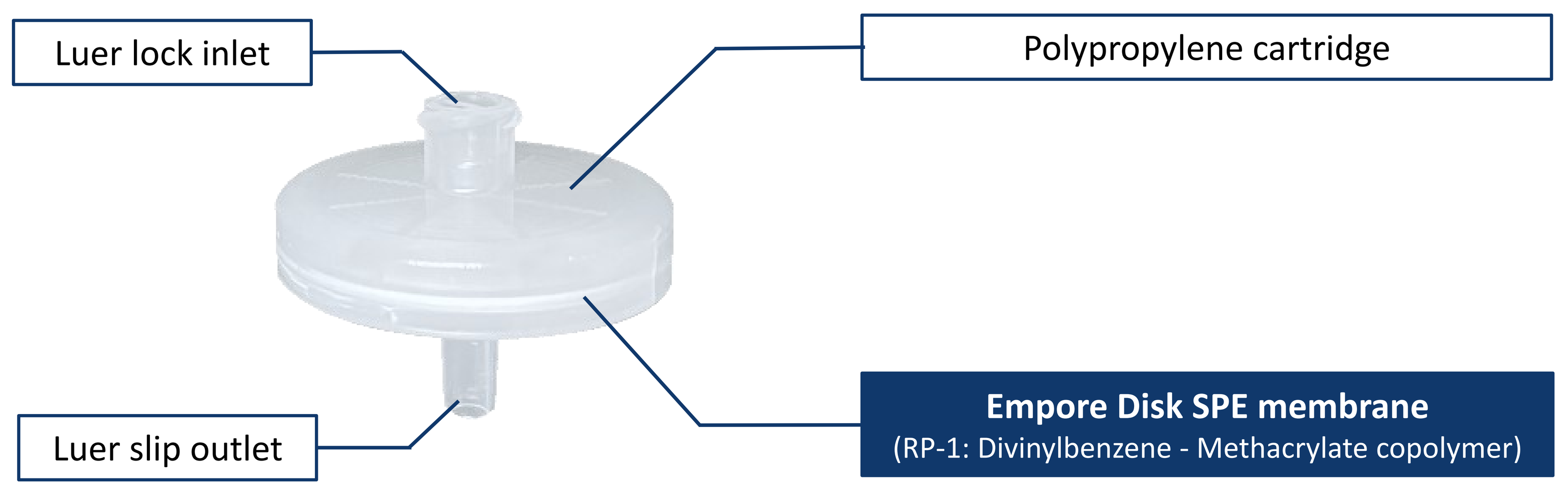
Rapid Sample Preparation and Analysis of 107 Pesticides in Water with the Solid Phase Extraction Disk Cartridge and Gas Chromatography Mass Spectrometer

Reika Takahara, Takumi Kunieda, Kazuyuki Ishii, Manabu Takayanagi, Hiroshi Hayashida,
GL Sciences Inc., Tokyo, Japan

Introduction

Gas chromatography mass spectrometer (GC-MS) and liquid chromatography mass spectrometer (LC-MS) are generally used for pesticide analysis in water, while solid phase extraction (SPE), which is easier to automate and uses less solvent, is preferred as a sample concentration method. SPE may concentrate analytes hundreds of times their concentration in the sample, allowing for the detection of analytes with very low concentrations. Conversely, SPE operation is complex, requiring conditioning of the SPE cartridge, sample application, washing, dehydration, elution, and distillation of the evaporation solvent as needed, and taking several hours for each preparation. If the number of samples is enormous, it may take up to an hour to apply the SPE cartridge. In this study, we report that the time for SPE in the analysis of 107 pesticides in water was greatly reduced using the new shape of SPE cartridge “EZ cartridge RP-1”. The EZ cartridge RP-1 has an SPE membrane fixed in a polypropylene housing. This membrane is composed of reversed-phase mode divinylbenzene - methacrylate copolymer particles and polytetrafluoroethylene (PTFE) fiber and is molded to a diameter of 25 mm and a thickness of 0.5 mm. Because of its large cross-sectional area, water sample passage at the same linear speed can theoretically be increased by approximately five times compared to a typical SPE cartridge. Due to the diameter of the solid phase particle being only 10 um, it is possible to strongly retain an analyte, preventing the analyte from breaking through.



