Rapid Solid-Phase Extraction of 136 Pesticides in Water Using Disk Cartridges and Alternative Solvents for GC-MS Analysis

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Introduction

Monitoring of pesticide residues in drinking water is essential for public health and regulatory compliance. Gas chromatography–mass spectrometry (GC-MS) is widely used due to its high sensitivity and selectivity. Prior to analysis, solid-phase extraction (SPE) is typically employed to achieve several hundred-fold concentration. Conventional SPE methods require approximately two hours to complete, with most of the time consumed by the sample loading step. In addition, dichloromethane (DCM)—a commonly used elution solvent—raises safety and environmental concerns due to its high toxicity. This study aimed to develop a faster and safer pretreatment method for GC-MS analysis of pesticides in drinking water by:

- Evaluating whether a disk-type SPE cartridge (EZ Cartridge RP-1) can significantly reduce sample loading time
- Establishing DCM-free elution conditions without sacrificing recovery efficiency

Methods

The analytical method used in this study was based on the official Japanese water quality testing procedures, specifically those described in the guidelines: *"Enactment of Ministerial Ordinance on Water Quality Standards, Partial Revision of Water Supply Law Enforcement Regulations, and Guidelines for Water Quality Management"*—Annex Methods 5 and 5-2. These are authorized procedures for pesticide monitoring in drinking water in Japan.

- SPE Cartridge : EZ Cartridge RP-1 (disk-type, GL Sciences Inc.)
- Target Pesticides : 136 compounds
- Sample Matrix : Ultrapure and tap water spiked at 1 µg/L
- Flow Rates Tested : 15, 50, 100 mL/min
- Elution Solvents:
    - Dichloromethane (DCM)
    - Acetone/Hexane (1:1)
    - Ethyl Acetate

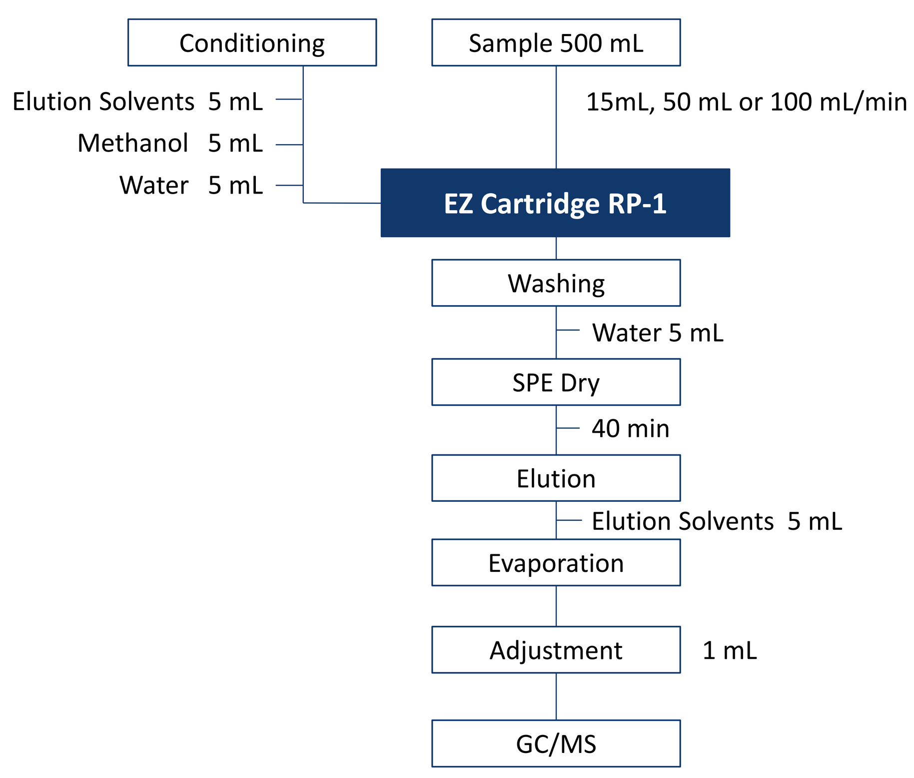
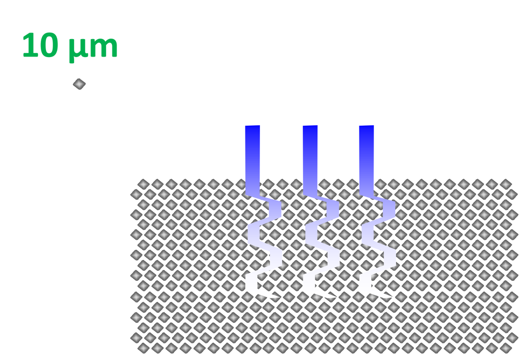
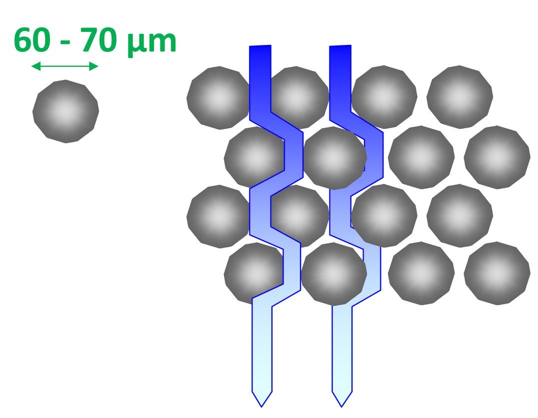
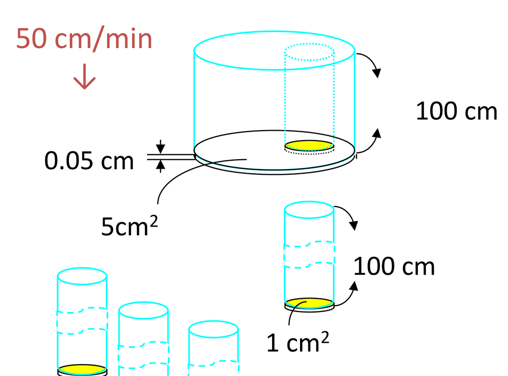
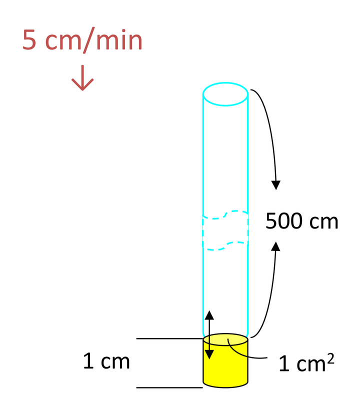


