

Applicability of Direct Extraction of Solid Phase Micro-Extraction to the Determination of 54 Volatile Organic Compounds in Drinking Water

Shiau-Chian Soh & Md Pauzi Abdullah

School of Chemical Sciences and Food Technology, Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia.

Abstract: The applicability of direct extraction of solid phase microextraction (SPME) to volatile organic compounds (VOCs) determination in drinking water samples was demonstrated by validating the method and confirmed the technique's capabilities consistent with what the application requires. Recovery of each VOC was well above 80%, which was in the range of 81 - 109% with mean recovery 85% for three different spiked concentrations (10, 50 and 100 µg/l) while the RSD were below 13%. The method detection limit is in the range of 0.005 to 1.0 µg/l. Upon consideration of the complete procedure from sample preparation to instrumental determination, the expanded uncertainty for all VOCs under study is in the range of 1.06 to 2.95 µg/l. SPME has proven to be a very powerful analytical tool that offers fast, sensitive, inexpensive, portable and solvent-free technique for extracting VOCs from aqueous samples, which can be used on a routine basis.

Abstrak: Aplikasi pengekstrakan secara terus teknik pengekstrakan mikro fasa pepejal (SPME) untuk penentuan sebatian organik meruap (VOCs) dalam sampel air minum didemonstrasikan dengan ujian pengesahan kaedah untuk memastikan teknik ini mempunyai keupayaan yang konsisten dengan kehendak dan tujuan aplikasinya. Perolehan kembali setiap sebatian VOC adalah melebihi 80%, iaitu dalam julat di antara 81 – 109% dengan min perolehan kembali 85% untuk tiga kepekatan sampel yang dipaku (10, 50 dan 100 µg/l), manakala nilai RSD pula adalah dibawah 13%. Had pengesanan kaedah adalah dalam julat 0.005 hingga 1.0 µg/l. Setelah mengambil kira keseluruhan prosedur analisis iaitu daripada langkah penyediaan sampel sehinggalah kepada penentuan menggunakan peralatan, nilai ketidakpastian keseluruhan untuk semua sebatian VOCs dalam kajian adalah di dalam julat 1.06 hingga 2.95 µg/l. Kaedah SPME terbukti merupakan suatu kaedah analisis yang baik yang mana ia adalah pantas, peka, murah, mudah alih dan bebas pelarut dalam pengekstrakan VOCs daripada sampel akueus, dan boleh digunakan sebagai rutin harian dalam makmal.

Received : 20.12.04 ; accepted : 18.04.05

Introduction

Volatile organic compounds (VOCs) are important environmental contaminants because many are mobile, persistent and toxic, even at very low concentrations [1]. Various extraction techniques have been developed to extract dissolved VOCs in aqueous samples for qualitative and quantitative determination [2]. In the first step of this analytical process the VOCs are separated from the aqueous matrix. The separation techniques can be divided into either concentration or isolation methods. In concentration method, water is removed and the substances are left behind whereas in isolation method the dissolved substances are removed from water. Nevertheless, isolation techniques are the more commonly used methods in the analysis of organics in water [3]. The techniques developed to extract VOCs includes static headspace, dynamic headspace, purge-and-trap, solid phase micro-extraction (SPME) and membrane inlet, which are then combined with gas chromatography (GC) and mass spectrometry (MS) for analysing dissolved VOCs [2].

Although volatiles are usually analysed by the use of purge and trap which is a U.S. Environmental Protection Agency (EPA) approved technique [4], SPME method has gained increasing

attention from various research disciplines, with constantly increasing numbers of new publications. SPME was first reported by Arthur and Pawliszyn in 1990 [5]. SPME technique has two steps. In the first step, the coated fibre is exposed to the sample or its headspace and the target analytes partition from the sample matrix to the coating. The second step is when the fibre bearing the concentrated analytes is transferred to the analytical instrument where desorption, separation, and quantification of the extracted analytes take place. Because of its unique characteristics, SPME has the potential to overcome the problems associated with liquid-liquid extraction, as it completely eliminated the use of organic solvents [6].

