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Solvent vapour monitoring in work space by solid phase micro extraction

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Abstract

Solid phase micro extraction (SPME) is a fast, solvent-less alternative to conventional charcoal tube sampling/carbon disulfide extraction for volatile organic compounds (VOC). In this work, SPME was compared to the active sampling technique in a typical lab atmosphere. Two different types of fibre coatings were evaluated for solvent vapour at ambient concentration. A general purpose 100 μm film polydimethylsiloxane (PDMS) fibre was found to be unsuitable for VOC work, despite the thick coating. The mixed-phase carboxen/PDMS fibre was found to be suitable. Sensitivity of the SPME was far greater than charcoal sorbent tube method. Calibration studies using typical solvent such as dichloromethane (DCM), benzene (B) and toluene (T) showed an optimal exposure time of 5 min, with a repeatability of less than 20% for a broad spectrum of organic vapour. Minimum detectable amount for DCM is in the range of 0.01 μg/l (0.003 ppmv). Variation among different fibres was generally within 30% at a vapour concentration of 1 μg DCM/l, which was more than adequate for field monitoring purpose. Adsorption characteristics and calibration procedures were studied. An actual application of SPME was carried out to measure background level of solvent vapour at a bench where DCM was used extensively. Agreement between the SPME and the charcoal sampling method was generally within a factor of two. No DCM concentration was found to be above the regulatory limit of 50 ppmv. © 2001 Published by Elsevier Science B.V.

Keywords: SPME; VOC; Air monitoring; Solvent vapour analysis; Charcoal sorbent

1. Introduction

In comparison to the charcoal sampling/carbon disulfide extraction (NIOSH method #1005), SPME is a rapid and simpler sample collection/preparation technique. By combining sample collection and concentration in one step, the adsorbed analytes can be easily thermally desorbed into an analytical instrument via the heated injection port, thus offering the benefits of minimal sample loss, maximum sample utilisation since, there is no dilution

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involved. It also reduces sample turn-around time and solvent usage as required in traditional sample extraction. In a more recent survey of their application in VOC analysis, it has been applied to detection of gasoline in fire debris [1], solvent in water [2], odours in drinking water [3], flavour and aroma volatiles in whole fruits [4].

The heart of SPME sampling technology is the liquid coating on the fibre, of which a variety of different chemistries are available for a variety of analytes to be measured. We have initially employed a general purpose 100 μm PDMS fibre which had been successfully applied to headspace/immersion SPME to concentrate VOC such as benzene, toluene, ethyl benzene and xylenes (BTEX) from water samples [5] as well as semi-volatiles such as PCB in water [6]. With its universality of adsorption characteristics for most organic compounds, it should be a good candidate for general analytical work. This approach reduces the cost and complexity of having to stock up on different fibres with various coating chemistries and thickness.

For comparison, we have also tried the carboxene 1006/PDMS SPME fibres with film thickness of 75 μm. The carboxene surface has a combination of micro-, meso-, and macro-pores ranging from 6 to 50 Å which retains low molecular weight VOC effectively [7].

The fibre is contained in a portable field sampler which has a built-in septum system that allows the exposed fibre to be retracted and protected during transit back to the lab for analysis without any loss or contamination. The sampler body is made from a lightweight polymer with an aluminum nosepiece that acts as a temperature shield during thermal desorption in the GC. There are five slots in the needle guide/depth gauge control the depth of needle insertion into a sample container, or into the injection port during fibre desorption.

In use, the fibre is simply extended and exposed for a pre-determined amount of time. The VOC in air diffuse freely into the liquid phase of the coating and upon completion of sampling, the fibre is retracted until analysis [6]. As a passive concentration device, it has good sensitivity because of the favourable partition coefficient of most organics for the carboxene/PDMS phase. This technique is far simpler to implement than collection on charcoal sorbent tubes and extraction using toxic carbon disulfide. To be useful for air monitoring work, the carboxen fibre was tested for repeatability over a period of time as well as lot to lot consistency. These criteria are important in field survey work since in most cases, more than one fibre is used and similar adsorption characteristics among fibres would reduce the calibration work required.

In this work, the use of SPME for measuring background level of solvent vapour in the lab space is described. We have investigated the performance characteristics of SPME and compared to charcoal tube sampling. Optimal exposure time was evaluated. Figures of merit such as detection limit, linearity range and repeatability studies were collected.

