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Determination of aromatic hydrocarbons in asphalt release agents using headspace solid-phase microextraction and gas chromatography–mass spectrometry

Bing Tang, Ulf Isacsson *

Division of Highway Engineering, Department of Civil and Architectural Engineering, Royal Institute of Technology, Brinellvägen 34, SE-10044 Stockholm, Sweden

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Abstract

The possibility of quantitative analysis of aromatic hydrocarbons in oil-based asphalt release agents was investigated using headspace solid-phase microextraction (HS-SPME) followed by gas chromatography–mass spectrometry (GC–MS). The target analytes studied were benzene, toluene, ethylbenzene, *p*-, *m*-, and *o*-xylene (BTEX) and 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene. Experimental parameters influencing HS-SPME efficiency were studied (equilibration time between sample and headspace and between headspace and SPME fiber, sample amount and sample matrice effects). A HS-SPME method using hexadecane as a surrogate matrice was developed. The detection limit was estimated as 0.03–0.08 ppm (w/w) for the target analytes investigated. Good linearity was observed ($R^2 > 0.999$) for all calibration curves at high, medium and low concentration level. The repeatability of the method (RSD, relative standard deviation) was found to be less than 10% (generally less than 5%) in triplicate samples and approximately 2% at eight consecutive tests on one and the same sample. The accuracy of the method given by recovery of spiked samples was between 85 and 106% (generally between 95 and 105%). The HS-SPME method developed was applied to four commercially available asphalt release agents. External calibration and standard addition approaches were investigated regarding accuracy. The results showed that standard addition generates higher accuracy than external calibration. The contents of target aromatic hydrocarbons in the asphalt release agents studied varied greatly from approximately 0.1–700 ppm. The method described looks promising, and could be a valuable tool for determination of aromatic hydrocarbons in different types of organic matrices.

Keywords: Headspace; Solid-phase microextraction; Asphalt release agents; Aromatic hydrocarbons; BTEX

1. Introduction

Asphalt release agents are widely used in road constructions to solve the problems of bituminous materials sticking to the metal surface of truck beds, paving machine or simple paving tools like shovels during road construction [1]. Most of the commercially available asphalt release agents can be categorized into three main groups according to the main active ingredients, i.e. petroleum oil, fatty oil and non-oil based agents, respectively. Traditionally, petroleum oils, such as diesel oil and kerosene were used as asphalt release agents. However, such products have been criticized from environmental as well as binder integrity reasons. Therefore, other products like fatty oil based agents (mostly natural or modified vegetable oils), claimed to be biodegradable and environmental-friendly, were used. Non oil-based products have also been proposed. This type of asphalt release agents varies with regard to active component(s) and is often emulsified in water for ease of application.

An asphalt release agent, especially a petroleum oil based one, is a complex mixture with considerably varied composition. The emission generated during application of this type of agents, especially when being used in hot-mix asphalt

* Corresponding author. Tel.: +468 7908700; fax: +468 4118432.
E-mail address: ulf.isacsson@byv.kth.se (U. Isacsson).

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production, contains a large number of organic compounds, some of which may be hazardous to the workers' health, e.g. aromatic hydrocarbons (benzene and alkylated benzenes) and polycyclic aromatic hydrocarbons (PAHs). Volatile aromatic hydrocarbons, especially BTEX, an acronym for benzene, toluene, ethylbenzene and the xylene isomers (*p*-, *m*-, and *o*-xylenes), are of primary concern with regard to health and environmental aspects and have been widely monitored [2–5]. Analytical techniques for determination of volatile aromatic hydrocarbons in oils have made major advances in the past years [6,7]. Due to complexity of oil composition, sample cleanup and fractionation are normally required [8]. For asphalt release agents, corresponding analytical methods were not found in the literature, and therefore, it is of great interest to develop a reliable and efficient method. In consideration of the nature of asphalt release agents, the method to be developed should satisfy the following requirements: (1) applicable for different types of asphalt release agents (no matter petroleum or fatty oil based); (2) a "direct" method without sample pretreatment procedure (to avoid the loss of target analytes); (3) relatively "clean" (to avoid introduction of large molecules into GC column and reduce the deterioration of GC column). SPME technique may provide such a possible approach.

SPME was introduced in the beginning of the 1990's as a solvent-free sampling and sample preparation technique [9]. It represents a rapid, sensitive and easily automated approach that simplifies the analysis of volatile and semi-volatile, polar and non-polar compounds in various matrices. A large number of papers as well as a few books have been published describing theoretical studies and applications of SPME during the last decade [10–14]. SPME technique has been widely applied in determination of aromatic hydrocarbons in different sample matrices such as air [15–23], water [24–32], oil [33–35] and solid samples [36–38]. However, no study has hitherto been published on the application of SPME technique to asphalt release agents.

In this paper the development of a HS-SPME method for extraction and analysis of aromatic hydrocarbons from oil-based asphalt release agent samples is presented. The target analytes includes BTEX, 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene. Experimental variables affecting HS-SPME procedure, such as analyte equilibration between headspace and sample matrice, extraction time profile of analytes, effects of sample amount as well as sample matrice, were studied. Different calibration approaches including external calibration and standard addition with and without internal standard were investigated, and the method developed was applied to four commercially available asphalt release agents. Although this study only covers the subject of aromatic hydrocarbons in asphalt release agents, it is believed that, the methodology may also be applied to characterization of other types of volatile organic compounds in different organic matrices.

