A New PVC-Activated Charcoal Fiber Coated on Silver Wire; Application in Determination of *n*-Alkanes in the Headspace of Soil Samples by SPME-GC

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In this study, a new solid phase microextraction (SPME) fiber based on activated charcoal and polyvinyl chloride (PVC) coated on silver wire is presented. This fiber is very mechanically and thermally stable. Unlike commercial fiber, which is coated on fused silica, this fiber has a metallic base to which the coating adheres very strongly. On the other hand, producing this fiber is very fast, and can be completed in less than 30 min. This compares favorably with the time to make a fiber based on fused silica, which may last several days, due to many steps, such as conditioning in HCl, drying, deactivation, impregnation with a binder and coating. Also, this fiber is stable up to 250°C. It has been successfully used for the analysis of *n*-alkanes in the gaseous phase and headspace of soil samples after optimization of the experimental parameters by capillary gas chromatography. The relatively high capacity of the sorbent allows 20–30% of the analytes to be transferred to a separative system during first extraction.

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Introduction

In recent years, environmental pollution by petroleum-type materials has increased with growing industries and demand for energy. Various hydrocarbons are the main constituents of petroleum, and contamination of air, soil and water by petroleum hydrocarbons is one of the most important environmental problems.

Due to the vital importance for analyzing this class of compounds, many standard methods have been presented by ASTM, EPA and API.^{1–11} In recent years, many advances have been made in the analysis of petroleum hydrocarbons. Capillary gas chromatography,^{12–14} high-performance liquid chromatography coupled with gas chromatography,¹⁵ size-exclusion chromatography,^{16–18} and many other advanced analytical methods have been used for this purpose.^{19,20}

Solid phase microextraction (SPME), which was first presented by Arthur and Pawliszyn in 1990, is a solvent-free alternative to the other common preconcentration and sample-preparation techniques.²¹ The use of various SPME fibers for environmental applications has been widely studied.²² Djozan and Assadi have reported on applications of an activated-charcoal coating on optical fiber using OV-1 silicon as a binder for the headspace microextraction of BTEX and PAHs compounds from water samples.^{23,24}

In this study, we introduced a new SPME fiber based on a solid sorbent (activated charcoal) in a polymeric matrix (PVC) coated on silver wire, and reported its application to the solid-phase microextraction of aliphatic hydrocarbons from the gaseous phase and the headspace of contaminated soil samples prior to their analysis by capillary gas chromatography. This

fiber is very durable; one fiber can be used for more than 100 samplings.

Experimental

Reagents and solutions

Extra-fine activated charcoal, polyvinyl chloride (PVC), *n*-undecane, *n*-pentadecane and THF were all of analytical grade and purchased from E. Merck (Germany). *n*-Decane, *n*-tetradecane and *n*-heptadecane were from Riedel-de Haen. He and H₂ (both with 99.999% purity) were prepared from Sabalan Co. (Tehran, Iran). Five milliliters of a standard solution of mixed analytes were prepared by weight percent; *n*-decane 14.7%, *n*-undecane 21.2%, *n*-tetradecane 9.8%, *n*-pentadecane 26.3%, *n*-heptadecane 6.7%.

Apparatus

A GC apparatus consisting of a Sanayeh Teif Gostar GC-101B, equipped with an FID detector, a data processor and a split/splitless injector was used. A Machery-Nagel Optima-17 capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm) was utilized. A laboratory-made SPME device was used in all experiments.

GC conditions

The initial column temperature was 30°C, held for 5 min, then raised at 15°C/min to 220°C and held for 5 min. Helium was used as a carrier-gas. The carrier-gas pressure was 1.2 bar, and the make-up gas pressure was 0.8 bar. The analytes were injected in the splitless mode.

Fiber preparation

First, 0.075 g of activated charcoal powder was poured into a solution of 0.025 g PVC powder in 5 mL THF and well-mixed.

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Fig. 1 Comparison of the extraction efficiencies using different compositions of activated charcoal:PVC coating.

After a few minutes, THF was evaporated until a viscose suspension was formed. A 1-cm length of silver wire, which was mounted in the laboratory-made SPME device, was successively introduced into the above-mentioned suspension. After evaporation of THF at room temperature, a very firm porous coating of the sorbent in a PVC matrix was formed on a silver wire. The fiber was then conditioned in an injection port of a gas chromatograph in 250°C for 15 min to remove any fiber contaminations.

