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Technical Report

Development of Solid-Phase Extraction Method for Simultaneous Analysis of Semi-Volatile Organic Compounds Using a GC-MS Database System

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Abstract:

Environmental pollution caused by a variety of chemicals is drawing attention to the need for a more efficient method of simultaneous multi-component analysis. One of the most effective methods of comprehensive, simultaneous multi-component analysis of semi-volatile organic compounds (SVOC) is by GC-MS in conjunction with an Automated Identification and Quantification System with a Database (AIQS-DB). As a comprehensive SVOC extraction method for environmental water samples using AIQS-DB, liquid-liquid extraction with dichloromethane has typically been used. In this research, however, we investigated the use of solid-phase SVOC extraction, which requires the use of less solvent. Here, an analytical method developed for comprehensive analysis of SVOCs in water samples using AIQS-DB is reported.

Keywords: GC-MS, SVOC, Simultaneous Multi-Residue Analysis, Solid-Phase Extraction, AIQS-DB

1. Introduction

Modern industrial civilization has been supported by the pervasive use of a wide variety of chemical substances. To understand the scope of this, more than 100,000 types of substances are registered in the European Inventory of Existing Commercial Chemical Substances, drawn up by the European Commission[1], and the annual worldwide production volume of these chemicals approximates 300 million tons[2]. During the manufacturing process, and over the course of their use and disposal, significant quantities of a wide range of substances may be released into the environment. In fact, even trace quantities of some manufactured compounds may exceed acceptable thresholds for environmental pollutants. To effectively address this problem, a very efficient simultaneous multi-component analytical method is required.

The Automated Identification and Quantification System with a Database (AIQS-DB)[3-5] is an identification and quantitative method which facilitates the determination of approximately 1000 chemical compounds registered in the database. Analysis is conducted based on data consisting of mass spectra, retention times and calibration curves acquired over the course of measurement of semi-volatile organic compounds (SVOCs) by capillary column GC-MS. AIQS-DB is a multi-component simultaneous measurement method that can be used to measure SVOCs quickly and with minimal environmental impact without using standards. However, since it does not include a sample pretreatment process, a method for comprehensive extraction of SVOCs from the sample is required.

The conventional method used for extraction of SVOCs from water samples has primarily been liquid-liquid extraction with dichloromethane (DCM-LLE)[6,7]. While there are reports of simulta-

neous analyses of separate groups of phenols and pesticides, etc. using solid-phase extraction (SPE), which require the use of only small amounts of solvent, there are few reported cases of comprehensive extraction applied to a wide variety of SVOCs that can be measured by GC-MS. If comprehensive, simultaneous extraction of all GC-MS target SVOCs by SPE were possible, this in conjunction with AIQS-DB would permit comprehensive SVOC analysis. Moreover, this approach would do so with a substantially lower environmental impact.

In this study, we investigated the SPE conditions that would permit comprehensive extraction of GC-MS detectable SVOCs from water samples. By combining this technique with an AIQS-DB for identification, a low-environmental-impact SVOC analytical method was developed for water samples[8].

2. Experiment

Reagents and Materials

The chemical standards used in this study were obtained from Kanto Chemical Co., Inc.; Wako Pure Chemical Industries, Ltd.; Hayashi Pure Chemical Ind., Ltd.; Wellington Laboratories, Inc.; and Sigma-Aldrich Japan K.K. The internal standard (IS) used for GC-MS measurement was a customized internal standard produced by Shimadzu GLC Ltd. Sodium chloride and anhydrous sodium sulfate (analytical grade reagents produced by Kanto Chemical) were used after conducting heat treatment in an electric furnace at 700°C for 6 hours. Buffer solutions at concentrations of 1 mol/L (pH 7.0), in addition to pH 3.0, 4.0, 6.0, 8.0, 10.0, and 11.0 were prepared using sodium hydroxide, potassium hydroxide, formic acid, aceticacid, sodium acetate, potassium dihydrogen phosphate, disodium hydrogen phosphate, and sodium hydrogen carbonate

(all analytical grade reagents produced by Kanto Chemical). The purified water used was prepared by filtering the water through an ultrapure water system (Milli-Q Advantage, produced by Merck Millipore), and then passing it through an Empore XD solid-phase extraction disk and activated carbon disk (each 47 mm in diameter, produced by 3M Company).

Model Compounds

The model compounds (MC) used for the study consisted of a representative SVOC group displaying a wide range of physical and chemical properties (boiling point 145 °C to 536 °C, polarity $\log P_{ow}$ – 0.65 to 15.07) (57 subgroups, 202 substances, Table 1).