2. Experimental

2.1. Chemicals and samples

Neat aromatic standards, benzene (Ben), toluene (Tol), *m*-, *p*- and *o*-xylene (Xyl), ethylbenzene (Etb), 1,3,5-trimethylbenzene (1,3,5-T) and 1,2,4-trimethylbenzene (1,2,4-T) (Supelco, Sweden) were used to prepare stock solution in *n*-hexane (>99% by GC, Merck, Germany). Throughout the study, ethylbenzene-d_{10} (Supelco, Sweden) was chosen as internal standard. In all cases, the concentration of the stock solution in *n*-hexane was 10 mg ml^{-1}. The stock solutions were diluted into various calibration standards using *n*-hexane. A standard mixture (revised PVOC/GRO mix, Supelco, Sweden), containing 10 compounds (methyl *tert*-butyl ether, benzene, toluene, ethylbenzene, *m*-, *p*-, *o*-xylene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, naphthalene) with each compound at a concentration of 2000 μg ml^{-1} in methanol, was used as a qualitative calibration standards after dilution in *n*-hexane. Among these 10 compounds, methyl *tert*-butyl ether and naphthalene were not studied, as not being target analytes in this investigation. Hexadecane ($C_{16}H_{34}$) (Supelco, Sweden) was used as the surrogate sample matrice during the method development. The four asphalt release agents studied (cf. Table 1, abbreviated to DIE, BIO, RME and AF1, respectively) were obtained from a contractor and tested without any further pretreatment.

2.2. HS-SPME device

The SPME device, consisting of a manual holder and a 100 μm polydimethylsiloxane (PDMS) fiber, was obtained from Supelco, Sweden. A crimp-top borosilicate glass vial (capacity about 24 ml, height 85 mm, diameter 23 mm, ScherfChroma, Germany), a 18 mm laminated butyl-PTFE septum (ScherfChroma, Germany) and a plastic screw cap with a hole in the middle were used as head space set-up. When the sample was introduced into the vial, the top of the vial was sealed immediately with septum and screwed tightly with the cap. Before SPME sampling, the septum was pierced

Table 1
Product information of asphalt release agents studied

Agents name	Product description
DIE	100% petroleum oil based products hydrocarbons: C_9–C_{20}; boiling point distribution: 163–357 °C
RME	100% based on derivatives of vegetable oil (rapeseed oil); flash point: 118 °C; solidifying point: −8 °C
BIO	50–100% mixture of petroleum oil and vegetable oil hydrocarbons: C_{11}–C_{16}; flash point: > 77 °C
AF1	100% vegetable oil from rapeseed and other vegetable plants, flash point: 140 °C; solidifying point: −12 °C

by a syringe needle to facilitate the passage of the SPME needle. After inserting the SPME needle into the HS vial through the precored septum, the fiber was exposed in the headspace above the sample. After sampling, the fiber was redrawn into the SPME needle and ready for GC–MS analysis.

2.3. Instrumentation of GC–MS

All the analysis was performed using a Varian 3400 gas chromatograph coupled with a Finnigan SSQ 7000 mass spectrometer. The GC column used was a DB-WAX polar capillary column (J&W Scientific, Folsom, CA, USA, 30 m × 0.25 mm I.D. and a film thickness 0.25 μm). Carrier gas was helium at a pressure of 68,950 Pa. The injector temperature was 215 °C (splitless injection for 45 s) and the transfer line was operated at 225 °C. The GC column was programmed from 40 °C (hold 3 min) to 80 °C at 5 °C min^{-1} (no hold) and then to 220 °C at 20 °C min^{-1} (hold 3 min). The mass spectrometer was operated at 70 eV EI mode. The source temperature was 150 °C and the manifold temperature 70 °C. MS full scan mode at a range of 45–400 *m/z* (2 scans s^{-1}) was used for qualitative screening analysis of the samples, whereas selected ion monitoring (SIM) mode was used for quantitative analysis. The ions monitored included *m/z* 78* for benzene; 91* for toluene; 91* and 106 for ethylbenzene and xylene isomers; 98* and 116 for ethylbenzene-d_{10}, 105* and 120 for 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene. If not indicated in the text, all peak areas were integrated based on the primary ion (marked with star) in SIM mode. The computer-based MS spectrum library used was the NIST mass spectral search program, version 1.7.

2.4. Testing procedures

A few key experimental variables of the HS-SPME procedure were studied, namely time required for the target analytes to reach equilibrium between headspace and liquid sample, extraction time profile for the target analytes as well as sample amount and sample matrice.

The equilibration time was investigated by performing HS-SPME on 1 g hexadecane containing 100 ppm of each of the aromatic standards at every 60 min up to 360 min, then at 520 min and finally at 24 h. During the course of this study, the SPME extraction time was kept constant (5 min).

The extraction time profile was obtained by performing HS-SPME on 1 g hexadecane containing 50 ppm of each of the aromatic standards. After introduction of the spiked hexadecane, the HS vial was sealed and equilibrated for 60 min. SPME sampling was performed consecutively at extraction time 10, 20, 40, 60, 120, 300, 600 and 1200 s, respectively. After each extraction, the sample was re-equilibrated for 60 min to make sure that the equilibrium between the sample and headspace was reached.

It should be noted that, in the investigation of equilibration time and extraction time, the analyte concentrations tested are comparably high (100 and 50 ppm, respectively), and the total amount of each analyte extracted after performing consecutive tests is less than 1%. Consequently, consecutive extractions of target analytes will not lead to significant decrease in concentration level, and the change of multiphase equilibrium can be considered negligible.

In order to find out if the sample amount affects the amount of analyte extracted, samples of different amount (0.5, 1, 2 and 4 g hexadecane spiked with each target analyte at 20 ppm) were analysed using the HS-SPME procedure (equilibration time of 60 min and extraction time of 5 min).

Sample matrice effects were investigated by spiking a series of internal standard of ethylbenzene-d_{10} in 1 g DIE, BIO, RME and AF1, respectively. The concentrations were 0.2, 2, 20 and 200 ppm, respectively. HS-SPME was performed following the procedure optimized in tests just described. The peak areas of ethylbenzene-d_{10} at *m/z* 116 were integrated.

A preliminary experimental study estimated that the content of individual aromatic hydrocarbons varied widely between different asphalt release agents studied: AF1 < 10 ppm, BIO and RME 1–100 ppm and DIE 100–1000 ppm (except benzene). However, for benzene, the contents measured for BIO, RME and DIE are much lower (about 1/10 of the low limit of the corresponding range). Based on the estimation, three series of calibration standards were prepared in hexadecane covering different concentration levels (low concentration level tested: benzene 0.00064–0.4 ppm, toluene 0.0064–4 ppm, *m*-, *p*-, *o*-xylenes and 1,3,5-trimethylbenzene 0.0032–2 ppm, 1,2,4-trimethylbenzene 0.0128–8 ppm; cf. Table 2 for medium and high concentration level, respectively). All these standards were analysed using the HS-SPME procedure based on testing parameters determined. Triplicate samples (hexadecane spiked with aromatic standards) were tested and linearity, detection limit, relatively standard deviation (RSD) and percentage of recovery of analytes were calculated.