SPME procedure from the gaseous phase

Five microliters of the analyte mixture were injected into a 10-mL vial, which was heated at 50°C. The fiber was then exposed to the gaseous phase. After 15 min the fiber was retracted and immediately transferred to the injection port of the gas chromatograph, and thermal desorption of the analytes was performed for 5 min at 250°C.

Headspace SPME procedure for soil samples

To a 10-mL vial, a 0.25 g volume of contaminated soil was added. After the vial was heated to 150°C for 5 min, its temperature was lowered to 50°C. The fiber was exposed to the headspace of the soil sample. After 15 min, extraction equilibrium was established and the fiber was retracted and transferred to the hot injection port of a gas chromatograph for thermal desorption of the analytes for 5 min at 250°C.

Results and Discussion

Selecting the optimum composition of coating

For this purpose, fibers with the following coating composition (weight percent) were prepared: activated charcoal:PVC of 25:75, 50:50, 75:25 and 90:10. The extraction procedure was performed as mentioned above, and the best composition was selected according to Fig. 1. As shown in this figure the coating with activated charcoal:PVC (75:25) composition had the maximum extraction efficiency compared with the other compositions in the adsorption of the analytes. It is mentioned that a fiber with a composition of 90:10 (activated charcoal:PVC) is very efficient in sampling lighter alkanes, but is very poor for heavier alkanes. Thus, the composition 75:25 (activated charcoal:PVC) was used in further studies.

Optimization of the microextraction temperature

In this study, the temperature had a dual effect. While high temperature is suitable for the evaporation of analytes until they are achievable to the fiber, adsorption of the analytes on the fiber is undesirable at high temperature. On the other hand, a high temperature is favorable for establishing the analyte

Fig. 2 Effect of the temperature on the amount of extracted alkanes.

Fig. 3 Effect of the temperature on the transfer of the analytes from the soil matrix to the headspace of the sample.

distribution equilibrium between the fiber and the gaseous phase. However, optimization of the extraction temperature is necessary. For this purpose, a 5 μ L standard mixture of *n*-alkanes was injected into a 10-mL vial and extraction was performed at 50, 100, 150 and 200°C. The obtained peak areas were plotted vs. temperature, and are presented in Fig. 2. As shown, *n*-decane, *n*-undecane and *n*-tetradecane have the maximum adsorption on the fiber at 50°C and all other alkanes, due to their higher boiling points, have maximum adsorption at 150°C. At all temperatures, there is a competition between the adsorption and the thermal desorption of the alkanes on the fiber, but at higher temperatures the desorption is dominated. Thus, amount of extracted alkanes at 200°C is very low. However, we selected 50°C as the experimental temperature for further studies because *n*-decane, *n*-undecane and *n*-tetradecane have maximum extraction yields at this temperature, and all others have relatively reasonable extraction yields. It is mentioned that, if 150°C would be selected as the experimental temperature, *n*-pentadecane and *n*-heptadecane would be extracted with high efficiency but all others would have very poor extraction yields. On the other hand, at 100°C, not only no obscure improvement was observed in the case of heavy alkanes, but also the extraction quantity of the light alkanes was enormously decreased. In the case of soil samples, a vial of the sample was heated at 30, 50, 100 and 150°C for 5 min and then extraction was performed after adjusting vial temperature at 50°C. The results are presented in Fig. 3. Due to the high boiling point of some analytes, the transfer of these analytes from the soil matrix to the headspace is more efficient at 150°C than at low temperatures. Thus, 150°C was selected as the experimental temperature to remove the analytes from the soil samples. Extraction was again carried out at 50°C by the fiber.

Optimization of the heating time in soil samples

For this study, the contaminated soil sample was heated at

Fig. 4 Effect of the heating time on the transfer of the analytes from the soil matrix to the headspace of the sample.

Fig. 5 Effect of time on the amount of extracted alkanes.

Fig. 6 Effect of temperature on the desorption of the analytes from the fiber.

150°C for 1, 3 and 5 min. After cooling the sample to 50°C, extraction was carried out by the fiber. Figure 4 shows that there were no considerable differences in the amount of the extracted alkanes for different heating times; therefore, the removal of alkanes from soil was very fast at 150°C. However, 5 min was selected as the heating time and was used in further studies.

