ELSEVIER

Journal of Chromatography A, 709 (1995) 319–331

JOURNAL OF CHROMATOGRAPHY A

Determination of organophosphorus pesticides in environmental samples by capillary gas chromatography–mass spectrometry

Tameo Okumura, Yoshinori Nishikawa*

Environmental Pollution Control Center, 62-3, 1 Chome, Nakamichi, Higashinari-ku, Osaka City 537, Japan

First received 29 November 1994; revised manuscript received 13 April 1995; accepted 18 April 1995

Abstract

Traces of fourteen organophosphorus pesticides in environmental samples such as river water, sediment and fish were determined by capillary GC–MS with selected-ion monitoring. The pesticides could be determined within the range 0.02–0.75 ng/ml in water with relative standard deviations (R.S.D.s) of 1.0–31.4% (except for MPP, 1.0–10.9%). The detection limits of the pesticides were 0.013–0.120 ng/ml in water. Their recoveries from river water, sea water, sediment and fish samples were 101–132%, 103–145%, 93–166% (except for isoxathion) and 67–101% (except for isoxathion and phosmet), with R.S.D.s of 1.1–8.0%, 0.9–8.2%, 6.2–28.5% and 4.2–10.8%, respectively.

1. Introduction

Organophosphates are well known as powerful insecticides and organophosphorus pesticides (OPs) have been widely used since the use of organochlorine pesticides was prohibited, as they do not have such adverse decomposition and bioaccumlative properties in the environment. However, care must be taken with the use of OPs because they are cholinesterase inhibitors in living bodies [1].

Chromatographic methods such as GC [2–7] and LC [8–10] have been used for the simultaneous determination of pesticides. However, it is very difficult to determine trace amounts in the presence of various kinds of interfering substances that occur in the environment, especially in fish samples. Moreover, few reports have appeared concerning detection limits, which are related to the standard deviations of the measured values at near zero concentrations of the analyte.

The aim of this study was to develop a practical method for the determination of the OPs in water, sediment and fish samples for use in an actual survey. In this work, fourteen OPs were selected for the survey on the basis of the amounts manufactured, their forms of use and other factors of concern to the Japan Environmental Agency. A convenient method is presented for determining these OPs in environmental samples by capillary GC–MS with selected-ion monitoring (SIM) and with detection limits at sub-ng/ml levels. The analytical methodologies were improved by using a clean-up pro-

* Corresponding author.

0021-9673/95/$09.50
SSDI 0021-9673(95)00477-7

cedure with both normal- and reversed-phase column chromatography for fish samples.

2. Experimental

2.1. Reagents and apparatus

OP standards were obtained as pure solids or liquids from Wako (Osaka, Japan). The structures of the fourteen OPs studied are shown in Fig. 1. Phenanthrene-d_{10}, fluoranthene-d_{10} and chrysene-d_{12}, used as internal standards, were obtained from MSD Isotopes (Montreal, Canada). Dichloromethane, acetone, hexane and methanol of pesticides grade and the other reagents used of special grade were purchased from Wako and Tokyo Kasei (Tokyo, Japan).

Wako gel C-200 and polyamide C-200 of column chromatographic grade were purchased from Wako. Hydrated silica gel columns were prepared as follows. Wako gel C-200 was activated overnight at 130°C and kept in a desiccator. A 100-g amount of the activated silica gel was placed in a stoppered conical flask, then 5 or 40 ml of pure water were added and the flask was shaken to ensure homogeneity and then allowed to stand for 4–5 h. A 2-g amount of the hydrated (100 + 5) silica or 5 g of the hydrated (100 + 40) silica was packed in a 1 cm I.D. column chromatographic tube using the hexane slurry method and anhydrous Na_2SO_4 was added to make a ca. 2 cm upper layer of the column packing. The polyamide column was prepared by packing 1 g of polyamide C-200 in 1 cm I.D. column chromatographic tube using the methanol–water (50:50) slurry method. The hydrated (100 + 5) silica columns were used to clean up sediment samples and the hydrated (100 + 40) silica and the polyamide columns were used for fish samples.