Table 1 Model compounds

No.	Compounds	No.	Compounds	No.	Compounds	No.	Compounds
1. Aliphatic HCs		50	Cholesterol	101	2-Nitrophenol	*44. Organochlorine pesticides*	
1	n-Pentadecane	*17. Phenols*		102	4-Nitrophenol	153	Endosulfan I
2	n-Triacontane	51	Phenol	103	4-Methyl-3-nitrophenol	154	Endosulfan II
2. Halogenated aliphatic HCs		52	1,4-Benzenediol	104	2-Methyl-4,6-dinitrophenol	155	p,p'-DDT
3	1,2-Dibromo-3-chloropropane	*18. Alkyl phenols*		*31. Nitroanilines*		156	trans-Nonachlor
4	Pentachloroethane	53	2-Methylphenol	105	2-Nitroaniline	*45. Organophosphorus pesticides*	
3. Alcohols		54	3-Methylphenol	106	3-Nitroaniline	157	DDVP
5	2-Heptanol	55	2,4-Dimethylphenol	107	4-Nitroaniline	*46. Organothiophosphorus pesticides*	
6	1-Octanol	56	2,6-Dimethylphenol	108	2,4-Dinitroaniline	158	Butamifos
7	1-Nonanol	57	4-tert-Butylphenol	*32. Nitrosoamines*		159	Chlorpyrifos
8	Benzyl alcohol	*19. Halogenated phenols*		109	N-Nitrosodiethylamine	160	Diazinon
4. Halogenated alcohol		58	2-Chlorophenol	110	N-Nitroso-di-n-butylamine	161	Diazinon oxon
9	1,3-Dichloro-2-propanol	59	3-Chlorophenol	111	N-Nitrosomorpholine	162	EPN
5. Ethers		60	2-Chloro-6-methylphenol	112	N-Nitrosopiperidine	163	Fenitrothion (MEP)
10	Bis(2-chloroethoxy)methane	61	4-Chloro-3-methylphenol	113	N-Nitrosopyrrolidine	164	Fenitrothion oxon
11	Bis(2-chloroethyl) ether	62	2,4-Dichlorophenol	*33. Heterocyclic HCs*		165	Fenthion
12	Bis(2-chloroisopropyl)ether	63	2,6-Dichlorophenol	114	Benzothiazole	166	Iprobenfos (IBP)
6. Aromatic ethers		64	2,4,5-Trichlorophenol	115	Safrole	167	Isofenphos
13	4-Chlorophenylphenyl ether	65	2,4,6-Trichlorophenol	116	Carbazole	168	Isofenphos oxon
14	4-Bromophenylphenyl ether	66	2,3,4,6-Tetrachlorophenol	117	Dibenzothiophene	169	Isoxathion
7. Ketone		67	2,3,5,6-Tetrachlorophenol	*34. Other HCs*		170	Pyridaphenthion
15	Isophorone	68	Pentachlorophenol	118	Triphenylmethane	171	Tolclofos-methyl
8. Aromatic ketone		69	Triclosan	*35. Phthalates*		*47. Organodithiophosphorus pesticides*	
16	Acetophenone	*20. Amines*		119	Dimethyl phthalate	172	Anilofos
9. Aliphatic esters		70	ε-Caprolactam	120	Dimethylterephthalate	173	Dimethoate
17	n-Butylacrylate	*21. Aromatic amines*		121	Di-n-butyl phthalate	174	Disulfoton
18	3-Methoxy-1-butyl acetate	71	Aniline	122	Di-n-octyl phthalate	175	Edifenphos
19	Bis(2-ethylhexyl) adipate	72	2-Methylaniline	123	Bis(2-ethylhexyl)phthalate	176	Malathion
20	Bis(2-ethylhexyl) sebacate	73	3,4-Dimethylaniline	124	Butyl benzyl phtalate	177	Methidathion
10. Sulfonate ester		74	2,6-Diaminotoluene	*36. Phosphates*		178	Phenthoate
21	Ethyl methanesulfonate	75	4-Dimethylaminoazobenzene	125	Trimethyl phosphate	179	Piperophos
11. Benzenes		76	Phenacetin	126	Tris(2-chloroethyl) phosphate	*48. Phenylurea pesticides*	
22	Benzyl chloride	77	Crotamiton	127	Tributyl phosphate	180	Methyldymron
23	1,2-Dichlorobenzene	78	m-Phenylenediamine	128	Tris(2-ethylhexyl) phosphate	181	Pencycuron
24	1,3-Dichlorobenzene	79	Diphenylamine	*37. Amide pesticides*		*49. Phthalimide pesticides*	
25	1,4-Dichlorobenzene	*22. Halogenated aromatic amines*		129	Bromobutide	182	Captan
26	1,2,4-Trichlorobenzene	80	4-Chloroaniline	130	Napropamide	*50. Pyrazole pesticides*	
27	Hexachlorobenzene	81	2,4-Dichloroaniline	131	Propyzamide	183	Tebufenpyrad
12. Biphenyl		82	4,4'-Methylene-bis(2-chloroaniline)	*38. Anilide pesticies*		*51. Pyrethroid pesticides*	
28	Biphenyl	*23. Amino-biphenyl*		132	Alachlor	184	Etofenprox
13. Halogenated biphenyls		83	4-Aminobiphenyl	133	Flutolanil	185	Tefluthrin
29	2,2',4,4',5,5'-Hexabromobiphenyl	84	Benzidine	134	Mefenacet	*52. Thiadiazine pesticides*	
14. PAHs		*24. Halogenated amino-biphenyls*		135	Mepronil	186	Buprofezin
30	Naphthalene	85	3,3'-Dichlorobenzidine	136	Metalaxyl	*53. Thiadiazole pesticides*	
31	Acenaphthylene	*25. Aminophenols*		137	Pretilachlor	187	Etridiazole (Echlomezol)
32	Acenaphthene	86	m-Aminophenol	138	Thenylchlor	*54. Thiocarbamate pesticides*	
33	Fluorene	*26. Amino PAHs*		*39. Carbamate pesticides*		188	Dimepiperate
34	Phenanthrene	87	1-Naphthylamine	139	Carbofuran	189	Esprocarb
35	Anthracene	88	N-Phenyl-1-naphthylamine	140	Fenobucarb	190	Molinate
36	Fluoranthene	89	2-Acetylaminofluorene	141	Isoprocarb	191	Pyributicarb
37	Pyrene	*27. Nitrobenzenes*		142	Terbucarb (MBPMC)	192	Thiobencarb
38	Benzo(a)anthracene	90	Nitrobenzene	*40. Chlorobenzene pesticides*		*55. Triazine pesticides*	
39	Chrysene	91	1,3-Dinitrobenzene	143	Chloroneb	193	Atrazine
40	Benzo(b)fluoranthene	92	1,4-Dinitrobenzene	144	Fthalide	194	Dimethametryn
41	Benzo(k)fluoranthene	93	2,4-Dinitrotoluene	*41. Dinitroaniline pesticides*		195	Simazine (CAT)
42	Benzo(e)pyrene	94	2,6-Dinitrotoluene	145	Benfluralin	196	Simetryn
43	Benzo(a)pyrene	95	1,3,5-Trinitrobenzene	146	Pendimethalin	*56. Triazole pesticides*	
44	Perylene	96	2,4,6-Trinitrotoluene	147	Trifluralin	197	Cafenstrole
45	3-Methylcholanthrene	*28. Halogenated nitrobenzenes*		*42. Diphenylether pesticides*		*57. Other pesticides*	
46	Indeno(1,2,3-cd)pyrene	97	4-Chloronitrobenzene	148	Bifenox	198	Dithiopyr
47	Dibenzo(a,h)anthracene	98	2,4-Dichloronitrobenzene	149	Chlornitrofen (CNP)	199	Iprodione
48	Benzo(ghi)perylene	99	Pentachloronitrobenzene	150	Pyriproxyfen	200	Isoprothiolane
15. Halogatened PAHs		*29. Nitro-PAHs*		*43. Nitrile pesticides*		201	Pyroquilon
49	2-Chloronaphthalene	100	1-Nitronaphthalene	151	Chlorothalonil (TPN)	202	Tricyclazole
16. Sterol		*30. Nitrophenols*		152	Dichlobenil		