Fig.1 Solid Phase Extraction Procedure

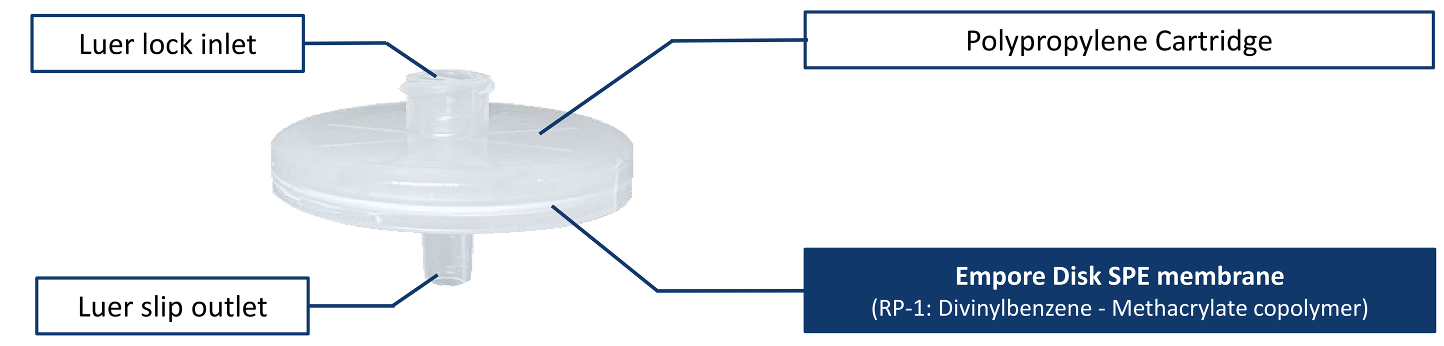
Table 1. Comparison of SPE Cartridge Structure and Sample Flow Rate

	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

Study 1: Effect of Sample Flow Rate on Recovery Rates

Ultrapure water samples were spiked with 136 pesticides at 1 µg/L each, and solid-phase extraction was performed using a disk-type SPE cartridge under three flow rate conditions: 15, 50, and 100 mL/min. The number of compounds recovered with ≥70% efficiency was 131 at 15 mL/min, 132 at 50 mL/min, and 121 at 100 mL/min (Table 3). These results indicate that even at a high flow rate of 100 mL/min, sufficient retention and recovery can be achieved for most compounds, demonstrating that faster flow rates are effective for reducing sample preparation time.