A Waters (Milford, MA, USA) Model 600E liquid chromatograph equipped with a Model 717 autosampler and a Nihonbunko (Tokyo, Japan) Model 870-UV absorbance detector adjusted to 210 nm was employed for the determination of *n*-octanol–water partition coefficients and for pesticide degradation tests. The analytical column used was a 25 cm × 4.6 mm I.D. stainless-steel tube packed with Develosil ODS-5 (Nomura Kagaku, Aichi, Japan).

A Branson B-220 ultrasonic extractor and a Poly Toron PT10-30 homogenizer were used for extraction from sediment and fish samples, respectively. A Tomy Seiko (Tokyo, Japan) LC06-SP centrifuge was employed for phase separation of sediment or fish samples.

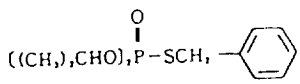
2.2. Gas chromatography–mass spectrometry

A Hewlett-Packard (Avondale, PA, USA) HP 5790 gas chromatograph and a Nihondenshi (Tokyo, Japan) JEOL-DX303 mass spectrometer with a DA-5000 data processing system were employed. The analytical column used was Ultra-2 cross-linked with 5% phenylmethylsilicone (25 m × 0.32 mm I.D., 0.52 μm film thickness). The GC temperature programme was an initial temperature of 70°C, increased at 3°C/min to 250°C. The temperatures of the injector, transfer line and ion source were 250°C. The carrier gas was helium at 7.5 p.s.i. (61 cm/s). Samples were injected in the splitless mode with 1.5 min purge off. The mass spectrometer was operated at 70 eV and 300 μA in the electron-impact mode using scanning or SIM. The ions of the pesticides and the internal standards monitored are shown in Table 1. As the retention times of the OPs vary widely, it is preferable to use several internal standards, and in this work three deuterated hydrocarbons whose retention times covered the appropriate interval were used. The *m/z* values monitored were selected in consideration of selectivity and sensitivity. Fig. 2 shows typical GC–MS total ion and SIM traces for the pesticides and the internal standards.

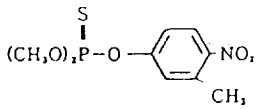
2.3. Analytical procedure

The procedure for the determination of the OPs in environmental samples is outlined in Fig. 3. A 1000-ml volume of water sample was added to 50 g of NaCl and extracted twice with 100 and 50 ml of dichloromethane, then the organic

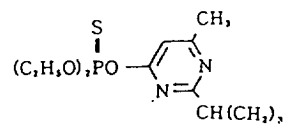
①IBP($C_{13}H_{21}O_3PS$:288.4)
S-benzyl O,O-diisopropyl phosphorothioate



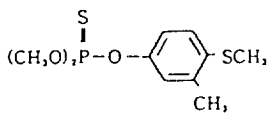
②MEP($C_9H_{12}NO_5PS$:277.2)
O,O-dimethyl O-4-nitro-m-tolyl phosphorothioate



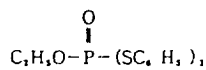
③Diazinon($C_{12}H_{21}N_2O_3PS$:304.4)
O,O-diethyl O-2-isopropyl-6-methylpyrimidine-4-yl phosphorothioate



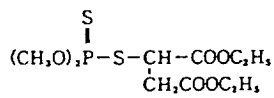
④MPP($C_{10}H_{15}O_3PS_2$:279.3)
O,O-dimethyl O-4-methylthio-m-tolyl phosphorothioate



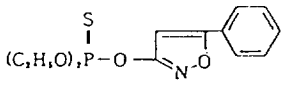
⑤EDDP($C_{14}H_{15}O_2PS_2$:310.4)
O-ethyl S,S-diphenyl phosphorodithioate



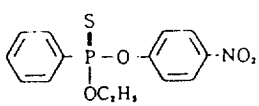
⑥Malathion($C_{10}H_{19}O_6PS_2$:330.4)
S-1,2-bis(ethoxycarbonyl)ethyl O,O-dimethyl phosphorodithioate



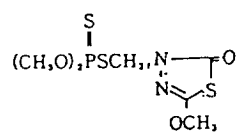
⑦Isoxathion($C_{13}H_{16}NO_4PS$:313.3)
O,O-diethyl O-5-phenylisoxazol-3-yl phosphorothioate



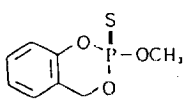
⑧EPN($C_{14}H_{14}NO_4PS$:323.3)
O-ethyl O-p-nitrophenyl phenyl phosphorothioate



