

Fig. 1. Phenobarbital structure.

sizes, shapes and forms. Sol–gel offers great advantages compared to conventional coating techniques: a strong adhesion between the coating and the bed, the coating's porous silica surface structure providing high surfaces areas and a compatible composition increasing sorbent selectivity. Recently, Malik and coworkers established a convenient pathway to surface coatings using sol–gel technology to overcome important drawbacks of conventional SPME coatings: low recommended operating temperature, instability and swelling in organic solvents, breakage of the fiber and expensive cost [13–15].

SPME applications to polar compounds species have been limited because of the neutral charge of conventional SPME fibers, which results in poor analyte extraction. Moreover, commercial SPME fibers have some disadvantages such as: fiber breakage; stripping of coatings and memory effects. SPME fibers are still comparatively expensive and have a limited lifetime.

The aim of this research was to improve on previous work through a simple and practical device that can overcome remaining main problems with ordinary SPME fibers like sample carryover. We have introduced a novel SPME technique that uses hollow fiber-supported sol–gel combined with MWCNTs and produced a high pre-concentration factor for phenobarbital. A silica-based, organic–inorganic polymer containing MWCNTs was prepared by sol–gel technology via the reaction of tetraethylorthosilicate (TEOS) with an acidic catalyst (HCl). Aromatic molecules are able to interact with the graphite surface of the CNTs through pi–pi stacking [16].

This sol was then injected into a polypropylene hollow fiber segment, and the gel formation process was implemented in situ. This disposable device was operated in direct immersion sampling mode during sample analysis.

2. Experimental

2.1. Chemical and reagents

Phenobarbital was purchased from the Doctor Abidi Company (Tehran, Iran) and was of pharmaceutical quality. Tetraethylorthosilicate (TEOS; the sol–gel precursor), ethanol (EtOH), methanol (MeOH), hydrochloric acid (37 w/w %) and the additive Triton X-100 were obtained from Merck (Darmstadt, Germany).

MWCNTs with the mean outer diameter ≤ 20 nm, lengths of 5–15 μm and purity greater than 95% were provided by the Research Institute of the Petroleum Industry (Tehran, Iran). The Q3/2 Accurel polypropylene microporous hollow-fiber membrane (200- μm wall thickness, 600- μm inner diameter, 0.2- μm pore size, 75% porosity) was obtained from Membrana (Wuppertal, Germany).

A stock standard solution of phenobarbital (1000 mg L⁻¹) was prepared by dissolving 5 mg of phenobarbital in 5 mL of methanol. Standard sample solutions were prepared daily at different concentrations by diluting the stock solutions with deionized water, which was purified in a Milli-Q filtering system (Mil-

Table 1
Composition of the sols.

Cocktail name	TEOS (mL)	EtOH (mL)	Acidified water (μL)	Triton X-100 (μL)	pH
Sol-1	1.07	1.07	386 ^a	120	1
Sol-2	1.07	1.07	386 ^b	120	5
Sol-3	1.07	1.07	193 ^c	120	4
Sol-1	1.07	1.07	386 ^a	120	1

^a 386 refers to 338 μL water and 48 μL concentrated HCl ($R=4$).

^b 386 refers to 338 μL water and 48 μL 0.1 M HCl ($R=4$).

^c 193 refers to 193 μL 0.1 M HCl ($R=2$).

lipore). The stock standard and sample solutions were stored at 4 °C.

2.2. Apparatus

The absorption spectra were recorded using a CECILCE7200 UV-Visible spectrophotometer (Cambridge, England). The HPLC system was a Knauer Smart Line (Berlin, Germany) with a Knauer (S-2500) UV detector. The column was a Perfectsil Target RP-18 column (4.6-mm diameter, 250-mm length, ODS3, 5 μm) from Knauer. An RP-18 guard column (4 \times 4 mm i.d., 5 μm) was fitted upstream of the analytical column. The mobile phase consisted of water:acetonitrile (1:1) and was run in isocratic mode at a flow rate of 1.0 mL min⁻¹. The mobile phase was filtered by a Milli-Q filtering system before use and delivered by a Knauer (S-1000) HPLC pump. Signals were monitored at 230 nm. A Metrohm 780 pH-meter equipped with a combined glass electrode was used to determine pH values during the experiment (Herisau, Switzerland).

