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Analysis of *n*-alkanes in water samples by means of headspace solvent microextraction and gas chromatography

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Abstract

A simple and efficient headspace solvent microextraction (HSME) was developed for the simultaneous determination of the trace concentrations of some *n*-alkanes in water samples. Therefore, a microdrop of an organic solvent was extruded from the needle tip of a gas chromatographic syringe to the headspace above the surface of the solution in a sealed vial. Then the volatile organic compounds are extracted and concentrated in the microdrop. Next, the microdrop was retracted into the microsyringe and injected directly into the gas chromatograph. Experimental parameters which control the performance of HSME such as the type of microextraction solvent, organic drop and sample volume, sample stirring rate, sample solution and microsyringe needle temperatures, salt addition and exposure time profiles were investigated and optimized. Finally, the enrichment factor, dynamic linear range (DLR), limit of detection (LOD) and precision of the method were evaluated. Using optimum extraction conditions, good linearity with correlation coefficients in the range of $0.995 < r^2 < 0.999$, suitable precision ($\%2.3 < \text{R.S.D.} < \%7.2$) and low detection limits (0.1–4.0 μg/l) were achieved. The HSME was performed for determination of *n*-alkanes in different types of natural water samples and acceptable recoveries were obtained. The results demonstrated that HSME is a rapid, accurate and effective sample preparation method and could be successfully applied for the determination of *n*-alkanes in water samples.

Keywords: Headspace solvent microextraction; *n*-Alkanes; Gas chromatography

1. Introduction

Environmental contamination by petroleum hydrocarbons is the most common site contamination issue encountered by environmental professionals [1]. In recent years, environmental pollution by petroleum-type materials has increased with the growth of industries and increased demand for energy [2]. The nature of petroleum hydrocarbon contamination is highly variable. Petroleum hydrocarbons themselves are diverse mixtures of chemical components. The more common functional categories of compounds found in petroleum products are *n*-alkanes, branched alkanes, cycloalkanes and aromatic compounds [1].

Organic contamination results from the uncontrolled releases from manufacturing and refining installations, spillage during transportation, underground storage tanks, above ground storage tanks, pumps or dispensers, fuel lines between the tanks and pumps, fill points and lines (normally remote from the tanks), air vent pipelines, waste oil tanks, drum storage and filling areas and storm water interceptors [3,4]. It has been estimated that around 20×10^6 t of petroleum hydrocarbons (mainly *n*-alkanes) impact marine waters and estuaries annually [5]. Therefore, analysis of environmental samples polluted by crude oil or petroleum products is important [3].

In order to determine trace level of these pollutants, an extraction and preconcentration step is necessary. The most difficult and time-consuming step in the determination of organic pollutants in environmental samples is extraction of the analytes from the matrix [6]. Trace enrichment can be performed by conventional techniques such as liquid–liquid extraction (LLE), purge and trap (P&T), solid-phase extraction (SPE) or solid-phase microextraction (SPME) and liquid phase microextraction (LPME) methods [7].

In view of the analysis of volatile organic compounds in water, conventional LLE often needs large amounts of toxic solvents and time-consuming procedures [8]. P&T method, also known as the dynamic headspace method, removes volatile com-

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pounds from the sample matrix by passing an inert gas such as helium or nitrogen through the matrix [9]. This method is, however, more time-consuming [10,11].

Solid phase extraction (SPE) is a more rapid and modern alternative to liquid–liquid extraction.

The drawbacks of SPE are:

- Although solvent use is small, its flow rate affects the recovery.
- For heavily contaminated samples, it is possible to get analyte break through.
- In order to have high and stable recovery rates, it is important to choose the most appropriate solid phase for the target compounds [9].

Solid-phase microextraction (SPME) was proposed in 1989 by Belardi and Pawliszyn [12]. This technique eliminates most drawbacks of the conventional extraction techniques. It is experimentally simple, fast and requires no solvents. Further, the sampling can be carried out directly under field or on-line conditions [13]. SPME has achieved tremendous success and has been widely used for drugs, food and environmental pollutants [14–17]. It also is regarded as a rugged, sensitive and accurate method. SPME has some disadvantages such as: (a) it is still relatively expensive, (b) the polymer coating is fragile and easily broken, and (c) the sample carryover is sometimes difficult or impossible to be eliminated [18].

