DEVELOPMENT OF A COMPREHENSIVE ANALYTICAL METHOD FOR SEMIVOLATILE ORGANIC MICROPOLLUTANTS IN WATER

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Abstract

In order to develop a rapid and comprehensive solid-phase extraction (SPE) method for semivolatile organic compounds (SVOCs) in environmental water, we systematically evaluated commercially available SPE materials using 99 representative SVOCs to determine which SPE materials show the highest performance for these representative compounds. Thereby it was demonstrated that the combination of a styrenedivinylbenzene polymer type and an activated carbon type show the highest performance; compounds with the molecular weight range 93.12–627.4, water solubility (logSw) -10–6.89, and logPow -0.66–15.07 could be extracted from distilled water by using this SPE combination; its performance was nearly equal to that of liquid-liquid extraction using dichloromethane (DCM-LLE). We also applied this combination of SPE materials to an actual river water sample; the result of SPE analysis of river water was essentially the same as that of DCM-LLE.

Introduction

In order to evaluate the effect of chemical substances on human health and ecosystems, it is desirable to determine the concentration of a variety of chemicals existing in environment as much as possible. In particular, some effective screening method is required as an initial assessment in certain areas or countries where unmonitored and rapidly growing industry is causing heavy environmental pollution. In that context, Kadokami et al[1] developed a novel GC/MS database for automatic identification and quantification of 888 kinds of SVOC micropollutants. The objective of the present study was to develop a rapid and comprehensive analytical method which covers whole SVOCs registered in the GC/MS database system.

For comprehensive analysis of SVOCs in water samples, DCM-LLE has conventionally been applied, [2,3] but a few methods using SPE, which has lower environmental impact, have been reported.[4] Therefore, in this study we selected 99 representative SVOCs as model compounds and evaluated 5 commercially available SPE materials, using the model compounds to determine which combination of SPE materials show the highest performance for the model compounds. We optimized our method with the best performing SPE and then conducted a screening analysis of an actual river water using the method that we developed.

Materials and Methods

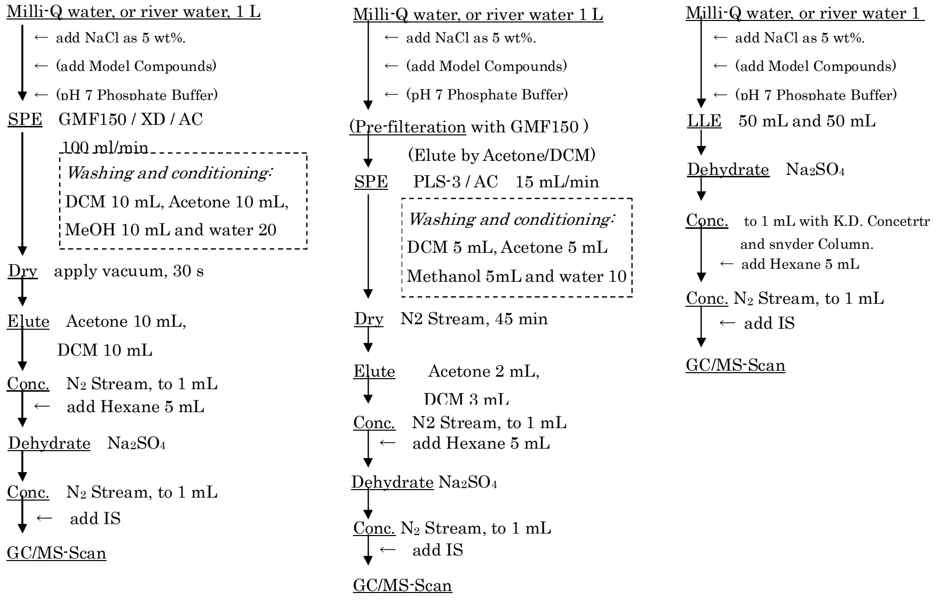
1) Model compounds: We selected 99 chemicals as model compounds from the groups of n-alkanes, benzenes, nitro compounds, amines, aromatic amines, polycyclic aromatic hydrocarbons, phenols, and pesticides on the basis of physicochemical properties such as molecular weight, boiling point, hydrophobicity, water solubility, functional group, and structure. Among the model compounds, molecular weight ranged from 89.09 to 627.4, water solubility from 0 to 7,720 g/L, and logPow from -0.66 to 15.07. We assumed that the model compounds represent SVOCs in general. We used a 2 μg/mL acetone solution of the model compound for experiments.

