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Applicability of headspace solid-phase microextraction to the determination of multi-class pesticides in waters

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Abstract

The applicability of headspace solid-phase microextraction (HS-SPME) to pesticide determination in water samples was demonstrated by evaluating the effects of temperature on the extraction of the pesticides. The evaluations were performed using an automated system with a heating module. The 174 pesticides that are detectable with gas chromatograph were selected objectively and impartially based on their physical properties: vapor pressure and partition coefficient between octanol and water. Of the 174 pesticides, 158 (90% of tested) were extracted with a polyacrylate-coated fiber between 30 and 100 °C and were determined with gas chromatograph–mass spectrometry. The extraction-temperature profiles of the 158 extracted pesticides were obtained to evaluate the effects of temperature on the extraction of pesticides. The pesticides were classified into four groups according to the shape of their extraction–temperature profiles. The line of demarcation between extractable pesticides and non-extractable pesticides could be drawn in the physical property diagram (a double logarithmic plot of their vapor pressure and partition coefficient between octanol and water). The plot also revealed relationships between classified extraction features and their physical properties. The new method for multi residue screening in which the analytes were categorized into sub-groups based on extraction temperature was developed. In order to evaluate the quantitivity of the developed method, the 45 pesticides were chosen among the pesticides that are typically monitored in waters. Linear response data for 40 of the 45 was obtained in the concentration range below 5 μg/l with correlation coefficients ranging between 0.979 and 0.999. The other five pesticides had poor responses. Relative standard deviations at the concentration of the lowest standard solution for each calibration curve of the pesticides ranged from 3.6 to 18%. The value of 0.01 μg/l in the limits of detection for 17 pesticides was achieved only under the approximate conditions for screening, not under the individually optimized conditions for each pesticide. Recoveries of tested pesticides in actual matrices were essentially in agreement with those obtained by solid-phase extraction.
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Keywords: Headspace analysis; Solid-phase microextraction; Water analysis; Automation; Pesticides

1. Introduction

Pesticides are used on a large scale for agricultural purposes. The adverse effects of pesticides on both human health and the environment are a matter of public concern. Thus, both the actual state and the transition of pesticide residues in various matrices including water, soil, and agricultural products should be extensively monitored. These researches should be undertaken using an efficient analytical system with a laborsaving and cost effective device, as pesticides as well as applicable fields of research range over a broad spectrum. Conventional sample preparation methods used to analyze pesticide residues in various matrices require expensive instrumentation, an expert analyst, and are very time costly. Efficient analytical systems that do not have these drawbacks are required.

Solid-phase microextraction (SPME), developed by Pawliszyn et al. [1], has received an increasing amount of attention at the analytical level in numerous scientific disciplines [2,3]. It is simple [4–6] and, as we will discuss later, offers great flexibility. The SPME consists of two extraction modes. One is the direct immersion mode (DI-SPME) in which analytes are extracted from the liquid phase onto a SPME fiber, and the other is the headspace mode (HS-SPME) in which analytes are extracted from the

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gaseous phase over liquid (headspace) onto the SPME fiber. In general, DI-SPME is more sensitive than HS-SPME for analytes present in a liquid sample, although HS-SPME gives lower background than DI-SPME [2]. Since it was previously thought that HS-SPME could be used to differentiate volatile compounds from less-volatile compounds [7], the use of HS-SPME extraction for semi- (and less-) volatile compounds has scarcely been applied [4]. Furthermore, pesticide extraction was not thought to be more efficient when the temperature increased to above 60 °C [4]; therefore, SPME extractions were usually conducted at room temperature [2]. However, the sensitivity to an analyte and the fundamental applicability of a method toward the analyte are two independent parameters.

We considered that it was necessary to recognize anew the applicability of SPME to the fields that researchers take little interest in before pursuing the sensitivity of the analytical system. We attempted to evaluate the applicability of HS-SPME to the determination of semi- (and less-) volatile pesticides in water samples, and to expand the application range to the pesticides in actual matrices. We reasoned that: if the time and temperature could be controlled through all steps of HS-SPME, and then if the minimum amount of analyte necessary for GC detection could be delivered into the GC detector without non-reversible coelutants, the HS-SPME technique could belong to the category of fur superior GC-injection techniques. Therefore first, we selected a commercial autosampler (Combi PAL model from CTC Analytics) as a SPME module, and mounted it on a GC–MS system. The autosampler could keep a vial oscillating at an optional fixed temperature during the extraction step, and could continuously insert a fiber into the GC-injection port in a short fixed interval. Then, a quadrupole ion trap mass spectrometer was adopted as a GC–MS detector because of its accurate identification of a target pesticide in both full scan and MS–MS modes [8]. The computer controlled all the movements of the autosampler and the GC–MS. Consequently, our HS-SPME system could provide superior productivity and reproducibility. The studies were performed in a stepwise manner as follows:

In the first step, more than 170 pesticides were selected objectively and impartially from a group of pesticides that are detectable by GC using a physical property diagram in which the values of two properties (vapor pressure and partition coefficient between octanol and water) were plotted on logarithmic scales. By varying the HS-SPME parameters (extraction time, fiber types, and salt addition), while increasing extraction temperature by ten degrees from 30 to 100 °C, the tests were carried out to determine whether the HS-SPME technique was useful for detecting each pesticide in pure water. This elaborate evaluation was successively conducted with the aid of the autosampler. Of the 174 pesticides, 158 were detected by the HS-SPME–GC–MS analytical system. The extraction-temperature profiles of the 158 pesticides were classified into four types according to the shapes of their profiles. Evaluating the physical property diagram elucidated the relationship between the features of the pesticide's extraction-temperature profile and its physical properties. These results have provided us with a useful guide to optimizing HS-SPME in actual matrices and estimating optimal conditions for pesticides not included in this study.

In the second step, we checked the system's ability to quantitatively detect the pesticides. Then, we confirmed whether the Ai theory [9] was practical especially under heated conditions, and concluded that our SPME quantifications were feasible even though adsorption equilibriums were not reached. We also confirmed that there was no difference between the calibration curves of pesticides prepared by single standard solutions and the calibration curves of corresponding pesticides prepared by mixed standard solutions at low concentrations. This shows that the HS-SPME–GC–MS system is applicable to extensive multi-residue analysis.

In the third step, we developed a new multiple simultaneous analytical system as opposed to the single simultaneous analysis used in a great number of pesticide residue monitoring. We tested the performance of the HS-SPME–GC–MS system using the 45 pesticides usually monitored in surface and drinking water. The recoveries of pesticides in actual matrices defined as the comparison with extracted yields of pesticides spiked in pure water were obtained, and the results were in good agreement with those obtained by solid-phase extraction (SPE).