HCs: hydrocarbons; PAHs: polycyclic aromatic hydrocarbons.

Solid-Phase Materials

For the solid-phase material, easy-to-handle solid-phase cartridges (Luer connection type) were used (Table 2). Seven types of solid-phase materials were used, including one type of octadecyl silica (ODS), 2 types of styrene divinyl benzene (SDVB) polymer solid phase, 3 types of solid phase consisting of SDVB polymer with included hydrophilic functional group (hereafter referred to as hydrophilic SDVB), and one type of activated carbon (AC) solid phase.

Table 2 Solid-phase extraction materials studied

Name (manufacturer)	Sorbent	Sorbent weight	Code
SepPak Plus C18 (Waters Corp.)	ODS	360 mg	-
SepPak PS-2 (Waters Corp.)	SDVB	265 mg	-
Autoprep PS@Liq (Showa Denko K.K.)	SDVB	250 mg	-
Oasis HLB Plus (Waters Corp.)	SDVB + N-vinylpyrrolidone	225 mg	-
Aqusis PLS-3 (GL Sciences, Inc.)	SDVB + N-vinylacetamide	200 mg	PLS3
InertSep RP-1 (GL Sciences, Inc.)	SDVB + methacrylate	230 mg	-
SepPak AC-2 (Waters Corp.)	Activated carbon	400 mg	AC2

ODS: octadecyl silica; SDVB: styrenedivinylbenzene polymer; AC: activated carbon

Solid-Phase Extraction Procedure

The procedure is shown in Fig. 1 (a). The PLS3 and AC2 solid phases were conditioned using dichloromethane, acetone, and purified water, then set in the high pressure solid-phase extraction instrument. One liter of sample water spiked with the model compound solution, a surrogate substance solution, and phosphate buffer solution were passed through the PLS3-AC2 combined solid phase. Following passage of the water, the solid phase was dried, the PLS3 was eluted with 2 mL of acetone and 3 mL of dichloromethane, and the AC2 was eluted with 3 mL of acetone. The eluates were then combined and concentrated to a volume of approximately 1 mL by streaming nitrogen gas. After adding 5 mL of hexane and dehydration by sodium sulfate, the combined eluate was again concentrated to less than 1 mL, then adjusted to a volume of 1 mL by adding IS solution and measured by GC-MS (Fig. 1 (a)).

