (a) and after extraction (b) using the proposed method under the optimized conditions.

Real sample analysis

In order to prove the performance of the proposed method, several plasma samples were spiked and analyzed by the proposed d-μ-SPE procedure. The results of the analysis showed that all unspikedreal samples were free of phenobarbital. However, the ability of the proposed method for the extraction and determination of the phenobarbital was investigated using various spiked samples at different concentrations (Table 2).

Figures of merits of the proposed method were compared with several reported techniques for the determination of phenobarbital (Table 3). Although, solvent assisted dispersive solid-phase microextraction (SA-DSPME) with GC-MS has low LOD and LOQ values than other methods, but the GC-MS is not a common analytical instrument in most laboratories. Compared to HPLC and spectrophotometric methods, analytical parameters of the proposed method are satisfactory.

Table 2. The precision and accuracy data for analyzed spiked plasma samples by the proposed method.

Plasma sample	Added conc. (ng/mL)	Found conc. (ng/mL)	RR (%)[a]	Precision, RSD (%)	
				intra-day (n=3)	inter-day (n=9)
#1	5.0	4.2	84.0	4.9	7.0
	10.0	8.9	89.0	4.5	6.8
	100.0	95.0	95.0	3.8	6.5
#2	5.0	4.4	88.0	5.2	7.2
	10.0	9.0	90.0	5.1	6.7
	100.0	94.0	94.0	3.5	5.4
#3	5.0	4.7	94.0	5.7	6.9
	10.0	9.8	98.0	4.6	5.7
	100.0	97.0	97.0	2.9	4.8

[a] Relative recovery

Table 3.Comparison of some analytical parameters of the proposed method with previously reports.

Matrix	Sample preparation	Analysis instrument	LOD (ng/mL)	LOQ (ng/mL)	RSD (%)	Recovery (%)	Ref.
Plasma	SBSE[a]	HPLC-UV	1.4	4.6	5.7-6.8	91.0-96.0	[12]
Plasma	MIP [b]	Spectrofluorometer	0.23	--	7.3	96.5-109.5	[14]
Urine	SA-DSPME[c]	GC-MS[d]	0.06	0.2	3.6-4.7	93.8-101.8	[15]
Plasma & urine	EME[e]	HPLC-UV	7.5	25.0	0.4-6.8	70.0-80.0	[16]
Plasma	Colorimetric nano-platform	Spectrophotometer	600.0	n.r[f]	4.3-5.2	94.0-98.0	[17]
Blood	FM-LPME [g]	LC-MS[h]	1.5	5.0	>20	n.r	[18]
Plasma	D-μ-SPE	HPLC-UV	1.4	5.0	3.5-7.2	84.0-98.0	C.W.[i]

[a] Stir bar sorptive extraction; [b] Molecularly imprinted polymer; [c] Solvent assisted dispersive solid-phase microextraction; [d]Gas chromatography- mass spectrometry; [e]Electromembrane extraction; [f] Not reported; [g]Flat membrane-based liquid-phase microextraction; [h] Liquid chromatography-mass spectrometry; [i]Current work.

Conclusion

In the present work, an effective adsorbent was developed for the extraction of phenobarbital from human plasma samples using d-μ-SPE procedure. The synthesis process of the adsorbent was simple and fast. The prepared adsorbent was characterized by various analytical techniques. Modification of GO by polymeric materials can enhance the sorption properties and thermal stability of this compound. However, uniform coating of polymeric materials on the surface of GO

reduces its porosity. As can be seen, the obtained analytical parameters by the proposed adsorbent for determination of phenobarbital are satisfactory. The prepared adsorbent was successfully applied for the determination of phenobarbital in plasma samples.

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