2. Experimental

2.1. Reagents and standards

The 174 pesticides used in this study are listed in Table 1. The pesticide standards (degrees of purity are >95%) were purchased from Kanto Kagaku (Tokyo, Japan), Dr. Ehrenstorfer Lab. (Augsburg, Germany), Wako (Osaka, Japan) and Hayashi Pure Chemical (Osaka, Japan). Several mixed standard solutions as vial packing were purchased from Kanto Kagaku. All solvents and anhydrous sodium sulfate (Na_2SO_4) were pesticide-analysis grade and were purchased from Kanto Kagaku. The standard stock solutions (1000 μg/ml) of each pesticide were prepared in acetone. Working standard mixtures were prepared by mixing the stock mixtures and solutions as needed. Thiobencarb-d_{10} and chlornitrofen-d_4 (CNP-d_4) (degrees of purity are >96%) were purchased from Hayashi, and were used as internal standards (I.S.). The I.S. stock solutions (1000 μg/ml) of each compound were accurately prepared in acetone. Pure water was obtained from the Milli-Q Gradient 10A system (Millipore, Tokyo, Japan).

2.2. Water samples

Water samples were pure water, commercially available natural mineral waters (Volvic, Evian, and Contrex) and

Table 1
CAS registry number, physical properties, type of extraction-temperature profile, and optimum extraction temperature of the studied pesticides

Compound	CAS registry number	$\log P_v$[a]	$\log P$[b]	Type of extraction-temperature profile	Optimum extraction temperature (°C)
Detectable					
Acrinathrin	101007-06-1	−4.36	5.00	3	100
Alachlor	15972-60-8	0.32	3.09	2	80
Aldrin	309-00-2	1.20	6.50	1	60
Bendiocarb	22781-23-3	0.66	1.72	1	70
Benfluralin	1861-40-1	0.94	5.29	1	80
Benfuresate	68505-69-1	0.16	2.41	2	90
α-Benzene hexachloride (BHC)	319-84-6	0.78	3.80	1	70
β-BHC	319-85-7	−1.32	3.78	1	70
γ-BHC	58-89-9	0.75	3.72	1	70
δ-BHC	319-86-8	0.67	4.14	1	70
Bifenox	42576-02-3	−0.49	4.50	2	80
Bifenthrin	82657-04-3	−1.62	6.00	3	100
Bitertanol	55179-31-2	−6.66	4.10	3	100
Bromobutide	74712-19-9	−1.08	3.47	2	80
Buprofezin	69327-76-0	0.10	4.30	2	90
Butachlor	23184-66-9	−0.41	4.50	2	90
Butamifos	36335-67-8	1.92	4.62	2	90
Butylate	2008-41-5	3.24	4.15	1	60
Cadusafos	95465-99-9	2.08	3.90	1	70
Carbaryl (NAC)	63-25-2	−1.39	1.59	2	80
Chlorfenapyr	122453-73-0	1.11	4.83	2	90
(*E*)-Chlorfenvinphos (α-CVP)	18708-86-6	0.00[c]	4.22	2	90
(*Z*)-Chlorfenvinphos (β-CVP)	18708-97-7	0.00[c]	3.85	2	90
Chlornitrofen (CNP)	1836-77-7	−1.15	4.97	2	90
Chlorobenzilate	510-15-6	−0.53	4.74	2	90
Chloroneb	2675-77-6	3.28	3.44	1	70
Chlorothalonil (TPN)	1897-45-6	−1.12	3.05	1	70
Chlorpropham	101-21-3	0.00	3.51	2	80
Chlorpyrifos	2921-88-2	0.43	4.70	2	80
Cinmethylin	87818-31-3	1.00	3.84	2	80
Clofentezine	74115-24-5	−3.89	4.10	2	70
Cyfluthrin	68359-37-5	−3.02	6.00	3	100
Cyhalofop-butyl	122008-85-9	−2.92	3.31	3	100
Cyhalothrin	68085-85-8	−3.00	6.80	3	100
Cypermethrin	52315-07-8	−3.64	6.60	3	100
Cyproconazole	94361-06-5	−1.46	2.91	3	100
DCIP	108-60-1	5.52	2.14	1	50
o,p′-DDD	53-19-0	–[d]	–[d]	2	80
p,p′-DDD	72-54-8	−0.74	6.02	2	80
p,p′-DDE	72-55-9	−0.10	6.51	2	80
o,p′-DDT	789-02-6	−0.74	6.79	2	80
p,p′-DDT	50-29-3	−1.67	6.91	2	80
Deltamethrin	52918-63-5	−4.91	4.60	3	100
Diazinon	333-41-5	1.08	3.30	1	80
Dichlofenthion (ECP)	97-17-6	1.87	5.14	1	80
Dichlofluanid	1085-98-9	−1.82	3.70	4	–
Dichrolvos (DDVP)	62-73-7	3.32	1.90	1	60
Dicofol	115-32-2	−1.28	4.30	2	70
Dieldrin	60-57-1	−0.11	5.40	2	80
Diethofencarb	87130-20-9	0.92	3.02	3	100
Difenoconazole	119446-68-3	−4.48	4.20	3	100
Dimethenamid	87674-68-8	1.56	2.15	2	90
(*E*)-Dimethylvinphos	71363-52-5	0.11[c]	3.12[c]	1	80
(*Z*)-Dimethylvinphos	67628-93-7	0.11[c]	3.12[c]	1	80
Dithiopyr	97886-45-8	−0.27	4.75	1	80
Edifenphos (EDDP)	17109-49-8	−1.49	3.83	1	80
Endrin	72-20-8	−0.40	5.20	2	80
α-Endosulfan	959-98-8	−0.40	3.83	1	80
β-Endosulfan	33213-65-9	−1.10	3.83	1	80
EPN	2104-64-5	−1.39	5.02	2	90

Table 1 (*Continued*)