2) SPE materials and GC/MS condition: We used 5 disk type and 2 cartridge-type SPE materials (Table 1), with SPE cartridges used as the reference. The Sep-Pak concentrator (Waters corp.) and the 3-station vacuum manifold (3M Company) were used for the extraction step. Samples were measured by Shimadzu QP-2010 GC/MS with the capillary column of J&W DB-5ms in scan mode. Quantification was conducted by the internal standard (IS) method using deuterium-labeled compounds.

Table 1 SPE materials used

No.	Name	Solid Phase
Disk type		
1	3M Empore disk AC	Activated carbon
2	3M Empore disk C18	Octadecyl silica
3	3M Empore disk SDB-XC	Styrenedivinylbenzene (SDB) polymer
4	3M Empore disk SDB-XD	SDB polymer
5	3M Empore disk RPS	Sulfonated SDB polymer
Cartridge type		
1	Waters Sep-Pak AC-2	Activated carbon
2	GL Science Aqusis PLS-3	SDB polymer + N-vinylacetoamide

3) Comparing SPEs and DCM-LLE extraction ability: Model compound-spiked water (MCSW) was



1) SPE disks **2) SPE cartridges** **3) DCM-LLE**

Figure 1 Analytical procedures

prepared as follows: 50 g of NaCl and 0.5 μg of the model compound were added to 1 L of Milli-Q water purified by Empore SPE disks (SDB-XD and AC). The extraction performance of each SPE disk was compared by the following procedure: 1 L of the MCSW was passed at 100 mL/min through the each SPE disk, which had been cleaned and conditioned with dichloromethane and acetone, methanol (10 mL each) and 20mL water. Disks were dried by applying a vacuum for 30 s and eluted with 10 mL acetone and 10 mL dichloromethane. The eluate was concentrated to 1 mL with a nitrogen stream and added to 10 mL of hexane, then dehydrated with small amount of anhydrous sodium sulfate, then again concentrated to 1 mL with a nitrogen stream. The IS was then added and measured by GC/MS (n=3). When SDB-XD was overlaid on AC, elution procedures were performed separately, and eluates from XD and AC were mixed later. The solvents used for elution were selected by testing four solvents—acetone, methyl acetate, diethylether and dichloromethane—that have lower boiling points than hexane, which was used as the final concentrated solution for GC/MS measurement. Among those, acetone and dichloromethane showed satisfactory performance.

The SPE cartridges were washed with 5 mL of dichloromethane and acetone, respectively, then conditioned with 5 mL methanol and 10 mL water. The MCSW was passed at 15 mL/min through two SPE cartridges (PLS-3, AC2) connected in tandem. Cartridges were dried with a nitrogen stream for 45 min, then each cartridge was eluted with 2 mL acetone and 3 mL dichloromethane. Eluates were mixed, concentrated, and dehydrated in the same way as the eluate of SPE disk, and then measured by GC/MS (n=7).

DCM-LLE was performed as follows: 1 L of the MCSW was extracted by shaking twice by 50 mL dichloromethane. The eluates were mixed and dehydrated with a small amount of anhydrous sodium sulfate and concentrated to about 5 mL using a Kuderna-Danish concentrator, then concentrated to 1 mL using a Snyder distilling column; the IS was then added and measured by GC/MS (n=4).

4) Comparing methods for extraction from Suspended Solids (SS): To analyze organochlorine pesticides and other pollutants by an SPE method, the U.S. Environmental Protection Agency employs a soaking extraction technique: SS are collected on a glass fiber filter, which had previously been overlaid on SPE disk(s). Target compounds absorbed on and inside the SS are extracted by soaking in an elution solvent for one minute at the same time as the SPE disk elution is performed (Soaking Extraction, SE).[5] On the other hand, for extraction of chemical substances absorbed in soil and sediments particulates, the ultrasonic extraction technique is also commonly used (Ultrasonic Extraction, UE). To determine the most effective analytical procedure, we compared the recovery rates of model compounds by SE and UE from SS containing river water by following procedure. Model compounds were added as 1 μg/L in 2.4 L river water that contained 20 mg/L of SS, then the river water was shaken well and left standing still for 1 h. The river water, while continually being shaken, was divided into six bottles, 400 mL each. Then the bottles of river water were filtered with one glass fiber filter (Whatman GMF-150) for each bottle. Three of six were extracted by SE (Figure 1: 1), and others were extracted by UE (Figure 1: 2). For UE, each glass fiber filter was soaked in 10 mL of acetone that had been exposed to ultrasound

for 10 min and repeated using 10 mL of dichloromethane. Then acetone and dichloromethane were mixed and treated in same way as SE and measured by GC/MS.

5) Recovery test for river water: Model compounds were added to 1 L of river water (SS: 20 mg/L) as 1 μg/L and pH was adjusted to 7 by adding phosphate buffer solution and treated (Figure 1, 3); the recovery rates were then confirmed.