Recently, headspace solvent microextraction (HSME) has been developed as a solvent-minimized pretreatment technique, which is fast, simple and inexpensive. This novel technique eliminates disadvantages of the conventional extraction methods such as LLE and P&T which are time-consuming and use specialized apparatuses. Since very little solvent is used, there is minimal exposure to the toxic organic solvent for the operator. At the same time, HSME combines extraction, concentration and sample introduction in one step [19]. HSME has been successfully applied for the determination of volatile organic compounds including alcohols [13], polycyclic aromatic hydrocarbons (PAHs) [20], aliphatic amines [21] and BTEX [6] from water samples.

The objective of the present study was to investigate the applicability of HSME to determine *n*-alkanes in aqueous matrices. The effect of several experimental variables such as extraction solvent, solvent volume, agitation speed of the sample and the temperature of the sample and microsyringe needle on the extraction efficiency were investigated and optimized. The optimized conditions were applied to the tap, river and waste water samples in order to evaluate the application of this method to real samples.

2. Experimental

2.1. Reagents

n-Alkanes were purchased from Ultrascientific and Merck companies. The stock standard solutions were prepared in acetone with the concentration level of 100 mg/l for heptane, octane, nonane, undecane, tetradecane, hexadecane and 200 mg/l for octadecane and docosan, and stored in a freezer at about −10 °C. Then, the working standard solutions were freshly prepared by diluting the mixed standard solution with doubly distilled water to the required concentration. The organic extractant was *n*-dodecane containing a fixed amount of toluene as internal standard.

2.2. Apparatus

The extraction and injection procedure were carried out using a Hamilton 10-μl syringe. The solution was stirred using a magnetic stirrer (heidolph MR 3001 K) and an 8 mm × 1.5 mm stirring bar. A circulating water bath (Frigomix, B. Braun UM-S) was used for adjusting the temperature of the syringe needle with the accuracy of ±0.1 °C. Also, a two compartment-recirculating cell fabricated from PVC and a small bore stainless steel tube (1/16′ o.d.) mounted inside the PVC cell, was used to control the temperature of microsyringe needle. In order to reach to a temperature very close to the temperature of the cooling bath, the internal surface of the inner tube was just touching the external surface of the microsyringe needle. A simple water bath, placed on a hot plate, was used for controlling the temperature of the samples.

Separation and quantification of *n*-alkanes were performed using a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector (FID) and a DB-5 (5% phenyl +95% methylpolysiloxane) fused-silica capillary column with a 20 m × 0.53 mm i.d. and 1.5 μm film thickness (J&W Scientific, Folsam, CA). The injector and detector temperatures were 260 and 270 °C, respectively. The GC split valve was open and helium was used as carrier gas to give a 5 ml/min column flow and 5 ml/min split line flow. The detector gasses flow rates were 300 ml/min of air and 30 ml/min of hydrogen.

The column temperature was held at 40 °C for 2 min, and then raised to 120 °C at a rate of 8 °C/min, followed by a second ramp (20 °C/min) to a final temperature of 260 °C for 5 min.

2.3. Extraction procedure

Aqueous standard solutions of *n*-alkanes at the concentration level of interest were prepared daily by spiking doubly distilled water. A 6 ml of the mixture was pipetted into a 10 ml vial with a PTFE-silicon septum (Supelco). A fixed concentration (20 mg/l) of toluene, as internal standard, was prepared in *n*-dodecane, as extracting solvent. The Hamilton syringe was completely washed with methanol, and then with acetone. After drying, it was rinsed and primed at least 10 times with the extracting solvent. After the uptake of 3 μl of the solvent, the needle of the syringe was inserted into the internal tube of the two-compartment cell above the extraction vial, pierced the vial septum and then was clamped in such a way that the position of the needle in the headspace was constant. The plunger was depressed to cause the solvent to form a drop suspended from the tip. After extracting for a prescribed period of time, the solvent drop was retracted into the microsyringe and directly injected into the GC for analysis. All quantifications made in

this study were based on the relative peak area of analyte to the internal standard (toluene) from the average of three replicate measurements.