EZ Cartridge RP-1
Solid Phase Extraction Disk Cartridge

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 °C (3 min hold) - 10 °C /min - 200 °C - 3 °C /min - 230 °C (5 min hold) - 5 °C/min - 300 °C (2 min hold)
Carrier Gas	He, 100 kPa
Injection	Pulsed Splitless, 1min, 250 °C
Detection	MS SIM
Interface Temp.	280 °C
Sample Size	1.0 µL

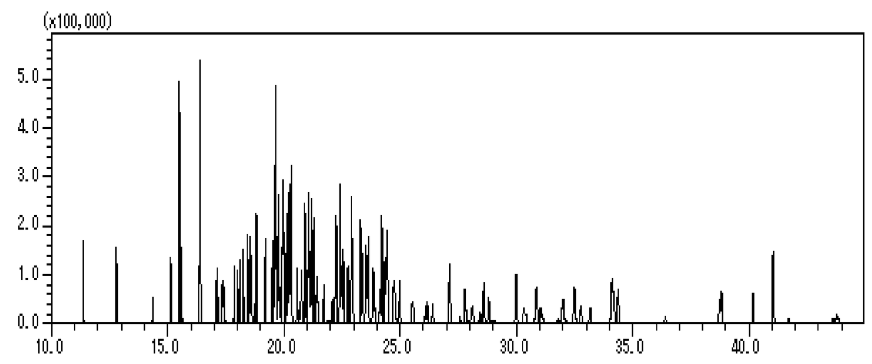


Fig.2 Total Ion Current Chromatogram (500ug/L each)

Table 3 Repeatability Linearity, and Recovery (Elution solvent; DCM)