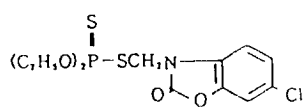
⑨Methidathion($C_6H_{11}N_2O_4PS_3$:302.3)
S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl O,O-dimethyl phosphorodithioate



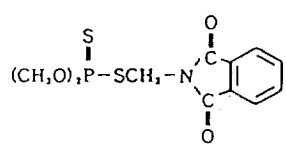
⑩Salithion($C_8H_9O_3PS$:216.2)
2-methoxy-4H-1,3,2-benzodioxaphosphinine



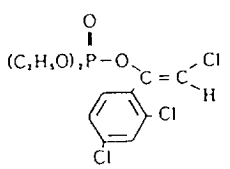
⑪Phosalone($C_{12}H_{15}ClNO_4PS_2$:367.8)
S-6-chloro-2,3-dihydro-2-oxobenzoxazol-3-ylmethyl O,O-diethyl phosphorodithioate



⑫Phosmet($C_{11}H_{12}NO_4PS_2$:317.3)
O,O-dimethyl S-phthalimidomethyl phosphorodithioate



⑬α-CVP($C_{12}H_{14}Cl_3O_4P$:359.6)
2-chloro-1-(2,4-dichlorophenyl)vinyl diethylphosphate



⑭β-CVP($C_{12}H_{14}Cl_3O_4P$:359.6)
2-chloro-1-(2,4-dichlorophenyl)vinyl diethylphosphate

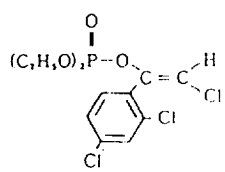


Fig. 1. Structures of the OPs studied.

Table 1
Monitor ions for the pesticides and the internal standards

No.	Compound	Monitor ion (m/z)	
a	Phenanthrene-d_{10}	188	
10	Salithion	(183)	216
3	Diazinon	(179)	304
1	IBP	204	(288)
b	Fluoranthene-d_{10}	212	
2	MEP	(260)	277
6	Malathion	(127)	173
4	MPP	(169)	278
13	α-CVP	323	(325)
14	β-CVP	323	(325)
9	Methidathion	(125)	145
7	Isoxathion	(177)	313
c	Chrysene-d_{12}	240	
5	EDDP	(173)	310
12	Phosmet	160	(317)
8	EPN	(169)	185
11	Phosalone	182	(367)

The monitor ions in parenthesis are used for identification, not for quantitation.

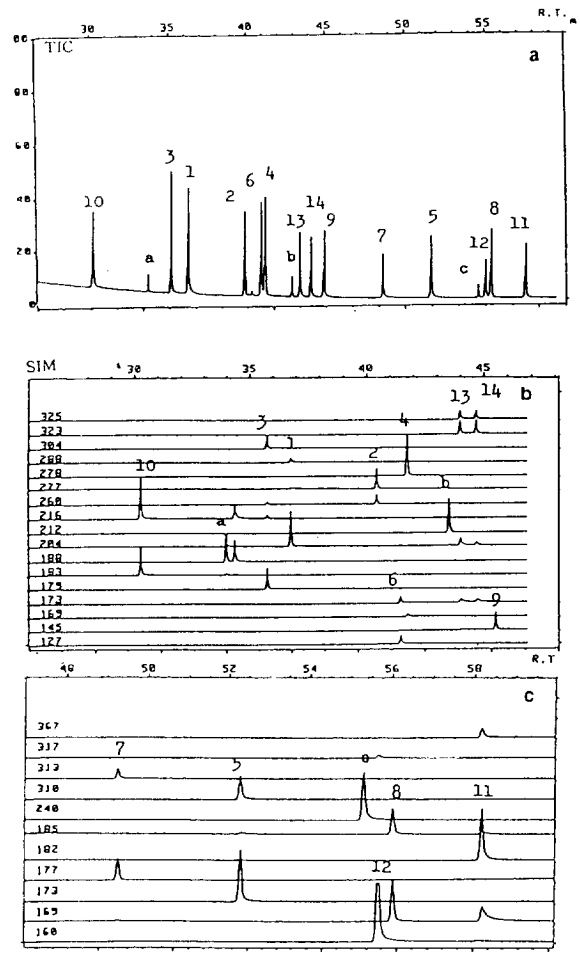


Fig. 2. Typical GC–MS TIC and SIM traces for the OPs and the internal standards. (a) Phenanthrene-d_{10}; (b) fluoranthene-d_{10}; (c) chrysene-d_{12}. Peaks: 1 = IBP; 2 = MEP; 3 = diazinon; 4 = MPP; 5 = EDDP; 6 = malathion; 7 = isoxathion; 8 = EPN; 9 = methidathion; 10 = salithion; 11 = phosalone; 12 = phosmet; 13 = α-CVP; 14 = β-CVP.