2. Procedure

2.1. Charcoal tube sampling and analysis

NIOSH method #1005 was used as a basis of comparison. The survey was carried out in November 1966 in response to a concern about the DCM vapour concentration in a lab in which crude oil interfacial tension testing was carried out. Air was drawn through a

two-stage (100/50 mg) SKC charcoal tube by a SKC Airchek sampler (model 224-PCXR7) at a flow rate of 0.1 l/min, the flow rate was calibrated and controlled by a variable orifice. Sample description and location are described as follows:

Sample 1 (collected on 16 November 1998)	Interfacial bench background, no tests and no other activities in the lab
Sample 2 (collected on 24 November 1998, morning)	Interfacial test bench, no tests but with other activities in the lab
Sample 3 (collected on 24 November 1999, afternoon)	Lab 345 near a GC/MSD, general lab background
Sample 4 (collected on 24 November 1999, afternoon)	Interfacial test bench, tests being conducted

As soon as the sampling was completed, the charcoal tubes were capped and stored in a fridge. To ascertain that there was no DCM breakthrough, the front and back portions (100/50 mg) of the tube were extracted separately in a 4 ml capped vial. Prior to extraction the charcoal was spiked with 100 μg of 1,2-dichlorobenzene as a recovery standard to assess any sample workup loss. A 1 ml aliquot carbon disulfide was added slowly and the contents were allowed to sit for 30 min with an occasional shaking. In parallel with the sample extraction, a matrix spike was also performed by spiking a blank charcoal tube with 132 μg DCM to measure any interference and overall accuracy of the methodology. Prior to analysis, 100 μg of d8-toluene was added to each vial as an internal standard to account for the difference in sample volume (nominally 1 ml) and variation in instrument response throughout the analysis.

Analysis was carried out on a bench top GC/MS system (HP 5890 Series II GC/GCD) equipped with a 30 M SPB-1 mega bore column (0.5 mm i.d., 1.5 μm film). The oven was kept at 30°C for 5 min and heated to a final temperature of 150°C at the rate of 15°C/min. The GCD was operated in selected ion monitoring mode, the ions were selected automatically with the injection of a solvent mixture standard in scan mode. Calibration of the system was by manual injection of 1 ml in splitless mode of a 132 ppm DCM standard together with 100 ppm of recovery and internal standard. The DCM peak eluted at 2.9 min just before the CS_2 peak. Ion mass at 85 was used to quantify the DCM in the extract, corrected for the response of internal standard. Instrumental detection limit was 10 μg DCM.

2.2. SPME

The 100 μm PDMS fibre was held in a manual SPME holder whereas the 75 μm carboxen/PDMS fibre was housed in a field sampling kit. Both were conditioned at 270°C in the heated injection port of another GC for 30 min prior to use. Daily the fibre was cleaned in the injection port for 5–10 min. The field sampling kit has a built-in septum sealing system that the fibre can be retracted into, thereby protecting the fibre from further exposure and also minimising evaporation loss. The fibres were deployed at the same sampling points as the charcoal tubes. Corresponding with sample #2, a duplicate SPME sample was also taken.

The fibre was inserted into the injection port of the same GC/GCD system and analysed with the same instrumental condition as described above. In contrast to other SPME application such as VOC analysis of water, an internal standard can often be added to the water sample to assess any variation in SPME and instrumental response. However, in air analysis, this is not possible and consistency of SPME response can only be monitored by calibration runs before and after sample analyses (external standard method). In this work, the SPME was calibrated by exposure in an enclosure with a known vapour concentration. This was carried out by making a nominal 50 ppm solution of different lab solvent in methanol. By adding aliquots of the solution to a Tedlar bag or a 1 l glass gas bulb equipped with a septum port, various vapour concentrations were generated. The fibre was inserted through the septum for the same amount of time the fibre was exposed in the lab atmosphere.

3. Results and discussions

3.1. Preliminary study

Calibration studies were carried out for carboxen fibre by exposing each fibre in a static atmosphere with known vapour concentration. Of the two types of enclosures investigated, the glass bulbs were easier to handle than Tedlar bags. They could also be cleaned much faster by washing with methanol and baked out in a hot oven. A typical calibration curve is shown in Fig. 1.

The static calibration method, though easy to carry out, is not the same as in an open atmosphere where a more complex and dynamic condition exists. In a typical lab environment there may be appreciable air current which might affect the sorption of vapour on SPME. Duplicating the real atmosphere for calibration purpose is much more difficult to carry out.

