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SPME–GC determination of methanol as a hydrate inhibitor in crude oil

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ABSTRACT

This work focused on the quantitation of methanol as a hydrate inhibitor in the crude oil. The novelty is microextraction of a polar compound from a complex non-polar matrix and selection of proper fiber with maximum selectivity, loading percent, and lifetime. This approach not only does not require specific instrumentation, such as multiple columns, and selective detectors, but also has eliminated the use of organic solvent and avoids the insertion of water inside the GC columns. The objective is optimization of extraction conditions, GC adjustments and data processing. Experiments were conducted on the real sample of Iranian offshore crude oil by a carboxen/PDMS fiber via a GC equipped with a cross-linked polyethylene glycol column and FID. The results revealed that this fiber adsorbed the alcohols among other light non-polar compounds of crude oil. Moreover, the interference effects of ethanol were solved by proper selection of thermal program. The LOD, LOQ and linear range of this approach were determined to be 3.9, 12.9 and 14–229 mg L^{-1} for methanol, respectively. Moreover, the sensitivity was 30 area-counts per mg L^{-1}. Using the standard calibration and the standard addition methods, the relative errors of 1.6–7.2 and 5.3–14.0% were determined, respectively.

1. Introduction

The two most common hydrate inhibitors added to crude oil are methanol (MeOH) and triethylene glycol. The main problems in performing a chromatographic analysis of methanol in crude oil are the pyrolysis of crude oil and the co-elution of aliphatic compounds with methanol. Therefore, several approaches have been used; as using two or more columns of different polarities, an oxygen selective detector and pre-extraction methods, in which injecting water into the gas chromatograph (GC) slightly damages the column.

Solid phase microextraction (SPME) solves this problem since no solvent is introduced into the GC column. It was invented by Dr. Pawliszyn in 1989 [1], allows solvents and interferences removal using a fiber.

SPME techniques are widely used for determination of trace materials, which some of them can be exampled as determination of volatile and semivolatile pollutants in soils [2], methyl *tert*-butyl ether in gasoline [3] and water [4], organophosphate esters in water [5], organochlorine pesticides in the water [6], organophosphorus pesticides in water [7], hydrocarbons in old creosote [8] and concentrated volatile products from thermal degradation of polymers [9].

For determination of methanol in organic matrices, Gorecki [10] attempted to use SPME–GC by a custom-made polar fiber, Kanai et al. [11] and Agarwal [12] used the organic solvent, and Pauls and McCoy [13] inserted water solvent to the GC. There are several approaches taken to determine methanol concentration in crude oil, either using chromatographic techniques, or using other techniques such as spectroscopy. Choquette et al. [14] used Fourier transform raman spectroscopy and showed that their method was capable to determine the common oxygenate additives in gasoline mixtures. Sarpal et al. [15] used ^{13}C nuclear magnetic resonance (^{13}C NMR) and Skloss et al. [16], Kalsi et al. [17], and Meusinger [18], have used ^{1}H NMR spectroscopes to analyze oxygenates in gasoline. Application of Fourier transform infrared (FTIR) spectroscopy was reported by Fodor et al. [19] and Iob et al. [20].

Based on the way they used to solve the co-elution problem, the chromatographic approaches are subdivided into three main categories including approaches using a pre-extraction step, two or more columns, and an oxygen-selective detector. The last two classes present the main problem of requiring specific instrumentation.

The matrix interferences are a major problem and need to be removed or eliminated. Agarwal [12] extracted the low molecular weight alcohols from an organic matrix using diethylene glycol. The extracted alcohols were analyzed by GC, while the propanol was used as the internal standard.

However, the proposed method had the disadvantage of using an organic solvent. Kanai et al. [11] analyzed some oxygen-containing compounds in an organic matrix via a pre-extraction step by acetonitrile to remove hydrocarbon interferences followed by GC/Mass (MS). Although the proposed approach was successful