The present work evaluated the applicability of direct extraction of SPME in extracting a wide range of VOCs in drinking water. Development of a performance based method and validation of SPME technique has been discussed for analysing 54 VOCs by using GC-MSD in drinking water.

Experimental

Reagents and standards

The pure standard solution of VOCs mixture for water analysis used in this study is listed in Table 1. The standards were purchased from TCI, Tokyo Kasei Kogyo Co. Internal standard used was

Table 1 : Compounds studied ordered by retention time (RT) and peak no. used, and its respective calibration equation and coefficient of determination (R^2).

Compound	CAS Registry No.	Peak No.	RT (min)	Calibration equation	R^2
1,1-Dichloroethylene	75-35-4	7	1.540	$y = 0.196\chi - 0.026$	0.999
Methylene chloride	75-09-2	8	1.580	$y = 0.027\chi + 0.001$	0.999
<i>trans</i> -1,2-Dichloroethylene	156-60-5	9	1.800	$y = 0.148\chi - 0.013$	0.999
1,1-Dichloroethane	75-34-3	10	1.850	$y = 0.133\chi - 0.017$	0.997
2,2-Dichloropropane	594-20-7	11	2.060	$y = 0.694\chi - 0.029$	0.998
<i>cis</i> -1,2-Dichloroethylene	156-35-4	12	1.930	$y = 0.135\chi - 0.007$	0.998
Chloroform	67-66-3	13	2.060	$y = 0.694\chi - 0.029$	0.998
Bromochloromethane	74-97-5	14	2.060	$y = 0.694\chi - 0.029$	0.998
1,1,1-Trichloroethane	71-55-6	15	2.360	$y = 0.835\chi - 0.099$	0.998
1,1-Dichloropropene	563-58-6	16	2.470	$y = 0.879\chi - 0.137$	0.998
Carbon tetrachloride	56-23-5	17	2.540	$y = 1.08\chi - 0.147$	0.998
1,2-Dichloroethane	107-06-2	18	2.540	$y = 1.08\chi - 0.147$	0.998
Benzene	71-43-2	19	2.540	$y = 1.08\chi - 0.147$	0.998
Trichloroethylene	79-01-6	20	3.100	$y = 0.808\chi - 0.045$	0.999
1,2-Dichloropropane	78-87-5	21	3.100	$y = 0.808\chi - 0.045$	0.999
Dichlorobromomethane	75-27-4	22	3.190	$y = 0.143\chi - 0.001$	0.997
Dibromomethane	74-95-3	23	3.100	$y = 0.808\chi - 0.045$	0.999
<i>cis</i> -1,3-Dichloropropene	10061-01-5	24	3.950	$y = 0.694\chi - 0.0649$	0.997
Toluene	108-88-3	25	4.570	$y = 5.33\chi - 0.248$	0.999
<i>trans</i> -1,3-Dichloropropene	10061-02-6	26	4.570	$y = 5.33\chi - 0.248$	0.999
1,1,2-Trichloroethane	79-00-5	27	4.670	$y = 1.19\chi - 0.223$	0.995