6) River water analysis: River water samples of 1 L each were treated by one of the three extraction methods (Figure 1: 1, 2, 3), using SPE disks (n=2), SPE cartridges (n=2) or DCM-LLE (n=1); the detected compounds and their concentrations by each method were then compared.

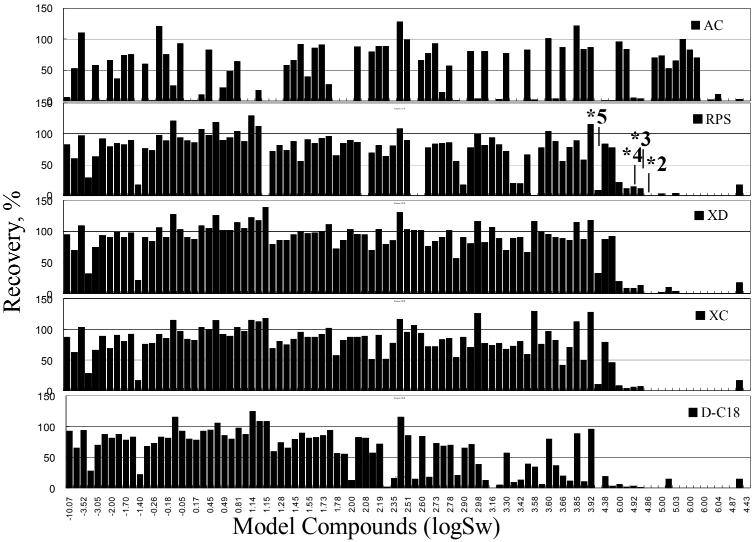


Figure 2 Recovery of SPE disks

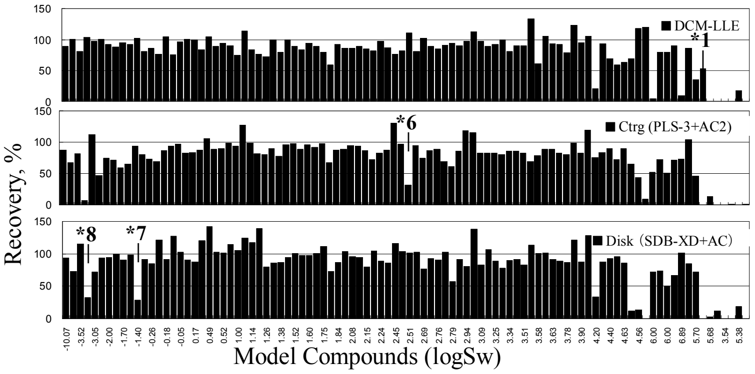


Figure 3 Recovery of combined disks, cartridges and DCM-LLE

Results and Discussion

1) Comparison of SPEs and DCM-LLE extraction ability: The extraction ability of the SPE disks was compared (Figure 2). C18 showed low recovery rates of water soluble compounds which had logSw greater than 2, such as nitrobenzenes, phenols and aromatic amines. SDB-XC and XD showed higher recovery rates for the most of the compounds that had logSw under 4.5. SDB polymers have been demonstrated to be more suitable than C18 for extraction of hydrophilic compounds. Recovery rates of 4-nitrophenol (*5, Figure 2) were low in all disks (0–33%) but XD in particular showed higher recovery rate (33%) compared to others. AC could extract very hydrophilic compounds that have logSw 5–7, which any other SPE disks could not extract. Therefore, it has been demonstrated that the combination of SDB-XD and AC will show highest performance for the comprehensive analysis using SPE disks.

We compared recovery rates for model compounds of combined SPE disks (SDB-XD+AC), SPE cartridges (PLS-3+AC2) and DCM-LLE (Figure 3). Phenol (*4, Figure 2) and aniline (*3), which had low recoveries with SPE disks, showed comparatively better recovery rates of 66% and 44%, respectively, with SPE cartridges, probably because PLS-3 has hydrophilic functional groups on its SDB polymer. Two model compounds, 2,6-diaminotoluene (*2) and methyl methanesulfonate (*1, Figure 3), were extracted only by DCM-LLE. Benzidine (*6) and 1,2,4,5-tetrabromobiphenyl (*7) showed lower recovery rates than other compounds on SPE cartridges and disks, respectively. Dibenzo(a,h)anthracene (*8), which is one of the very hydrophobic compounds, showed lower recovery rates with both the SPE disks and cartridge compared with DCM-LLE.

As mentioned above, some compounds that have a strong hydrophilic or hydrophobic property showed lower recovery rates compared with DCM-LLE. However, it has been demonstrated that the combined SPE material, SDB polymer and activated carbon, can extract as wide a wide range of compounds (logSw: -10 to 6.89) that

DCM-LLE can extract, and thus can be applied to a comprehensive analysis.