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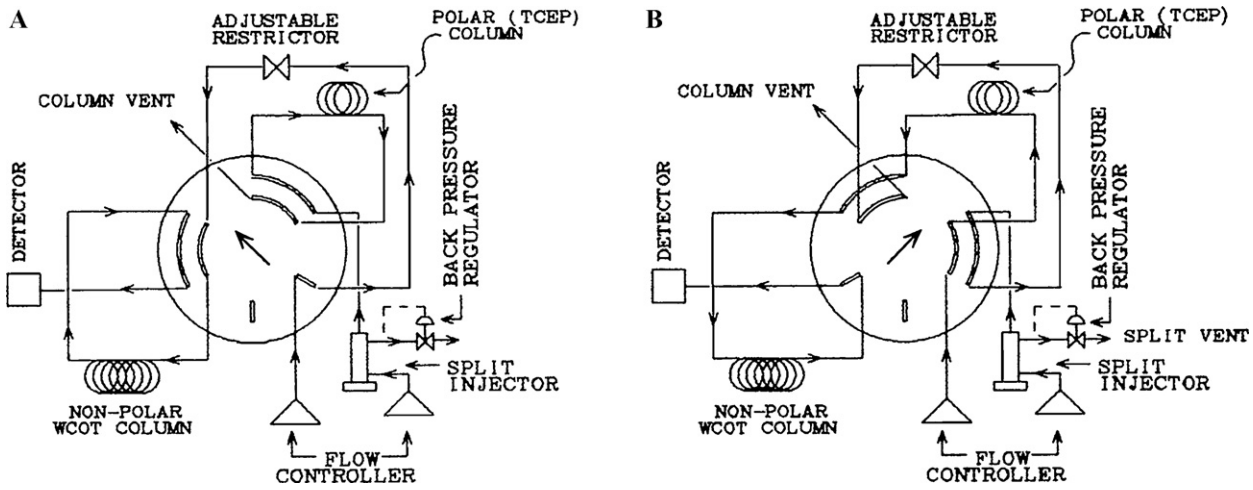

Fig. 1. Schematic of two-column chromatographic system for analysis of oxygenates in gasoline.

in removing the hydrocarbon interferences, however, it led to just 12% recovery. Pauls and McCoy [13] used a water pre-extraction step and analyzed methanol, ethanol, *t*-butanol, and methyl *t*-butyl ether in gasoline by a GC equipped with a packed-column and using isopropanol as the internal standard. The disadvantage of their method was introducing of water into the GC column and decreasing the column's lifetime.

Frysinger and Gaines [21] used two-dimensional GC and determined some oxygenates in gasoline. The first column separated the compounds based on their volatility, while the second one separated them based on their polarity. The output chromatogram organized the analytes by volatility and polarity properties.

The ASTM-D4815-04 [22] has discussed the standard test method for determination of methanol and similar compounds in gasoline using two columns and a column-switching valve. A two-column chromatographic system presenting the switching valve in the reset (scheme A) and the back-flash (scheme B) positions is depicted in Fig. 1. In this procedure, the sample is passed through a polar column, in which the light non-polar compounds are eliminated and vented. Then the valve is switched and the remainder of the sample is passed through a non-polar column, in which the alcohols are eluted before the heavier hydrocarbons. Finally, the valve is switched back and the heavy hydrocarbons are back-flushed. However, this method is complicated and requires some specific hardware.

The approaches based on the oxygen-selective detectors, all require some modifications on the chromatographic instrument. Verga et al. [23] and Di Sanzo [24] used some oxygen-selective detectors for determination of some oxygenates in gasoline range hydrocarbons by capillary column gas chromatography. Diehl et al. [25] reported the application of FTIR spectroscope and atomic emission detector (AED) [26] on the GC. Goode and Thomas [27] used a microwave-induced plasma (MIP) GC detector.

Determination of methanol, ethanol, and 2-propanol in unleaded gasoline and water has been reported by Gorecki [10] using SPME with a custom-made polar fiber, coated with Nafion perfluorinated resin. Although the fiber adsorbed the MeOH, it did not allow good quantification of 2-propanol and ethanol in water. Not only they did not explain the technique's details, but also they observed a non-linear response at long sampling times. Indeed, owing to the limited number of adsorption sites on the coating surface, the analytes with lower affinity were eventually displaced.

They achieved better linearity by using a short extraction time with vigorous stirring and an extraction time (with no stirring) for which some analytes did not reach equilibrium. Shirey [28] used the carboxen/polydimethyl siloxane (Car/PDMS) fiber for the analysis of methyl *tert*-butyl ether (MTBE) and C_1–C_8 alcohols in water and reported the linear ranges of respectively 1–500 and 10–1000 $\mu g\,L^{-1}$. However, the Car/PDMS fiber does not behave such as other adsorption type fibers, and no extraction theory is available for it yet [29].

Carboxen is only available suspended in PDMS and attempts to suspend it in carbowax (CW) resulted in poor analyte recovery. Moreover, there is one fiber available that contains a combination of divinyl benzene (DVB)–PDMS layered over Car/PDMS, which has a similar surface area as DVB, while the major difference is the much higher percentage of micropores. This material has a fairly even distribution of macro, meso and micro pores and is also a more rigid carbon based material.

Carboxens differ from other porous carbons since the pores are not sealed but pass entirely through the particle. The pores taper as they approach the center of the particle than expand as they approach the perimeter. This pore structure allows analytes to desorb more efficiently than with sealed pores common with carbon molecular sieves such as charcoals. Fig. 2 shows the comparative GC responses by using different fibers for both volatile and semi-volatile compounds.