Compound	CAS registry number	$\log P_v$ [a]	$\log P$ [b]	Type of extraction-temperature profile	Optimum extraction temperature (°C)
EPTC	759-94-4	3.51	3.20	1	60
Esprocarb	85785-20-2	1.00	4.60	2	80
Ethiofencarb	29973-13-5	−0.35	2.04	1	60
Ethion	563-12-2	−0.05	5.07	2	80
Ethofenprox	80844-07-1	−3.04	7.05	3	100
Ethoprophos	13194-48-4	1.67	3.59	1	70
Etobenzanid	79540-50-4	−1.68	4.30	3	100
Etoxazole	153233-91-1	−2.66	5.59	3	100
Etridiazole	2593-15-9	1.12	3.37	1	60
Etrimfos	38260-54-7	0.81	3.30	1	70
Fenarimol	60168-88-9	−1.19	3.69	3	100
Fenitrothion (MEP)	122-14-5	1.18	3.50	1	80
Fenobucarb (BPMC)	3766-81-2	0.20	2.79	1	70
Fenpropathrin	39515-41-8	−0.14	6.00	3	100
Fensulfothion	115-90-2	0.82	2.23	3	100
Fenthion	55-38-9	−0.13	4.84	2	80
Fenvalerate	51630-58-1	−1.72	5.01	3	100
Flucythrinate	70124-77-5	−2.92	6.20	3	100
Fludioxonil	131341-86-1	−3.41	4.12	2	80
Flusilazole	85509-19-9	−1.41	3.74	3	100
Flutolanil	66332-96-5	−2.19	3.70	3	100
Fluvalinate	69409-94-5	−7.05	4.26	3	100
Folpet	133-07-3	−1.68	3.11	4	–
Fthalide	27355-22-2	−2.52	3.20	4	–
Furametpyr	123572-88-3	−2.33	2.36	3	100
Halfenprox	111872-58-3	−3.11	4.10	3	100
Heptachlor	76-44-8	1.72	6.10	1	60
Heptachlor Epoxide	1024-57-3	0.41	4.98	2	80
Hexaconazole	79983-71-4	−1.74	3.90	3	100
Imazalil	35554-44-0	−0.80	3.82	3	100
Imibenconazole	86598-92-7	−4.07	4.94	3	100
Iprobenfos (IBP)	26087-47-8	−0.61	3.21	1	80
Isofenphos	25311-71-1	−0.66	4.04	2	90
Isofenphos P=O	31120-85-1	– [d]	– [d]	3	100
Isoprocarb	2631-40-5	0.45	2.30	1	70
Isoprothiolane	50512-35-1	1.27	3.30	3	100
Isoxathion	18854-01-8	−0.88	3.88	2	90
Kresoxim-methyl	143390-89-0	−2.64	3.40	2	80
Malathion	121-75-5	0.72	2.75	1	70
Mefenacet	73250-68-7	−3.19	3.23	3	100
Mepanipyrim	110235-47-7	−1.63	3.28	2	90
Mepronil	55814-41-0	−1.25	3.66	3	100
Metalaxyl	57837-19-1	−0.13	1.65	2	90
Methabenzthiazuron	18691-97-9	−2.23	2.64	3	100
Methiocarb	2032-65-7	−1.82	3.08	1	80
Methyldymron	42609-73-4	– [d]	3.01	1	80
Metolachlor	51218-45-2	0.62	2.90	2	90
Metribuzin	21087-64-9	−1.24	1.60	3	100
Molinate	2212-67-1	2.87	3.21	1	60
Myclobutanil	88671-89-0	−0.67	2.94	3	100
Napropamide	15299-99-7	−1.64	3.36	3	100
Paclobutrazol	76738-62-0	−3.00	3.20	2	90
Parathion	56-38-2	−0.05	3.83	2	80
Parathion-methyl	298-00-0	−0.70	3.00	1	80
Pencycuron	66063-05-6	−6.30	4.68	– [e]	–
Pendimethalin	40487-42-1	0.60	5.18	2	80
Pentoxazone	110956-75-7	−1.95	– [d]	1	80
Permethrin	52645-53-1	−1.15	6.10	3	100
Phenthoate	2597-03-7	0.72	3.69	1	70
Phosalone	2310-17-0	−1.22	4.01	2	90
Pirimicarb	23103-98-2	−0.01	1.70	3	100
Pirimiphos-methyl	29232-93-7	−0.17	5.00	2	80

Table 1 (*Continued*)

Compound	CAS registry number	log P_v[a]	log P[b]	Type of extraction-temperature profile	Optimum extraction temperature (°C)
Pretilachlor	51218-49-6	−0.88	4.08	2	90
Propiconazole	60207-90-1	−1.25	3.72	3	100
Propyzamide	23950-58-5	−1.24	3.43	2	90
Prothiofos	34643-46-4	−0.52	5.67	2	80
Pyraclofos	89784-60-1	−2.80	3.77	3	100
Pyributicarb	88678-67-5	−0.57	3.69	3	100
Pyridaben	96489-71-3	−0.60	6.37	3	100
Pyridaphenthion	119-12-0	−2.83	3.20	2	90
(*E*)-Pyrifenox	83227-22-9	0.23[c]	3.70[c]	3	100
(*Z*)-Pyrifenox	83227-23-0	0.23[c]	3.70[c]	3	100
Pyrimidifen	105779-78-0	−3.80	4.59	3	100
(*E*)-Pyriminobac-methyl	147411-69-6	−1.46	2.98	3	100
(*Z*)-Pyriminobac-methyl	147411-70-9	−1.57	2.70	3	100
Pyriproxyfen	95737-68-1	−0.05	5.55	3	100
Quinalphos	13593-03-8	−0.46	4.44	2	90
Quinomethionate	2439-01-2	−1.59	3.78	1	60
Silafluofen	105024-66-6	−2.60	8.20	3	100
Simazine (CAT)	122-34-9	−2.53	2.18	3	100
Simetryne	1014-70-6	−1.02	2.80	3	100
Tebuconazole	107534-96-3	−2.77	3.70	3	100
Tebufenpyrad	119168-77-3	−2.00	4.61	3	100
Tefluthrin	79538-32-2	0.90	6.50	1	80
Terbucarb (MBPMC)	1918-11-2	0.72	5.28	2	80
Terbufos	13071-79-9	1.54	2.77	1	70
Tetraconazole	112281-77-3	−0.74	3.56	3	100
Thenylchlor	96491-05-3	−1.55	3.53	3	100
Thiobencarb	28249-77-6	0.47	3.42	1	80
Thiometon	640-15-3	0.35	3.15	1	70
Tolclofos-methyl	57018-04-9	1.76	4.56	1	80
Tralomethrin	66841-25-6	−5.32	5.00	3	100
Triadimenol	55219-65-3	−3.22	3.08	2	90
Trichlamide	70193-21-4	1.00	–[d]	3	100
Triclopyr-2-butoxyethyl	64700-56-7	–[d]	–[d]	1	70
Triflumizole	68694-11-1	−0.73	5.10	3	100
Trifluralin	1582-09-8	0.79	5.34	1	70
Uniconazole P	83657-17-4	0.72	3.28	3	100
Non-detectable					
Acephate	30560-19-1	−0.65	−0.89		
Acetamiprid	160430-64-8	−3.00	0.80		
Bensulide (SAP)	741-58-2	−0.97	4.20		
Cafenstrole	125306-83-4	−5.52	3.21		
Captafol	2425-06-1	−3.06	3.80		
Captan	133-06-2	−1.92	2.80		
Dimethoate	60-51-5	−0.60	0.70		
Fosthiazate	98886-44-3	−0.25	1.68		
Iprodione	36734-19-7	−3.30	3.00		
Lenacil	2164-08-1	−3.70	2.31		
Methamidophos	10265-92-6	0.36	−0.80		
Oxamyl	23135-22-0	−1.29	−0.44		
Probenazole	27605-76-1	0.19	1.40		
Propamocarb	24579-73-5	2.86	0.84		
Trichlorfon (DEP)	52-68-6	0.02	0.51		
Tricyclazole	41814-78-2	−1.57	1.40		

[a] Logarithmic value of vapor pressure (mPa).
[b] Logarithmic value of octanol–water partition coefficient.
[c] Data as mixture of (*E*)- and (*Z*)- isomers.
[d] No data.
[e] Not determined.

surface water collected from the river Katsuura located in Tokushima prefecture in Japan. The natural mineral waters and the surface water were tested to ensure that they were free from the selected pesticides, and stored at 4 °C before use.