1,3-Dichloropropane	142-28-9	28	5.190	$y = 0.701\chi - 0.118$	0.997
Tetrachloroethylene	127-18-4	29	5.940	$y = 2.71\chi - 0.214$	0.998
Dibromochloromethane	124-48-1	30	5.450	$y = 0.459\chi - 0.030$	0.997
1,2-Dibromoethane	106-93-4	31	5.770	$y = 0.343\chi - 0.049$	0.997
Chlorobenzene	108-90-7	32	7.100	$y = 5.51\chi - 0.618$	0.995
1,1,1,2-Tetrachloroethane	630-20-6	33	7.240	$y = 1.93\chi - 0.277$	0.996
Ethylbenzene	100-41-4	34	7.650	$y = 1.20\chi - 0.027$	0.996
1,3-Xylene	108-38-3	35	7.920	$y = 19.2\chi + 0.791$	0.997
1,4-Xylene	95-47-6	36	7.920	$y = 19.2\chi + 0.791$	0.997
1,2-Xylene	106-42-3	37	8.670	$y = 11.4\chi - 0.048$	0.995
Styrene	100-42-5	38	8.600	$y = 5.30\chi + 0.258$	0.995
Isopropylbenzene	98-82-8	39	9.730	$y = 15.2\chi - 0.124$	0.996
Bromoform	75-25-2	40	8.30	$y = 0.351\chi - 0.012$	0.997
1,1,1,2-Tetrachloroethane	79-34-5	41	9.340	$y = 1.10\chi - 0.075$	0.998
1,2,3-Trichloropropane	96-18-4	42	9.530	$y = 1.03\chi - 0.077$	0.995
<i>n</i> -Propylbenzene	103-65-1	43	10.660	$y = 24.0\chi + 1.02$	0.997
Bromobenzene	108-86-1	44	9.830	$y = 4.66\chi + 0.110$	0.996
1,3,5-Trimethylbenzene	108-67-8	45	11.130	$y = 13.1\chi - 0.145$	0.996
2-Chlorotoluene	95-49-8	46	10.530	$y = 11.3\chi + 0.209$	0.996
4-Chlorotoluene	106-43-4	47	10.710	$y = 10.2\chi + 0.164$	0.995
<i>tert</i> -Butylbenzene	98-06-6	48	11.890	$y = 13.5\chi + 0.070$	0.996
1,2,4-Trimethylbenzene	95-63-6	49	11.890	$y = 13.5\chi + 0.070$	0.996
<i>sec</i> -Butylbenzene	135-98-8	50	12.430	$y = 21.3\chi + 1.08$	0.997
<i>p</i> -Isopropyltoluene	89-83-8	51	12.860	$y = 1.51\chi + 0.057$	0.995
1,3-Dichlorobenzene	541-73-1	52	12.190	$y = 6.92\chi - 0.118$	0.995
1,4-Dichlorobenzene	106-46-7	53	12.430	$y = 21.3\chi + 1.08$	0.997
<i>n</i> -Butylbenzene	104-51-8	54	13.790	$y = 18.5\chi + 0.629$	0.997
1,2-Dichlorobenzene	95-50-1	55	13.070	$y = 6.86\chi - 0.197$	0.995
1,2-Dibromo-3-chloropropane	96-12-8	56	14.460	$y = 8.54\chi + 0.019$	0.995
1,2,4-Trichlorobenzene	120-82-1	57	17.110	$y = 5.26\chi + 0.198$	0.995
Hexachlorobutadiene	87-68-3	58	18.210	$y = 2.60\chi + 0.096$	0.996
Naphthalene	91-20-3	59	17.270	$y = 1.67\chi + 1.080$	0.996
1,2,3-Trichlorobenzene	87-61-6	60	18.040	$y = 5.34\chi + 0.199$	0.996