2.5. Determination of aromatic hydrocarbons in asphalt release agents

To further evaluate the applicability of the HS-SPME method for asphalt release agent samples, two different calibration approaches (external calibration and standard addition) were investigated for determination of aromatic hydrocarbons in DIE. Besides hexadecane, AF1 was also used as a surrogate matrice for preparation of external calibration standards at high concentration level. The signal of a target analyte in DIE spiked with internal standard was compared with the corresponding external calibration curve obtained using hexadecane and AF1 as sample matrices, after which the concentration was calculated. As for standard addition approach, a linear regression curve was formed by interpolation (the signal of target analyte in pure sample was deducted from the signal in sample spiked with standards), and the concentration of target analyte was calculated from

Table 2
Validation of the HS-SPME method for determination of aromatic hydrocarbons at low, medium and high concentration level in spiked organic matrice (hexadecane)

Analytes	LOD	Linear range	Spiked concentration	No I.S.				I.S.			
				R^2	Mean	RSD%	Rec.%	R^2	Mean	RSD%	Rec.%
Low concentration level											
Ben	0.032	0.032–0.4	0.032	0.9994	0.0323	4.3	101	0.9998	0.0272	3.9	85
Tol	0.08	0.32–4	0.32	0.9998	0.318	3.6	100	0.9999	0.310	4.6	97
Etb	0.04	0.16–2	0.16	0.9999	0.174	2.9	109	0.9993	0.167	0.9	104
p-Xyl	0.04	0.16–2	0.16	0.9997	0.150	5.1	94	0.9991	0.143	2.0	89
m-Xyl	0.04	0.16–2	0.16	0.9992	0.150	6.9	94	0.9998	0.145	4.5	91
o-Xyl	0.04	0.16–2	0.16	0.9996	0.158	5.1	99	0.9999	0.152	3.0	95
1,3,5-T	0.04	0.16–2	0.16	0.9996	0.156	1.2	98	0.9997	0.150	2.6	94
1,2,4-T	0.032	0.64–8	0.64	0.9996	0.618	2.4	97	0.9998	0.601	2.7	94
Medium concentration level											
Ben		0.2–4	0.8	0.9999	0.83	5.8	104	0.9997	0.83	3.2	103
Tol		2–40	8	0.9998	8.0	3.0	100	0.9998	8.0	2.6	99
Etb		1–20	4	0.9998	4.1	3.0	102	0.9999	4.1	0.4	102
p-Xyl		1–20	4	0.9994	4.1	3.9	104	0.9997	4.1	1.2	103
m-Xyl		1–20	4	1.0000	3.9	3.2	98	0.9999	3.9	0.9	98
o-Xyl		1–20	4	0.9999	4.1	4.4	102	0.9999	4.1	1.8	103
1,3,5-T		1–20	4	0.9997	4.2	3.2	104	0.9998	4.1	1.3	103
1,2,4-T		4–80	16	0.9999	17.0	3.4	106	0.9998	16.9	1.2	106
High concentration level											
Ben		10–500	100	0.9999	102.5	4.7	103	0.9998	97.7	2.9	98
Tol		10–500	100	0.9999	101.0	3.9	101	0.9998	103.1	1.6	103
Etb		10–500	100	1.0000	98.9	2.5	99	0.9999	101.2	0.2	101
p-Xyl		10–500	100	0.9999	98.2	2.7	98	0.9998	100.5	0.7	100
m-Xyl		10–500	100	0.9999	95.8	3.1	96	0.9997	98.1	0.9	98
o-Xyl		10–500	100	0.9999	95.0	3.0	95	0.9999	97.3	0.8	97
1,3,5-T		10–500	100	0.9998	98.3	2.7	98	0.9996	100.1	0.5	100
1,2,4-T		10–500	100	0.9998	96.1	3.3	96	0.9995	98.3	1.1	98

Note: The calculated mean was based on triplicate samples ($n = 3$). I.S.: internal standard. The concentrations of internal standard are 0.1, 1 and 100 ppm for low, medium and high concentration level, respectively.

the interpolated regression curve. A conventional analytical method (syringe injection) was also applied for DIE as a control method. The conventional method used the calibration standards in *n*-hexane varying in the concentration range from 0.08 to 80 $\mu g\,ml^{-1}$ for target analytes. DIE was dissolved in hexane to give a concentration of 20 $mg\,ml^{-1}$. All calibration standards, as well as the DIE solution, contain 1 $\mu g\,ml^{-1}$ ethylbenzene-d_{10}. The GC–MS instrumentation parameters were the same as those used in the HS-SPME method, except that the liquid sample (1 μl) was directly injected using a syringe and a 3 min solvent delay was applied in MS detection. Due to the fact that the other studied asphalt release agents contain polar compounds (e.g. fatty acid methyl esters) with comparably higher boiling points and increased risk of deterioration of the GC column may occur, the syringe injection was not performed for the other asphalt release agents.

After the comparison of the results obtained from different calibration approaches for DIE, standard addition approach was chosen for determination of aromatic hydrocarbons in the other asphalt release agents, BIO, RME and AF1. In these cases, corresponding series of calibration standards at medium or low concentration range was used.