Dichloromethane Liquid-Liquid Extraction Procedure

We used the DCM-LLE method for comparison with the SPE method (Fig. 1 (b)). One liter of the water sample was transferred to a separatory funnel, phosphate buffer solution, sodium chloride (except in the case of sea water samples), and dichloromethane were added, and extraction was conducted for 10 minutes while shaking the funnel (2 iterations). The extracts were combined, and after dewatering with a small amount of anhydrous sodium sulfate, the volume was concentrated to about 5 mL. After concentrating further to less than 1 mL with 1 mL of hexane, IS solution was added to adjust the volume to 1 mL, and measurement was conducted by GC-MS.
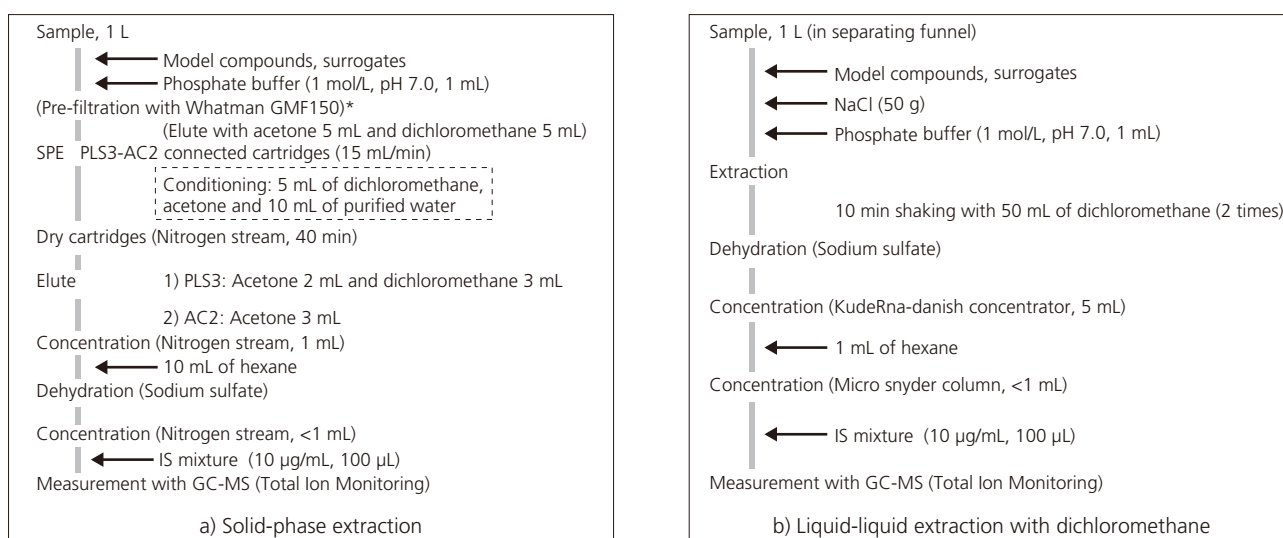

Sample, 1 L
      ← Model compounds, surrogates
      ← Phosphate buffer (1 mol/L, pH 7.0, 1 mL)
(Pre-filtration with Whatman GMF150)*
          (Elute with acetone 5 mL and dichloromethane 5 mL)
SPE   PLS3-AC2 connected cartridges (15 mL/min)
      Conditioning: 5 mL of dichloromethane, acetone and 10 mL of purified water
Dry cartridges (Nitrogen stream, 40 min)
Elute   1) PLS3: Acetone 2 mL and dichloromethane 3 mL
      2) AC2: Acetone 3 mL
Concentration (Nitrogen stream, 1 mL)
      ← 10 mL of hexane
Dehydration (Sodium sulfate)
Concentration (Nitrogen stream, <1 mL)
      ← IS mixture (10 µg/mL, 100 µL)
Measurement with GC-MS (Total Ion Monitoring)

a) Solid-phase extraction

Sample, 1 L (in separating funnel)
      ← Model compounds, surrogates
      ← NaCl (50 g)
      ← Phosphate buffer (1 mol/L, pH 7.0, 1 mL)
Extraction
      10 min shaking with 50 mL of dichloromethane (2 times)
Dehydration (Sodium sulfate)
Concentration (KudeRna-danish concentrator, 5 mL)
      ← 1 mL of hexane
Concentration (Micro snyder column, <1 mL)
      ← IS mixture (10 µg/mL, 100 µL)
Measurement with GC-MS (Total Ion Monitoring)

b) Liquid-liquid extraction with dichloromethane

Fig. 1 Procedures for Solid-Phase Extraction and Liquid-Liquid Extraction with Dichloromethane
* Pre-filteration should be performed if needed but not in this study.