fluorobenzene (FB) and surrogate standard used was 4-bromofluorobenzene (BFB), which was purchased from Supelco. The deionised water used for preparing standard solutions was purified by Arium 611DI system from Sartorius AG.

Calibration

Intermediate calibration standard solution, 200 mg/l was prepared by diluting 1.0 ml calibration stock standard, 2000 mg/l to 10 ml in a volumetric flask with methanol. A series of working standard solutions (10 - 100 µg/l) were prepared appropriately in a 50 ml volumetric flask using deionised water. The intermediate internal calibration standard and surrogate standard (200 mg/l) were prepared in the same procedure as preparing the calibration stock standard.

Water samples

The samples were collected in 100 ml amber glass vials equipped with Teflon-faced septa. Water tap was opened and allowed the system to flush until the water temperature has stabilised. Five drops of 10% sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) was added to the sample bottle before sample bottle was filled to overflowing. No air bubbles should pass through the sample as the bottle was filled or be trapped in the sample when the bottle was sealed. The pH was adjusted to < 2 by carefully adding two drops of 1:1 acid hydrochloride (HCl) for each 100 ml sample volume. The sample bottles were sealed and shake vigorously for 1 min.

Samples were allowed to warm to room temperature (30°C). About 40 ml sample was poured into a 50 ml volumetric flask followed by 20 µl of internal calibration standard (FB) and surrogate standard (BFB) at 200 mg/l and then top up to exactly 50 ml. The sample was transferred to a 40 ml glass vial with magnetic stirrer inside and capped with a hole cap and a Teflon-faced silicone rubber septum.

SPME-GC-MSD

SPME device was purchased from Supelco America (Bellefonte, PA) with approximately 7.5 cm of fibre (coated with a 100 µm thick stationary phase of polydimethylsiloxane) attached to a 15 cm of stainless steel needle that is inserted inside the plunger of a Hamilton syringe (Model, 7005) was used. The SPME fibre was previously conditioned according to the manufacturer's recommendations (280°C for 30 min in a GC injector). The fibre was exposed into the sample for 5 min at ambient temperature under stirring condition. 5 min absorption time was found to be the optimum time to extract all VOCs in water sample. After sampling time, the SPME fibre was withdrawn into the needle and removed from the sample matrix. The fibre was then immediately inserted into the heated GC injection port. A desorption time of 10

min was allowed for the analytes to be desorbed from the fibre and get introduced into the GC column for analyses. Although for non-polar volatile compounds, desorption is virtually complete in a few seconds, desorption should be continued for a few minutes to ascertain that no carryover occurs when a blank is inserted after a sample [7]. A fused-silica capillary column CP SIL 8CB (30 m x 0.25 mm, $d_f = 0.25 \mu\text{m}$; Varian, Inc.) was used on a HP 5890 GC system equipped with mass spectrometry detector (MSD). The oven temperature program started from 35°C holds for 4 min and increased to 160°C at 6°C/min, holding at 160°C for 5 min. The total run time was 30 min. Injector temperature was set at 220°C. The MSD acquisition was performed in scan mode from 35 to 260 a.m.u. and in time scheduled selected ion monitoring mode was used.

Results and Discussion

Performance validation and quantitative evaluation of SPME-GC-MSD technique

Linearity of calibration curve

Internal standard quantification was carried out using a five-point calibration at concentrations of standard solutions in the range of 10 to 100 µg/l using three replicate injections. A linear curve fit was obtained using the linear least squares regression procedure. The coefficient of determination (R^2) was close to unity (> 0.994), as shown in Table 1.

Accuracy and Precision

Determination of accuracy is done by spiking drinking water samples with known amounts of VOCs standard mixture to obtain 10, 50 and 100 µg/l concentrations. Table 2 summarises the results of spiked drinking water samples with VOCs standard mixture. As for precision, the ISO defined it as the closeness of agreement between independent test results obtained under stipulated conditions [8]. Therefore, precision in this case can be expressed in terms of the percent relative standard deviation (RSD). It is assessed using three different spiked concentrations (10, 50 and 100 µg/l) and seven replicates for each concentration. The results of each VOC are also shown in Table 2.

Recovery of each VOC was well above 80%, which was in the range of 81 - 109% with mean recovery 85% for three different spiked concentrations while the RSD were below 13%. These ranges or results were within the limit set by the Association of Official Analytical Chemists (AOAC) [9] i.e. for 100 µg/l spiking concentration; the acceptable mean recovery is 80 - 110% and RSD less than 15%.

Table 2 : Mean recovery, RSD, MDL and LOQ of each VOC using SPME-GC-MSD.