2.3. Automated HS-SPME–GC–MS system

2.3.1. GC–MS

Analysis of the pesticides was performed using a GC–MS system (Trace GC 2000-Polaris brand from Thermoquest, Austin, TX, USA) with an ion trap mass spectrometer. It was equipped with a programmable temperature vaporizing (PTV) injector fitted with a glass insert (1 mm I.D.). It was used in the PTV splitless mode with a splitless time of 3 min, and used with the following temperature program: 50 °C hold for 0.5 min, 10 °C/s to 250 °C hold for 3 min, 5 °C/s to 260 °C hold for 28 min. An Rtx-5MS fused silica capillary column (30 m × 0.25 mm I.D., 0.25 μm: Restek, Bellefonte, PA, USA) was used with the following temperature program: 50 °C hold for 1 min, 25 °C/min to 125 °C, 10 °C/min to 300 °C hold for 7 min. The carrier gas was helium at a constant flow (1 ml/min). The transfer line was held at 260 °C and the ion source at 200 °C. The full scan mode (scan range: 50–500 *m/z*) for all pesticides and the MS–MS mode for 11 pesticides (bitertanol, cyproconazole, fenvalerate, fludioxonil, isofenphos-oxon, metribuzin, myclobutanil, paclobutrazol, propiconazole, pyraclofos, pyridaphenthion) were used for detection and confirmation of the pesticides. One or two ions were selected from the spectrum of each pesticide to quantify the response. The ion energy used for electron impact (EI) was 70 eV.

2.3.2. Automated HS-SPME procedure

Automation of the HS-SPME procedures was achieved with an autosampler (Combi PAL brand from CTC Analytics, Basel, Switzerland). Using the Combi PAL autosampler, all movements of the SPME fiber in the processes of adsorption, desorption, and cleaning could be precisely controlled. A sample vial on the sample tray was transported into the agitating attachment to the Combi PAL, which keeps the vial oscillating at an optional fixed temperature during the extraction step. After extraction onto the fiber was completed, the Combi PAL continuously inserted the fiber into the GC-injection port in a short fixed interval, and then the GC measurement started simultaneously. The sample vial was then returned to the sample tray and the fiber was thoroughly cleaned at 270 °C under nitrogen for 10 min in the cleaning attachment to the Combi PAL, ready for the next extraction. The Combi PAL was fully controlled with Cycle Composer software (CTC Analytics). Details of the Combi PAL, including a photograph has been presented by Zini et al. [13].

2.3.3. Sample preparation

A 10-ml volume of a water sample and 4 g of anhydrous sodium sulfate (Na_2SO_4) were placed in a 20-ml crimp-top headspace vial equipped with a PTFE-coated magnetic stir bar, and the solution was stirred with a magnetic stirrer at 600 rpm. For preparing the spiked water samples over the concentration range of 0.01–10 μg/l, the appropriate amounts of the mixed standard solutions of pesticides at 0.01–10 μg/ml in acetone were spiked into each water-sample vial. The vials were sealed with both a blue silicon/PTTE septa and an open centered magnetic cap, and the solutions stirred again. In the calibration and quantitation studies, the mixed I.S. solution was also added to each sample. The total concentration of acetone in each sample vial throughout the study was controlled within 0.05% (v/v).

2.3.4. SPME fiber

The five SPME fibers (85 μm polyacrylate (PA), 100 μm polydimethylsiloxane (PDMS), 65 μm PDMS–divinylbenzene (PDMS–DVB), 65 μm Carbowax DVB (CW–DVB), 75 μm Carboxen–PDMS (CAR–PDMS) for use with the autosampler were purchased from Supelco Co. (Bellefonte, PA, USA). Fibers were conditioned before use according to the supplier's instructions with the fiber cleaning attachment to the Combi PAL.

2.4. SPE procedure

A 500-ml volume of water was spiked with 0.5 ml of the mixed standard solution of pesticides at 0.5 μg/ml in acetone and mixed well. A Sep-Pak PS-2 plus cartridge obtained from Waters (Milford, MA, USA) was conditioned by sequentially rinsing with 5 ml of dichloromethane, 5 ml of methanol, and 5 ml of pure water. The 500-ml water sample was then pulled through the SPE cartridge at a flow rate of 10 ml/min. The SPE cartridge was dried by introducing air into the cartridge for more than 30 min to dislodge the bound water. The SPE cartridge was then eluted with 3 ml of dichloromethane. The dichloromethane eluant was evaporated under nitrogen until its volume was condensed to less than 0.5, and 0.5 ml of the solution containing [$^2H_{10}$] thiobencarb and [$^2H_4$] CNP at 0.5 μg/ml was added as internal standards. One micro liter of the solution adjusted to 1 ml with dichloromethane was then injected into the GC–MS system.

3. Results and discussion

3.1. Overview of the applicability of HS-SPME to pesticide analysis

To investigate the applicability of HS-SPME, 174 pesticides (see Table 1) detectable by GC were selected at random according to their physical properties: vapor pressure (P_v) and partition coefficient (P) between octanol and water. These values were taken from literature [10,11] not determined in this study. Since the P_v and P vary widely,

it is convenient to express them on a logarithmic scale. The $\log P_v$ values range from −7.0 to 5.5, and partition coefficient ($\log P$) values range from −0.6 to 8.2. We investigated how many pesticides could be detected by the HS-SPME–GC–MS analytical system while changing the system's parameters such as the extraction temperature (30–100 °C), extraction time (10–60 min), fiber types (five different SPME fibers), and salt addition (seven concentrations of Na_2SO_4). As a result, 158 of the 174 pesticides were detectable at a concentration of 10 μg/l in pure water. The other 16 pesticides could not be detected at 10 μg/l under any condition used in this study. The HS-SPME procedures were performed automatically with the Combi PAL autosampler throughout this study. Since the movements of the GC–MS system and the autosampler were independent of each other, different procedures for two samples (GC procedure for *n*th sample and SPME procedure for $(n+1)$th sample) could be performed simultaneously. Moreover, GC measurements for samples could be consecutively carried out by synchronizing the end of GC–MS procedure for the former sample with the start of GC injection in SPME procedure for the latter sample. The HS-SPME technique reduces background adsorption and matrix effects, and consequently enhances the life expectancy of the SPME fiber, because the fiber is not in contact with the sample [12]. In this study, one fiber could be used repeatedly more than one hundred times.