EZ Cartridge RP-1
Solid Phase Extraction Disk Cartridge

Methods

Solutions and mixtures for sample preparation were extracted and analyzed as shown in Table 3. The standard sample was prepared by diluting a pesticide standard mixture (Hayashi Pure Chemical Ind., Ltd.) and adding it to the sample water. The SPE cartridge, EZ Cartridge RP-1 (GL Sciences, Inc.), is filled with a reverse mode SPE membrane made of methacrylate divinylbenzene copolymer. The 500 mL sample was concentrated using the procedure shown in Fig.1. The flow rates to the SPE cartridge were 50 mL/min and 100 mL/min, respectively, and the other procedures were the same. The analytes were eluted with 5 mL dichloromethane, then nitrogen gas was sprayed while the eluate was concentrated to 0.5 mL before being adjusted to 1 mL with dichloromethane. The entire process, from conditioning the SPE cartridge to evaporating the elution solvent, is performed automatically by the Aqua Trace ASPE899 (GL Sciences, Inc.). The GCMS-QP2020 NX was used to examine the material (Shimadzu). The internal standard was a mixture of Anthracene-d10, Chrysene-d12, and 9-Bromoanthrancene, with 9-Bromoanthrancene for correction. The InertCap 5MS/Sil capillary column was employed, which is a low-polar column having a liquid phase of 5% diphenyl (equiv.) - 95% dimethyl silphenylene siloxane.

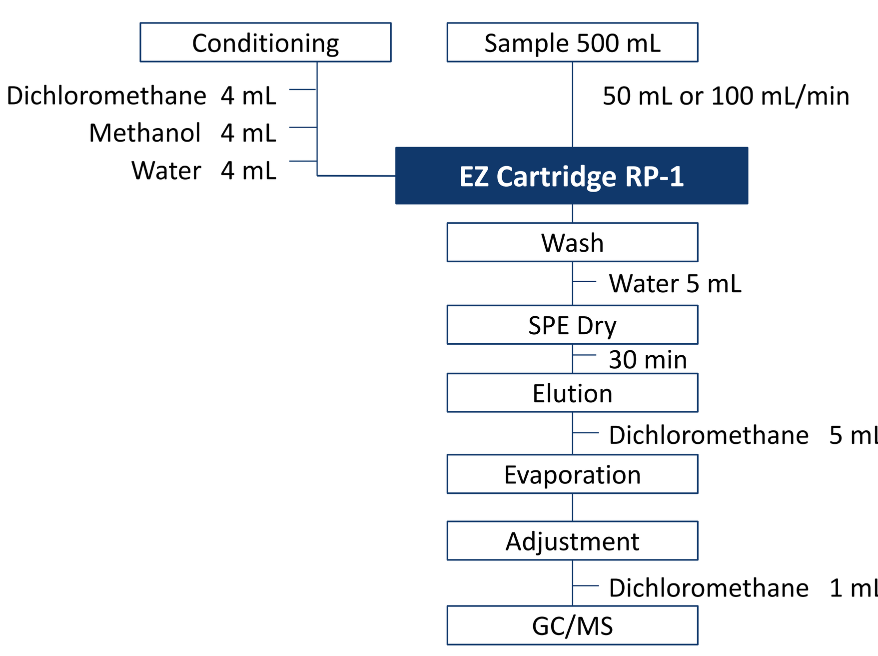
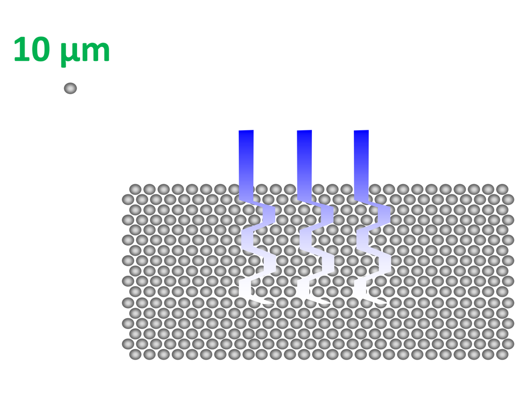
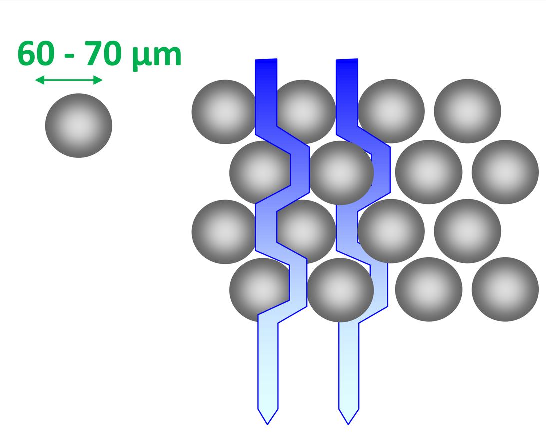
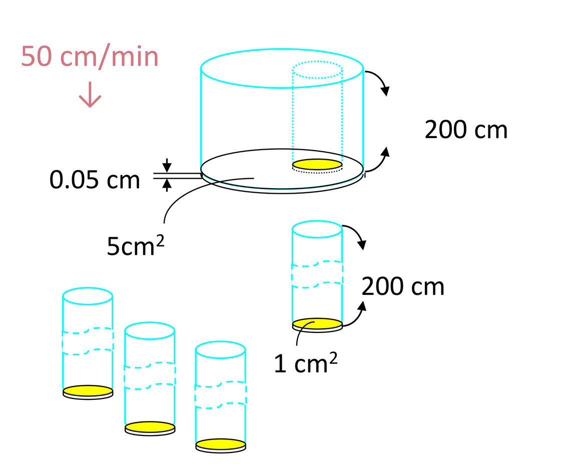
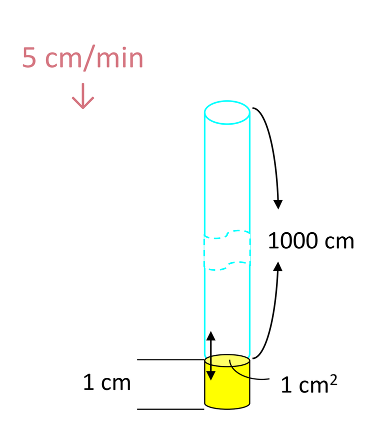