No.	Compounds	15 mL/min Recovery Rate (%)	15 mL/min CV (%, n = 3)	50 mL/min Recovery Rate (%)	50 mL/min CV (%, n = 3)	100 mL/min Recovery Rate (%)	100 mL/min CV (%, n = 3)
1	Dichlorvos	84.4	8.1	82.8	2.9	74.9	6.7
2	Trichlorfon(DEP)	84.4	9.3	82.7	2.1	73	6.7
3	Dichlobenil	81.3	6.8	81.8	2.4	73.8	2.6
4	Etridiazole	82.9	10.2	80	4.3	71.1	4.9
5	Chloroneb	91.9	5.8	81.3	0.9	83.5	0.1
6	Isoprocarb	87.2	5.2	88.9	1.9	83.8	1.8
7	Molinate	80.6	5.2	82.5	1.2	77.1	3.3
8	Fenobucarb	86.8	4.9	90.4	3	85	1.4
9	Propocur(PHC)	83.4	4.6	92.8	4.6	79.4	1.4
10	Trifluralin	72.5	4.7	75.8	4.1	58.6	2.5
11	Benfluralin	67.1	6.1	70.8	6.3	53.8	3.6
12	Cadusafos	79	6.7	83.6	5.4	75.8	4.3
13	Pecycuron	88.6	9	95.9	5.7	88.2	0.3
14	Dimethoate	91.1	8.8	96.2	1.7	63.2	2.8
15	Simazine	87.6	5.2	81.8	5.4	85.3	0.8
16	Atrazine	85.9	4.8	93.9	5.5	86.5	1.5
17	Diazinon Oxon	92.8	8.2	91	7.9	83	2.6
18	Cyanophos(CYAP)	80.5	4.2	89.6	5.6	77.9	0.4
19	Propyzamide	89.8	7.1	92.9	7.1	87.7	0.4
20	Diazinon	81.1	3.6	87.1	6.2	81.6	2.8
21	Pyroquilon	84.4	3.9	91.7	3.7	81.7	0.4
22	Chlrothalonil(TPN)	74.1	4.1	83.4	5.7	78.7	2.8
23	Anthracene-d10	-	-	-	-	-	-
24	Ethylthiometon	80.7	4	42.9	3.5	75.9	0.6
25	Iprobenfos	87.9	6.8	91.1	7.9	79.4	0.6
26	Tolclofos-methyl Oxon	94.3	8.2	94.4	7.2	84.4	0.4
27	Benfuresate	83.9	5.8	93.6	4.7	82.1	2.1
28	Dichlofenthion	76	3.7	83.3	5.6	68.7	0.5
29	MEP Oxon	97.8	10.6	96.6	8.2	82.6	0.1
30	Terbucarb	85.8	6	93.9	6.2	85.9	1.4
31	Propanil(DCPA)	86.4	5.6	98.4	3.7	86.3	3.7
32	Bromobutide	85	6.3	92.3	7.5	84.4	0.8
33	Chlorpyrifos-methyl	77.7	4.8	86.8	6.1	75.5	1.4
34	Metribuzin	84.1	7.1	94.8	6.6	80.6	0.8
35	Malaoxon	88.2	15.5	111.6	8.7	89.3	1.8
36	Simeconazole	83.1	7.7	94.4	8.7	80.8	1.2
37	Alachlor	85.4	5	91.8	5.7	85.3	1.1
38	Tolclofos-methyl	82	3.1	87.7	4.7	79.6	1.7
39	Simetryne	80.8	7.4	84.1	9.4	82.2	0.3
40	Metalaxyl	86.9	7.2	95.5	6.1	85.2	1.7
41	Ametryn	79.8	6.9	91.1	8.3	81.7	1.7
42	Cinmethylin	78.9	3.5	88.4	4.1	80.2	0.4
43	Prometryn	77.3	6.8	90.8	7.4	79.1	0.6
44	Dithiopyr	73.4	4.7	83.6	7.8	67.3	2
45	MPP Oxon	90.7	8.5	73.6	6.5	80.1	0.7
46	Pirimiphos-methyl	76	4.7	86.9	6.8	75.1	0.8
47	Fenitrothion	91.2	8.3	94.4	8.4	83.6	1.9
48	Bromacil	86.2	11.2	100.5	9.6	81.4	0.6
49	(E)-Dimethylvinphos	84	6.7	98.7	9.9	83.9	1.4
50	Esprocarb	82.7	4	89.6	4.4	82.1	2
51	Malathon	86.8	6.1	95.2	6.4	87.5	1.6
52	Chlorpyrifos Oxon	93.1	11.6	101.1	10.2	86.7	1.2
53	Quinoclamine(ACN)	67.9	5.5	96.5	5.5	76.7	2.1
54	Metolachlor	78.6	4.4	91.9	6.4	81.3	2.1
55	Chrorpyrifos	77.8	4.1	85.4	6.9	71	2
56	Thiobencarb	82.6	3.2	87.6	4	85	1.8
57	(Z)-Dimethylvinphos	82.7	8.2	91.2	8.3	82.7	1.5
58	Cyanazine	83.2	7.6	91.4	6.5	82.3	1.4
59	Fenthion	83.4	3.8	75.9	5.3	82.4	2.2
60	Chlorthal-dimethyl(TCTP)	79.2	2.8	85.2	5.1	77	3.2
61	Isofenphos Oxon	95.3	13	98.6	10.9	81.5	0.1
62	Tetraconazole	80.3	9.3	91.5	8.7	80.9	1.6
63	Fthalide	86.5	4.6	90.7	3	84.9	4.6
64	Fosthiazate	86.2	9.7	105.4	6.9	85.5	0.2
65	Thiamethoxam	70.1	15.2	88.7	2.7	39.3	2.5
66	Pendimethalin	79.6	5.7	81.7	7.4	63.5	2
67	Cyprodinil	79.8	5.7	87.6	6.2	79.2	0.3
68	Dimethametryn	82.7	8.5	87.5	8.3	84.7	0.5