In this work, two methods of SPME including the direct-SPME and the head space-SPME were used. The methanol concentration in crude oils (were taken from Iranian offshore oil reservoirs) were determined by both methods. Minimum extraction time for the direct approach was calculated and discussed. Moreover, two methods of data predicting including standard calibration and standard addition were used and the results were compared.

2. Experimental procedure

2.1. Materials

The oil samples were collected from one of the Iranian offshore fields and their physical properties and chemical characteristics are presented in Tables 1 and 2, respectively. Table 3 presented the characteristics of crude oil.

2.2. Sample preparation and mixing procedure

The mixing procedure was consisted of five steps including: (1) mixing 2 mL of crude oil with 2 mL of high performance liquid chromatography (HPLC) grade water, (2) shaking them for 1 min, (3) staying it for 4 min until the phase separation occurred, (4)

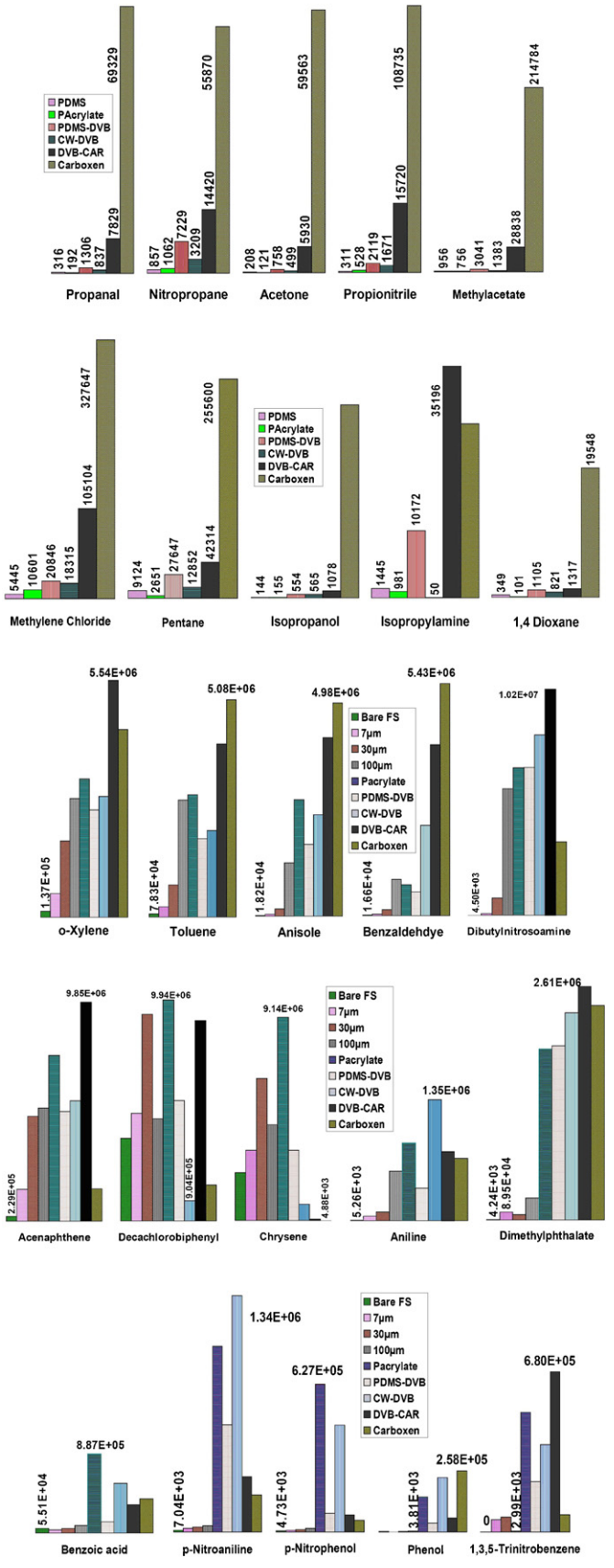

Fig. 2. Comparison of area responses by fiber type. The volatile and semi-volatile compounds are presented in the upper and the lower rows, respectively.

Table 1
Physical properties of the blend crude oil used in the experiments.