Fig.1 Solid Phase Extraction Procedure

Table 1 Comparison of SPE cartridge structure and sample flow rate

	EZ Cartridge	Conventional SPE Cartridge
Structure		
Particle size and diffusion efficiency		
Sample Volume	500 mL	500 mL
Flow Rate	100 mL/min	10 mL/min
Time	5 min	50 min
Relationship between liner velocity and sample passage area		

Results

Pesticides in water were concentrated from 500 mL to 1 mL using an EZ cartridge RP-1 and analyzed using GC-MS. As shown in Table 3, the EZ cartridge had a good recovery rate. The number of pesticides with a recovery rate of 70% or higher in 107 pesticides was 101 components when the sample was passed at 50 mL/min and 104 components when the sample was passed at 100 mL/min.

Table 2 GC-MS Conditions

System	GCMS-QP2010 Plus (Shimadzu)
Column	InertCap 5MS/Sil (GL Sciences Inc.) 0.25 mm I.D. × 30 m df = 0.25 µm
Col. Temp.	50 ℃ (3 min hold) - 10 ℃/min - 200 ℃ - 3 ℃/min - 230 ℃ (5 min hold) - 5 ℃/min - 280 ℃ (2 min hold)
Carrier Gas	He, 100 kPa
Injection	Splitless, 1min, 250 ℃
Detection	MS SIM
Interface Temp.	280 ℃
Sample Size	1.0 µL