2.3. Preparation of the sol–gel

The sol–gel composites were obtained through modification of the method reported by Oter et al. [17]. One of the advantages of the sol–gel technique is the possibility of using different precursors. In the current work, tetraethylorthosilicate (TEOS) was used as the precursor. Two major sets of reactions take place during sol–gel processing: (I) hydrolysis of the precursor and (II) polycondensation of the hydrolyzed products [18].

The sols were prepared by the acid-based catalyzed method from a solution containing TEOS, HCl solution, ethanol (EtOH) and Triton X-100. Equal volumes of TEOS and EtOH were added to a clean glass vial and stirred for 10 min. Then, the HCl solution was added and the mixture was stirred to promote the hydrolysis and condensation reactions. After 20 min, 120 μL of Triton X-100 was added into the sol, and the mixture was stirred for an additional 120 min. The ageing time is therefore 120 min. The molar ratios of TEOS, ethanol and water were either 1:1:4 or 1:1:2. The exact compositions of the sols are given in Table 1. The solutions were aged at room temperature in closed glass vials.

FT-IR spectra of the sol–gels are shown in Fig. 2. The low frequency peak near 434 cm⁻¹ is assigned to Si–O–Si out-of-plane bending. The bands at 804 and 1070 cm⁻¹ are ascribed to Si–O–Si symmetric and anti-symmetric stretching vibrations, respectively. The peaks at 956 and 1150 cm⁻¹ are related to Si–OH and Si–O–C, respectively.

2.4. MWCNT functionalization

Functional groups like carboxylic acids allow the CNTs dissolve in various solvents. The dimensions of the nanotubes and their concentration in solution can be altered to observe how these variables affect what phase the nanotubes will form in aqueous sol solutions. Different surfactants can also be added to the solution to better disperse the nanotubes and prevent their re-aggregation.

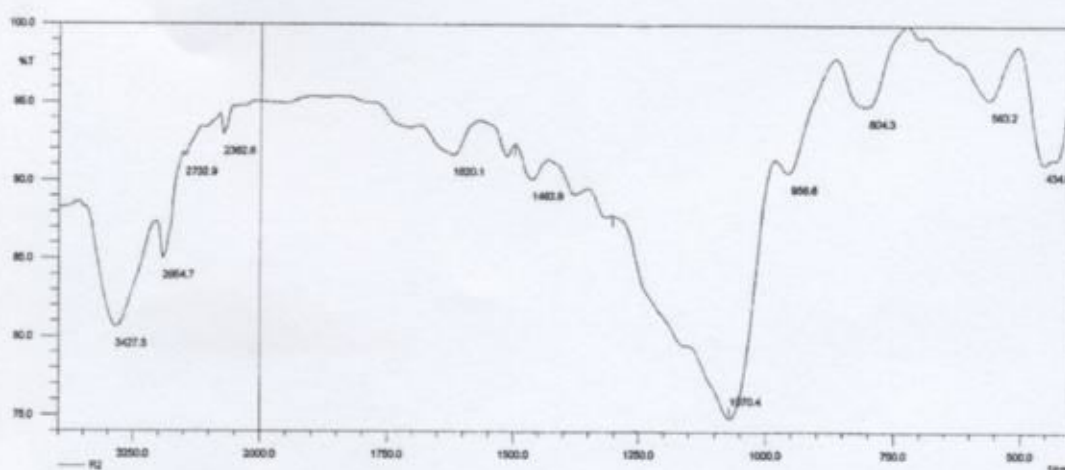


Fig. 2. FT-IR spectrum of the sol-gel. The low frequency peak near 434 cm^{-1} is assigned to Si-O-Si out of plane bending. The bands at 804 cm^{-1} and 1070 cm^{-1} are ascribed to Si-O-Si symmetric and anti-symmetric stretching vibration. The peaks at 956 and 1150 cm^{-1} are related to Si-OH and Si-O-C, respectively.

Untreated MWCNTs were heated in an oven at $350\text{ }^{\circ}\text{C}$ for 30 min to remove amorphous carbon. After thermal treatment, a half-gram of CNTs was dispersed into a flask containing 20 mL of a 70% sodium hypochlorite solution (6 mL of H_2O + 14 mL of NaClO). The solution was then shaken in an ultrasonic cleaning bath for 20 min. The resulting solution was filtered through a $0.45\text{-}\mu\text{m}$ Nylon fiber filter, yielding the activated CNTs. Finally, the CNTs were washed thoroughly with double distilled water several times until the pH of the filtrate was neutral. The filtered solid was dried in the oven at $70\text{ }^{\circ}\text{C}$, obtaining carboxylic acid-functionalized MWNTs (MWNT-COOH) [13–15,19].