3. Results and discussion

3.1. Optimization of HS-SPME procedure

3.1.1. Selection of a surrogate sample matrice

When developing a HS-SPME procedure for a given type of materials to be tested, the selection of the sample matrice is of outmost importance. For example, for aqueous samples, pure water is often used as a standard matrice [24,25,30], and a certified solid soil can be used as a standard matrice for soil samples [36]. However, no standard or certified sample matrice for asphalt release agents was found in practice. The requirements of such standard matrice at least include: (1) having chemical and physical properties similar to the samples tested; (2) containing no or negligible amount of target analytes; (3) being not reactive with the target analytes; (4) containing no or negligible interfering compounds. Based on these considerations, neat hexadecane (no aromatic compounds were found by GC–MS checking) was selected throughout the experiment. Hexadecane is a long-chain non-polar alkane solvent with a high boiling point (283–286 °C) and volatility lower than the target analytes. It has been used as a standard sample matrice for determination of volatile

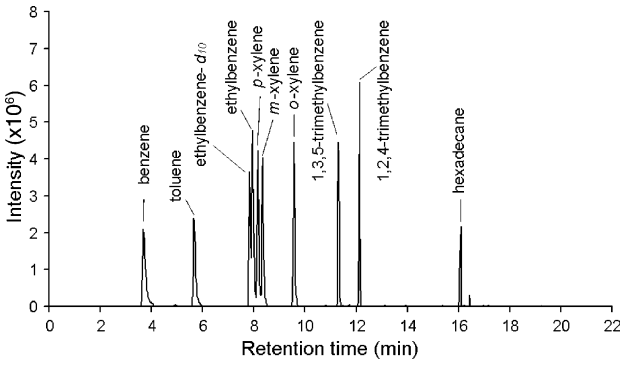

Fig. 1. Total ion chromatogram of hexadecane spiked with aromatic standards (100 ppm each in 1 g hexadecane) by HS-SPME (sample equilibration time 60 min, SPME extraction time 5 min).

organic compounds in packaging materials by HS-SPME [38]. The total ion chromatogram of hexadecane spiked with aromatic standards (100 ppm each in 1 g hexadecane) by HS-SPME is shown in Fig. 1. Hexadecane peak is far away from the peaks of target analytes. Furthermore, the amount of hexadecane extracted by SPME fiber is less than target analytes at a concentration level of 100 ppm. Therefore, hexadecane could be a suitable surrogate sample matrice.

3.1.2. Equilibration of samples

In order to obtain the proportional relationship between extracted amount of analytes by HS-SPME and initial concentration of analytes in the sample, multiphase equilibrium should be reached. The equilibration process involves the three phases: fiber coating, the headspace and the liquid sample matrice.

The equilibration of target analytes between headspace and liquid sample matrice was studied. The results in Fig. 2 clearly shows that the extracted amount of target analytes at different equilibration time (from 60 min up to 24 h) are kept almost constant, indicating that equilibrium in practice was already reached at 60 min for all target analytes. Although a slight increase of extracted amount from 60 to 120 min was observed, this increase was considered to be practically

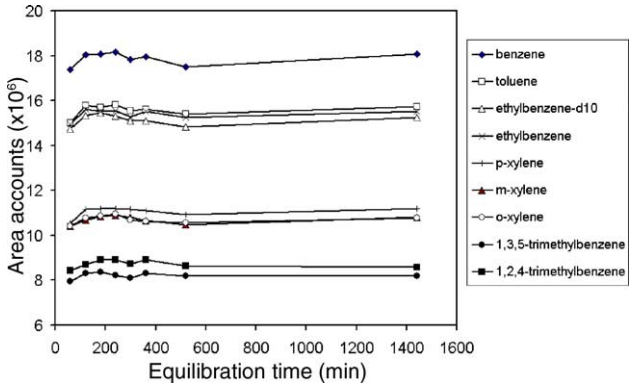

Fig. 2. Equilibration of spiked aromatic hydrocarbons (100 ppm each) in hexadecane (1 g) between head space and hexadecane (SPME extraction time 5 min).

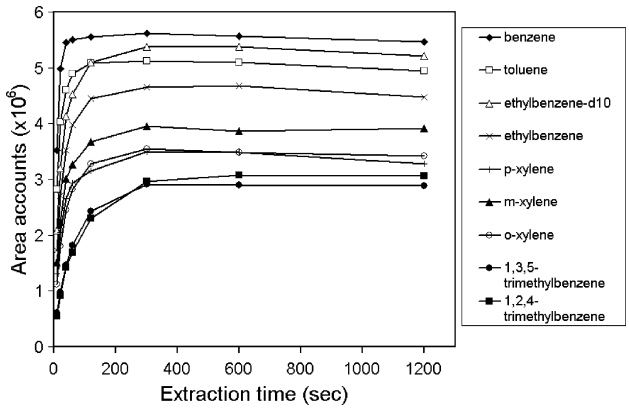

Fig. 3. Extraction time profile of spiked aromatic hydrocarbons (50 ppm each) in hexadecane (1 g).

insignificant. Less equilibration time will also shorten the overall analysis process. Therefore, a 60 min equilibration time was used for all HS-SPME tests. For repeated SPME extractions of the same sample, re-equilibration was 60 min.

3.1.3. Extraction time profile

The aromatic hydrocarbons studied normally reach equilibrium on the SPME fiber very fast (in a few minutes) with the headspace phase as described in literature [11,15]. The same thing was observed in our tests as shown in the extraction time profile (cf. Fig. 3). As expected, more volatile analytes like benzene and toluene reach equilibrium faster (40–60 s) than less volatile compounds like 1,3,5- and 1,2,4-trimethylbenzene (approximately 5 min). Based on the results presented in Fig. 3, 5 min was chosen consistently in all SPME extraction procedures. The desorption time, 5 min, was chosen based on regular checking of the cleanness of the SPME fiber by GC–MS.

3.1.4. Effect of sample amount

SPME theory indicates that sample amount (volume) may affect the amount of analytes extracted in a confined vial [11]. However, the test results (RSDs of the area accounts vary from 1 to 8% at different sample amounts for each analyte) indicate that such effects on amount of target analytes extracted is not significant in the range of sample amount investigated. To remain the consistency of experimental procedure, 1 g sample was chosen in all tests.