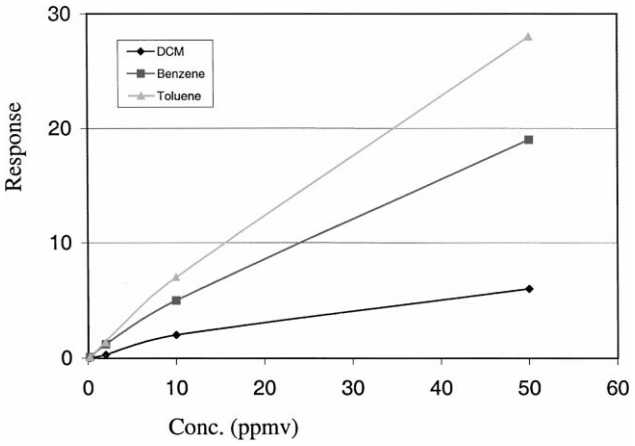

Fig. 1. 75 mm, carboxen/PDMS fibre 1 l sampling bulb, fibre #4, 5 min exposure.

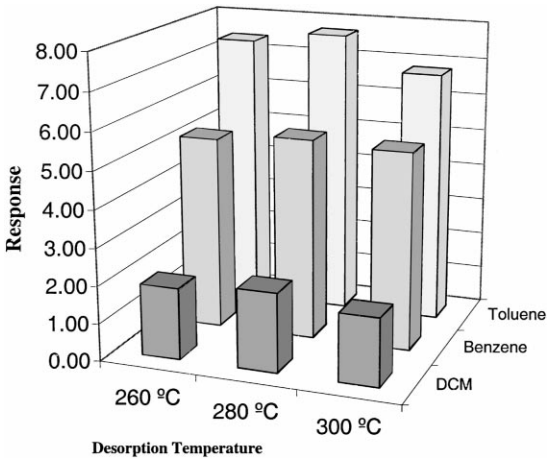

Fig. 2. Effect of desorption temperature.

To investigate the effect of desorption temperature, the injection port temperature was varied between 260, 280 and 300°C. The SPME was exposed in a glass bulb with a nominal vapour concentration of 10 ppmv. There was no significant difference in the response between the three desorption temperatures within experimental errors (Fig. 2). Subsequently, 260°C was used for the rest of the study.

3.2. Adsorption study, PDMS versus carboxen

Low molecular weight VOC vapour such as DCM was poorly retained by the 100 μm PDMS fibre, leading to unsatisfactory detection limits. By comparison, the carboxen/PDMS phase retains DCM well. The pores of carboxen, a chemically modified charcoal, are tapered (private communication, Supelco) so the smaller gaseous molecules diffuse deeper into the pore structures relative to the heavier molecules and remains adsorbed until desorption by heat.

Comparison of the two types of fibres was conveniently carried out on a lab bench in an open atmosphere. Vapour at background levels was generated from about 10 capped vials (40 ml) of various solvent used to make standards. The solvents includes pentane, hexane, *iso*-octane, benzene, toluene, xylenes, DCM, methanol, ethanol and carbon disulfide. Levels of DCM, benzene and toluene was determined to be nominally 10–30 ppmv by comparing the amount adsorbed to that derived from a static calibration method. After 5 min, the fibres were desorbed and analysed by GC/GCD. While the carboxen fibres showed measurable amounts of most solvents, the PDMS fibre had mostly non-detectable or only trace level of the vapour.

To measure the repeatability of the carboxen SPME, a fibre was exposed for 5 min in the same environment. Five replicate measurements were made. For clarity only results of DCM, benzene and toluene data were used to illustrate (Fig. 3). Repeatability of the same fibre for five runs was about 20% relative standard deviation (R.S.D.). The repeatability

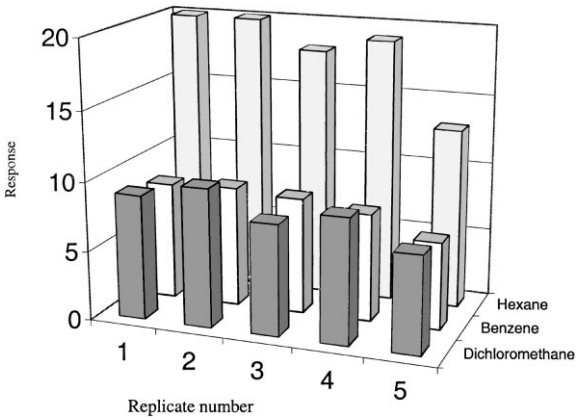

Fig. 3. Repeatability for a carboxen fibre on bench, 5 min exposure.

reflected the variation in an uncontrolled environment, typical that of a lab, as well as the overall measurement process of adsorption/analysis. The data also showed the vapour concentration at that bench was reasonably constant despite the open atmosphere.