2.5. Fabrication of the sol-gel/MWCNT/SPME device

The -COOH grafted onto the surface of the MWNT enhances its dispersion and compatibility. 0.03 g of the functionalized MWCNTs (F-MWCNTs) were added to 1.0 mL of sol. The mixture was agitated thoroughly for 30 min in a glass vial. Here the functionalized CNTs contribute during sol-gel fabrication by improving their solubility. Using non-functionalized CNTs, a stable homogenous solution could not be obtained. In addition, in the gelification step, SiOR chains formed in the polymerization process and contributed to the formation of the matrix structure [20].

The polypropylene microporous hollow-fiber tubes were cut into 2.0-cm segments. Each piece was used only once to decrease the memory effect. Liquid sol containing functionalized MWCNTs was injected into the fibers with a $25\text{-}\mu\text{L}$ Hamilton syringe. The pores of the hollow fiber wall were previously filled with 1-octanol. This solvent is compatible with polypropylene and easily occupies the pores. During extraction, analyte molecules use these channels for direct contact with the sorbent. Meanwhile, the pores can cause a kind of dimensional selectivity to the analyte molecules. The fiber segments were left to dry at room temperature for 1.0 hour. The solutions were aged at room temperature until the gel was formed into the fiber segments (Fig. 3).

2.6. Extraction procedure

For each experiment, 5 mL of the aqueous sample ($\text{pH} = 7$) containing the analytes was poured into a 25-mL sample vial, and the vial was placed on a magnetic stirrer. For extraction, the fiber that was impregnated with MWCNT-reinforced sol-gel was plunged into the sample solution, and the analyte travels from the donor phase to the extractor phase. Extraction was done for the optimized period of time, 20 min, at the appropriate agitation speed, 400 rpm.

After extraction, the hollow fiber was removed and plunged into 3 mL of methanol in a closed vial, and the analyte desorbed from the fiber with sonication. The extractor was measured by UV-vis spectrophotometry and HPLC. The volume of methanol as the extractor solvent for HPLC and UV-vis analysis was $40\text{ }\mu\text{L}$ (the HPLC loop volume was $20\text{ }\mu\text{L}$) and 2.5 mL, respectively.

Some of initial optimization experiments were re-checked by UV-vis spectrophotometer, but final results are related to HPLC analysis.

3. Results and discussion

3.1. Optimization

Several parameters that influence the extraction efficiency were investigated for their effect on the ageing properties: sol-gel ageing time, pH and volume of the aqueous feed, extraction time, amount of MWCNTs, agitation speed and surfactant type.

3.1.1. Effect of surfactants on sol-gel ageing time

The silicon alkoxide precursors are generally pre-hydrolyzed before the surfactants are introduced to the solution. This pre-hydrolysis step is carried out at a low pH where the hydrolysis of the alkoxide is rapid, but condensation of the silica oligomers is slow. The optimum length of pre-hydrolysis time varies from minutes to days, depending on sol concentration, water content and pH. When surfactants are added, the solution pH is also frequently adjusted to a lower value, increasing the rate of silica condensation. The sol is then aged, increasing its viscosity. This viscosity increase is often referred to gelation. The ageing time required to produce a homogeneous gel depends on the surfactant used. Surfactants like Triton X-100 that accelerate the gelling of the silica solution produce more uniform films.

Despite the fact that temperature was not carefully controlled, heating was more homogeneous, and gelation time was greatly reduced. We also found that the sol viscosity and the ability to wet substrates was related to the initial precursor decomposition in solution and the start of the polymerization process. Distinct differences were observed in sorbent characteristics when later aggregation and agglomeration processes occurred.