GC-MS Analysis

GC-MS analysis was conducted using the Shimadzu GCMS-QP2010 Ultra. The analytical conditions used are shown in Table 3. Quantitation of the MC and surrogate substances was conducted using a calibration curve generated with standard solutions (MC: 0, 0.01, 0.1, 10 µg/mL, IS: 1.0 µg/mL), and recoveries were obtained using the following expression.

$$\text{Recovery (\%)} = 100 \times (A - B) / C$$

Where:

A: Spiked sample detection concentration (µg/L); B: Unspiked sample detection concentration (µg/L); C: Spike concentration (µg/L)

Table 3 Analytical Conditions

GC-MS	: GCMS-QP2010 Ultra		
Column	: DB-5ms (30 m length, 0.25 mm I.D., df = 0.25 µm)		
[GC]		[MS]	
Injection Temp.	: 250°C	Interface Temp.	: 300°C
Column Oven Temp.	: 40°C (1 min) → (8°C /min) → 310°C (4 min)	Ion Source Temp.	: 200°C
Injection Mode	: Splitless		
Sampling Time	: 1 min	Scan Measurement	
Carrier Gas Control	: He, Linear velocity (40 cm/sec)	Event Time	: 0.3 sec
Injection Volume	: 1 µL	Mass Range	: m/z 45–600

Solid-Phase Selection Testing and Optimum Extraction pH Investigation

To select a solid-phase material suitable for comprehensive extraction, 1 L of MC-spiked purified water (0.5 µg/L) was subjected to extraction using each of the solid-phase materials, and the recovery rates were compared. In addition, buffer solution was used to prepare MC-spiked purified water solutions (1 L, 0.5 µg/L) with pH values of 3.0, 4.0, 6.0, 7.0, 8.0, 10.0 and 11.0, respectively. Extraction was conducted using PLS3-AC2 combined solid phase with each of these solutions to determine the optimum extraction pH. In this case, the target recovery rate and target MDL were set to values of 50 % or greater and 0.05 µg/L or less, respectively.

Low Concentration Spike and Recovery Test

To evaluate the extraction performance by SPE, 1 L of MC-spiked purified water (0.1 µg/L, n = 7), and 1 L each of MC-spiked sea water, river water, and sewage treatment plant (STP) effluent water (0.1 µg/L, n = 2 for each) were analyzed using PLS3-AC2 combined solid phase. In addition, MC-spiked purified water (0.1 µg/L, n = 2) was analyzed using DCM-LLE, and the results were compared with those obtained using SPE.

Analysis of Unspiked Actual Sample Combined with AIQS-DB

To confirm the effectiveness of the SVOC comprehensive extraction method using a combination of SPE and AIQS-DB, actual samples (sea water, river water and STP effluent water) were subjected to analysis using this SPE method and the DCM-LLE method, and then analyzed using the Shimadzu AIQS-DB Simultaneous Analysis Database (for environmental samples, 940 substances registered)[5].

Accuracy Management

This SPE method is typically directed at substances with a wide range of physicochemical properties, including polarity, boiling point, and functional groups. Therefore, lower recovery with some of these target substances can be expected due to adsorption to interior walls of instruments, volatilization and oxidative decomposition during solid-phase drying, as well as matrix effects within the sample. Therefore, to verify that SVOC comprehensive extraction has been accomplished effectively for each sample, we utilized 17 types of stable isotope-labeled substances, shown in Table 4, as surrogate compounds.

Table 4 Surrogate compounds

No.	Surrogate compound	Recovery criteria, %	No.	Surrogate compound	Recovery criteria, %
1	*n*-Eocosan-*d*42	50	10	2-Chlorophenol-*d*4	50
2	1,2-Dichlorobenzene-*d*4	50	11	2,4-Dichlorophenol-*d*3	50
3	Bis(2-chloroethyl)ether-*d*8	50	12	2-Nitrophenol-*d*4	50
4	3,3'-Dichlorobenzidine-*d*6	50	13	4-Nitrophenol-*d*4	50
5	2-Methyl-4,6-dinitrophenol-*d*2	50	14	Dibenzo(a,h)anthracene-*d*14	50
6	Diphenylamine-*d*10	50	15	Anthracene-*d*10	60
7	4-Chloroaniline-*d*4	50	16	Fenitrothion-*d*6	60
8	Phenol-*d*5	30	17	Thiobencarb-*d*10	60
9	Bisphenol A-*d*14	50			

3. Results and Discussion

Solid-Phase Selection Test

We compared MC recovery rates with the various solid phases. MC was extracted at a recovery rate greater than 50% with ODS solid phase: $\log P_{ow} > 3$; SDVB solid phase: $\log P_{ow} > 1$; hydrophilic SDVB solid phase: $\log P_{ow} > 1$; and Aniline ($\log P_{ow}$ 0.9), such that extraction was accomplished over a wide polarity range of MC, in the order of ODS < SDVB < hydrophilic SDVB. Among the three types of hydrophilic SDVB solid phase, PLS3 showed the best recovery, whereas for high-polarity MC with $\log P_{ow} < 1$, extraction was accomplished only with AC2. From this, we concluded that simultaneous extraction of MCs could be accomplished with the widest range of polarity by concat-coupling the PLS3 and AC2 solid phases.