Optimization of the extraction time

For optimization of the extraction time, the fiber was exposed to the headspace of a soil sample for 5, 10, 15 and 25 min. The fiber was then transferred to the injection port of the GC and the desorbed analytes were determined. As shown in Fig. 5, after 15 min the extraction equilibrium was established for all analytes.

Optimization of the desorption temperature

As mentioned above, after extraction, the fiber was immediately transferred to the injection port of the gas chromatograph. Thermal desorption was carried out at 100, 150, 200 and 250°C for 5 min. The results are shown as the peak area vs. desorption temperature in Fig. 6. At 200°C or higher, thermal desorption of the analytes from the fiber was

Fig. 7 Effect of time on the amount of desorbed alkanes from the fiber.

Fig. 8 Extraction efficiency at the SPME from a gaseous sample. Eight sequential extractions were performed.

completed. In this study we selected 250°C as the desorption temperature for further studies. It is mentioned that the fiber was completely stable at this temperature and that no additional peaks were introduced in the chromatograms from the fiber.

Optimization of the desorption time

For studying the effect of time on the amount of desorbed analytes, after adsorption of the analytes on the fiber, it was placed in the injection port of GC for 1, 3, 5 and 10 min. As shown in Fig. 7, after 1 min the desorption was completed. Owing to the rapid desorption of the analytes, no considerable peak broadening occurred.

Study of the extraction efficiency from the gaseous phase and the headspace of soil samples

In the case of the gaseous phase, eight sequential extractions were performed on a single sample. As shown in Fig. 8, the extraction efficiency of the analytes was between 20–30% in the first extraction. In most cases, commercial SPME fibers have very low capacities and rarely adsorb more than 1% of the analyte in each extraction. Therefore, in this study the fiber had a relatively high capacity, which allowed the limit of the detections to be lowered. In a soil sample, ten sequential extractions were carried out on its headspace; the results are shown in Fig. 9. The extraction efficiency for all analytes was between 15–20% at first extraction. Due to the nature of SPME, there was no need for a quantitative extraction, and the analysis could be carried out after establishing a distribution equilibrium between the gaseous phase or the headspace and the fiber.

Fig. 9 Extraction efficiency of the SPME from the headspace of a soil sample. Ten sequential extractions were performed.

Table 1 Study of the reproducibility of the proposed method in the gaseous phase and soil samples

Compound	Gaseous sample/ $\mu\text{g mL}^{-1}$			Soil sample/ $\mu\text{g g}^{-1}$		
	Added	Found	RSD, % ^a	Added	Found	RSD, %
C ₁₀ H ₂₂	4.35	4.34 $\pm$ 0.07 ^b	1.61	87.0	87.0 $\pm$ 3.15	3.62
C ₁₁ H ₂₄	6.28	6.30 $\pm$ 0.42	6.66	126	126 $\pm$ 5.29	4.19
C ₁₄ H ₃₀	2.92	2.90 $\pm$ 0.14	4.82	58.5	58.6 $\pm$ 3.51	5.98
C ₁₅ H ₃₂	7.78	7.75 $\pm$ 0.21	2.70	156	154 $\pm$ 12.45	8.09
C ₁₇ H ₃₆	2.00	1.99 $\pm$ 0.01	0.50	40.1	40.3 $\pm$ 2.82	6.99

a. Relative standard deviation ($n = 3$).

b. Mean concentration $\pm$ standard deviation ($n = 3$).

Table 2 Quantitative characteristics of the proposed method for gaseous samples

Compound	Calibration curve equation	r^a	LOD ^b	LDR ^c
C ₁₀ H ₂₂	$A = 6.06 \times 10^5 C + 6.62 \times 10^{4d}$	0.994	0.20	0.70 – 216
C ₁₁ H ₂₄	$A = 4.04 \times 10^5 C + 1.13 \times 10^5$	0.994	0.10	0.30 – 314
C ₁₄ H ₃₀	$A = 9.50 \times 10^4 C + 5.23 \times 10^4$	0.995	0.02	0.07 – 292
C ₁₅ H ₃₂	$A = 7.30 \times 10^4 C + 1.22 \times 10^5$	0.995	0.05	0.20 – 776
C ₁₇ H ₃₆	$A = 5.53 \times 10^4 C + 1.23 \times 10^4$	0.996	0.05	0.20 – 150

a. Correlation coefficient.

b. Limit of detection ($\mu\text{g mL}^{-1}$).

c. Linear dynamic range ($\mu\text{g mL}^{-1}$).

d. A and C are peak area and concentration of the analytes ($\mu\text{g mL}^{-1}$), respectively.