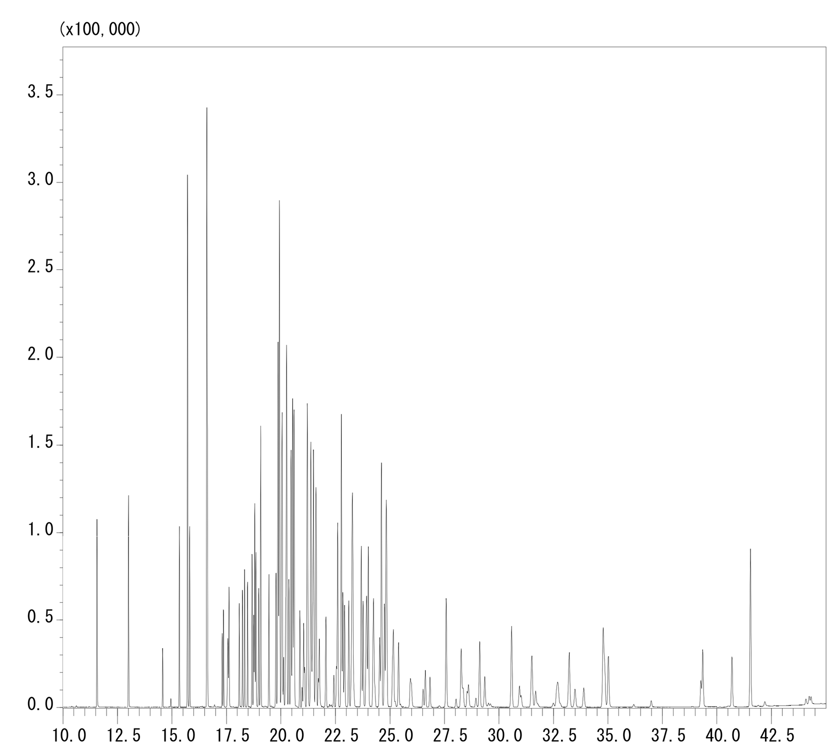


Fig.2 Total Ion Current Chromatogram

Table 3 Repeatability Linearity, and Recovery

	Flow Rate	100 mL/min		50 mL/min	
NO.	Compounds	Recovery Rate (%)	CV (%, n = 3)	Recovery Rate (%)	CV (%, n = 3)
1	Dichlorvos	75.8	9.6	76.3	2.8
2	Etridiazole	65.9	11	70.4	4.3
3	Chloroneb	81.1	10.5	81.8	1.9
4	Isoprocarb	81.1	8.4	78.6	2.6
5	Fenobucarb	82	7.8	79.1	2.6
6	Propoxur (PHC)	77.9	4.2	80.3	3.2
7	Pecycuron	86.1	8.1	78.3	5.5
8	Simazine	83.5	4.9	67.6	4.6
9	Atrazine	83.4	5	77.8	4.4
10	Diazinon Oxon	82.3	5.9	76.2	6.6
11	Cyanophos (CYAP)	74.7	6.4	74.7	4.1
12	Propyzamide	85.3	5.6	76	4.9
13	Diazinon	77.3	7.8	73.7	4.3
14	Pyroquilon	79.1	6.8	78.8	2.8
15	Chlorothalonil (TPN)	75.2	4.3	71.7	3.9
I.S 1	Anthracene-d10	-	-	-	-
16	Ethylthiomethon	74.9	8.1	74.9	3.6
17	Iprobenfos	78.8	6	76.4	5
18	Tolclofos-methyl Oxon	83	5.2	78.4	4.5
19	Benfuresate	79	6.5	77.6	3.7
20	MEP Oxon	81	6	80.5	4.9
21	Terbucarb	83.3	5.8	78	5.4
22	Propanil (DCPA)	84.6	5.3	82.4	4.1
23	Bromobutide	80.6	4.8	75.5	6.6
24	Metribuzin	78.6	4.3	77.4	5.3
25	Malaoxon	88.4	11.8	91.9	7.3
26	Simeconazole	78.8	5.1	76.2	5.9
27	Alachlor	82.5	5.6	77.7	4.2
28	Tolclofos-methyl	75.9	6.3	75.3	3.6
29	Simetryne	77.9	4.5	69.3	6.3
30	Metalaxyl	84.2	6.6	80.2	4.6
31	Ametryn	79.5	5.7	75.7	5.1
32	Cinmethylin	76.6	5.9	78.4	3.5
33	MPP Oxon	79.8	4.4	79.9	6.1
34	Fenitrothion	81.4	5.9	77.2	5.5
35	Bromacil	79.6	4.7	78.8	7
36	(E)-Dimethylvinphos	82.2	5.2	82.7	7.3
37	Esprocarb	79.5	6.9	78.5	3.2
38	Malathion	85.9	4.8	79.6	5.3
39	Chlorpyrifos Oxon	86.9	7.2	81	6.7
40	Quinoclamine (ACN)	74.2	4.4	76.7	4.5
41	Metolachlor	78.2	5.8	75.4	4.9
42	Thiobencarb	81.8	5.9	79.3	1.8
43	(Z)-Dimethylvinphos	79.6	3.9	79.2	3.5
44	Cyanazine	78.8	3.4	79.4	3.9
45	Fenthion	79.9	5.8	77.5	3.3
46	Chlorthal-dimethyl (TCTP)	73.2	4.6	76.9	2
47	Isofenphos Oxon	83.2	8.8	76.3	7.7
48	Tetraconazole	76.9	5	73.6	5.9
49	Fthalide	81.5	4	79.1	2.7
50	Fosthiazate	83.2	6.3	89.9	3.7
51	Cyprodinil	75.2	5.2	74.3	3.8
52	Dimethametryn	80	6.2	72.5	5.8
53	Isofenphos	79.6	5.1	76.4	4.3
54	Methyldymron	80.2	4.5	77.9	3.5