Specification	Quantity	Test method
Density/at 60 °F	0.8092/g cm^{-3}	ASTM D-4053
Density/at 70 °F	0.8035/g cm^{-3}	ASTM D-4054
Density/at 80 °F	0.7989/g cm^{-3}	ASTM D-4055
Viscosity/at 60 °F	2.2139/cp	ASTM D-445
Viscosity/at 70 °F	1.9608/cp	ASTM D-445
Viscosity/at 80 °F	1.7133/cp	ASTM D-445
Acidity number	0.29/mg KOH g^{-1} oil	ASTM D-664

discarding the top layer of crude oil, (5) sampling 10 μL of aqueous layer and diluting it to 100 mL using HPLC grade water. In this work, the salt adding was discarded since the salt can penetrate to the fiber and it is difficult to be removed. Moreover, there is an accumulation of salt in the liner, which needs to be taken out of the GC and be cleaned. Furthermore, methanol as a moderately water-soluble compound may be salted out and go into the headspace.

2.3. SPME conditions

A Supelco fiber-holder with 0.75 mm internal diameter (id) was used instead of the other conventional splitless liners (2 mm id), in order to allow a faster flow-rate through the liner. Hence, the analytes focused at the beginning of the column, resulting in narrower chromatographic peaks. Since methanol is the analyte of interest, the polar fiber of Car/PDMS was used. This fiber does not behave exactly like the other adsorption type fibers; therefore, no adsorption kinetic model is available for it.

As discussed before, several fibers have been evaluated, however, this was the fiber of choice since not only this was the one showing the least amount of interfering peaks, but also is one of the most polar fibers that is sensitive to volatile compounds. Carboxen is a carbon molecular sieve, consisting of solid particles (2–10 μm thick) embedded in a PDMS phase. Its small pores allow separation of small analytes by retention in the pores. This is another interesting feature of this fiber since methanol (MW_{MeOH} = 32 Da) is relatively small. Both direct and head space methods were examined and compared.

2.4. GC conditions

The gas chromatograph from Tief Gostar Faraz Co., equipped with a flame ionization detector (FID). In order to confirm peak

Table 2
Chemical characteristics of the blend crude oil used in the experiments.

Component	Flashed liquid (mol%)	Flashed gas (mol%)	Stream liquid (mol%)
N_2	00.00	00.31	00.04
CO_2	00.00	02.78	00.35
H_2S	00.00	04.52	00.57
CH_4	00.00	30.14	03.76
C_2H_6	00.00	12.02	01.50
C_3H_8	01.18	21.90	03.77
i-C_4H_{10}	01.16	07.25	01.92
n-C_4H_{10}	06.49	12.40	07.23
i-C_5H_{12}	02.73	03.21	02.79
n-C_5H_{12}	03.94	02.81	03.80
C_6	08.08	01.86	07.30
C_7	09.91	00.68	08.76
C_8	10.97	00.12	09.61
C_9	10.02	00.00	08.77
C_{10}	07.71	00.00	06.75
C_{11}	04.12	00.00	03.60
C_{12+}	33.69	00.00	29.48
Total sulfur	00.85/mass%		
Asphaltenes	00.32/mass%		
Waxes	05.00/mass%		

Table 3
Characteristics of the individual oil wells and the exported blend pipe-line.

Well no.	Productivity range (BPD)[a]	Water content (%)	Well head pressure (bar)	Well head temperature (°C)	GOR[b] (SCF BBL^{-1})[c]
Bl 2P	400–500	0	14	41	200
Bl 4P	4200–4400	25	30	66	266
Bl 5P	9400–10,000	1	55	68	309
Bl 6P	7100–7500	23	18	67	347
Bl 12P	3200–3600	5	18	49	0
Export line	25,000–26,000	0	19	52	–

[a] Barrels per day.
[b] Gas oil ratio.
[c] Standard cubic feet per barrel.

identities, we used a HP Model 6890 gas chromatograph, equipped with a mass selective detector HP Model. A cross-linked polyethylene glycol column (HP-INNOWAX) with 30 m length, 1.0 μm film thickness and 0.53 mm id was used. The oven temperature was programmed to stay 4 min in 65 °C and then, to be raised to 200 °C by the slope of 60 °C min^{-1}. The temperatures of injector and FID detector were set to 260 and 290 °C, respectively. The operating mode of splitless, with purge valve open after 1 min was used, while the column head-pressure, the linear velocity and flow-rate of gas were 2.0 psi, 5.4 mL min^{-1} and 40 cm s^{-1}, respectively.

Table 4
Data set for determination of MeOH using the standard calibration method.