3.1.5. Effect of sample matrice

As shown in Fig. 4, the total ion chromatograms of the four asphalt release agents differ from each other, indicating different sample matrices among these agents. The complexity of the sample matrice not only increases the difficulty of chromatographic separation but also competitive extraction of non-target compounds on SPME fibers. Therefore, the SPME extraction efficiency may vary in different sample matrices. In Fig. 5, effects of sample matrices are clearly illustrated. In general, matrice effects may be attributed

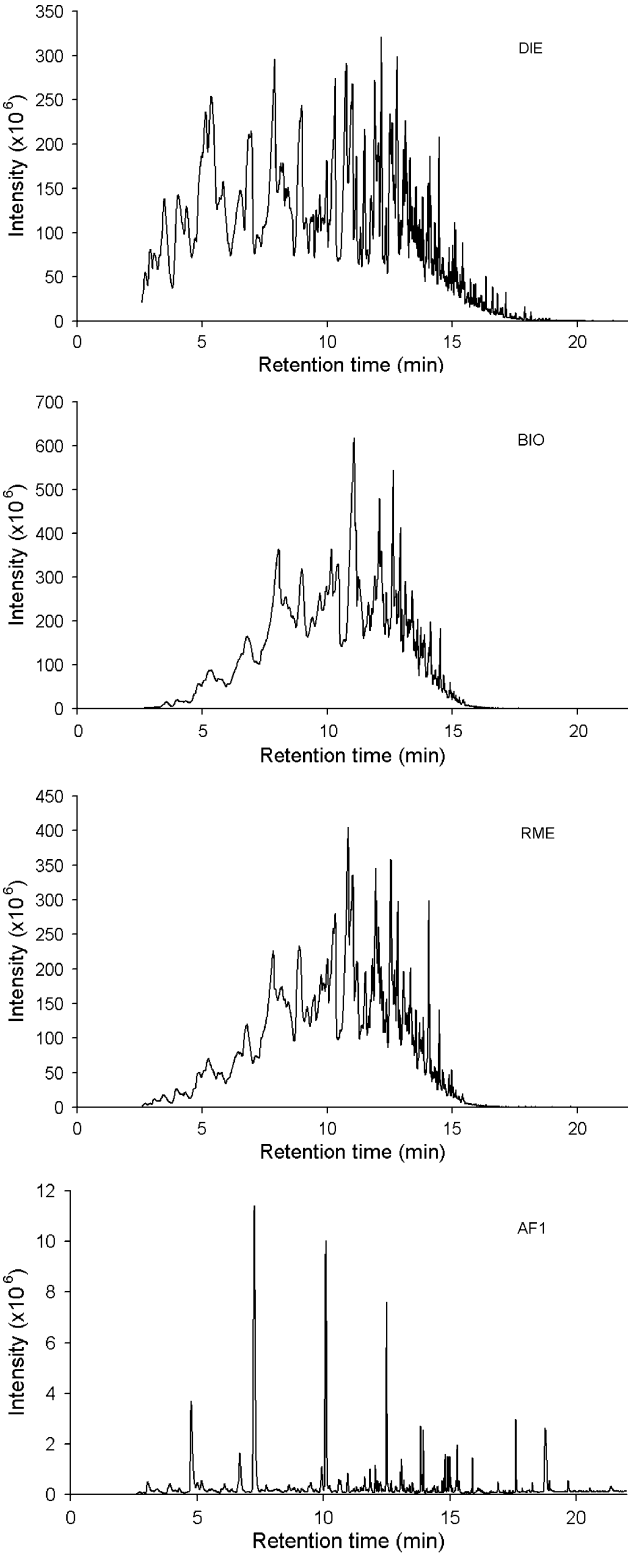

Fig. 4. Total ion chromatograms of asphalt release agents extracted by HS-SPME and analysed using GC–MS full scan mode (*m*/*z* 45–400) (sample amount, 1 g; sample equilibration time, 60 min; extraction time, 5 min; desorption time, 5 min).

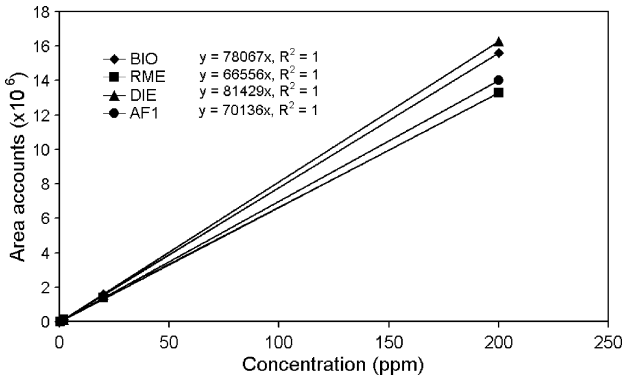

Fig. 5. Sample matrix effects on extraction of ethylbenzene-d_{10} (peak area at *m*/*z* 116 was integrated) in asphalt release agents at different concentration level (0.2, 2, 20 and 200 ppm, respectively).

to competitive extraction of other organic compounds co-existing with the target analytes, as well as physico-chemical properties of the sample matrice [11]. In principle it is impossible to find a standard matrice for all types of asphalt release agents as these products may vary considerably with regard to chemical composition (cf. Fig. 4), and therefore, the standard addition method could be an alternative approach. On the other hand as illustrated in Fig. 5, the range of variation in the target analyte response at 200 ppm is about 10% due to the different sample matrices (at 0.2 ppm, the corresponding variation range is 20%). These figures indicate that external calibration using a surrogate matrice may be feasible at least for semi-quantitative analysis. For comparison purpose, both external calibration using hexadecane and calibration of standard addition were used in this study for determination of aromatic hydrocarbons in asphalt release agents.

3.2. Validation of the HS-SPME method based on hexadecane

The validation of the HS-SPME method was conducted by determining the concentration of target analytes spiked in surrogate sample matrice (hexadecane) at different (low, medium and high) concentration levels. The linearity, detection limit, accuracy as well as repeatability were investigated.

3.2.1. Linearity

In general, SPME methods show wide ranges of linearity. For example, for fuel related hydrocarbons in water samples, the ranges of the linearity observed between 3 and 6 orders of magnitude have been reported [24].

The linearity of the calibration curve covering different concentration levels for target analytes in hexadecane was investigated. As shown in Table 2, all of the squares of correlation coefficient are greater than 0.999 for low, medium and high concentration level no matter with or without internal standard. The results indicate very good linearity at the use of the HS-SPME procedure.