3.2. Selection of extraction fibers, effect of salt additions and pH adjustments

Five different commercially available SPME fibers (PA, PDMS, PDMS–DVB, CW–DVB, and CAR–PDMS) were tested for efficiency in HS-SPME extraction of pesticides from water samples. Although the optimum fibers differed depending on the pesticide, all 158 pesticides could be sufficiently extracted with the PA fiber, with the exception of pencycuron. The chromatogram of pencycuron extracted with the PA fiber was not suitable for quantitative treatment because of the small peak and the band broadening. The PA fiber was selected for the subsequent experiments in consideration of the purpose of the study: not to pursue the sensitivity of analytical system but to recognize the applicability of the SPME technique to pesticides over a very wide range. The details on the results with the other four fibers (PDMS, PDMS–DVB, CW–DVB and CAR–PDMS) will be reported in our following paper. The effect of the salt addition in HS-SPME can be explained as follows: The salt increases the ionic strength of the solution, consequently decreasing the solubility of analyte, and the affinity of analyte to gaseous phase increases. The pure water samples (10 ml) spiked with the studied pesticides at 1 μg/l contained no salt, 5, 10, 20, 30, 40, or 50% (w/v) of Na_2SO_4. The extractions from these samples were carried out with the PA fiber for 30 min at 80 °C. The 40% (w/v) Na_2SO_4 concentration was selected for subsequent experiments because the increase in the extraction yield for most pesticides declined when more than 40% (w/v) of Na_2SO_4 was added. In addition, it was observed that the rates of increase for pesticides with $\log P$ values below four ($\log P < 4$) were higher than those for pesticides with $\log P$ values above four ($\log P > 4$). There was no change in the value of pH for each mixture solution, in which the 40% (w/v) of Na_2SO_4 was already added, between before and after the working standard mixture was added. Therefore, no pH adjustment for tested solution was carried out.

3.3. Extraction-temperature profiles

The autosampler device allowed us to obtain the extraction-temperature profiles and extraction-time profiles with excellent reproducibility. These extraction profiles were obtained by triplicate extractions with PA fiber from pure water samples (10 ml) spiked with the studied pesticides at 10 μg/l contained 40% (w/v) of Na_2SO_4, while the extraction time was increased in 10-min steps from 10 to 60 min, and the extraction temperature was increased in 10 °C steps from 30 to 100 °C. The optimum extraction temperature for each pesticide (see Table 1) was determined after due consideration of not only the extraction-temperature profile but also the extraction-time profile.

3.4. Classification of extraction-temperature profiles

In addition to the enhancement of applicability, the automatic survey revealed that extraction-temperature profiles were classified into four types according to their shapes as shown in Table 1. The characteristics of each type are as follows. (1) Type 1: a peak shape is a characteristic feature of this type. The profile has one peak in which the apex lies at 60–80 °C. The extraction yield increases by elevating temperature from 30 °C to the apex level at 60–80 °C. As the temperature increases to a value higher than the apex-temperature, the extraction yield rapidly decreases. We have not yet confirmed the mechanism behind their profiles experimentally. As a typical example of type 1, the profile of fenobucarb is shown in Fig. 1a. (2) Type 2: a plateau shape is a typical feature of this type. In contrast to type 1, the profile of this type does not have a well-defined peak. The extraction yield increases with elevating temperature until it reaches a maximum at 60–80 °C. The extraction yield is steady or slightly decreases as temperature increases to higher than the maximum temperature. As a typical example of type 2, the profile of EPN is shown in Fig. 1b. (3) Type 3: a steep slope is a characteristic feature of this type. An outstanding characteristic of this type is its uniqueness. There was no or a poor extraction yield of each pesticide that belonged to type 3 at the room temperature. Over the boundary temperature (about 60 °C), the extraction yield of the pesticides continues to increase with temperature until 100 °C. As a typical example of type 3, the profile of ethofenprox is shown in Fig. 1c. (4) Type 4: this type has no defining

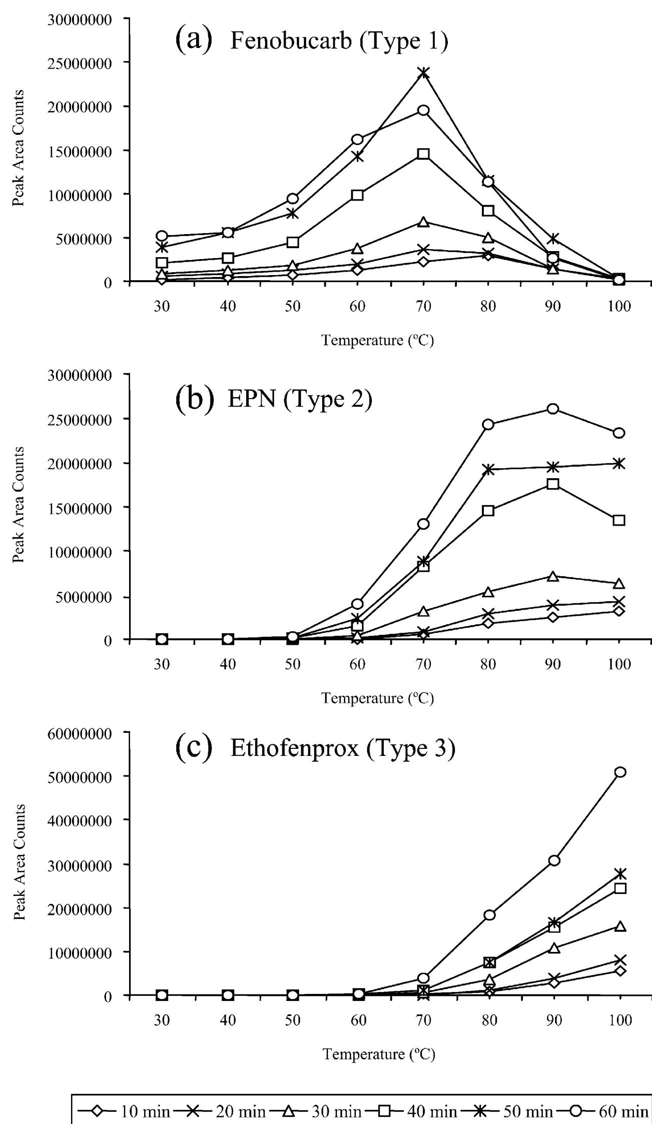

Fig. 1. Examples of the extraction profiles given by analyzing pure water samples (10 ml) spiked at 1 μg/l of each pesticide. Each point represents an average of triplicate extractions with a PA fiber.

feature. The profiles of three pesticides (dichlofluanid, folpet, and fthalide) were classified into this type as shown in Table 1. The phenomenon caused by hydrolysis was observed in folpet as follows: in the extraction-time profile at 30–50 °C, the extraction yields of folpet started decreasing at 40–60 min, whereas continued to increase from 10–30 min. There were no pesticides observed in the extract over the course of the extraction (10–60 min) at temperatures higher than 50 °C.