3. Results and discussion

This study explored the applicability of HSME to the analysis of *n*-alkanes in aqueous matrices. To develop HSME method for determining *n*-alkanes, several parameters controlling optimum performance, such as type of the organic solvent used as extractant, temperature of microdrop and sample solution, stirring rate, ionic strength, microdrop and aqueous solution volumes and extraction time were assessed. Also the parameters related to HSME were optimized utilizing the univariant method for simplifying the optimization procedure.

3.1. Selection of organic solvent

The selection of an appropriate extraction solvent is of great importance for the optimization of HSME process. The extraction solvent has to confirm three requirements: to have low volatility in order to be stable at the extraction period, to extract analytes well and to be separated from the analyte peaks in the chromatogram [13,20]. Accordingly, several extracting solvents were investigated, including benzene, toluene, 1-butanol, benzyl alcohol, *n*-heptane and *n*-dodecane, of which, *n*-dodecane was found to get the best extraction efficiency, while its chromatographic peak was easily separated from the sample peaks. Also because of its low vapor pressure at the extraction condition, the microdrop was stable at the extraction period. Therefore, *n*-dodecane was selected as the extraction solvent.

3.2. Sample solution and microsyringe needle temperature

In headspace mode sampling, the analytes need to be transported through the barrier of air before reaching the drop. Temperature has a significant effect on both the kinetics and the thermodynamics of the process. Temperature affects the kinetics of sorption in the microdrop by changing the vapor pressure of the analytes and diffusion coefficient values in all three phases [6]. In this work, we used a device that allows the sample to be heated and the microdrop to be cooled independently. This process facilitates mass transfer of the analytes from the sample to the microdrop, and thus increases the efficiency of the extraction.

The effect of sample solution temperature on the extraction efficiency in the range of 23–45 °C was studied by exposing an *n*-dodecane drop for 7 min in the headspace of the water samples (at a level of 100 μg/l for each *n*-alkane). Experimental results showed that, by increasing the temperature, the extraction efficiency was increased (Fig. 1). This can be explained by the fact that at higher temperatures, the vapor pressure of the analytes and, hence, their concentrations in the headspace increase. The amounts of the extracted analytes decreases above 35 °C, probably due to the decreasing of the partition coefficients of analytes between head space and the extraction phase. On the other hand, high temperatures can cause solvent drop damage and decrease the reproducibility of HSME procedure [21,22]. Thus, in further experiments the sample vial temperature was held at 35 °C. Variations of the extraction efficiency with microsyringe needle temperature in the range of −8 to 10 °C is shown in Fig. 1. According to this observation, maximum extraction occurred at −4 °C. By decreasing the microsyringe needle temperature, the extraction efficiency was increased; because extracting into the microdrop is an exothermic process, so decreased temperature enhanced the partition coefficients and the flux of the analytes into the microdrop [20]. At low temperatures (<−4 °C), viscosity of *n*-dodecane increases and the partition coefficients of the analytes into the extraction phase decreases. Consequently, all the other experiments were carried out at microsyringe needle temperature of −4 °C.