Compound	10 µg/l		50 µg/l		100 µg/l		MDL (µg/l)	LOQ (µg/l)
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)		
1,1-Dichloroethylene	89	13	90	10	90	8	0.925	2.775
Methylene chloride	93	10	90	9	92	9	1.121	3.363
<i>trans</i> -1,2-Dichloroethylene	92	11	96	10	103	10	1.069	3.207
1,1-Dichloroethane	88	12	90	11	91	8	0.999	2.997
2,2-Dichloropropane	85	13	86	12	98	11	0.210	0.630
<i>cis</i> -1,2-Dichloroethylene	88	10	89	10	100	8	0.712	2.136
Chloroform	85	13	86	12	95	11	0.210	0.630
Bromochloromethane	85	13	86	12	88	11	0.210	0.630
1,1,1-Trichloroethane	86	13	85	11	85	11	0.150	0.450
1,1-Dichloropropene	85	12	85	12	109	12	0.089	0.267
Carbon tetrachloride	89	13	89	11	90	10	0.015	0.045
1,2-Dichloroethane	89	13	89	11	102	10	0.015	0.045
Benzene	89	13	89	11	90	10	0.015	0.045
Trichloroethylene	92	10	90	8	91	8	0.195	0.585
1,2-Dichloropropane	92	10	90	8	91	8	0.195	0.585
Dichlorobromomethane	85	9	85	9	85	9	0.779	2.337
Dibromomethane	92	10	90	8	91	8	0.195	0.585
<i>cis</i> -1,3-Dichloropropene	88	8	89	9	85	8	0.482	1.446
Toluene	95	9	92	9	96	7	0.015	0.045
<i>trans</i> -1,3-Dichloropropene	95	9	92	9	96	7	0.015	0.045
1,1,2-Trichloroethane	85	8	86	8	85	7	0.897	2.691
1,3-Dichloropropane	83	9	86	9	89	7	0.594	1.782
Tetrachloroethylene	85	10	85	9	86	8	0.101	0.303
Dibromochloromethane	83	7	85	8	96	7	0.456	1.368
1,2-Dibromoethane	85	9	86	9	88	9	0.896	2.688
Chlorobenzene	85	10	86	10	89	8	0.769	2.307
1,1,1,2-Tetrachloroethane	85	8	87	9	86	8	0.188	0.564
Ethylbenzene	84	9	85	8	85	8	0.012	0.036
1,3-Xylene	90	10	89	8	92	6	0.009	0.027
1,4-Xylene	90	10	89	8	92	6	0.009	0.027
1,2-Xylene	88	11	89	10	85	10	0.013	0.039
Styrene	86	6	85	6	85	6	0.052	0.156
Isopropylbenzene	87	9	85	8	86	8	0.006	0.018
Bromoform	85	7	86	8	85	9	0.298	0.894
1,1,2,2-Tetrachloroethane	85	8	85	8	84	7	0.187	0.561
1,2,3-Trichloropropane	83	6	85	7	82	6	0.096	0.288
<i>n</i> -Propylbenzene	82	9	83	9	82	9	0.103	0.309
Bromobenzene	81	10	85	9	85	10	0.088	0.264
1,3,5-Trimethylbenzene	86	8	89	7	83	7	0.029	0.087
2-Chlorotoluene	87	6	88	6	93	6	0.059	0.177
4-Chlorotoluene	83	10	85	10	96	10	0.061	0.183
<i>tert</i> -Butylbenzene	89	8	92	6	93	6	0.024	0.072
1,2,4-Trimethylbenzene	89	8	92	6	93	6	0.063	0.189
<i>sec</i> -Butylbenzene	88	6	86	5	89	6	0.005	0.015
<i>p</i> -Isopropyltoluene	82	10	85	10	97	8	0.087	0.261
1,3-Dichlorobenzene	86	6	85	6	93	6	0.016	0.048
1,4-Dichlorobenzene	88	6	86	5	89	6	0.005	0.015
<i>n</i> -Butylbenzene	87	5	86	6	91	5	0.009	0.027
1,2-Dichlorobenzene	86	5	85	6	94	5	0.026	0.078
1,2-Dibromo-3-chloropropane	87	9	85	10	89	9	0.106	0.318
1,2,4-Trichlorobenzene	86	8	85	8	87	8	0.064	0.192
Hexachlorobutadiene	85	5	85	6	83	6	0.029	0.087
Naphthalene	84	8	85	8	93	8	0.069	0.207
1,2,3-Trichlorobenzene	83	8	84	8	90	7	0.085	0.255