69	Isofenphos	82.9	6.1	87.8	4.8	81.6	1
70	Methydymron	86	6.4	91	4.5	82.6	1.1
71	Phenthoate	85.8	7.3	88.1	7.3	81.5	0.3
72	Captan	84.8	4.2	89.2	3.6	80.9	2
73	Procymidone	86.4	4.7	92.1	4.3	88.7	1.3
74	Dimepiperate	84.4	6.2	89.3	6.9	79.6	0.7
75	Triflumizole	73.3	10.3	82.2	9.5	66	1.4
76	Butamifos Oxon	94.8	11.9	92.6	9.7	75.7	0.7
77	Methidathion	87.1	7.8	90.9	5.2	87.6	1.2
78	Propaphos	80.7	10.1	62.8	7.2	73.7	0.7
79	Tetrachlorvinphos(CVMP)	83.3	8.6	91.9	8.7	81.4	1
80	Paclobutrazol	85.9	9.9	91.2	7.6	81.4	0.9
81	Butachlor	79.1	6	87.2	5.9	77.1	1.9
82	alpha-Endsulfan	82.7	4.5	85.8	5.2	76.9	1.2
83	9-Bromoanthrancene	-	-	-	-	-	-
84	Butamifos	89.2	8.5	90.1	8	80.6	1.4
85	Napropamide	88.4	6.9	91.7	5.3	89.9	2.8
86	Flutolanil	89.6	9	94.5	5.6	91.3	1
87	(E)-Metominostrobin	86.6	9.2	94.1	5.4	84.2	1.3
88	Pretilachlor	86.8	7.3	90.3	5.6	86.3	1.4
89	Isoprothiolane	88.3	7.3	91.9	4.5	86.9	2.2
90	Isoxathion Oxon	86.5	7.8	77.7	5.5	85.8	0.5
91	Uniconazole P	84.8	10.4	91.7	7.4	80.4	0.6
92	Thifluzamide	82.3	10.8	92.3	6.7	81.7	1
93	MPP Oxon Sulfoxide	94.5	14.4	150.2	5	84.4	10.4
94	MPP Oxon Sulfone	91.3	13.8	101.6	6.8	83.4	3.4
95	Buprofezin	83.9	6.8	88.7	4.8	78.8	0.4
96	Cyproconazole	83.3	9.2	89.5	7.8	79.9	1.5
97	Isoxathion	86.1	7	89.8	4.9	74.5	1
98	(Z)-Pyriminobac-methyl	82.2	11.2	92.2	5.8	82.5	0.8
99	MPP sulfoxide	93.6	11.3	107.8	3.9	81.4	2.5
100	beta-Endsulfan	85.4	6.2	91.1	4.6	76.5	4.5
101	MPP sulfone	92.4	10.8	94.1	6.8	82.5	0.9
102	Mepronil	91.8	10.9	92.7	3.4	87.8	0.7
103	Chlornitrofen(CNP)	90.8	9	88.9	5.4	72.6	4.9
104	Edifenphos	92	8.9	92.1	4.8	91	0.1
105	Propiconazole1	90.8	10.4	90.8	6.5	88.4	0.7
106	Endsulfate	88.2	6.8	91.3	6.9	77.9	4.4
107	(E)-Pyriminobac-methyl	83.3	10.2	88.6	6.7	84.5	0.9
108	Propiconazole2	86.9	9.6	90.3	6.8	88.5	0.9
109	EPN Oxon	99.1	11.9	101.7	5.8	85.8	3.1
110	Thenylchlor	92.6	8.6	91.7	4.7	90.4	1.1
111	Tebuconazole	85.3	9.4	93.9	6.7	80.9	0.7
112	Propargite(BPPS)	59.4	9.3	77.7	7.1	41.3	1.3
113	Pyributicarb	82.9	10.7	77.8	7.9	60.6	0.4
114	Pyridaphenthion	87.5	14.5	89.6	8.7	79.3	0.1
115	Acetamiprid	84.7	14.4	91.4	11.1	70.6	6.1
116	Iprodion	86.2	10.1	90.3	5.1	83.5	0.1
117	Chrysene-d12	-	-	-	-	-	-
118	EPN	91.2	9.7	90.2	6.5	75	1.4
119	Piperophos	82.6	12.4	84.6	10.3	72.5	0.4
120	Cumyluron	81.5	11.5	88.4	7.5	69.3	3.4
121	Indanofan	83.1	11.1	54.2	8.4	75	1.7
122	Anilofos	85.8	13.2	88.2	9.3	76.7	0.2
123	Orysastrobin	83.5	12.9	89.7	8.4	74.5	1.6
124	Bifenox	94	16.7	91.1	8.5	68.7	3.4
125	Furametpyr	82.4	11.1	89.6	6.2	81.4	0.4
126	Iprodion-t	93.2	9.3	89.6	5.6	74.4	1.3
127	Phosalone	80.8	10.7	87.5	7.7	74	0.3
128	Pyriproxyfen	77.9	7.6	82.9	4.4	64.2	0.9
129	Mefenacct	89.3	10	91.4	6.4	81.9	0
130	Cyhalofop-butyl	55.5	9.3	70.4	4.4	44.7	0.4
131	CNP-amino	92	11.1	92.4	2.4	86.5	3.3
132	Pyraclofos	174.9	50.8	83.8	48.1	128.1	2
133	Etobenzanid	93.5	14.9	88.6	5.6	82.3	1.8
134	Cafenstrole	97.4	12	91.8	5.6	91	0.5
135	Boscalid	95.6	13	87.4	3.5	86.7	1
136	Ethofenprox	54.5	10.8	49.2	4	35.4	0.6
137	Thiacloprid	91.3	8.4	97.6	2.1	79.5	7
138	Difenoconazole	86	11.8	83.7	6	70.8	4.2
139	Pyrazoxyfen	91.6	9.9	91.3	4.7	82.3	1.3