No.	SPME extraction time	MeOH (mg L^{-1})			MeOH retention times (ave.)	Error (%)	R^2
		Original	Added	RSD (%)			
1	10 min	3.9	0	19.5	3.56		
2	10 min	3.9	0.4	7.3	3.28		
3	10 min	3.9	1.1	4.2	3.33		
4	10 min	3.9	1.9	12.3	3.44		
5	10 min	3.9	2.7	8.2	3.29	=5.3	=0.8717
6	10 min	4.5	0	4.6	3.34		
7	10 min	4.5	1.6	5.4	3.35		
8	10 min	4.5	3.1	3.0	3.27		
9	10 min	4.5	4.7	4.5	3.29		
10	10 min	4.5	6.2	2.1	3.24	=9.1	=0.9915
11	10 min	17.0	0	3.1	3.13		
12	10 min	17.0	4.5	2.9	3.26		
13	10 min	17.0	7.0	4.4	3.24		
14	10 min	17.0	8.5	2.3	3.37		
15	10 min	17.0	10	1.9	3.34	=5.4	=0.9923
16	12 h	3.9	0	22.0	3.36		
17	12 h	3.9	0.4	16.0	3.35		
18	12 h	3.9	1.1	8.6	3.28		
19	12 h	3.9	1.9	11.6	3.41		
20	12 h	3.9	2.7	9.2	3.40	=6.0	=0.8214
21	12 h	4.5	0	4.8	3.39		
22	12 h	4.5	1.6	4.7	3.43		
23	12 h	4.5	3.1	6.1	3.48		
24	12 h	4.5	4.7	12.2	3.38		
25	12 h	4.5	6.2	4.9	3.49	=8.9	=0.8989
26	12 h	17.0	0	2.9	3.36		
27	12 h	17.0	4.5	15.5	3.50		
28	12 h	17.0	7.0	7.9	3.44		
29	12 h	17.0	8.5	8.8	3.47		
30	12 h	17.0	10	10.4	3.28	=6.0	=0.90.67
31	48 h	3.9	0	17.8	3.34		
32	48 h	3.9	0.4	11.1	3.52		
33	48 h	3.9	1.1	8.5	3.28		
34	48 h	3.9	1.9	13.2	3.50		
35	48 h	3.9	2.7	17.1	3.30	=14.0	=0.8513
36	48 h	4.5	0	9.7	3.46		
37	48 h	4.5	1.6	33.4	3.46		
38	48 h	4.5	3.1	19.8	3.34		
39	48 h	4.5	4.7	8.8	3.38		
40	48 h	4.5	6.2	16.0	3.25	=11.8	=0.8042
41	48 h	17.0	0	14.6	3.28		
42	48 h	17.0	4.5	9.7	3.43		
43	48 h	17.0	7.0	9.1	3.47		
44	48 h	17.0	8.5	9.4	3.53		
45	48 h	17.0	10	14.8	3.36	=10.2	=0.8815

2.5. Data processing

Two methods were used for quantitation of methanol in crude oil including standard calibration curve and the method of standard addition. In the method of standard addition, different volumes of MeOH were spiked in the samples of crude oil and the resulted solutions contained different concentrations of MeOH. The detector response was plotted against the added concentration of MeOH and then, it was referred to a standard addition curve.

In the method of standard calibration, some selected standard solutions with different alcohol concentrations (Table 4) were prepared in water. The calibration curve was constructed by plotting the detector responses (peak areas) versus the MeOH concentration.

The linear portion of trace was used to find the alcohol concentration in the unknown sample. This method worked well if the standard solutions were prepared in the same matrix as the actual samples. However, it was not accurate in the present study, since the extraction of alcohols in crude oil from water was done in a slightly different matrix than the extraction of pure alcohols from water, and the calibration curve was varied slightly. Furthermore, there is the possibility of errors due to non-quantitative MeOH transfer in the mixing stage. However, this method is preferred whenever non-alcohol base crude oils are available.

3. Results and discussion

3.1. Effect of extraction time

In this section it is discussed that how the area counts for MeOH vary with different extraction times. For this aim, two curves of extraction time using both direct and headspace sampling of 4.5 mg L^{-1} MeOH (in water dilute solution) are presented. At any time, the amount of analyte extracted by the fiber is directly proportional to its initial concentration and hence, it is not necessary to choose a sampling time. However, where the slope is low, owing to minimize the error propagation, it is important to choose an extraction time.

The minimum sampling time required to achieve a certain degree of accuracy in analyte amount extracted was determined as the following procedure. Let τ, n, and ε be the sampling time, the amount of analyte extracted, and the maximum relative error in analyte amount extracted. The aim is calculating Eq. (1)

$$\varepsilon \geq \frac{\Delta n}{n} \tag{1}$$

Let us derive an expression for $\Delta n/n$. First, using well-known derivatives, we have Eq. (2)

$$\frac{dn}{dt} \cong \frac{\Delta n}{\Delta t} \tag{2}$$

Dividing both sides of Eq. (2) by n, we get Eq. (3)

$$\frac{1}{n}\left(\frac{dn}{dt}\right) \cong \frac{\Delta n}{n}\left(\frac{1}{\Delta t}\right) \tag{3}$$