3.5. Rearrangement classified characteristics in the physical property diagram

The characteristic profiles are divided into four types as determined by the effects of temperature on each pesticide. This classification did not necessarily reveal the relationship between these features in extraction and their physical properties. The relationship between the characteristic features in extraction and their physical properties did not become clear until the values were marked again with the corresponding symbols in the diagram. Fig. 2 shows that the physical property values of the pesticides classified into the same type aggregate into a cluster. Moreover, the boundary line of the applicability simultaneously comes into view. The distribution of three types and boundary lines are described as follows. (1) Type 1: $\log P_v$ values and $\log P$ values of the pesticides in this type range from −2.0 to 5.5 and 1.7 to 6.5, respectively. The physical property values of the pesticides in this type are distributed in circle A with one exception (DCIP). (2) Type 2: $\log P_v$ values and $\log P$ values of the pesticides in this type range from −3.9 to 1.9 and 1.6 to 6.9, respectively. The physical property values of the pesticides in this type are distributed in circle B. Circle B lies on the upper and left side of the circle A. (3) Type 3: $\log P_v$ values and $\log P$ values of the pesticide in this type are range from −7.1 to 1.3 and 1.6 to 8.2, respectively. The physical property values of the pesticides in this type are distributed in circle C with a few exceptions, a larger area than both circles A and B. Circle C is upward and to the left of circles A and B. The discovery of type 3 contributed greatly to the enhancement of applicability from the viewpoint that the physical properties are spread over a wide range of values. Although the regions in the circles overlap each other, this diagram is useful for estimating extraction feature in pesticides that have not been examined. (4) The boundary line of the applicability: a line of demarcation separating detectable pesticides and non-detectable pesticides can be drawn. The observation that the demarcation line is curved upper and leftward suggests that the hydrophobic pesticides are apt to be extracted more easily than hydrophilic pesticides as the vapor pressure of pesticide becomes lower.

3.6. Multi-group analysis

We developed a new multiple simultaneous analytical system. Multi-group analysis is the name given to multiple simultaneous analyses as opposed to a single simultaneous analysis in great number of pesticide residue analysis. In HS-SPME, multi-group analysis is composed of several group analyses. A group analysis means a single simultaneous analysis for pesticides that are similar in optimum temperature in their extraction profiles and are classified into the same group. The grouping is done flexibly, not restrictively: The temperature for grouping can be chosen from not the only optimum temperature of the pesticide but also adjacent temperatures to the optimum. Therefore, it is also possible for a pesticide to belong to more than one group. In the actual procedures for comprehensive monitoring, the same sample is divided into several vials. Each vial is sequentially examined by each group method in turn. Generally, simultaneous analysis is essential for multi-residue monitoring,

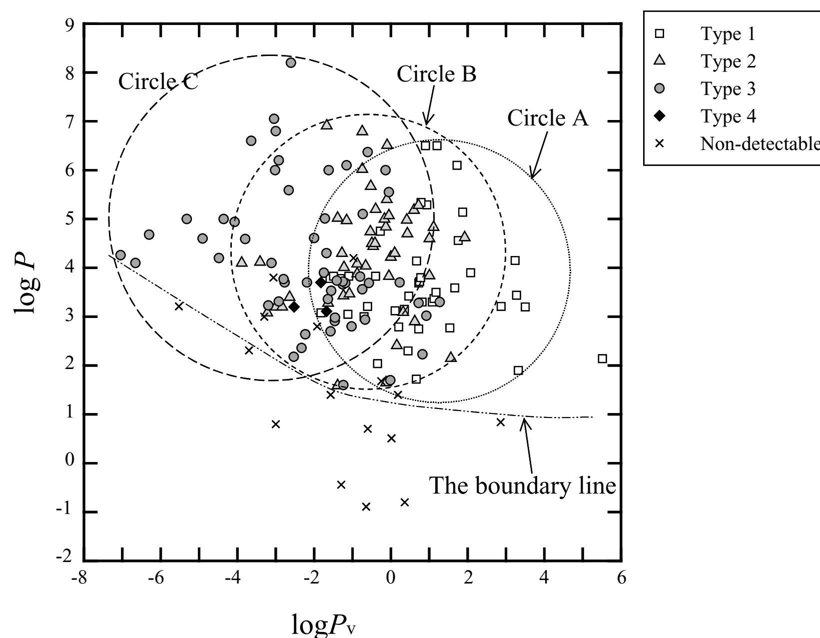

Fig. 2. Physical property diagram rearranged according to the classification of extraction temperature profiles of the selected pesticides. log P_v: logarithmic value of vapor pressure (mPa). log P: logarithmic value of octanol-water partition coefficient.

but has two inevitable weak points: (1) the uniform condition adopted in simultaneous analysis does not necessarily coincide with the optimum condition for each analyte, so it often happens that when obscure results have been obtained each analyte should be reexamined by an optimized individual method. (2) The simultaneous analysis becomes more inadequate for various matrices as the number of analytes increase. However, multi-group analysis can improve these weaknesses as follows: (1) the decision of analytical condition for a pesticide in multi-group analysis does not necessarily coincide with the optimization for the pesticide, but is more simple and flexible than the fractionation adjustment in the conventional sample preparations such as liquid–liquid extraction and solid-phase extraction. When a new pesticide should be added in a monitoring list, it is easy to select the grouping temperature for the pesticide because the pre-examination for obtaining the extraction profile of the pesticide can be rapidly carried out by the autosampler device. Therefore, new pesticides can be easily classified into the suitable group without altering the conditions established for already existing pesticides. (2) The connection between the simultaneous method and the individual optimum methods will be easily built up if the related extraction profiles can be rapidly obtained, because the methodologies of the group (simultaneous) analysis and the individual optimum analysis belong to the same category in HS-SPME. (3) Multi-group analysis takes more labor than a single simultaneous analysis because the repetition of similar procedures increases. Although adoption of the multi-group analysis system seems to be counter productive to the pursuit of efficiency required to meet the demand of the times, the remarkable advantage of simplicity and superior reproducibility in this automated system can more than compensate for these disadvantages.