Having established the repeatability of a single fibre, five randomly-chosen fibres of the same type were then exposed simultaneously at the same location. After exposure each fibre was stored in the field sampler body sealed by a septum until analysis. Results showed response of the fibres was generally within 23–30% (Fig. 4). This showed variation among different lots of fibre is not significantly worse than that of a single fibre. For field survey work, a number of fibres can be set up simultaneously. The lot to lot consistency greatly simplifies calibration and permit quantitation to be made. These positive attributes however, can change depending on the age and physical condition of the fibre. During use

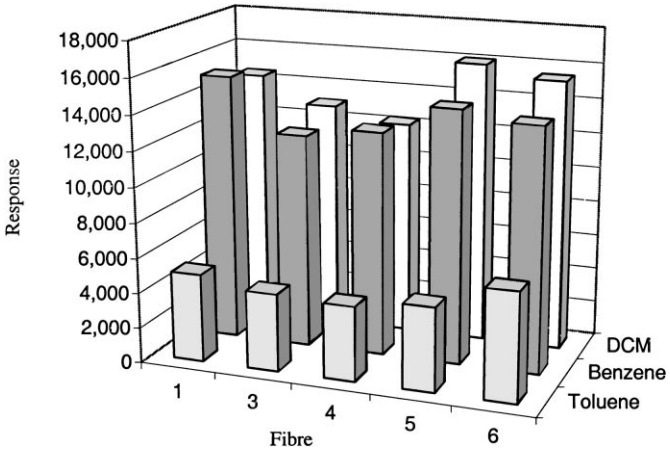

Fig. 4. Variation among six carboxen fibres on bench, 5 min exposure.

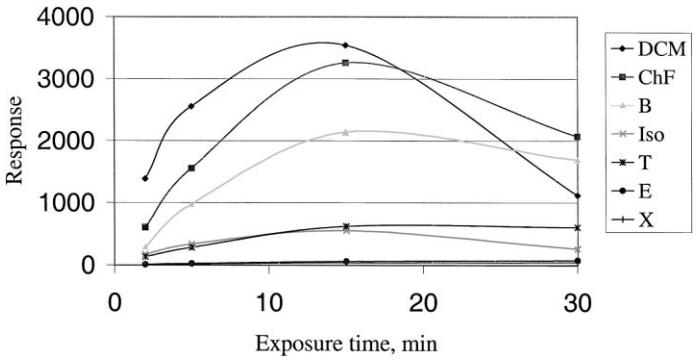

Fig. 5. Response of various solvent vapour vs. exposure time.

the fibre is subjected to abrasion, chipping, heat stress and general wear. The coating can also be affecting by irreversible adsorption or poisoning. It is interesting to note fibre #5 in the uniformity test was a brand new one. The amount of VOC adsorbed and within fibre variation was not significantly different than the other four, which had been in constant use and each had about 100 adsorption/desorption cycles.

To assess the effectiveness of the built-in septum as effective barrier to VOC, one fibre was placed on the bench in the retracted position, another one was co-located with the fibre exposed. The pair was left on the bench overnight. Analysis of the fibres showed the amount of VOC adsorbed on the protected fibre was less than 0.1% of that of the exposed one. Effectiveness of the sealing system depends on the ambient vapour concentration as well as the integrity of the replaceable septum. If the septum is worn or contaminated, it can actually contribute to the background of the SPME fibre.

3.3. Time exposure study

A time exposure experiment was then conducted on the bench described above at times ranging from 2 to 30 min. The time adsorption study is shown in Fig. 5, illustrating a general increasing adsorption profile, peaking at 15 min. for most solvent vapours. It is interesting to note with most volatile solvents, exposure time as short as 2 min produced a measurable amount of VOC. In practice, exposures anywhere between 2 and 15 min can be employed. The short exposure time is obviously advantageous in providing a ‘snap shot’ of fast-changing vapour concentration or in a hazardous situation where a short sampling time is essential for safety consideration.