2) Comparing extraction methods from suspended solids: Several hydrophobic model compounds, such as trans-Nonachlor and 4,4′-DDT, were extracted from SS on glass fiber filters by both extraction methods, SE and UE (Table 2). Comparing the average concentrations from SE and UE, respectively, the rates between average concentrations have given from 0.8 to 1.2. No notable difference was observed between the two extraction techniques in this instance. Therefore, the SE technique was employed for the ensuing studies.

3) Recovery test for river water: Three aromatic amines - 3,3′-dichlorobenzidine, 4,4′-methylenebis (2-chloroaniline) and benzidine—showed low recoveries at 27%, 24% and 0%, respectively. It has been suggested that the low recovery rates were caused by pH adjustment or some other procedure, because these compounds showed recovery rates of 123%, 124%, and 102%, respectively, in the study of MCSW recovery test, which included no pH adjustment. Phenol and aniline compounds showed relatively higher recovery at 31% and 64%, even though these compounds showed low recovery rates of 10% and 14%, respectively, in the MCSW test. The other 88 compounds, with the exception of aromatic amines and phenols, showed an average recovery of 85%. Therefore, we demonstrated that almost all the model compounds, except some amines, could be quantitatively extracted from the river water containing 20 mg/L SS by using the combined SPE disks.

4) River water analysis: In our analysis of the three extraction methods (Table 3), some compounds detected from the blank sample, such as n-alkanes and phthalates, were omitted from further consideration. For beta-sitosterol, cholestanol and caffeine, concentrations from SPE disks were 1.4–1.6 times higher than that of DCM-LLE. The cause of that difference is under investigation. This study shows that the three methods are comparable: The same compounds are extracted by each method and the concentrations determined were approximately the same.

References

1. Kadokami K, Sato K, Hanada Y, Shinohara R, Koga M, Shiraishi H. *Analytical Sci.* 1995; 375:384.
2. Method 8270, US Environmental Protection Agency, Washington, D.C., 1989
3. Kadokami K, Tanada K, Taneda K, Nakagawa K. *J. Chromatogr. A* 2005; 219:226.
4. Method 525.2, US Environmental Protection Agency, Washington, D.C., 1995
5. Method 3535A, US Environmental Protection Agency, Washington, D.C., 1998.

Table 2 Comparing extraction methods from Suspended Solids (SS)

Compounds	logSw	logPow	Soaking Extraction, ug/400mL				Ultrasonic Extraction, ug/400mL				Rate
			1	2	3	Ave.1	4	5	6	Ave.2	Ave2/1
n-Triacontane	-10.07	15.07	0.080	0.097	0.088	0.088	0.077	0.090	0.082	0.083	0.9
Tris(2-ethylhexyl) phosphate	-0.22	9.49	0.044	0.045	0.048	0.045	0.049	0.054	0.054	0.052	1.2
4,4'-DDT	-1.60	6.91	0.126	0.119	0.126	0.124	0.117	0.122	0.114	0.118	0.9
Dibenzo(a,h)anthracene	-3.22	6.5	0.045	0.042	0.050	0.046	0.034	0.044	0.035	0.038	0.8
Tefluthrin	-1.70	6.5	0.152	0.146	0.155	0.151	0.144	0.145	0.128	0.139	0.9
Benzo(e)pyrene	-2.20	6.44	0.615	0.610	0.611	0.612	0.548	0.607	0.547	0.567	0.9
trans-Nonachlor	-2.00	6.35	0.102	0.075	0.097	0.091	0.061	0.091	0.059	0.070	0.8
2,2',4,4',5,5'-Hexabromobiphenyl	-1.96		0.173	0.180	0.192	0.182	0.168	0.169	0.146	0.161	0.9

Ave1 and Ave2 are the averages of 1-3 and 4-6, respectively. Ave2/1 is the ratio of Ave 2 to 1.

Table 3 River water analysis µg/L

	Cartridges		Disks		LLE
	1 Ctrg	2 Ctrg	3 Disk	4 Disk	LLE
2-Nitrophenol	0.037	0.040	0.048	0.044	0.033
Simazine (CAT)	0.17	0.19	0.17	0.20	0.14
Caffeine	0.29	0.29	0.37	0.39	0.23
Terbcarb (MBPMC)	0.031	0.029	0.031	0.032	0.032
Cyanazine	0.057	0.058	0.045	0.042	0.040
Bromacil	0.088	0.085	0.063	0.11	0.089
Lenacil	0.027	0.026	0.030	0.028	0.021
Cholestanol	0.12	0.11	0.16	0.15	0.14
Cholesterol	3.9	3.5	5.1	5.1	3.1
beta-Sitosterol	2.1	2.1	3.2	3.6	2.1