	Flow Rate	100 mL/min		50 mL/min	
NO.	Compounds	Recovery Rate (%)	CV (%, n = 3)	Recovery Rate (%)	CV (%, n = 3)
55	Phenthoate	77.4	6.7	73.6	5.2
56	Captan	78.7	3.4	78.4	2.2
57	Procymidone	85.4	4.9	81.4	2.3
58	Dimepiperate	77.6	5.6	76.4	4.5
59	Butamifos Oxon	75.2	8.5	74.3	7.2
60	Methidathion	84.7	4.8	77.1	4.8
61	Propaphos	75.5	6.8	73.1	5.7
62	Tetrachlorvinphos (CVMP)	78.2	5	79.1	5.8
63	Paclobutrazol	81.6	6.4	76.8	5.3
64	Butachlor	75	6.5	75	4.9
65	alpha-Endosulfan	73.1	5.5	77.7	2.4
I.S 2	9-Bromoanthracene	-	-	-	-
66	Butamifos	78.4	5.3	74.9	6.3
67	Napropamide	87.3	6.3	79.1	4.6
68	Flutolanil	88.9	5.4	80.1	5.6
69	(E)-Metominostrobin	83.7	6.2	79.9	5.7
70	Pretilachlor	84.6	6	77.4	4.4
71	Isoprothiolane	86.7	5.1	81.5	2.8
72	Isoxathion Oxon	85.5	5.6	67.4	1.9
73	Uniconazole P	80.3	7.3	74.1	5.2
74	Thifluzamide	80.5	5.9	75.8	5.7
75	MPP Oxon Sulfoxide	81.3	5.3	91.6	4.2
76	MPP Oxon Sulfone	80.9	12.8	81.9	6.1
77	Buprofezin	77.4	6.1	77.4	3.2
78	Cyproconazole	78.1	8.4	73.4	6
79	(Z)-Pyriminobac-methyl	80.5	7.1	74.8	4.8
80	MPP sulfoxide	78.6	5.1	78.9	3.3
81	beta-Endosulfan	73.7	5.4	78	2.8
82	MPP sulfone	78.7	5.7	78.4	5.4
83	Mepronil	88.5	6.5	79.3	4.4
84	Chlornitrofen (CNP)	68.2	8.9	76.6	6.4
85	Edifenphos	87.7	4.8	79.2	5.8
86	Propiconazole1	85.1	6.1	74.9	7.3
87	Endsulfate	69.8	3.4	81.8	8.6
88	(E)-Pyriminobac-methyl	80.2	6.1	71.2	6.8
89	Propiconazole2	82.8	7.1	72.6	6.4
90	EPN Oxon	84.2	9.8	81.1	7.3
91	Thenylchlor	87.3	5.2	78.1	6.6
92	Tebuconazole	80	7.2	76.7	4.6
93	Pyridaphenthion	79	8	69.5	8.2
94	Acetamiprid	70.4	6	70.6	7.8
95	Iprodion	79.3	5.2	74.5	6.8
I.S 3	Chrysene-d12	-	-	-	-
96	EPN	73	9.4	77.9	6.9
97	Piperophos	71.7	10.1	66	7.8
98	Indanofan	72.3	11.5	29.6	6.4
99	Furametpyr	79	6.7	73	7.2
100	Iprodion metabolite	71.5	7.2	74.3	5.2
101	Mefenacet	79.2	6.4	74.7	6.9
102	CNP-amino	87.1	5.4	78.4	4.4
103	Etobenzanid	84.4	8	78.1	5.7
104	Cafenstrole	91.7	6	83.2	4.8
105	Boscalid	87.2	6.2	77.5	4.5
106	Thiacloprid	80.7	4.7	81.8	6.2
107	Pyrazoxyfen	81.5	6.4	79.9	4.2

Conclusions

Using an EZ cartridge in the sample preparation for pesticide analysis in water, it was possible to reduce the time required for solid phase extraction from 162 min to 80 min. The EZ cartridge RP-1 is packed with reversed-phase polymers and is highly versatile; thus, it is likely to be applied with hydrophobic chemical compounds other than pesticides.

References

1. Standard test method in water, Ministry of Health, Labor and Welfare, Japan
2. Water Supply Test Method 2011 Edition, Japan Water Works Association

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