Sol viscosity and surface morphology of the sorbent were directly related to the age of the sol. Also, the sorbent properties were correlated to the amount of polymerization of the precursors dissolved in solution. Ageing for an extended period, however, led to a gradual decrease in the viscoelasticity of the gel, likely driven by

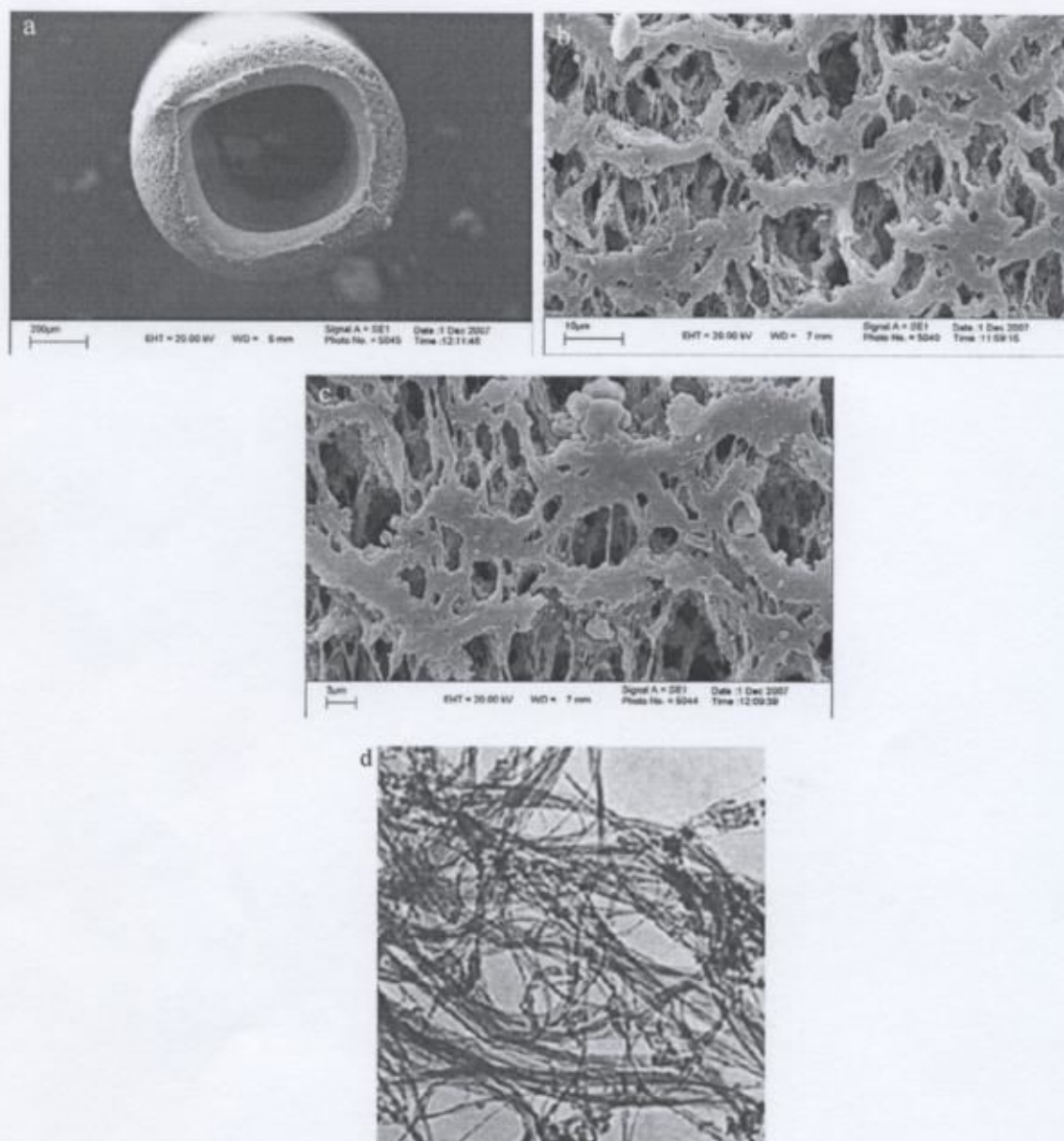


Fig. 3. SEM of a polypropylene hollow fiber. (a) Scale: 200 μm, (b) scale: 10 μm, (c) scale: 3 μm and (d) TEM of MWCNTs.

the expulsion of liquid from the gel, a phenomenon called syneresis [21].

The produced sols gradually increase in the viscosity and finally form gels. However, the ageing characteristics of such highly concentrated sols have not been well known. Furthermore, the addition of the appropriate amount of water during ageing can reduce the speed of the gelling.

The average sorption properties of the nanocomposites show an increase at around 120 min. It should also be noted that the ageing times depend dramatically on the TEOS concentration. It is expected that the increase in the viscosity might cause the formation of the network structure of silica particles.