Solving for $\Delta n/n$ in Eq. (3), we obtain Eq. (4)

$$\frac{\Delta n}{n} \cong \frac{1}{n}\left(\frac{dn}{dt}\right)\Delta t \tag{4}$$

From Eqs. (1) and (4), and dividing both sides by Δt, it follows as Eq. (5)

$$\frac{1}{n}\left(\frac{dn}{dt}\right) \leq \frac{\varepsilon}{\Delta t} \tag{5}$$

According to Eq. (6), the amount of analyte extracted by direct sampling is an increasing function of time and is related to sampling time.

$$n = n^{\infty}(1 - e^{-t/\tau}) \tag{6}$$

where, n depicts the amount of analyte extracted at equilibrium and τ is the time constant for direct sampling. Taking the derivative of n with respect to t and dividing both sides by n in Eq. (6), we get Eq. (7)

$$\frac{1}{n}\left(\frac{dn}{dt}\right) = \frac{n^{\infty}}{n}\left(\frac{e^{-t/\tau}}{\tau}\right) \tag{7}$$

Substituting the left side of Eq. (5) by the right side of Eq. (7) we get Eq. (8)

$$\frac{n^{\infty}}{n}\left(\frac{e^{-t/\tau}}{\tau}\right) \leq \frac{\varepsilon}{\Delta t} \tag{8}$$

Substituting n in Eq. (8) with its expression in Eq. (6), and simplifying the obtained equation, we have Eq. (9)

$$\left(\frac{1}{1 - e^{-t/\tau}}\right)\left(\frac{e^{-t/\tau}}{\tau}\right) \leq \frac{\varepsilon}{\Delta t} \tag{9}$$

Multiplying both sides of Eq. (9) by τ, ($\tau > 0$), we get Eq. (10)

$$\frac{e^{-t/\tau}}{1 - e^{-t/\tau}} \leq \frac{\varepsilon\tau}{\Delta t} \tag{10}$$

Let us introduce a new variable, z, such as Eq. (11)

$$z = e^{-t/\tau} \tag{11}$$

When t varies from 0 to ∞, z varies from 0 to 1, and $(1 - z)$ varies from 1 to 0. Substituting this new variable into Eq. (10), we obtain Eq. (12)

$$\frac{z}{1 - z} \leq \frac{\varepsilon\tau}{\Delta t} \tag{12}$$

Multiplying both sides of Eq. (12) by $(1 - z)$, $(1 - z > 0)$, and developing the right side of new equation, adding $(\varepsilon\tau/\Delta t)z$ to both sides, and factoring out z, we obtain Eq. (13)

$$z\left(1 + \frac{\varepsilon\tau}{\Delta t}\right) \leq \frac{\varepsilon\tau}{\Delta t} \tag{13}$$

Dividing both sides of Eq. (13) by the term in parentheses (positive), and simplifying it, we obtain Eq. (14)

$$z \leq \frac{\varepsilon\tau}{\Delta t + \phi\tau} \tag{14}$$

Substituting z in Eq. (14) by its expression in Eq. (11), taking the natural log of the expressions on both sides, multiplying both sides of resulted equation by $-\tau$ (negative), and rearranging, we get Eq. (15)

$$t \geq \tau \ln\left(1 + \frac{\Delta t}{\varepsilon\tau}\right) \tag{15}$$

The error in sampling time measurements (Δt) was assumed to be 5 s, while the time constant of sampling was 3.3 min. The maximum relative error in analyte amount extracted was assumed to be 1%. Therefore, using Eq. (15), the sampling time was determined to be 4.2 min (at least). With a conservative approach, the sampling time of 10 min was chosen. Fig. 3 depicted the trace of extraction time in direct sampling method, in which the amount of extracted analyte increased quickly during the first 5 min.

Obviously, in headspace sampling, the amount of MeOH extracted increased rapidly during the first 60 min. After that, instead of increasing more slowly and reaching a steady state, it started decreasing, which may be characteristic of the Car/PDMS fiber, as it saturates with the components of crude oil. Fig. 4

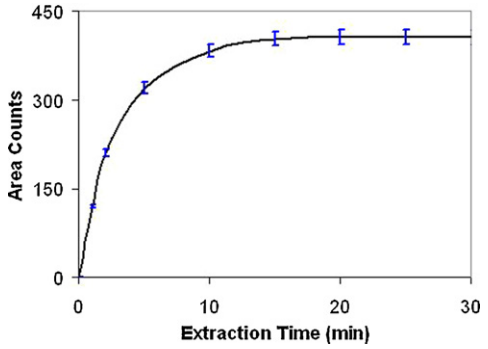

Fig. 3. Plot of extraction performance of MeOH by direct SPME.

depicted the amount of MeOH as well as other compounds extracted by the fiber during the same analysis.