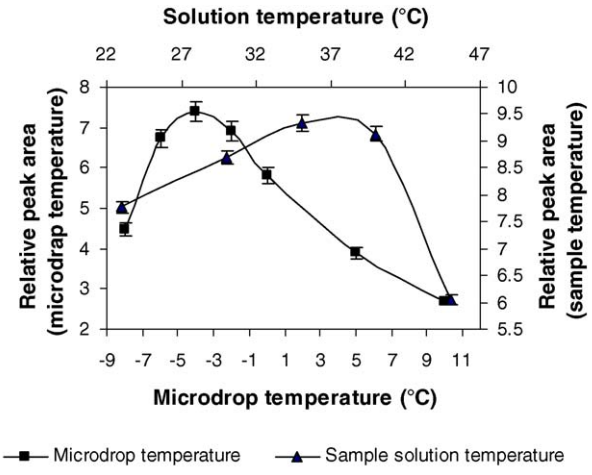

Fig. 1. The effect of aqueous sample and microsyringe needle temperatures on the relative peak area. Extraction conditions: microdrop volume, 3 μl; sample volume, 6 ml; stirring speed, 500 rpm; extraction time, 10 min and without salt addition.

3.3. Microdrop volume

The volume of extraction solvent has great effect on the extraction efficiency. For studying the effect of organic drop volume on the analytical signal, some experiments was performed by increasing the drop volume from 1.0 to 3.0 μl (at 100 μg/l level of each *n*-alkane). The effect of microdrop volume on the analytical signal is shown in Fig. 2. As it was expected, an increase in the volume of the microdrop (up to 3 μl) resulted in a sharp increase in the extraction efficiency of the system. However, at larger volumes (i.e. >3 μl), the microdrop revealed a great tendency to fall down from the tip of the microsyringe. Therefore, the drop volume of 3.0 μL was selected for the subsequent experiments [4].

3.4. Sample volume

During the headspace extraction process, sample volume can influence the magnitude of the headspace, and thus might influence the extraction efficiency. In order to study the effect of the sample volume on the extraction efficiency, some experiments were carried out using 10 ml vials and the volumes of samples were increased from 2 to 8 ml. The results showed that the largest

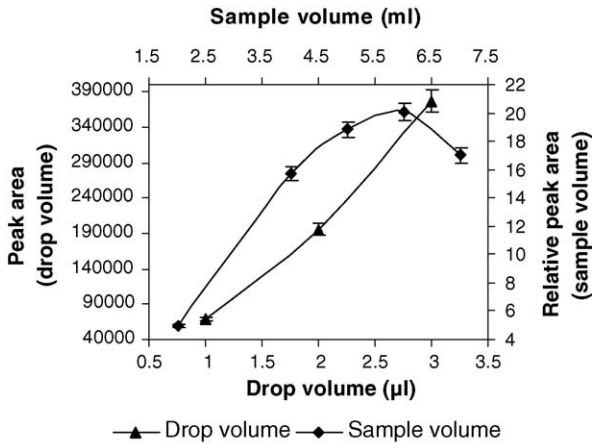

Fig. 2. The effect of microdrop and sample volumes on the peak area and relative peak area, respectively. Extraction conditions: microsyringe needle and sample temperatures, −4 and 35 °C, respectively; stirring speed, 500 rpm; extraction time, 10 min and without salt addition.

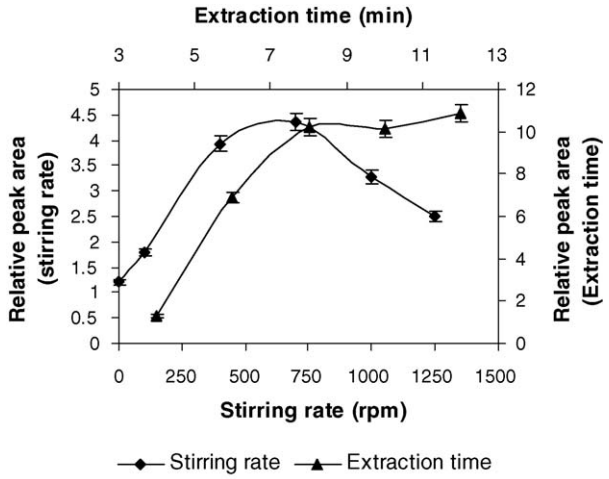

Fig. 3. The effect of stirring rate and extraction time on the relative peak area. Extraction conditions: microsyringe needle and sample temperatures, −4 and 35 °C, respectively; microdrop volume, 3 µl; sample volume, 6 ml and without salt addition.

analytical response was obtained at the sample volume of 6 ml (Fig. 2). Further increasing of the sample volume resulted in the decreasing of the peak area. At the beginning, by increasing the sample volume, the headspace volume decreases which accelerates the diffusion of the analytes into the drop until saturation. Upon stirring the solution at a fixed rate with a large volume, the convection is not as good in the aqueous phase, resulting in less extraction. Therefore, the volume of 6 ml was chosen as the optimal sample volume [20,23].