The times of the gelling strongly depend on the concentration of TEOS, excessive value of acid (catalyses) and temperature.

Fig. 4 shows the effect of ageing time on the extraction efficiency. Different ageing times (30–150 min) were studied at room temperature. The pre-concentration for phenobarbital

increased up to 120 min, and then decreased with additional ageing time.

After the optimal ageing time, viscosity increased due to multi-dimensional network formation and polymer growths in a limited volume (inside the fiber), led to polymer network distortion, and pores disruption. Thus extraction efficiency decreased. Therefore, 120 min was selected as the optimal ageing time.

3.1.2. Effect of pH

The pH value plays an important role in this technique. A suitable pH can improve the extraction efficiency and reduce matrix interferences. To extract the basic compounds into the solid phase from the aqueous phase, the pH of the feed was basified to convert the analytes to their molecular form [19].

When the pH was lowered to 5, the amount of analyte extracted was significantly reduced due to the ionization of phenobarbital ($pK_a = 7.63$). When the pH was adjusted to higher values, the

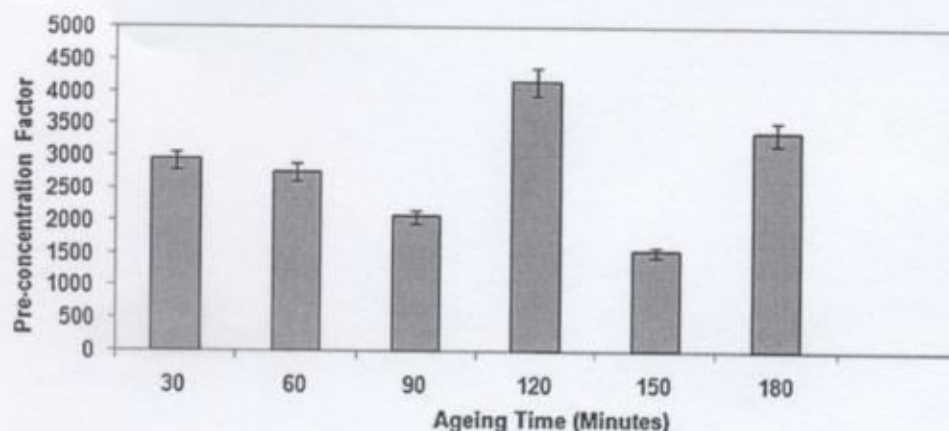


Fig. 4. Effect of sol-gel ageing time on extraction efficiency. Extraction conditions: analyte concentration, $1 \mu\text{g mL}^{-1}$; dispersed CNTs in sol-gel, 30 mg mL^{-1} ; feed solution volume, 5 mL; extraction time, 30 min; desorption time, 10 min; stirring speed, 400 rpm; temperature, $22 \pm 0.5^\circ\text{C}$.

amount extracted also decreased. These results indicate that the suitable pH for phenobarbital extraction was in the range of 6–8. Since this is the pH range of most natural water samples, it was not necessary to adjust sample pH in subsequent experiments.

On the other hand, the solubility of the MWCNTs in aqueous solution increases with decreasing pH. We studied the pH effect between 3 and 11, and the results are depicted in Fig. 5. The selected optimum pH was 7.0 for the feed solution.

3.1.3. Extraction time

Mass-transfer is a time-dependent process, and its rate affects the equilibrium conditions [22]. Since SPME is an equilibrium extraction mode, the maximum amount of analyte that can be extracted by the sorbent is achieved at equilibrium. Thus, the extraction time was examined to give the highest microextraction efficiency. Sol-gel is a porous material in which mass transfer is a process of diffusion through the pores. Therefore, the porosity of the sol-gel should strongly affect the equilibrium time for analyte extraction.

The extraction time was attributed to both the thickness and porosity of the sorbent chosen. For a thicker sorbent, the time needed for analyte diffusion into the sorbent was longer than for the thinner materials. However, a thicker sorbent provided better sensitivity because the kinetics of microextraction is dependent on diffusion of the analyte in the bulk solution and the sorbent. Analytes will diffuse faster through a thinner, porous coating than a thicker, non-porous one. But the sol-gel network is porous, and this compensates for the effect of sorbent thickness. Different extrac-

tion times of 10–40 min were evaluated at room temperature, and the extraction efficiency for phenobarbital increased up to 20 min. After this time, no significant change in extraction efficiency was observed. Therefore, an extraction time of 20 min was chosen as the optimal time.