3.7. *Quantitative evaluation of the HS-SPME technique*

In order to determine whether the automated HS-SPME–GC–MS system was quantitatively useful for detecting multi residue pesticides in waters, 45 of the 158 detectable pesticides were selected. The selected pesticides and the selected ions (*m/z*) for the determination of each pesticide with the mass chromatograms under full scan and MS–MS modes are listed in Table 2.

3.7.1. *HS-SPME conditions*

It was difficult to carry out the simultaneous determination of 45 pesticides under one set of conditions because their optimum conditions were different from each other as shown in Table 1. Therefore, multi-group analysis was adopted for the simultaneous determination of 45 pesticides. The 45 pesticides were divided into three groups and extracted at 60, 80, or 100 °C, as shown in Table 2. The pesticides were extracted with the PA fiber for 40 min in such a way that each sample could be analyzed within one hour. The values for the quantitative evaluations were obtained under the conditions for the multi-group method, not under the optimum conditions for each pesticide.

3.7.2. *Linearity of calibration curve*

The calibration curves were prepared as follows: the ratio of the peak area for the target pesticide to the peak area for the internal standard was plotted on the *y*-axis, and the initial concentration of the target pesticide was plotted on the

Table 2
Quantitation ion, limits of detection (LOD), linearity and precision data for 45 pesticides by HS-SPME

Compound	Quantitation ion (m/z)	Extraction temperature (°C)	LOD (μg/l)	Linearity		R.S.D.[d] (%)
				Correlation coefficient	Concentration range (mg/l)	
Dichlorvos (DDVP)	185	60	0.05	0.999	0.1–2	6.1
Etridiazole	211 + 183	60	0.01	0.995	0.05–2	7.7
Chloroneb	193	60	0.01	–[b]	–	–
Molinate	126	60	0.01	0.999	0.05–2	16.9
Fenobucarb (BPMC)	121	80	0.05	0.998	0.1–2	10.1
Benfluralin	292	80	0.01	0.999	0.05–2	4.9
Simazine (CAT)	201	100	0.1	0.995	0.2–5	11.9
Propyzamide	173	100	0.01	0.997	0.05–2	8.6
Diazinon	179	80	0.01	0.996	0.05–2	13.6
Chlorothalonil (TPN)	266	80	0.05	0.992	0.1–2	4.6
Iprobenfos (IBP)	204	80	0.01	0.995	0.05–2	9.2
Dichlofenthion	279	80	0.01	0.992	0.05–2	9.4
Bromobutide	232	100	0.01	0.986	0.05–2	2.5
Terbucarb (MBPMC)	205	80	0.01	0.995	0.05–2	3.6
Simetryne	213	100	0.1	0.992	0.2–5	15.4
Tolclofos-methyl	265	80	0.01	0.990	0.05–2	3.6
Carbaryl (NAC)	144	100	0.2	0.990	0.5–5	6.6
Metalaxyl	160	100	0.5	0.989	1–5	5.4
Dithiopyr	354	80	0.01	0.990	0.05–2	9.5
Fenitrothion (MEP)	260	80	0.05	0.991	0.1–2	14.4
Esprocarb	222	80	0.01	0.988	0.05–2	5.0
Malathion	173	100	10	–[c]	–	–
Thiobencarb	100	80	0.01	0.994	0.05–2	5.3
Chlorpyrifos	314	80	0.01	0.991	0.05–2	7.8
Fthalide	243	60	5	–[c]	–	–
Pendimethalin	252	80	0.01	0.994	0.05–2	6.1
Methyldymron	106	100	0.5	0.983	1–5	17.0
Isofenphos	213	100	0.05	0.990	0.1–2	18.2
Butamifos	286	100	0.05	0.995	0.1–2	15.2
Flutolanil	173	100	0.05	0.979	0.1–2	9.1
Napropamide	128	100	0.1	0.997	0.2–5	14.4
Isoprothiolane	204	100	0.05	0.990	0.1–2	13.2
Pretilachlor	262	100	0.05	0.982	0.1–2	14.9
Edifenphos (EDDP)	310	80	10	–[c]	–	–
Buprofezin	175	100	0.05	0.988	0.1–2	9.9
Triclopyr-2-butoxyethyl	184	80	0.1	0.997	0.2–5	7.5
Isoxathion	177	80	0.1	0.990	0.2–5	18.1
Mepronil	119	100	0.2	0.991	0.5–5	6.3
Chlornitrofen (CNP)	317	80	0.01	0.984	0.1–1	15.5
Propiconazole	191 (259)[a]	100	0.1	0.984	0.2–1	9.1
Pyributicarb	165	100	0.05	0.996	0.1–2	15.4
Pyridaphenthion	156 (199)[a]	100	0.5	0.992	1–5	11.8
EPN	169	100	0.05	0.992	0.1–2	6.6
Mefenacet	192	100	5	–[c]	–	–
Ethofenprox	163	100	0.05	0.987	0.1–2	11.2

[a] Product ion (precursor ion) selected in MS–MS mode.
[b] Nonlinear calibration curve was observed in the range of 0.05–2 μg/l.
[c] No calibration curve was determined.
[d] $n = 3$ determinations.

x-axis. The correlation coefficients were calculated from the 15 data (triplicates in five points) on the calibration curve, and ranged between 0.979 and 0.999 as shown in Table 2.

Ai [9] reported "The expression also provides a directly proportional relationship between the amount of analyte adsorbed by the SPME fiber and its initial concentration in sample matrix. This relationship indicates that SPME quantification is feasible before an adsorption equilibrium is reached, once the agitation condition and the sampling time are held constant." We confirmed whether the Ai theory was practical in our examinations and especially under heated conditions. We concluded that our HS-SPME–GC–MS analytical system fitted the theory. In addition, we confirmed that the linearity of calibration curve was effective not only at the optimum temperature but also at adjacent temperatures to the optimum. Furthermore, there was no difference

Table 3
Recoveries and relative standard deviations (R.S.D.) for 38 pesticides in water samples by HS-SPME and SPE