Optimal Extraction pH

For most of the MCs, there was no obvious tendency for recovery rates to vary due to the extraction pH. However, in the case of PAH compounds and aromatic amines on the one hand, and phenols, nitrophenols as well as some pesticides (Captan, Iprodione) on the other, low recoveries were seen at acidic and alkaline pH levels, respectively. Therefore, we adopted a single extraction pH of 7.0, the pH at which most of the types of MC were readily extracted.

Low Concentration Spike and Recovery Test

The results are shown in Fig. 2. In the purified water spike and recovery tests, of the 202 MC substances in 57 groups, the target recovery was exceeded for 193 substances in 54 groups using this SPE method. Using the DCM-LLE method, 196 substances in

55 groups exceeded the target recovery rate, but the recoveries of some polar substances, including nitrophenols, etc., were lower than those obtained by SPE. Thus, the comprehensive extraction performance using the SPE method was found to be approximately equivalent to that of DCM-LLE. MCs which exhibited recoveries lower than 50 % in the purified water spike and recovery test by SPE were Nos. 1, 4, 21, 52, 71, 74, 78, 84 and 86. The results suggested that possible factors causing these low recoveries might be high water solubility, loss of volatiles during solid-phase drying, and acidification decomposition during pretreatment, among others. Considering the range of possible factors, individual analysis of these substances might be necessary.

In spike and recovery testing of actual river water samples, recovery rates greater than 50% were obtained with 3 samples (average recovery was 90%), including 184 substances in 51 groups, corresponding to 92% of the entire MC list. This SPE method has thus been shown to be applicable for comprehensive extraction of SVOCs in actual samples. However, in testing of actual samples (in addition to the substances in the purified water mentioned above), some aromatic amines, nitrophenols, and pesticide substances showed recoveries of less than 50%. These were not a problem in the purified water spike testing, and because of the great variation in recoveries among the actual samples, it was surmised that the effects of sample matrix could be a factor. For these substances, it may be necessary to verify recovery for each sample by using surrogate substances.

Calculation of the minimum detection limit (MDL) by this SPE method using the results of the purified water spike and recovery testing[8] indicated MDL values from 0.012 to 0.082 (average 0.029) µg/L for the above-mentioned 193 substances. Of these, the target MDL was satisfied for 169 substances.
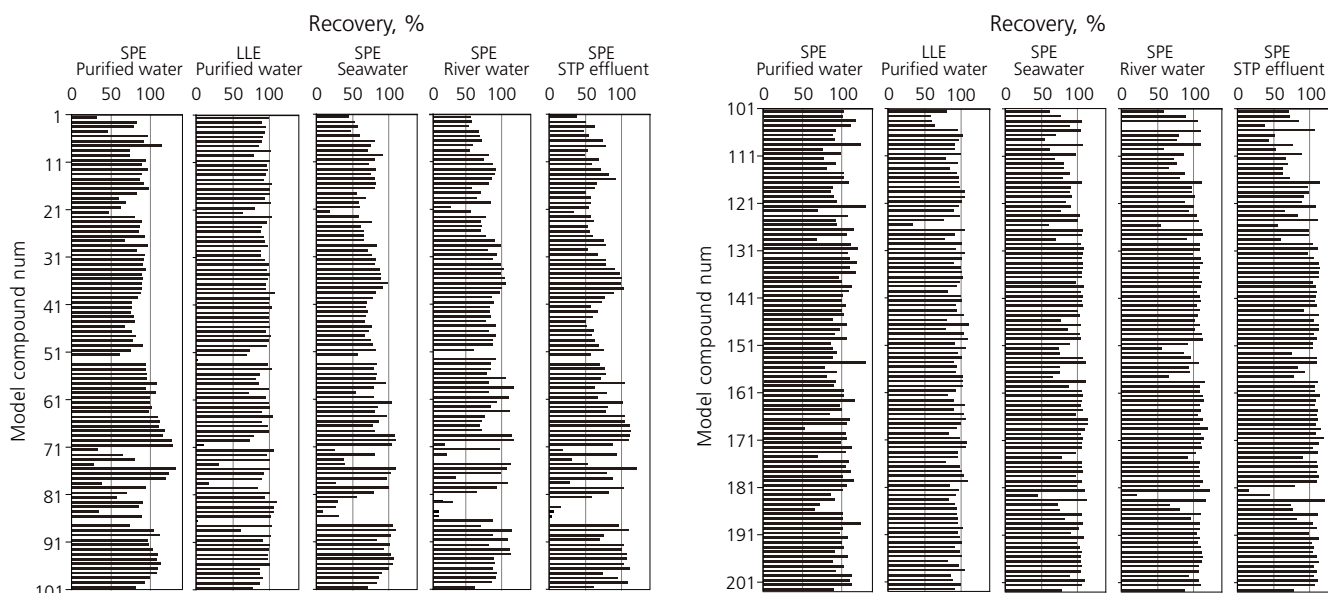

Fig. 2 Results of low concentration spike tests by solid-phase extraction method and liquid-liquid extraction using dichloromethane
Spiked amounts of model compounds were 0.1 µg in 1L samples.
Recoveries are the averages of dupulicated tests of n=7 (SPE, purified water) and n=2.