3.1.4. Desorption conditions

The membrane was put into a test tube with proportional amount of methanol as the re-extractor phase. The volume of methanol was optimized in the range 1.0–5.0 mL and 3.0 mL yielded the best answer.

The compound extracted by the membrane was desorbed ultrasonically for the appropriate amount of time and analyzed. Different desorption times of 10–40 min were studied at room temperature. There was no significant difference between the tested times, thus a desorption time of 10 min was chosen as the optimal time.

3.1.5. Role of the amount of MWCNTs in extraction

10–50 mg of functionalized MWCNTs were evaluated in 1 mL of sol solution. The extraction efficiency dramatically increased with increasing MWCNTs, but with increasing the amount of MWCNTs (up to 50 mg), the injection of massive reinforced composite into the fiber was difficult. Moreover the air bubbles occupied the fiber spaces. Thus, 50 mg of nanotubes per 1 mL of sol solution was chosen as the optimal amount.

3.1.6. Volume of the feed solution

The volume of the donor phase was optimized, while the acceptor phase was held constant. Different donor phase volumes (1–7 mL) were studied, and 5.0 mL was selected as the optimum volume. Commonly, the extraction efficiency can be improved by increasing the volume ratio of donor to acceptor phase, but a larger sample volume can be disadvantageous due to poorer mass transfer kinetics that result in a poor extraction efficiency. This would lead to a decrease in the microextraction output [23–25].

3.1.7. Agitation speed

Agitation of the solution increases mass transfer in the donor phase, reduces the time needed to reach equilibrium, reduces the extraction time and accelerates the extraction kinetics [26,27]. Different stirring rates (200–800 rpm) were tested to determine their effects on the pre-concentration of phenobarbital. According to the experimental results, 400 rpm was selected as the optimum agitation speed. At higher agitation speeds, no significant changes were observed.

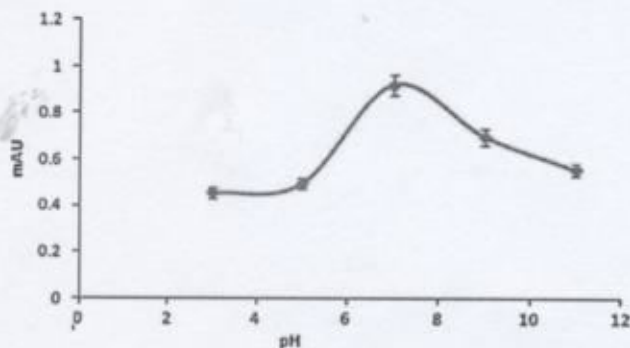


Fig. 5. Effect of feed solution pH on extraction efficiency. Extraction conditions: analyte concentration, $1 \mu\text{g mL}^{-1}$; dispersed CNTs in sol-gel, 30 mg mL^{-1} ; feed solution volume, 5 mL; extraction time, 30 min; desorption time, 10 min; stirring speed, 400 rpm; temperature, $22 \pm 0.5^\circ\text{C}$.

Table 2
Performance of the HF-SPME method.^a

Compound	Pre-concentration factor	RSD% (n = 3)	Linear range, ng mL ⁻¹	Correlation coefficient, r	LOD, ng mL ⁻¹ (n = 5)	LOQ, ng mL ⁻¹ (n = 9)
Phenobarbital	2100	2.9	0.5–5000	0.9913	0.32	0.5

^a Regression equation: $Y = 0.456X + 0.207$.