phases were combined and dehydrated by passing through anhydrous Na_2SO_4. The organic phase was concentrated to 3–5 ml in a Kuderna–Danish (KD) evaporative concentrator and further evaporated to 0.5 ml under a stream of nitrogen. A 0.5-ml volume of internal standard solution (each 1 mg/l) was added and then an aliquot was analysed by GC–MS–SIM.

For sediments, 10 g of sample were added to 30 ml of acetone with stirring and then sample was extracted twice in an ultrasonic extractor for 10 min and then centrifuged at 3000 rpm (1600 *g*) for 10 min. The supernatant solutions were combined in a separating funnel and 200 ml of 5% NaCl solution and 50 ml of dichloromethane were added, then the mixture was extracted, dehydrated and concentrated to dryness. One should be careful not to over-dry with heating, otherwise the recovery will be low. Hexane (2 ml) was added to the dry sample, which was subjected to hydrated (100 + 5) silica column chromatography. The column was first washed with 20 ml of hexane and then the fourteen OPs were eluted with 30 ml of acetone–hexane (10:90). The eluate was treated using the same procedure as for water samples.

For fish samples, 10 g of sample were homogenized, centrifuged, extracted and concentrated to dryness in a similar manner to sediment. Next, 2 ml of azobenzene in hexane solution (500 mg/l) were added to the dry sample and subjected to hydrated (100 + 40)