According to Fig. 4, as the amount of extracted MeOH started to decrease, the amount of other compounds still increased. This confirms the presence of displacement effects. Owing to the small pores in the carboxen coating, capillary condensation could occur and leading to a greater adsorption capacity for some volatile analytes. This capillary condensation can occur in addition to the replacement effects (where analytes with low affinity for the fiber are displaced by analytes with higher affinity for the fiber) common to adsorption type fibers. The capillary condensation effect is negligible if the analytes' concentrations are low. Thus, as long as the amount of MeOH stays above the limit of detection, a more dilute water extracted bitumen solution is recommended. Also, using a more polar fiber may improve the relative standard deviation (RSD) of method.

3.2. Chromatograms of real samples

Both direct and headspace sampling were considered, but direct sampling was preferred owing to better sensitivity. The linear range of this quantitative method was determined to be 14–229 mg L^{-1} for methanol in water and is shown in Fig. 5.

Using this procedure, the limit of detection (LOD), which is defined as the injected quantity giving S/N of 3 (in terms of peak area), was determined to be 3.9 mg L^{-1} MeOH in water (Fig. 6). Moreover, the limit of quantitation (LOQ), was defined as the injected quantity giving S/N of 10 (in terms of peak area), was found to be 12.9 ppm. For each solution, three replicate SPME–GC analyses were utilized and the average concentration, standard deviation of concentration and related RSD's, which are presented in Tables 4 and 5, were determined. Moreover, the dynamic linear range was determined to be in the range of 14–229 mg L^{-1}

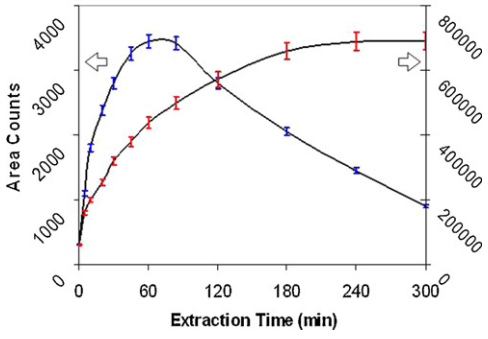

Fig. 4. Plot of extraction performance by headspace SPME. The left and right hand traces depicted the extraction loading of MeOH and light non-polar compounds on the fiber, respectively.

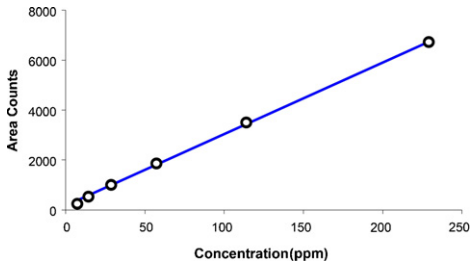

Fig. 5. The linearity curve of methanol concentration.

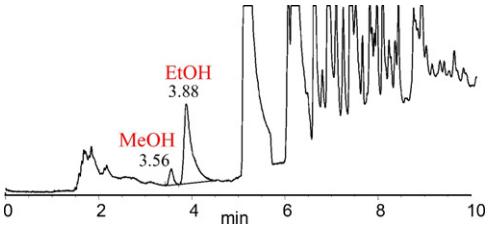

Fig. 6. GC chromatogram of 4.3 mg L^{-1} MeOH (LOD) and EtOH in water.

for MeOH. According to the calibration line, the sensitivity of this approach was calculated and was 30 area-counts per mg L^{-1}.

The chromatogram in Fig. 7 depicted significantly the peak areas for each of two alcohols (methanol and ethanol) even though they were spiked into water at similar concentrations of 17.0 mg L^{-1}. According to Figs. 6 and 7, the water extraction procedure was shown to be effective in eliminating the interfering hydrocarbon peaks. However, just the interfering effect of ethanol (EtOH) remains in the solution. Selection of right program for oven temperature allowed obtaining proper separation of MeOH and EtOH as depicted in Figs. 6 and 7.

3.3. Method of standard addition

The method of standard addition was used to determine the amount of MeOH in the stock solution, which first extracted with water and then diluted with water to the corresponding mg L^{-1} amount. The standard addition predictions were obtained using the added mg L^{-1} amounts of the MeOH in the water fraction and then, the weight percent of MeOH in the stock solution of crude oil was calculated.