Quantitative characteristics of the proposed method

In additional studies, further experiments were performed to assess the reproducibility of the method. For this purpose, three replicate determinations were carried out, and the relative standard deviations were calculated (Table 1). These results show that the RSD% for all compounds was less than 9%, which indicates that the proposed method is reproducible. Also, other characteristics, such as the calibration curve equations, correlation coefficients, limits of detection (LOD) and linear dynamic ranges, are summarized in Tables 2 and 3. The correlation coefficients were higher than 0.994 for all compounds in gaseous samples and higher than 0.995 for them in the headspace of soil samples. Relatively low detection

Fig. 10 Typical gas chromatogram of a) *n*-alkanes standard mixture in gaseous phase, b) gaseous sample containing kerosine, c) *n*-alkanes in headspace of a soil sample.

Table 3 Quantitative characteristics of the proposed method for soil samples

Compound	Calibration curve equation	r^a	LOD ^b	LDR ^c
C ₁₀ H ₂₂	$A = 1.58 \times 10^4 C + 2.47 \times 10^{4d}$	0.995	16.00	50 – 7000
C ₁₁ H ₂₄	$A = 1.52 \times 10^4 C + 4.74 \times 10^4$	0.998	6.00	20 – 25000
C ₁₄ H ₃₀	$A = 2.53 \times 10^4 C + 4.94 \times 10^3$	0.999	4.00	15 – 8700
C ₁₅ H ₃₂	$A = 2.35 \times 10^4 C + 1.00 \times 10^4$	0.999	6.00	20 – 15000
C ₁₇ H ₃₆	$A = 3.92 \times 10^4 C - 1.20 \times 10^4$	0.997	7.00	25 – 1000

a. Correlation coefficient.

b. Limit of detection ($\mu\text{g g}^{-1}$).

c. Linear dynamic range ($\mu\text{g g}^{-1}$).

d. A and C are peak area and concentration of the analytes (mg g^{-1}), respectively.

limits (0.02–0.2 $\mu\text{g mL}^{-1}$ for gaseous samples and 4–16 $\mu\text{g mL}^{-1}$ for soil samples) and extent linear ranges are two other advantages of the presented method. It is mentioned that the upper limits of the linear ranges are limited by the constant adsorption capacity of the fiber.

Analysis of real samples

To evaluate the efficiency of the proposed method in real samples, a gaseous sample contaminated with kerosine and a soil sample collected from around of a domestic fuel reservoir were selected, and this method was used to determine some *n*-alkane contents of these samples. The obtained results from two of the above samples are listed in Table 4. Also, typical chromatograms of the extracted *n*-alkanes from the gaseous phase and the headspace of the soil sample are shown in Fig. 10.

Table 4 Results obtained from the analysis of real samples

Compound	$C \pm SD^a$	
	Gaseous sample/mg mL ⁻¹	Soil sample/mg g ⁻¹
C ₁₀ H ₂₂	ND ^b	ND
C ₁₁ H ₂₄	ND	ND
C ₁₄ H ₃₀	ND	0.43 $\pm$ 0.01
C ₁₅ H ₃₂	ND	1.01 $\pm$ 0.08
C ₁₇ H ₃₆	0.15 $\pm$ 0.01	0.54 $\pm$ 0.02

a. Mean concentration $\pm$ standard deviation ($n = 3$).

b. Not detected.

Conclusions

In this study, a very durable, high-capacity fiber based on activated charcoal and PVC was presented. It was used for sampling *n*-alkanes from the gaseous phase and the headspace of soil samples. Equilibration between the gaseous phase and the sorbent was established in less than 15 min for all analytes. The proposed method is simple, rapid, cheap and solvent-free. By this method, the alkane content of the real samples could be successfully analyzed.

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