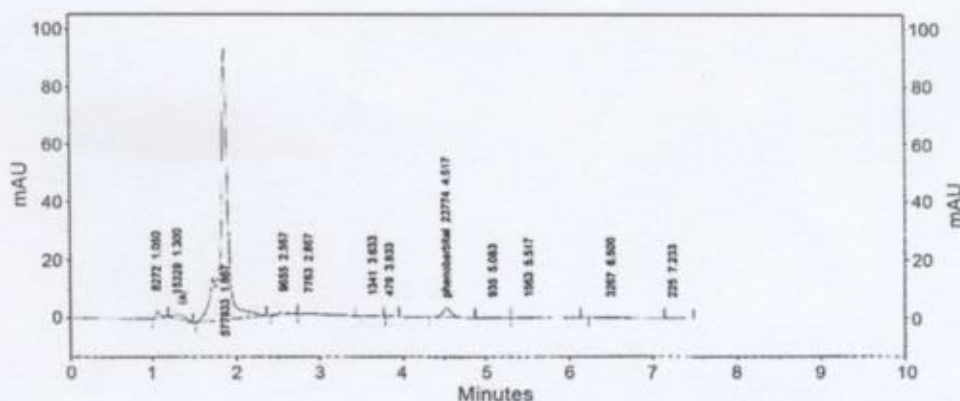


Fig. 6. HPLC chromatogram of clinical wastewater, Mashhad, Iran (spiked with 1.0 ng mL⁻¹ of analyte) from the determination of phenobarbital.

3.2. Validation of the method

The pre-concentration, correlation coefficient, repeatability, linearity and limit of detection (LOD) for the extraction of the phenobarbital from aqueous solutions were calculated experimentally under the optimized conditions. The results are summarized in Table 2. The linearity range was 0.50–5000 ng mL⁻¹ with $r = 0.9913$. The HPLC limits of detection and quantification were 0.32 ng mL⁻¹ ($n = 5$, $S/N = 3$) and 0.5 ng mL⁻¹ ($n = 5$, $S/N = 10$), respectively.

Pre-concentration factor of 2100 was obtained for phenobarbital. The chromatogram peak area after extraction of 1 $\mu\text{g mL}^{-1}$ of analyte was divided by the peak area before extraction under the same conditions. Specifically, after extraction of the analyte into the fiber, it was desorbed with 3000 μL of methanol. The peak area after this extraction was divided by the peak area of the sample before extraction and multiplied by a dilution factor ($3000/2 = 1500$). The volume of donor phase was 5.0 mL, and 2 μL was the volume of the solid sorbent spaces that were occupied by analyte molecules (i.e., the acceptor phase volume).

3.3. Environmental water sample analysis

The standard solution of phenobarbital was spiked into water samples to demonstrate the potential of this method as a viable

Table 3
RSD% and relative recovery% (RR%) of phenobarbital in clinical waste water.

Analyte	Real sample	RSD%	RR%
Phenobarbital ^a	Clinical wastewater	2.4	102

^a Spiked amount of analyte: 1.0 ng mL⁻¹.

extraction technique for environmental samples. The relative recovery of phenobarbital from clinical wastewater was determined as the ratio of the concentration in the environmental and distilled water samples spiked at the same concentration level (1.0 ng mL⁻¹) [28,29]. An average relative recovery of $102 \pm 6.4\%$ (mean \pm S.D.) was obtained for clinical wastewater samples at three concentration levels (1.0, 100.0 and 2000.0 ng mL⁻¹, $n = 5$). Samples were taken from a hospital in Mashhad, Iran. An HPLC chromatogram of a sample is shown in Fig. 6, and results are summarized in Table 3.

3.4. Method comparison

A review of selected methods used in the determination of phenobarbital in environmental and biological samples is shown in Table 4. Compared to other conventional sample-preparation methods, the developed method has the merits of improved

Table 4
Comparison of some methods which were used for determination of Phenobarbital.

No.	Date	Matrix	Extraction method	Detection	LOD (ng mL ⁻¹)	LOQ (ng mL ⁻¹)	DLR (ng mL ⁻¹)	r	RSD%	Recovery (%)	Ref.
1	1997	Human urine	SPME	GC-MS	1	-	10–1000	0.99	6.5	93–104	[30]
2	2003	Human urine	SPE	HPLC-PDA ^a	-	-	-	-	5.1	81	[31]
3	2004	Human whole blood	DI ^b -SPME	GC-MS	300	-	500–50,000	0.995	5.1–6.6	-	[32]
4	2004	Human urine	DI-SPME	GC-MS	150	-	250–25,000	0.995	4.2–7.7	-	[32]
5	2006	Plasma	SPME	LC-UV	-	5000	5000–40,000	0.997	Less 10	-	[33]
6	2006	Pork	SPE	GC-MS	0.5 ($\mu\text{g kg}^{-1}$)	1 ($\mu\text{g kg}^{-1}$)	0.5–25 ($\mu\text{g kg}^{-1}$)	-	1.6–12	84–103	[34]
7	2007	Pork	-	GC-MS-MS	0.1 ($\mu\text{g kg}^{-1}$)	0.5 ($\mu\text{g kg}^{-1}$)	0.5–50 ($\mu\text{g kg}^{-1}$)	-	2.1–7.8	75–96	[35]
8	2008	Plasma	SBSE ^c	HPLC-UV	80	-	80–40,000	-	Less 8.8	72–86	[36]
9	2008	Plasma	MIS ^d SPE	HPLC-UV	62,000	18,600	-	0.997	-	75	[37]
	2008	Water	MIS-SPE	HPLC-UV	10,000	30,000	-	-	-	-	[37]

^a PDA (photo diode array).