3.5. Stirring rate

Agitation of the sample enhances the extraction rate, and therefore reduces the extraction time because the equilibrium between the aqueous and vapor phases can be achieved more rapidly [24]. In this work, the samples with a volume of 6 ml were continuously agitated at different stirring rates (0, 100, 400, 700, 1000, 1250 rpm) with a 8 mm stirring bar on a stirrer plate. According to Fig. 3, the relative peak area increases with increasing stirring rate up to 700 rpm. Faster stirring rates were avoided as they resulted in dislodgement of the organic drop from the needle. Hence, a stirring rate of 700 rpm was chosen for further studies [21].

3.6. Ionic strength

The effect of ionic strength of the sample solutions on the extraction efficiency was evaluated by increasing NaCl concentration from 0 to 4 mol/l in spiked water samples (at a 100 µg/l level of each *n*-alkane). The results showed that the headspace extraction efficiency of *n*-alkanes was not changed with the increasing concentration of NaCl. Hence, further extractions were performed in the absence of any salt addition.

3.7. Extraction time

For increasing the precision of the HSME method, it is necessary to choose a suitable extraction time in which the equilibrium between the microdrop, the headspace and sample solution is reached [13]. A series of experiments were performed to determine the optimum extraction time. As Fig. 3 shows, the relative peak areas increase by increasing the exposure time. It also shows that the analytical signal increases by the increase of the extraction time from 1 to 8 min, and then remains constant. The first stage corresponds only to the analyte extraction from the headspace. As soon as the headspace concentration of the analyte falls below the equilibrium value with respect to the aqueous phase, analyte molecules begin to diffuse from the aqueous phase to the gaseous phase, which is a rate-determining step. Since it is not practical to wait the equilibrium to occur, the extraction time should be just long enough in order to slow down the extraction rate, and consequently to improve the precision. Thus, an exposure time of 8.0 min was selected for the subsequent experiments [6].

3.8. Evaluation of method performance

Linearity of the proposed HSME method for determining *n*-alkanes in the water samples was evaluated using GC-FID under optimal experimental conditions. Calibration curves were prepared between 0.5 and 800 µg/l. At each concentration, at least three runs were carried out with the independent samples. The corresponding regression equations, correlation coefficients (r^2) and dynamic linear ranges (DLR) are listed in Table 1. Detection limits (LODs) were calculated based on the signal that differed three times from the blank average signal. The obtained LODs were in the range of 0.1–4 µg/l (Table 1).

In order to investigate the preconcentration factors of each *n*-alkane, three replicate extractions were performed at optimal conditions from the aqueous solutions containing 100 µg/l of each *n*-alkane. The preconcentration factor was calculated as the ratio of the final concentration of the analytes in the microdrop and their concentration in the original solution. To obtain the

Table 1
Limit of detections, regression equations, correlation coefficients, dynamic linear ranges, relative standard deviation and preconcentration factors for HSME of *n*-alkanes

Analyte	LOD (μg/l)	r^2	Regression equation[a]	DLR (μg/l)	%R.S.D.	Preconcentration factor
n-Heptane	0.1	0.9974	$Y=0.0032C+0.026$	0.5–400	6.1	809
n-Octane	0.1	0.9969	$Y=0.0037C+0.044$	0.5–400	5.7	475
n-Nonane	0.2	0.9957	$Y=0.0032C+0.046$	1–400	7.2	297
n-Undecane	0.4	0.9973	$Y=0.0018C+0.026$	1–400	6.5	169
n-Tetradecane	1.1	0.9982	$Y=0.0003C+0.002$	5–300	2.3	87
n-Hexadecane	2.0	0.9978	$Y=0.0004C-0.001$	5–200	2.7	81
n-Octadecane	2.7	0.9976	$Y=0.0003C+0.002$	5–200	2.7	63
n-Eicosane	4.0	0.9993	$Y=0.0001C+0.0014$	10–200	3.4	55