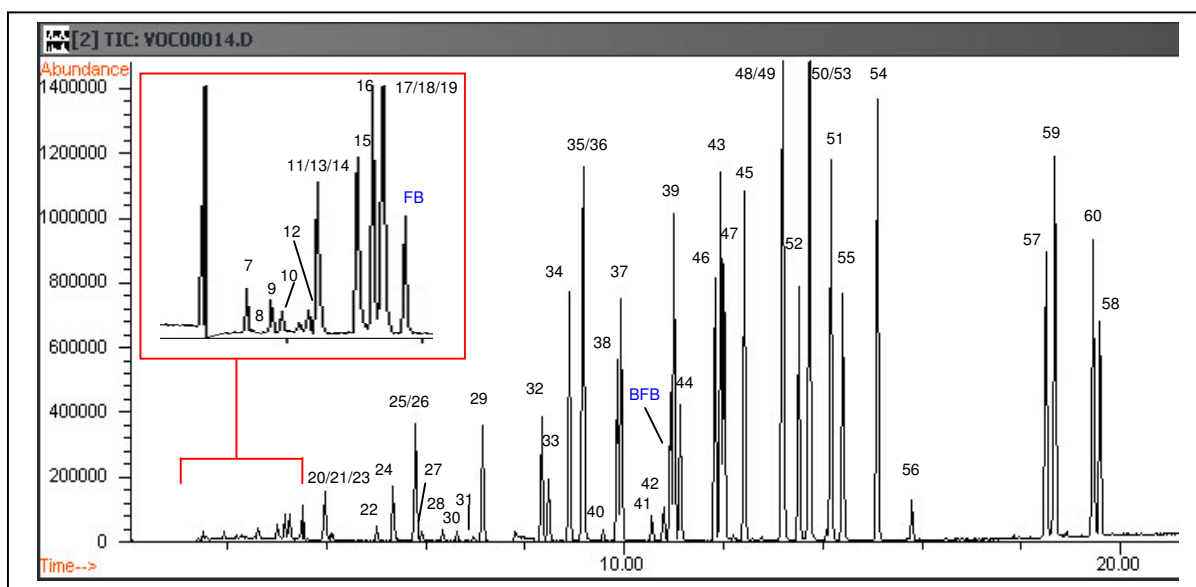


Figure 1 : Chromatogram (SPME-GC-MSD) of spiked drinking water sample with VOCs standard at 10 µg/l.

Specificity or selectivity

Specificity, which defined by the ICH documents, is the ability to assess unequivocally the analyte in the presence of components, which may be expected to be present such as impurities, degradation products and matrix components, whereas, other reputable international authorities (IUPAC, AOAC) have preferred the term selectivity, reserving specificity for those procedures that are completely selective [10]. The selectivity of the analytical method in this research was determined by comparing the results from the analysis of drinking water sample containing impurities with the result obtained from deionised water sample. Figure 1 shows a chromatogram of spiked drinking water sample. VOCs were well separated despite the presence of other components or impurities in the sample. SPME is an equilibrium method which is more selective if it was to compare with other exhaustive methods as it takes full advantage of differences in extracting phase/matrix distribution constants to separate the VOCs from interferences. This SPME technique has proved its selectivity as it does not require an additional cleanup step to remove interference.