3.2.2. Detection limit

The limit of detection (LOD) was estimated by analysis of a series of spiked hexadecane with calibration standards at low concentration level. The detection limit was estimated as the concentration with a signal/noise ratio (S/N) at 3:1. As shown in Table 2, the detection limits for all target analytes investigated are in the same order of magnitude (0.032–0.08 ppm). However, it should be noted that the estimated detection limits are solely valid for hexadecane as a surrogate sample matrice. Severe background interference on target analytes in asphalt release agents may cause substantially increased detection limit.

3.2.3. Accuracy

The accuracy of the testing procedure was studied by analyzing spiked samples at low, medium and high concentration level, respectively. The accuracy was estimated by determining the analyte recovery (amount of analyte measured divided by amount of analyte spiked in percent). As shown in Table 2, the mean recovery (Rec.%) is between 85 and 106%, which can be considered acceptable. Generally, the accuracy at high and medium concentration levels is better compared to the accuracy at low level. The internal standard calibration does not seem to contribute to higher accuracy. In conclusion, the results presented in Table 2 indicates that the HS-SPME procedure developed can be used for accurate quantitative determination of aromatic hydrocarbons in oil-based samples, at least in a concentration range from 0.1 to 500 ppm.

3.2.4. Repeatability

The repeatability of the HS-SPME method developed was evaluated in two different ways by analysing triplicate aliquots of spiked samples and the same sample at consecutive time. The results obtained are given in Tables 2 and 3. Table 2 shows that the relative standard deviation (RSD) at triplicate tests for all target analytes at different spiked concentration levels are below 5%, when using internal standard, and up to 7% without internal standard. It is also observed that the repeatability of the method is marginally better at high and medium concentration level compared to low concentration level. The results presented in Table 2 indicates very good repeatability of HS-SPME method used. As calibration with internal standard gives higher repeatability (cf. Table 2), this calibration approach is recommended.

The repeatability of the HS-SPME method using one and the same sample (each target analyte at 100 ppm in 1 g hexadecane) was estimated based on eight consecutive analysis within 24 h. The results are given in Table 3. As can be seen, RSD value is below 2% in most of the cases, indicating very good repeatability.

3.3. Determination of aromatic hydrocarbons in asphalt release agents

3.3.1. DIE sample

In proceeding section, a HS-SPME method based on the use of surrogate sample matrice (hexadecane) was described. To further evaluate the applicability of the method for asphalt release agent samples, different calibration approaches were investigated for determination of aromatic hydrocarbons in DIE: (1) external calibration using hexadecane as surrogate matrice; (2) external calibration using AF1 as surrogate matrice; (3) standard addition. In all these cases, calibration with and without internal standard was used. The use of AF1 as a surrogate sample matrice for DIE was based on assumption that the low content of target analytes (maximum around 1% of that in DIE) might not lead to significant effects of the test results. For comparison purpose, analysis using conventional method (syringe injection) with internal standard calibration was also conducted. The test results are given in Table 4. Due to solvent effects, benzene was not determined using the conventional method. As shown in Table 4, the content of individual aromatic hydrocarbons (except benzene) in DIE varies from approximately 100 to 700 ppm. The content of benzene is much lower (around 10 ppm).

The different calibration approaches for the HS-SPME method were evaluated with regard to repeatability as well as accuracy. As shown in Table 4, all calibration approaches, with or without internal standard, show very good precision with RSD value less than 5%. In most cases (cf. Section 3.2.4), the repeatability is improved by the use of internal standard.

Table 3
Successively repeated extraction on the same sample (100 ppm each analyte in hexadecane) by HS-SPME

Analytes	Area accounts ($\times 10^7$) at different test number									
	1	2	3	4	5	6	7	8	Mean	RSD%
Ben	1.739	1.805	1.808	1.818	1.785	1.797	1.750	1.808	1.789	1.6
Tol	1.502	1.579	1.569	1.583	1.554	1.563	1.541	1.574	1.558	1.7
Etb-d_{10}	1.476	1.534	1.546	1.530	1.510	1.511	1.482	1.526	1.514	1.6
Etb	1.496	1.563	1.552	1.555	1.528	1.552	1.524	1.553	1.540	1.5
p-Xyl	1.053	1.116	1.119	1.121	1.116	1.110	1.093	1.119	1.106	2.1
m-Xyl	1.041	1.070	1.083	1.089	1.080	1.065	1.048	1.081	1.070	1.6
o-Xyl	1.042	1.077	1.087	1.095	1.069	1.064	1.055	1.077	1.071	1.6
1,3,5-T	0.794	0.833	0.836	0.823	0.810	0.830	0.819	0.821	0.821	1.7
1,2,4-T	0.843	0.872	0.892	0.891	0.873	0.890	0.866	0.860	0.873	2.0

Table 4
Comparison of HS-SPME methods based on different calibration approaches with conventional method of syringe injection at determination of aromatic hydrocarbons in DIE samples

Analytes	Quantitative ion	Concentrations determined by HS-SPME (ppm)												Concentration determined by conventional method (ppm)
		External calibration using AF1 as a surrogate matrice				External calibration using hexadecane as a surrogate matrice				Standard addition approach				
		No I.S.[a]		I.S.		No I.S.		I.S.		No I.S.		I.S.		I.S
		Mean	RSD%	Mean	RSD%	Mean	RSD%	Mean	RSD%	Mean	RSD%	Mean	RSD%	Mean	RSD%
Ben	78	11.0	1.6	12.1	1.5	11.3	1.5	10.2	1.6	9.9	1.9	10.2	1.8	nd	nd
Tol	91	196.8	1.3	213.0[b]	0.8	216.1[b]	1.3	203.4[b]	0.8	198.3	2.0	199.5	1.2	193.8	2.4
Etb	105	95.1[b]	2.6	102.5	1.4	111.1[b]	2.5	104.6	1.4	104.5	3.4	105.0	1.8	105.7	0.4
p-Xyl	105	92.2[b]	2.6	99.3	1.5	111.1[b]	2.6	104.7	1.5	97.6	3.4	98.1	2.2	102.0	1.0
m-Xyl	105	286.0	0.8	309.9[b]	1.1	340.3[b]	0.8	321.2[b]	1.1	294.8	1.4	297.2	2.1	291.8	1.8
o-Xyl	105	183.8[b]	1.5	198.8[b]	0.2	209.0[b]	1.5	197.1	0.2	189.7	2.4	190.8	0.2	191.3	1.1
1,3,5-T	120	190.2[b]	1.4	205.5	1.3	246.8[b]	1.4	231.3[b]	1.3	213.7	2.1	215.1	2.2	213.5	3.8
1,2,4-T	120	615.7	1.9	668.1	1.0	747.4[b]	1.9	704.6[b]	1.0	614.9	5.0	621.3	2.3	637.1	1.7

[a] I.S.: internal standard; nd: not determined.
[b] The mean difference is significant at 0.05 level by Dunnett's pairwise multiple comparison *t* test (different calibration approaches against the conventional method, $n = 3$, two-sided).