3.4. DCM measurement in lab atmosphere

Before the actual sampling, a comparison was conducted between the charcoal and SPME method. A 5 l Tedlar bag was prepared with 265 ppmv DCM. Two separate charcoal tube samples were taken each with 2.5 l sample volume. Extraction and analysis was carried out as described in the experimental section. The average value was 232 ppmv. There was

Table 1
DCM in lab air, pump/charcoal vs. SPME method[a]

	Location		Charcoal tubes	SPME
Sample 1 (16 November)	Interfacial bench background	frt	17	34
		bk	0	
Sample 2 (24 November morning)	Interfacial test bench ('clean': non active)	frt	0	4 (9 duplicate)
		bk	0	
Sample 3 (24 November afternoon)	Lab 345 near GC/MSD; background	frt	0	6
		bk	0	
Sample 4 (24 November afternoon)	Interfacial test bench ('dirty': active)	frt	78	50
		bk	3	

[a] Results in μg DCM/l; charcoal tube sampling flow rate 0.1 l/min for 30 min, SPME (carboxen) exposed for 30 min.

no breakthrough of DCM from the first stage of 100 mg charcoal tube, as evident from non-detectable amount of DCM in the back half. A blank charcoal tube was exposed for 30 min in lab air without connecting to the pump. It was analysed in the same manner and found to be below detection limit. Surrogate recovery standard showed recoveries between 53 and 68% in the extraction method. Instrument detection limit was 10 μg per sample. For a sample volume of 5 l, the charcoal method detection limit is 2 μg/l or approximately 0.6 ppmv of DCM vapour in air.

Prior to actual use, the fibres were calibrated using a 5 l Tedlar bag with a DCM vapour concentration of 265 ppmv. Results of lab air samples are summarised in Table 1, showing the charcoal tube and the corresponding SPME values. Only sample #1 and #4 had measurable amount of DCM on the charcoal tubes. In most cases there was non-detectable amount of DCM in the back portion of the tube, signifying no breakthrough occurred at a sampling rate of 0.1 l/min during the 30 min sampling interval. The only exception is in sample #4 collected during active duties at the interfacial lab. The back half had 3 μg/l (1 ppmv), which amounts to less than 4% of the total collected. This is at the detection limit of the method and can be considered insignificant.

The corresponding SPME results are also shown in Table 1. Duplicate SPME at the site where sample #2 was collected showed the DCM concentration to be at 4 and 9 μg/l (1.1 and 2.6 ppmv). Agreement was in general, good, considering the rather poor sensitivity of liquid injection of DCM in CS_2 by GC/GCD. Examination of SPME sample chromatograms of the GC/GCD analyses typically showed the DCM peak at several hundred thousand counts, at least 100 times higher than the same from wet chemical extraction. In the latter case, at such low concentrations, peak shapes were also poorly formed, making quantitation difficult. In addition, the CS_2 peak eluted between 3 and 6 min, and presented a significant stress on the filament in the ion source of the GCD.

The recovery of the 1,2-dichlorobenzene (recovery standard) added to the charcoal samples was generally good at 75% with a variation of 11%. Recovery of native DCM from the matrix spike was 46–26%, respectively for front/back half, showing the fairly high degree of variation in the analysis of DCM due to the low instrument sensitivity.

As expected, the 'dirtiest' sample corresponded to the period when the interfacial tests were performed had a DCM concentration of 78 μg/l (26 ppmv) by the NIOSH method and

50 μg/l (16 ppmv) by SPME. Background concentration ranged from 17 μg/l (6 ppmv) to non-detectable (<1 ppmv). They are all below the regulatory limit.

4. Conclusions

The NIOSH official method for lab solvent vapour measurement using charcoal tube sampling with subsequent GC/GCD analysis is not well suited for background levels of DCM analysis due to the high background introduced by the solvent. The SPME method using carboxen/PDMS fibre is far more sensitive and easier to use. In field application, the simplicity of deployment, short sampling time, stability of the VOC on the fibre and reasonably precise measurement are significant advantages. Problems, however, exist with proper calibration of the fibre to reflect the dynamic nature of the atmosphere. When used in conjunction with a bench-top GC/MS in a mobile laboratory, the SPME is an excellent field screening tool or a general monitoring device for VOC in air, providing quick, unequivocal identification and quantitation of most VOC encountered in emergencies situations.

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