Method Detection Limit (MDL), Limit of Quantitation (LOQ) and Measurement uncertainty for test result

MDL is the lowest concentration of analyte in sample that can be detected but not necessarily quantified, under the stated conditions of the test [9]. LOQ, also known as the limit of reporting, is the lowest concentration of an analyte that can be determined with acceptable precision and accuracy under the stated conditions of test [11].

To determine the MDL, drinking water samples were spiked with freshly prepared VOCs standards, each at a concentration of 1 µg/l. It was

then analysed with SPME-GC-MSD method at optimum experimental conditions. The MDL value was calculated from the standard deviation of seven replicates studies results multiplied by the appropriate Student's-t value for 99% confidence interval (3.707). For this case MDL does not account for the variation in sample composition and only achieves under ideal conditions [12]. Quantitation limit is 3.33 times MDL [12]. Table 2 shows the values of MDL and LOQ of each VOC under study.

Upon consideration of the complete procedure from sample preparation to instrumental determination, the expanded uncertainty for all VOCs under study is in the range of 1.06 to 2.95 µg/l.

Field samples

The optimised SPME method was used to analyse the presence of VOCs in drinking water samples, which was collected fortnightly for 3 months (January to March 2004) at Semenyih River Water Treatment Plant.

Results from drinking water samples showed significantly high concentrations of trihalomethanes (THMs). Overall, chloroform was the highest followed by bromodichloromethane and dibromochloromethane. THMs with the lowest concentration were bromoform.

Of all VOCs compounds tested (exclude THMs compounds), 1,3-dichloropropene had a percent positive rate of 86%, chlorobenzene with 72%, toluene with 69%, dichlorobenzenes with 65%. Other VOC compounds ranged from 3% to 15%. Nevertheless, the mean VOCs concentrations did not exceed the guideline values stated in the Guidelines of Malaysia Drinking Water Standard 2001.

Overview of the applicability of SPME to multi VOCs group analysis

Benzene, toluene, ethylbenzene and the xylenes (BTEX) are a subset of commonly regulated volatile organic compounds but nevertheless they are the most frequently requested in environmental monitoring. As by-products of petrochemical refining, coal burning operations, and leaks from underground storage tanks, they are routinely demanded as a unique set of parameters. It follows that a significant amount of work has been devoted to optimisation of SPME extraction of these compounds [2,13,14]. Apart from BTEX compounds, SPME technique has also proved to be efficient in extracting trihalomethanes (THMs) compounds [15]. THMs are disinfection by-products of chlorination of drinking water that are suspected and known to be carcinogens. The same concept of extraction applies to BTEX and THMs analysis as to the larger set of multi volatiles organic compounds group. Polydimethylsiloxane (PDMS) with 100 μm film thickness is used due to its favourable polarity.

The standard conventional chromatographic injectors of GC require large volume liners to accommodate the expansion of the evaporated solvent introduced during injection. However, in SPME introduction, no solvent is present and therefore the split opening, which allows injection band sharpening and removal of solvent vapours, is unnecessary. Hence, by using a narrow bore liner of 0.75mm internal diameter will practically generate high linear flow rates to facilitate sharp SPME injection bands.

The selection of the SPME extraction mode is made by considering the sample matrix, analyte volatility and its affinity to the matrix. Drinking water samples can be considered as clean matrices, therefore direct sampling is preferred. As SPME technique is an equilibrium method, the most universal approach for sample preparation technique is to cool the fibre coating [7]. The fibre temperature needs to be kept low and constant during the experiment. In order to make aqueous extraction faster, agitation is necessary. These approaches are needed to reduce the effects of fluid shielding and small diffusion coefficients of analytes in liquid matrixes in the zone close to the fibre [5]. Care must also be taken when using a magnetic stirrer to ensure that the rotation speed of the bar is constant and the base plate is thermally isolated from the vial containing the sample.