Study 2: Comparison of Elution Solvents

Three elution solvents were evaluated: dichloromethane (DCM), acetone/hexane (1:1), and ethyl acetate. DCM and acetone/hexane yielded comparable recovery results across most compounds, indicating that acetone/hexane is a suitable alternative to DCM. In contrast, ethyl acetate resulted in significant degradation of Ethylthiometon, leading to poor recovery. These findings support the selection of acetone/hexane (1:1) as the preferred DCM-free elution solvent.

Study 3: Validation with Tap Water Samples

Tap water samples spiked with 136 pesticides at 1 µg/L were processed at a flow rate of 100 mL/min and eluted with acetone/hexane (1:1). The results showed that the recovery of 125 compounds was over 70% as in the case of dichloromethane as the eluent. The performance was similar to that observed with ultrapure water, confirming the method's applicability to actual water samples..

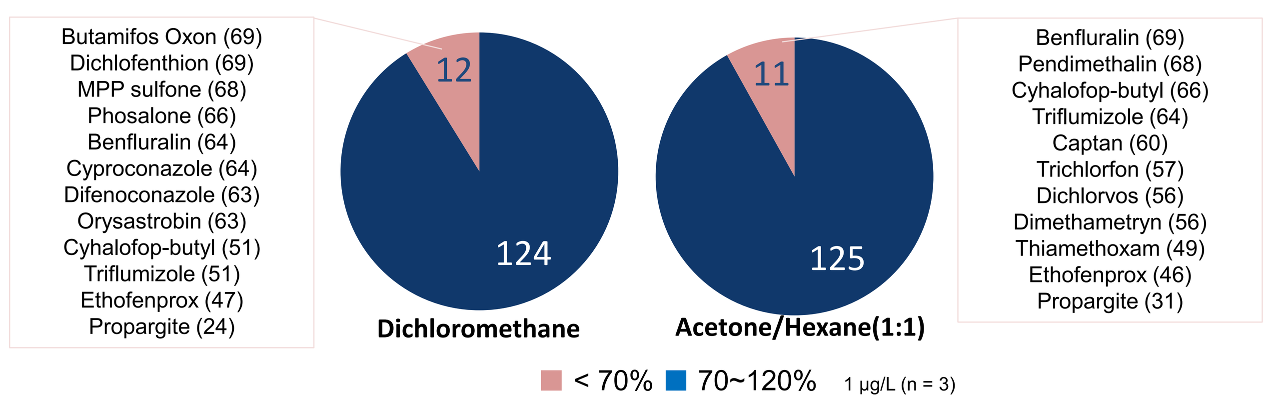


Fig 3. Recovery Rate of the Pesticides from Tap Water Samples by Each Solvent

Conclusions

This study demonstrated that using a disk-type SPE cartridge (EZ Cartridge RP-1) allows sample flow rates to be significantly increased (up to 100 mL/min) while maintaining good recovery rates. Specifically, 125 out of 136 pesticide compounds showed ≥70% recovery, indicating that pretreatment time can be substantially reduced without sacrificing performance. Additionally, replacing hazardous dichloromethane (DCM) with acetone/hexane (1:1) achieved similar recovery results while improving safety. These results confirm that the developed method is a practical and efficient GC-MS pretreatment technique for pesticide residue analysis in drinking water, offering both speed and safety.

References

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www.glsciences.com
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