Analysis of Unspiked Real Samples Combined with AIQS-DB

The results are shown in Table 5. The substances detected by this SPE method and by DCM-LLE were nearly identical: 39 types of environmental contaminant substances associated with 21 compound groups were detected in 3 samples. By sample type, industrial chemicals such as 1,2-dichlorobenzene, etc., were detected in seawater samples from industrial areas, pesticides in river water samples from rice field regions, and domestic origin pollutants such as caffeine, aspirin and sterols were detected in effluent from sewage treatment plants (STP). The applicability of comprehensive analysis was demonstrated in the wide range of physico characteristics represented, with logP_{ow} values of the detected samples ranging from −0.07 (caffeine) to 14.6 (squalane), and boiling points ranging from 176 °C (1,3-dichloro-2-propanol) to 404°C (pyrene).

Table 5 Results of comprehensive analysis of real samples by using AIQS-DB coupled with SPE and DCM-LLE

Compounds	Class[a]	Detected concentrations (µg/L, n=2) and recoveries of surrogates (%, n=2)					
		Seawater[b]		River water[b]		STP effluent[b]	
		SPE	DCM-LLE	SPE	DCM-LLE	SPE	DCM-LLE
Detected compounds							
Squalane	1	0.10	0.12	0.057*	0.051*	0.18	0.28
1,3-Dichloro-2-propanol	4	0.81	0.64	-	-	-	-
Anthraquinone	8	-	-	-	-	0.028*	0.028*
1,2-Dichlorobenzene	11	0.066	0.10	-	-	-	-
Acenaphthene	14	0.022	0.029*	-	-	-	-
Fluoranthene	14	0.029	0.032*	-	-	-	-
Pyrene	14	0.028	0.028*	-	-	-	-
Cholestanol	16	0.10*	0.11*	0.13*	0.13*	0.13*	0.29*
Coprostanol	16	0.29	0.24	-	-	0.27	0.60
beta-Sitosterol	16	0.16*	0.40	0.57	0.89	0.13*	0.10*
Stigmasterol	16	-	-	0.30*	0.35*	0.20*	0.55
Cholesterol	16	1.1	1.3	1.7	1.1	0.92	1.2
Bisphenol A	17	0.072	0.14	-	-	-	0.037*
Triclosan	19	-	-	-	-	0.079	0.088
2-Methylaniline	21	0.034*	0.042	-	-	0.033*	0.044
Aniline	21	0.027*	0.24	-	-	-	-
Carbamazepine	21	0.040	0.045	-	-	0.15	0.24
Crotamiton	21	0.55	0.51	-	-	3.1	2.7
2-Chloroaniline	22	0.028*	0.028*	-	-	-	-
Nitrobenzene	27	0.034	0.028*	-	-	-	-
2-Nitrophenol	30	0.027	0.026*	-	-	-	-
2-(Methylthio)-benzothiazol	33	0.058*	0.068*	-	-	0.094*	0.099*
Caffeine	34	0.37	0.27	0.19	0.14	0.063	0.079
Aspirin	34	-	-	-	-	4.9	2.6
Tris(1,3-dichloro-2-propyl)phosphate	36	-	-	-	-	0.065*	0.086*
Tris(2-chloroethyl)phosphate	36	0.14	0.13	-	-	0.49	0.47
Tributyl phosphate	36	0.025	0.019*	-	-	0.26	0.24
Bromobutide	37	0.053	0.052	-	-	-	-
Diethyltoluamide	37	0.11	0.11	-	-	0.029*	0.033*
Thifluzamide	38	0.040	0.045	0.057	0.055	0.063	0.050
Terbucarb	39	-	-	0.046	0.045	-	-
Fenobucarb	39	0.041	0.040	-	-	-	-
Iprobenfos	46	-	-	0.033	0.028*	-	-
Fenitrothion	46	-	-	0.043	0.040	-	-
Cafenstrole	56	-	-	0.034	0.032*	-	-
Tricyclazole	57	-	-	0.15	0.17	-	-
Pyroquilon	57	0.057	0.052	0.55	0.49	-	-
Bromacil	57	-	-	0.18	0.13	-	-
Lenacil	57	0.035*	0.033*	-	-	0.014*	0.017*
Surrogates							
Bis(2-chloroethyl)ether-d_8	5	70	103	62	96	61	96
1,2-Dichlorobenzene-d_4	11	64	98	63	96	52	89
Benzylchloride-d_7	11	58	96	24	94	45	88
Anthracene-d_{10}	14	99	106	84	101	99	102
Dibenzo(a,h)anthracene-d_{14}	14	71	117	72	103	57	104
Phenol-d_5	17	60	40	62	36	55	35
Bisphenol A-d_{14}	18	44	88	33	78	10	89
2-Chlorophenol-d_4	19	71	101	71	97	61	89
2,4-Dichlorophenol-d_3	19	84	107	77	101	79	103
Diphenylamine-d_{10}	21	109	98	96	91	109	93
4-Chloroaniline-d_4	22	40	118	32	116	34	126
3,3'-Dichlorobenzidine-d_6	24	3	103	-	59	-	72
2-Nitrophenol-d_4	30	71	100	55	96	76	101
4-Nitrophenol-d_4	30	112	21	82	9	77	29
2-Methyl-4,6-dinitrophenol-d_2	30	106	75	-	61	106	69
Fenitrothion-d_6	46	109	113	92	107	120	125
Thiobencarb-d_{10}	54	101	114	99	109	99	108