The basic objective of the SPME experiments, in principle, is to reach distribution equilibrium in the system. The equilibrium time is defined as the time after which the amount of extracted analyte remains constant and corresponds within experimental error to the amount extracted at infinite extraction time. Care must be taken to control the exposure time as timing is very critical in order to obtain good precision. However,

constant convection and temperature in the system needs to be ensured to obtain reproducible data.

Conclusion

SPME is a very powerful analytical tool that offers fast, sensitive, inexpensive, portable and solvent-free technique for extracting VOCs from aqueous samples. However, validation of SPME-GC-MSD method is vital before any further applications and analysis done because the process of confirming an analytical requirement will prove the technique's capabilities consistent with what the application requires and is fit for purpose. This paper has proved that direct extraction of SPME is applicable for the determination of 54 VOCs in drinking water and can be used on a routine basis.

Acknowledgements

The authors gratefully acknowledged Universiti Kebangsaan Malaysia for the laboratory facilities. The financial support from Malaysian Government under R & D grant, IRPA program 08-02-02-0009EA179 is gratefully acknowledged. Ministry of Sciences, Technology and the Environment is also acknowledged for financial support to SC Soh.

References

1. Malaysia (2001) *Malaysia environmental quality report 2001*. Kuala Lumpur, Malaysia: Ministry of Sciences, Technology and the Environment.
2. Yang, K.L., Lai, C.H. and Wang, J.L. (2004) Construction and validation of an automated spray-and-trap gas chromatograph for the determination of volatile organic compounds in aqueous samples. *J. Chromatogr. A.*, **1027**, 41-48.
3. Louch, D. Motlagh, S. and Pawliszyn, J. (1992) Dynamics of organic compound extraction from water using liquid-coated fused silica fibers. *Anal. Chem.*, **64**, 1187-1199.
4. Clesceri, L.S., Greenberg, A.E. and Trussell, R.R. (1998) Standard methods for the examination of water and wastewater. 17th ed. Washington, D.C., American Public Health Association.
5. Arthur, C.L. & Pawliszyn, J. (1990) Solid phase microextraction with thermal desorption using fused silica optical fibres. *Anal. Chem.*, **62**, 2145-2148.
6. Fatima Alpendurada, M.D. (2000) Solid phase microextraction: a promising technique for sample preparation in environmental analysis. *J. Chromatogr. A.*, **889**, 3-14.
7. Wercinski, S.A.S. (1999) Solid phase microextraction : A practical guide. New York: Marcel Decker, Inc.
8. EURACHEM. (1998). The fitness for purpose of analytical methods: A laboratory guide to method validation and related topics. Teddington, UK: EURACHEM.

9. AOAC. (1993) Peer verified methods program, manual on policies and procedures. Arlington, VA: AOAC.
10. Candela, M., Ruiz, A. & Feo, F.J. (2000) Validation of an analysis method for 4-amino-3-hydroxybutyric acid by reversed-phase liquid chromatography. *J. Chromatogr. A.*, **890**, 273–280.
11. NATA. (1998) Format and content of test methods and procedures for validation and verification of chemical test methods. Australia: National Association of Testing Authorities.
12. US EPA. (1994). Method detection limit. USEPA definition in 40 CFR, Part 136, Appendix B, 7-1-94 edition.
13. Arthur, C.L., Killam, L.M., Motlagh, S., Lim, M., Potter, D.W. & Pawliszyn, J. (1992) Analysis of substituted benzene compounds in groundwater using solid-phase microextraction. *Environ. Sci. Technol.*, **26**, 979-983.
14. Zhang, Z & Pawliszyn, J. (1993) Headspace solid-phase microextraction. *Anal. Chem.*, **65**, 1843-1852.
15. Md. Pauzi Abdullah, Yew, C.H., Mohamad Salleh & Rahmah Ali (2002) Validation of solid phase microextraction technique for analysis of trihalomethanes (THMs) in Malaysian drinking water. *Malaysian Journal of Chemistry*, **4**, 27-34.