Each experiment comprised five solutions, which the first was the original solution (diluted from the stock solution) and the other four were the spiked ones (diluted from the spiked stock solution). For each solution, three replicate SPME–GC analyses were utilized and the average concentration, standard deviation and RSD were determined. The above mentioned results were plotted as the graph of area counts versus the added concentration (mg L^{-1}) of MeOH

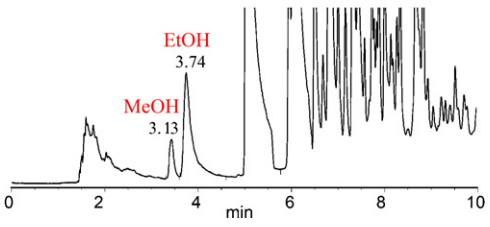

Fig. 7. GC chromatogram of a real sample presents 17.0 mg L^{-1} MeOH and EtOH in the water phase after mixing with crude oil.

Table 5
Data set for determination of MeOH using the standard addition method.

No.	SPME extraction time	MeOH (mg L^{-1}) in		RSD (%)	MeOH retention times (ave.)	Error (%)	R^2
		Standard solutions	Unknown solutions				
1	10 min	2.1	3.9	5.1	3.48		
2	10 min	3.2	3.9	6.0	3.52		
3	10 min	4.2	3.9	2.9	3.49		
4	10 min	5.0	3.9	3.6	3.54	=7.2	=0.8905
5	10 min	3.2	4.5	3.7	3.50		
6	10 min	4.2	4.5	1.4	3.40		
7	10 min	5.0	4.5	1.8	3.39		
8	10 min	6.0	4.5	1.0	3.28	=1.6	=0.9902
9	10 min	6.0	17.0	3.3	3.33		
10	10 min	12.2	17.0	2.4	3.30		
11	10 min	20.0	17.0	1.6	3.13		
12	10 min	26.8	17.0	2.1	3.24	=1.7	=0.9989
13	12 h	2.1	3.9	3.0	3.28		
14	12 h	3.2	3.9	5.6	3.35		
15	12 h	4.2	3.9	2.3	3.38		
16	12 h	5.0	3.9	4.0	3.42	=2.0	=0.9830
17	12 h	3.2	4.5	7.1	3.46		
18	12 h	4.2	4.5	4.1	3.38		
19	12 h	5.0	4.5	3.2	3.28		
20	12 h	6.0	4.5	7.9	3.31	=1.9	=0.9648
21	12 h	6.0	17.0	4.4	3.50		
22	12 h	12.2	17.0	4.8	3.48		
23	12 h	20.0	17.0	5.2	3.54		
24	12 h	26.8	17.0	6.0	3.44	=1.7	=0.9652
25	48 h	2.1	3.9	3.1	3.37		
26	48 h	3.2	3.9	8.5	3.28		
27	48 h	4.2	3.9	3.2	3.36		
28	48 h	5.0	3.9	2.1	3.41	=1.6	=0.9855
29	48 h	3.2	4.5	5.4	3.37		
30	48 h	4.2	4.5	2.8	3.31		
31	48 h	5.0	4.5	4.8	3.27		
32	48 h	6.0	4.5	1.0	3.25	=2.8	=0.9910
33	48 h	6.0	17.0	3.7	3.41		
34	48 h	12.2	17.0	2.1	3.46		
35	48 h	20.0	17.0	0.4	3.38		
36	48 h	26.8	17.0	2.8	3.32	=1.7	=0.9943

in water. In the first set of results (extraction time was 10 min), the RSDs were reasonable.

According to the first zone of Table 4, using samples 1–5, the MeOH concentration in the extracting water was found to be 3.9 mg L^{-1}, which corresponded to a 6.0 wt% of MeOH in the reference crude oil. The actual weight percent of MeOH in crude oil was 5.7%, and the results reflected a 5.3% error with respect to the true MeOH concentration in the crude oil. Other zones in Table 4 show more information by increasing the concentration of unknown samples from 3.9 mg L^{-1} (zone 1) to 4.5 mg L^{-1} (zone 2) and 17.0 mg L^{-1} (zone 3). The zones 1–3 were repeated after 12 and 48 hrs and the relevant results are depicted in the zones 4–6 and 7–9, respectively. Owing to displacement effects of light non-polar compounds, with increasing the extraction time, the error percent and RSD were increased.

3.4. Method of standard calibration

Since the crude oil samples, obtained from the reservoirs, do not contain injected MeOH, it is possible to use this method. Standard solutions with known amounts of MeOH were prepared. Stock solutions, were used previously with known amounts of MeOH, were analyzed to test the accuracy of this method. The results are tabulated in Table 5.

4. Conclusions

Using a novel approach based upon SPME-CG, the interfering agents were eliminated and the linear range of MeOH quantitation in the water extracted crude oil was determined. EtOH, which was transferred to the water solution, was removed using an optimized temperature program in the column. Two methods of standard calibration and standard addition were used to predict the MeOH concentrations. Their relative errors were determined to be in the range of 1.6–7.2% and 5.3–14.0%, respectively. The linear range of 14–229 mg L^{-1} for methanol was obtained.

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