−: Not detected (under the IDL[8]). Numbers with asterisk are detected concentrations under MDLs[8].
a Class numbers are llisted in Table 1.
b Suspended solid (mg/L): 3.6 (seawater), 8.0 (river water), 0.6 (sewage treatment plant (STP) effluent).

Conclusion

A method was developed for comprehensive analysis of SVOC in water samples using SPE in conjunction with AIQS-DB. Using the optimum SPE conditions determined in the investigation of 202 types of typical SVOCs (MC) (solid-phase material: hydrophilic SDVB polymer and activated carbon solid phase, extraction pH: 7.0), the results obtained in purified water spike and recovery testing (0.1 µg/L) confirmed that extraction performance was about the same as that by DCM-LLE. In addition, the results of spike and recovery testing (0.1 µg/L) using actual samples indicated that except for aromatic amines and some other substances, extraction was achieved with an average recovery of 90% for 184 MC substances. The results of comprehensive analyses of unspiked actual samples by both SPE and DCM-LLE methods in conjunction with AIQS-DB indicate that detection of contaminants with a wide range of physiochemical properties is possible with both extraction methods. This therefore demonstrates that SPE combined with AIQS-DB offers a low-environmental impact method for comprehensive analysis of SVOCs in water samples.

Because this method makes it possible to analyze nearly 1000 types of SVOC while eliminating the expense and effort typically required to purchase standards and prepare solutions for calibration curves, it represents a useful technique for conducting primary screening to further an overall understanding of environmental pollution, or the state of contamination due to accidental and other types of emergency situations. This method is also ideal for applications such as surveys in countries and regions where obtaining reagents is problematic.

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GC-MS Database Software for Simultaneous Analysis

The GC-MS Database Software for Simultaneous Analysis (2nd Edition), the Automated Identification and Quantification System with a Database (AIQS-DB), designed by Professor Kiwao Kadokami of the University of Kitakyushu (formerly associated with Kitakyushu City Institute of Environmental Sciences), was jointly commercialized by Professor Kadokami and Shimadzu Corporation. This database, containing the mass spectra, retention times and calibration curves for about 1,000 substances, permits simultaneous identification and quantification of these 1,000 plus substances without the use of chemical standards.

Maximizing the performance of this database calls for a high-sensitivity instrument together with feature-rich quantitative software. The GCMS-QP2010 Ultra and GCMSsolution software is a GC-MS system optimized for AIQS-DB to fully satisfy these demands

Environmental Pollutants Comprising 942 Registered Compounds

The database contains retention indices, mass spectra and calibration curve information for all the target compounds, which include 194 hydrocarbons (PAHs, PCBs, etc.), 150 oxygenated compounds, 113 nitrogen-containing compounds, 12 sulfur-containing compounds, 8 phosphorus-containing compounds, 14 PPCPs (Pharmaceuticals and Personal Care Products), and 451 agricultural chemicals (insecticides, herbicides, fungicides, etc.). Highly reliable component identification is even further supported by the inclusion of n-alkanes to assist in retention time prediction.

Evaluation of the operational condition of the instrument and whether or not maintenance is required using substances for instrument evaluation is also supported. The internal standard method is supported for obtaining approximate quantitative values.

Easy Operation with GCMSsolution

The Database Software for Simultaneous Analysis allows creating methods for the standard GCMSsolution software. This permits analysis and data processing using the same procedures as in a typical analysis. The method created using the GC-MS Database Software for Simultaneous Analysis is switched to Scan/Selected Ion Monitoring (SIM) mode for SIM measurement of regulated target substances. The regulated substances can be measured with high sensitivity using SIM, while pollutants can be comprehensively screened using Scan measurement. This permits a quick response in the event of accidents, e.g., contamination of tap water and source water by pollutants.

High-Sensitivity GC-MS Optimized for AIQS-DB

In typical environmental analysis, high-sensitivity SIM is used as the MS measurement mode. However, when using the AIQS-DB, measurement must be conducted in Scan mode due to the use of mass spectra. Therefore, it is important that scan measurement is conducted with high sensitivity. The Shimadzu high-sensitivity ion source ensures that high sensitivity is achieved with the GCMS-QP2010 Ultra in both Scan and SIM mode analysis.

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