[a] Concentration unit is (μg/l).

final concentration of *n*-alkanes in the microdrop, the standard solutions of *n*-alkanes were prepared in *n*-dodecane as solvent and the solutions were injected into GC-FID injection port and calibration curves were obtained. Finally the extracted analytes were injected into GC-FID and the actual concentration of each extracted analyte in *n*-dodecane was calculated from the related calibration curve and the preconcentration factors were determined and summarized in Table 1.

Finally, the proposed HSME method was applied to determine the concentrations of *n*-alkanes in different spiked real samples (tap water, waste water, river water and two well waters). Table 2 shows that results of five replicate analysis of each water sample obtained by the proposed method and the added amount of *n*-alkanes are in satisfactory agreement. On the other hand, the proposed method revealed good reproducibilities with percent relative standard deviations (R.S.Ds.) value in the range of 2.3–7.2%. Fig. 4 shows the chromatogram of the real and spiked water samples after headspace extraction with a 3 μl drop of *n*-dodecane containing 20 mg/l toluene, as internal standard, at optimum working conditions (extraction time: 8 min; drop volume: 3 μl; stirring rate: 700 rpm; sample temperature: 35 °C; microsyringe needle temperature: −4 °C; sample volume: 6 ml, spiked concentration of *n*-heptane, *n*-octane, *n*-nonane and *n*-undecane is 15 μg/l and for *n*-tetradecane, *n*-hexadecane, *n*-octadecane and *n*-eicosane is 30 μg/l).

It is worth to note that the concentrations of some *n*-alkanes such as dodecane to eicosane reported here are higher than their solubility (1–4 $\mu g\,l^{-1}$) in aqueous solution [26]. As we mentioned in the introduction section, annually several million tons of hydrocarbons enter into marine waters. This large amount of hydrocarbons is not soluble in water but they exist as emulation or floating forms. In a HSME there is equilibrium between microdrop, headspace and mixture, thus we are able to evaluate the concentration of the hydrocarbons in the mixture. Concentration as high as 4500 $\mu g\,l^{-1}$ have been reported for *n*-alkanes in water samples using headspace SPME [3,25]. Similar results have been obtained for determination of PAH's in aqueous solutions using HSME [20].

Table 2
Determination of *n*-alkanes in spiked water samples (spiked concentrations of *n*-heptane, *n*-octane, *n*-nonane and *n*-undecane is 15 μg/l and for *n*-tetradecane, *n*-hexadecane, *n*-octadecane and *n*-eicosane is 30 μg/l)

Sample		*n*-Heptane	*n*-Octane	*n*-Nonane	*n*-Undecane	*n*-Tetradecane	*n*-Hexadecane	*n*-Octadecane	*n*-Eicosane
Well water 1	Concentration	77.1	20.0	22.5	94.3	12.2	10.6	21.8	16.5
	Found	94.3	33.4	39.5	107.6	39.9	42.8	49.8	44.7
	%Recovery	114.7	89.3	113.3	88.7	92.3	107.3	93.3	94.0
Well water 2	Concentration	–	–	–	–	–	–	–	–
	Found	13.9	16.3	15.6	14.7	27.9	29.8	33.1	31.7
	%Recovery	92.7	108.7	104.0	98.0	93.0	99.3	110.3	105.6
Tap water	Concentration	–	–	–	–	–	–	–	–
	Found	15.3	17.1	14.7	16.1	31.7	32.9	29.1	28.3
	%Recovery	102.0	114.0	98.0	107.0	106.6	109.6	97.0	94.3
Waste water	Concentration	–	–	–	–	–	–	–	–
	Found	12.3	13.7	12.9	15.3	27.3	26.8	25.2	26.1
	%Recovery	82.0	91.3	86.0	102.0	91.0	89.3	84.0	87.0
River water	Concentration	–	–	–	–	–	–	–	–
	Found	14.2	16.3	15.3	13.9	33.2	29.7	34.4	28.2
	%Recovery	94.7	108.7	102.0	92.7	110.7	99.0	114.7	94.0
Sea water	Concentration	–	–	–	–	–	–	–	
	Found	13.4	14.1	12.3	13.7	27.1	29.2	26.9	27.6
	%Recovery	89.3	94.0	82.0	91.3	90.3	97.3	89.7	92.0