Accuracy of the three calibration approaches can normally be evaluated by comparing the concentration measured with either the "true" concentration or the concentration determined using a reference method. In this study, the "true" concentration of target analytes in DIE was not available, and therefore, a reference method (the conventional method using syringe injection) was used. To find out if there are significant differences in means determined by different calibration approaches and means determined by the reference method, a statistical post hoc test, Dunnett's pairwise multiple comparison *t* test, was conducted. Dunnett's test compares a set of treatments against a single control mean and is widely used in natural and social science research [39]. Dunnett's test ($n = 3$, at 0.05 level) was performed for all analytes (except benzene) using the statistical software, SPSS 12.0, and the test results were given in Table 4. It is observed that no significant difference exists between the concentration mean of a given analyte determined by standard addition approach (with or without internal standard) and the mean obtained using the conventional method. Based on the results presented in Table 4, it can be generally concluded, that the standard addition approach is the most appropriate one among the three approaches studied. The significant differences observed using external calibration may be partially attributed to matrice effects, since no surrogate matrice could be identical to the sample analysed. Consequently, in the following section, the HS-SPME method using standard addition approach was used for determination of aromatic hydrocarbons in the other asphalt release agents investigated. However, if the requirement of accuracy is not of the main concern (e.g. semi-quantitative analysis), the external calibration approach using a surrogate matrice is recommended as this approach saves a lot of labour work compared to standard addition approach, especially when a large batch of samples are to be analysed.

3.3.2. BIO, RME and AF1 samples

Standard addition (at medium concentration level) approach using internal standard (1 ppm) was used for determination of aromatic hydrocarbons in BIO and RME samples. The results in form of mean concentration and relative standard deviation obtained from triplicate samples are shown in Table 5. For BIO sample, a large variation (RSD 9–20% for all analytes) was observed without internal standard. However, the RSD was reduced to less than 7% after internal standard calibration. For RME, the RSD is less than 10% in all cases. Both BIO and RME show similar content of benzene (around 0.1–1 ppm), ethylbenzene and *p*-, *m*, and *o*-xylene (around 4–12 ppm). However, higher content of toluene was found in BIO and higher contents of 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene in RME.

As was the case for BIO and RME, determination of aromatic hydrocarbons in AF1 was measured by standard addition but at low concentration level (internal standard 0.1 ppm). The results are shown in Table 5. The content of

Table 5
HS-SPME determination of aromatic hydrocarbons at medium concentration levels in BIO and RME samples and at low concentration level in AF1 using standard addition approach

Analytes	Determination of aromatic hydrocarbons in BIO, RME and AF1 samples (ppm)											
	BIO				RME				AF1			
	No I.S.		I.S.		No I.S.		I.S.		No. I.S.		I.S.	
	Mean	RSD%	Mean	RSD%	Mean	RSD%	Mean	RSD%	Mean	RSD%	Mean	RSD%
Ben	0.53	14.2	0.59	3.6	0.27	7.0	0.27	5.2	nd	nd	nd	nd
Tol	12.5	19.0	14.3	1.7	4.6	3.3	4.6	1.3	0.15	12.9	0.15	12.9
Etb	3.6	12.5	4.0	4.0	5.3	7.7	5.4	5.4	0.39	2.2	0.37	3.2
p-Xyl	3.5	11.8	3.9	4.8	3.8	4.1	3.9	2.0	0.43	1.9	0.41	2.7
m-Xyl	7.8	13.9	9.0	6.8	11.7	10.0	11.9	7.0	0.92	5.8	0.88	1.8
o-Xyl	5.1	13.3	5.8	4.7	11.7	5.0	11.9	1.9	0.78	4.2	0.72	1.4
1,3,5-T	2.7	10.5	3.0	3.4	25.9	5.0	26.3	2.5	1.32	2.0	1.26	2.3
1,2,4-T	10.1	18.2	11.9	3.8	74.1	7.3	81.6	1.7	7.32	14.2	6.41	4.1

I.S.: internal standard; nd: not determined as less than the detection limit.

benzene was below the detection limit (0.032 ppm), as given in Table 2. The contents of toluene, ethylbenzene and *p*-, *m*-, and *o*-xylene are between 0.1 and 1 ppm, while 1,3,5-trimethylbenze and 1,2,4-trimethylbenzene are in the range of 1–10 ppm. All RSD are below 15%, indicating the repeatability of HS-SPME for analysis at low concentration level is still acceptable.

3.3.3. Comparison of the results

BTEX is widely monitored in environmental and industrial hygiene studies [2–5]. In this study, the sum of BTEX determined by HS-SPME using the standard addition approach was calculated and the results are shown in Fig. 6. DIE contains significantly higher level of BTEX (around 900 ppm) than the other release agents studied. In the case of BIO and RME, BTEX content is less than 40 ppm BTEX. However, if trimethylbenzene is considered, BIO would be a better choice as an asphalt release agent than RME, which contains considerably more 1,3,5- and 1,2,4-trimethylbenzenes. For AF1, the BTEX content is less than 3 ppm. The results presented indicate that the HS-SPME method used is a valuable tool for characterizing health risk potential of asphalt release agents.