Compound	HS-SPME									SPE	
	Extraction temperature (°C)	Volvic		Evian		Contrex		Katsuura river		Katsuura river	
		Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
Dichlorvos (DDVP)	60	125.9	15.6	87.8	4.7	110.5	8.7	73.2	4.9	117.8	7.1
Etridiazole	60	95.6	5.8	45.2	6.4	87.6	4.2	99.4	5.9	96.5	5.6
Chloroneb	60	94.1	4.1	54.3	6.8	94.2	3.4	125.5	6.9	89.5	1.6
Molinate	60	97.7	4.0	72.7	8.5	100.0	7.3	108.5	5.3	82.5	2.6
Fenobcarb (BPMC)	80	135.9	5.7	153.6	2.7	159.7	4.9	93.9	7.9	89.7	5.2
Benfluralin	80	100.7	3.9	109.3	3.3	96.8	7.3	94.3	6.7	80.4	9.3
Simazine (CAT)	100	83.9	10.4	108.4	9.3	103.7	11.4	117.5	2.3	100.4	6.0
Propyzamide	100	91.8	6.7	99.1	1.6	97.7	7.5	107.2	3.0	97.5	2.9
Diazinon	80	93.2	2.6	109.7	2.0	89.4	3.7	92.4	2.6	98.6	5.6
Chlorothalonil (TPN)	80	80.6	17.2	140.0	3.9	141.1	5.1	90.9	5.7	239.2	5.8
Iprobenfos (IBP)	80	84.3	3.0	92.0	3.4	100.2	6.7	80.0	9.9	91.9	10.9
Dichlofenthion	80	79.9	4.8	117.5	1.8	104.5	7.7	103.9	2.3	88.3	8.8
Bromobutide	100	80.7	6.8	93.5	2.5	114.0	8.3	103.3	1.4	97.0	6.5
Terbucarb (MBPMC)	80	83.2	3.4	112.2	2.8	102.1	4.3	97.1	3.2	95.1	4.0
Simetryne	100	80.6	8.4	101.8	5.9	113.0	10.8	130.9	3.7	88.0	5.5
Tolclofos-methyl	80	75.0	3.1	108.3	2.6	103.6	6.6	95.5	2.2	77.9	5.5
Carbaryl (NAC)	100	91.2	15.1	90.6	15.9	117.8	8.5	105.7	5.4	78.7	13.0
Dithiopyr	80	86.9	4.1	88.5	3.8	102.1	4.2	101.6	1.1	79.0	6.8
Fenitrothion (MEP)	80	107.3	5.9	124.9	4.8	66.1	12.5	88.1	11.7	115.2	4.6
Esprocarb	80	83.7	2.8	88.6	3.3	94.7	7.9	97.2	6.7	90.6	5.2
Thiobencarb	80	96.9	3.9	90.4	5.5	93.2	4.9	99.0	3.2	93.8	7.5
Chlorpyrifos	80	92.2	5.1	75.4	3.8	78.4	4.1	96.1	3.9	87.4	7.6
Pendimethalin	80	76.4	2.5	106.1	6.5	80.9	6.7	86.4	7.0	81.0	1.6
Isofenphos	100	95.4	5.7	89.6	8.1	76.5	7.6	98.6	3.0	73.3	8.0
Butamifos	100	94.5	2.9	87.5	6.9	87.1	9.3	91.9	5.3	101.0	5.0
Flutolanil	100	114.5	5.8	112.7	15.4	101.5	3.2	118.1	9.2	102.8	7.8
Napropamide	100	112.7	5.4	111.6	4.2	100.2	4.7	102.8	3.9	117.0	4.1
Isoprothiolane	100	114.7	10.1	111.1	11.1	98.0	6.9	104.0	5.5	132.0	6.0
Pretilachlor	100	92.0	4.6	95.1	5.2	87.5	8.2	92.5	5.4	120.0	4.4
Buprofezin	100	89.5	5.4	94.1	6.5	93.1	8.9	99.8	6.6	105.6	3.8
Triclopyr-2-butoxyethyl	80	112.5	2.7	120.2	5.8	96.7	7.4	71.8	8.3	102.3	4.3
Isoxathion	80	86.4	3.9	88.2	6.9	70.5	6.5	77.0	4.4	106.2	7.6
Mepronil	100	119.0	4.9	120.6	12.7	107.2	7.8	128.4	8.3	106.8	6.7
Chlornitrofen (CNP)	80	77.4	5.4	101.2	4.3	86.3	8.2	93.4	6.4	85.1	6.0
Propiconazole	100	82.1	9.7	51.3	6.8	60.8	7.4	96.0	8.9	111.1	6.8
Pyributicarb	100	96.4	3.6	66.5	12.6	91.1	8.8	98.5	3.2	80.6	5.0
EPN	100	113.9	7.4	108.4	6.6	78.8	9.1	68.0	12.5	117.2	5.2
Ethofenprox	100	91.1	10.1	108.5	5.7	110.0	10.4	132.7	6.9	65.3	9.6

Spiking level of 0.5 μg/l, $n = 5$ determinations.

between the calibration curve prepared by single standard solutions and the calibration curve prepared by mixed standard solutions. This indicates that the HS-SPME–GC–MS system is also practical for multi-residue analysis of a wide range of pesticides.

3.7.3. Limit-of-detection (LOD) and precision

The LOD was calculated as the concentration giving a signal-to-noise ratio of three ($S/N = 3$). Pure water samples that were spiked with target pesticides at concentration levels ranging from 0.01 to 10 μg/l were analyzed to estimate the LOD. The LOD values for each pesticide are given in Table 2. The values of 0.01 μg/l in LOD for the 17 pesticides were achieved only under approximate conditions for screening not under optimized conditions for each pesticide. The precision of the method was evaluated by calculating the relative standard deviation (R.S.D.). The R.S.D. values for each pesticide in pure water were obtained by triplicate analysis of the target pesticides at the concentration of the lowest standard solution for each calibration curve. The R.S.D. values ranged from 3.6 to 18% as shown in Table 2.

3.7.4. Recovery and comparison between HS-SPME and SPE

The recovery examinations were performed by analyzing water samples (pure water, three different natural mineral waters, and surface water) spiked with tested pesticides at 0.5 μg/l. Seven of the 45 pesticides tested (metalaxyl, malathion, fthalide, methyldymron, edifenphos, pyridaphenthion, and mefenacet) were excluded from the subsequent examinations because the LOD values for these seven pesticides were more than 0.5 μg/l. The recovery for target pesticides was determined as the ratio of peak area in each tested sample to that in pure water under the same conditions. The mean recovery values and the R.S.D. values for the 38 selected pesticides in water samples at the concentration of 0.5 μg/l were obtained with five replicate analyses as shown in Table 3. The recovery values and the R.S.D. values on the HS-SPME technique were compared with those values on the solid-phase extraction (SPE) technique by analyzing pure water and surface water samples (five replicates) spiked with the tested pesticides at 0.5 μg/l. The results were in good agreement with those obtained by SPE as shown in Table 3.

4. Conclusions

The combination of an automated device with a heating module in the HS-SPME system proved to be an extremely powerful coupling method for the determination of multi-class pesticides in various water samples. The unexpected applicability of HS-SPME to less volatile compounds has revealed HS-SPME as an effective technique for pesticide residue identification not only in specific cases but also in usual cases. While it has not yet been theoretically useful, the physical property diagram may prove to be a valuable tool in inductively predicting adaptability of untested compounds in the HS-SPME system. The automated heating HS-SPME–GC–MS system with the multi-group technique appears to be a flexible and low-cost approach for multi residue analyses in various matrices.

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