^b Direct immersion.

^c Stir bar-sorptive extraction.

^d Molecularly imprinted silica.

simplicity, extraction efficiency, pre-concentration, precision and sensitivity.

4. Conclusions

We have outlined the successful development and application of a new SPME method for the determination of phenobarbital in aqueous samples. MWCNTs reacted with a silica-based sol via its functional groups, and these silane-modified MWCNTs were used to prepare silica-coated MWCNTs. Due to strong interactions between modified CNTs and TEOS, a firm silica shell with a controllable uniform thickness was produced. The CNT-reinforced sol was supported by a macro-porous polypropylene membrane wall that protected the composite network structure. Functionalized MWCNTs are also compatible with the polypropylene fiber structure.

In desorption stage, the pore structure of the polypropylene fiber allows rapid exit of the analyte from the sorbent in the enriched solvent. The disposable nature of the hollow fiber completely eliminates the possibility of sample carry-over and ensures high reproducibility. In addition, the small pore size prevents large molecules in the matrix and unsolved particles in the donor solution from entering the acceptor phase, thus yielding a very clean extract [38,39].

This method is rapid, simple inexpensive, providing a high degree of sensitivity and pre-concentration. The operation is easy to handle because the receiving phase is protected by the polypropylene hollow fiber segment. Under the optimized conditions, this technique provided limits of quantitation in the ng mL^{-1} range and acceptable precision and linearity. Therefore, this method is a suitable alternative to other microextraction methods proposed for the analysis of phenobarbital in environmental samples. This technique is a novel and simple application of SPME to a wide range of analytes (i.e., metal ions to large biomolecules) due to the selective and flexible nature of the sol-gel technique and unique features of carbon nanotubes.

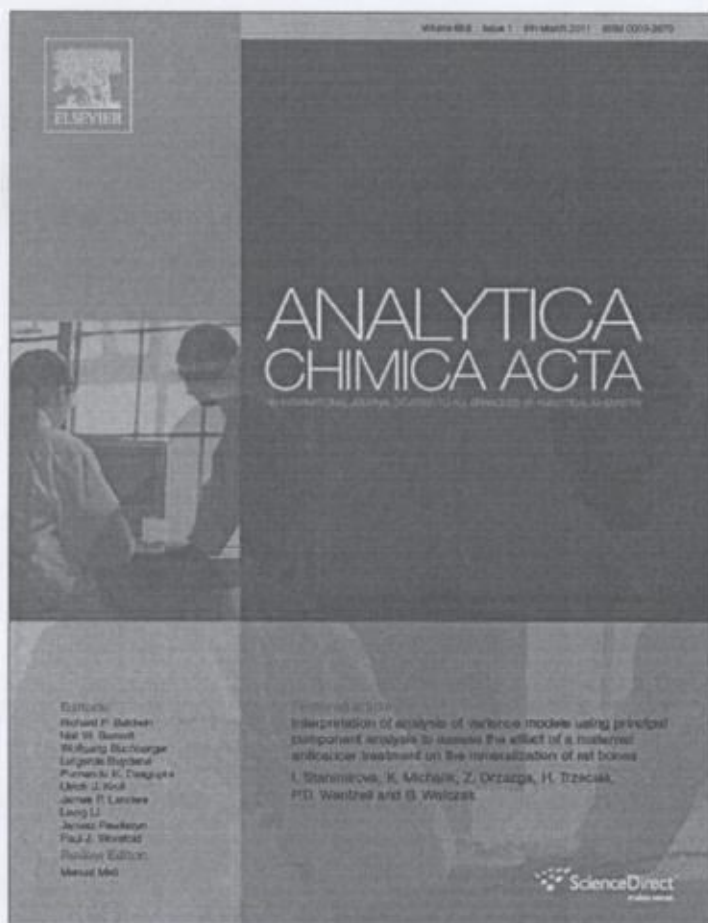
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