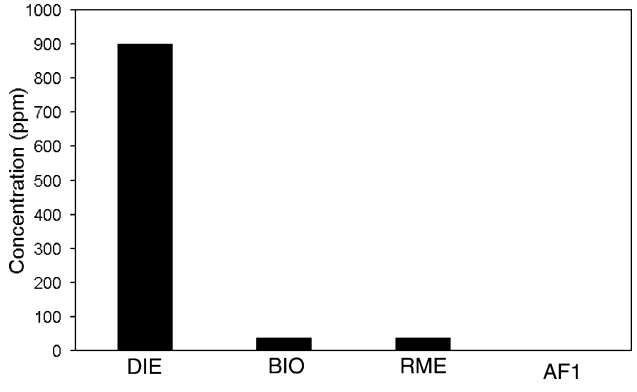

Fig. 6. BTEX content (ppm) in asphalt release agents.

4. Conclusions

The present work describes the development of a method using HS-SPME followed by GC–MS for determination of aromatic hydrocarbons in oil-based asphalt release agents. The use of an organic solvent (e.g. hexadecane) as a surrogate sample matrice facilitates the optimization of HS-SPME parameters. Repeatable and accurate results on spiked organic matrices under optimized experimental conditions were obtained. Both external calibration approach and standard addition approach were considered. Statistical evaluation showed that the standard addition approach generates better agreement with the reference method, when determining aromatic hydrocarbons in a given asphalt release agent. If the accuracy is not of major concern, external calibration using a surrogate organic matrice is also feasible. The HS-SPME method developed using the standard addition approach was successfully applied to the determination of aromatic hydrocarbons in a broad concentration range (approximately 0.1 ppm up to at least 700 ppm). The methodology described looks promising, and could be a valuable tool for determination of aromatic hydrocarbons (possibly even for other types of volatile organic compounds) in different types of organic matrices.

References

[1] B. Tang, On chemical characterization of asphalt release agents, Licentiate thesis, Royal Institute of Technology, Stockholm, 2002.
[2] Environmental and Health Criterial 150—Benzene, World Health Organization, Geneva, 1993.
[3] Environmental and Health Criterial 52—Toluene, World Health Organization, Geneva, 1985.
[4] Environmental and Health Criterial 186—Ethylbenzene, World Health Organization, Geneva, 1996.
[5] Environmental and Health Criterial 190—Xylenes, World Health Organization, Geneva, 1997.
[6] N. Kosal, A. Bhairi, M.A. Ali, Fuel 69 (1990) 1012.
[7] Z. Wang, M. Fingas, J. Chromatogr. A 774 (1997) 51.
[8] Z. Wang, M. Fingas, M. Landriault, L. Sigouin, N. Xu, Anal. Chem. 67 (1995) 3491.

[9] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[10] R. Eisert, K. Levsen, J. Chromatogr. A 733 (1996) 143.
[11] J. Pawliszyn, Solid-Phase Microextraction—Theory and Practice, Wiley-VCH, New York, 1997.
[12] J. Pawliszyn, Applications of Solid-Phase Microextraction, Royal Society of Chemistry, Cambridge, 1999.
[13] H. Lord, J. Pawliszyn, J. Chromatogr. A 885 (2000) 153.
[14] M. Alpendurada, J. Chromatogr. A 889 (2000) 3.
[15] J. Namieśnik, B. Zygmunt, A. Jastrzębska, J. Chromatogr. A 885 (2000) 405.
[16] M. Chai, J. Pawliszyn, Environ. Sci. Technol. 29 (1995) 693.
[17] D. Gorlo, L. Wolska, B. Zygmunt, J. Namieśnik, Talanta 44 (1997) 1543.
[18] K. Elke, E. Jermann, J. Begerow, L. Dunemann, J. Chromatogr. A 826 (1998) 191.
[19] D. Gorlo, B. Zygmunt, M. Dudek, A. Jaszek, M. Pilarczyk, J. Namieśnik, Fresenius J. Anal. Chem. 363 (1999) 696.
[20] F. Augusto, J. Koziel, J. Pawliszyn, Anal. Chem. 73 (2001) 481.
[21] F. Parreira, C. Carvalho, Z. Cardeal, J. Chromatogr. Sci. 40 (2002) 122.
[22] G. Xiong, Y. Chen, J. Pawliszyn, J. Chromatogr. A 999 (2003) 43.
[23] J.A. Koziel, P.A. Martos, J. Pawliszyn, J. Chromatogr. A 1025 (2004) 3.
[24] J. Langenfeld, S. Hawthorne, D. Miller, Anal. Chem. 68 (1996) 144.
[25] S. Thomas, R. Ranjan, G. Webster, L. Sarna, Environ. Sci. Technol. 30 (1996) 1521.
[26] T. Nilsson, R. Ferrari, S. Facchetti, Anal. Chim. Acta 356 (1997) 113.
[27] R.B. Gaines, E.B. Ledford, J.D. Stuart, J. Microcol. Sep. 10 (1998) 597.
[28] M. Llompart, K. Li, M. Fingas, J. Chromatogr. A 824 (1998) 53.
[29] K. Sukola, J. Koziel, F. Augusto, J. Pawliszyn, Anal. Chem. 73 (2001) 13.
[30] C. Almeida, L. Boas, J. Environ. Monit. 6 (2004) 80.
[31] A. Paschke, P. Popp, J. Chromatogr. A 1025 (2004) 11.
[32] I. Arambarri, M. Lasa, R. Garcia, E. Millán, J. Chromatogr. A 1033 (2004) 193.
[33] D. Page, G. Lacroix, J. Chromatogr. A 873 (2000) 79.
[34] S. Harris, M. Whiticar, M. Eek, Organ. Geochem. 30 (1999) 721.
[35] M.T. Clasadonte, A. Zerbo, J. Commod. Sci. 38 (1999) 3.
[36] M. Llompart, K. Li, M. Fingas, Talanta 48 (1999) 451.
[37] Ó. Ezquerro, G. Ortiz, B. Pons, M.T. Tena, J. Chromatogr. A 1035 (2004) 17.
[38] Ó. Ezquerro, B. Pons, M.T. Tena, J. Chromatogr. A 985 (2003) 247.
[39] D. Montgomery, G. Runger, Applied Statistics and Probability for Engineers, Wiley-VCH, New York, 2003.