Table 3
Comparison of HSME and SPME in determination of *n*-alkanes

Ext. method	Detection technique	LOD (μg/l)	DLR (μg/l)	r^2	R.S.D.%	Ext. time (min)	Ref.
Proposed method	GC-FID	0.1–4	0.5–400 to 5–200	0.9957–0.9993	2.3–7.2	8	–
Direct SPME	GC-FID	0.1–0.3	0.5–30	0.990–0.999	4.78–9.54	20	[3]
Headspace SPME	GC-FID	50–150	150–3000 450–4500	0.990–0.998	2.3–8.6	20	[25]

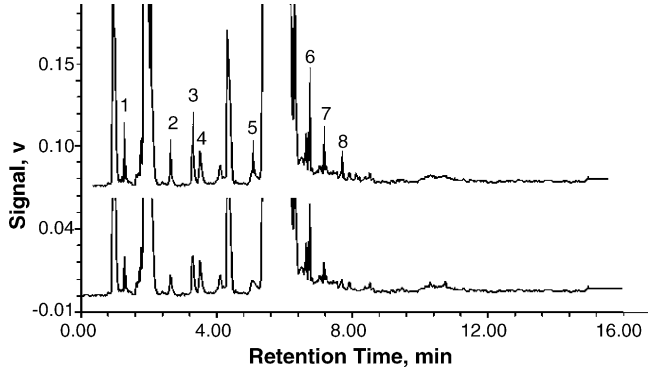

Fig. 4. Chromatogram of the well water and spiked well water after HSME at optimum conditions. Column temperature programming: 40 °C for 2 min, then raised to 120 °C at 8 °C/min, and to 260 °C at 20 °C/min, then held at 260 °C for 5 min. (1) *n*-Heptane; (2) *n*-octane; (3) internal standard (toluene); (4) *n*-nonane; (5) *n*-undecane; (6) *n*-tetradecane; (7) *n*-hexadecane; (8) *n*-octadecane and (9) *n*-eicosane.

4. Conclusions

HSME technique coupled with capillary column gas chromatography-flame ionization detector was successfully applied to determine *n*-alkanes in water samples. After optimization of the extraction conditions for the target analytes, the detection limits of 0.1–4 μg/l were achieved. The relative recoveries, obtained in several real water samples, were between 82 and 114.7% and the R.S.D. values were found to be in the range of 2.3–7.2% for drinking water. In comparison with the other methods of *n*-alkanes determination, HSME integrates sampling, extraction, concentration and sample introduction into a single step [20]. The developed headspace solvent microextraction technique has a number of advantages including: (1) renewable drop (no sample carryover); (2) high sensitivity and low detection limit; (3) good precision; (4) wide selection of available solvents; (5) low cost; (6) simplicity and ease of use; (7) minimal solvent use; (8) short extraction time; (9) possibility of automation; (10) no conditioning required; and (11) no need for instrument modification [6]. A comparison between SPME [3,25] and HSME methods (Table 3), for the extraction of *n*-alkanes revealed that although they have similar capabilities in terms of precision, speed of analysis, and LODs, the latter has no limitation on the selection of solvents. It also requires negligible cost for microliter amounts of the solvent. In addition, the absence of the solvent peak in the headspace SPME chromatogram is an obvious advantage; however, this advantage is offset by the high cost and more elaborate apparatus, comparing to the HSME apparatus [3,20].

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