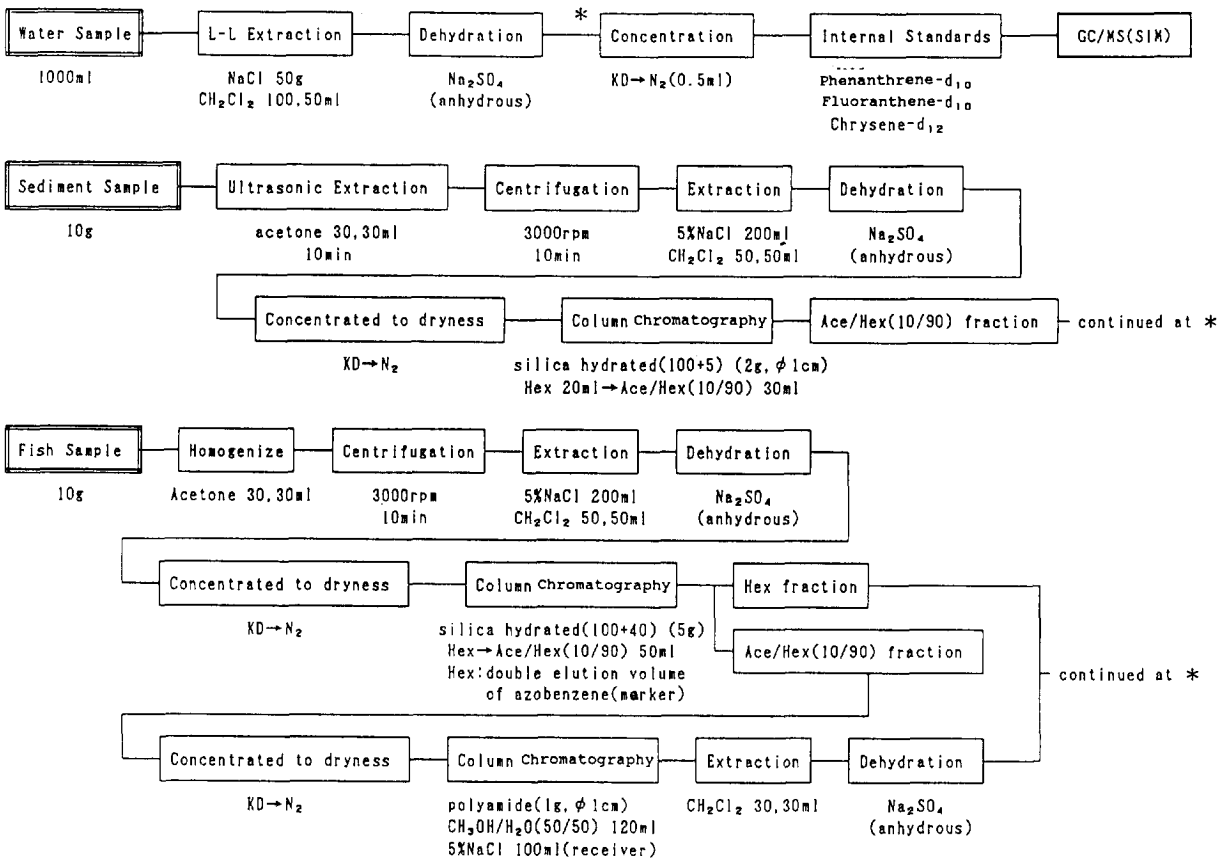


Fig. 3. Flow scheme for the determination the OPs in environmental samples.

silica column chromatography. Azobenzene was used as an elution marker, being observed visually as a yellow band in the column. The hexane fraction was obtained using double the volume (14 ml) used in azobenzene elution. As it was difficult to charge the sample on the column due to its low solubility in CH_3OH–H_2O (50:50), the acetone–hexane (10:90) fraction (50 ml) was concentrated to dryness 0.3 g of polyamide was added to the residue and then the adsorbed particles were charged on the polyamide column. The charged sample was washed on the column with 120 ml of CH_3OH–H_2O (50:50) to remove interfering biota components. The eluate was extracted twice with 30 ml of dichloromethane and then the organic phase was dehydrated with anhydrous Na_2SO_4. The organic phase and the preceding hexane fraction were combined and the procedure was continued from the asterisk marked in Fig. 3.

3. Results and discussion

3.1. Octanol–water partition coefficients

The *n*-octanol–water partition coefficients (P_{ow}) of organic chemicals are an important parameter for predicting bioconcentration factors for fish and their water solubility. It is easy to calculate log P_{ow} as a function of the logarithm of the capacity factor with the use of a

reversed-phase HPLC system [11,12]. Benzene, bromobenzene and biphenyl were used for calibration. The analytical column was used Develosil ODS-5 (25 cm × 4.6 mm I.D.). The mobile phase was CH_3OH–H_2O (70:30) at a flow-rate 1.0 ml/min. The log P_{ow} data for the OPs are summarized in Table 2. The calculated values of log P_{ow} were 1.90–3.97 and the experimental values were 1.8–4.30.

3.2. Degradation test

In any method, it is necessary to elucidate the stability of the analytes. A degradation screening test for the pesticides was investigated under different pH conditions. Table 3 shows residual percentage of the OPs after 1 h and 5 days at pH 5, 7 and 9, adjusted using the buffer solutions 65 m*M* KH_2PO_4, 65 m*M* KH_2PO_4–65 m*M* Na_2HPO_4 (40:60) and 65 m*M* Na_2HPO_4, respectively. The pesticides did not decompose under acidic conditions (pH 5), but EDDP, salithion and phosmet decomposed at pH 7 and 9 and malathion at pH 9. MPP decomposed on exposure to light.

3.3. Clean-up procedure for column chromatography

Clean-up of sediment extracts was carried out with the use of the hydrated (100 + 5) silica column. Fig. 4 shows typical elution pattern of the OPs with hexane and acetone–hexane (10:90) as eluents. The OPs were not eluted with 20 ml of hexane, but they completely eluted with 30 ml of acetone–hexane (10:90). For fish or biota samples, it is difficult to apply a clean-up procedure similar to that for sediment owing to unavoidable interfering components in the samples. Most OPs are relatively polar compounds, so the hydrated (100 + 40) silica column was used. The polar acetone–hexane (10:90) fraction was further cleaned up by means of polyamide column chromatography in order to separate biota interferents.

3.4. Calibration

The calibration graph for the OPs was obtained by plotting the concentration ratio against peak-area ratio of the analyte to internal stan-

Table 2
HPLC capacity factors and calculated log P_{ow} values for the pesticides

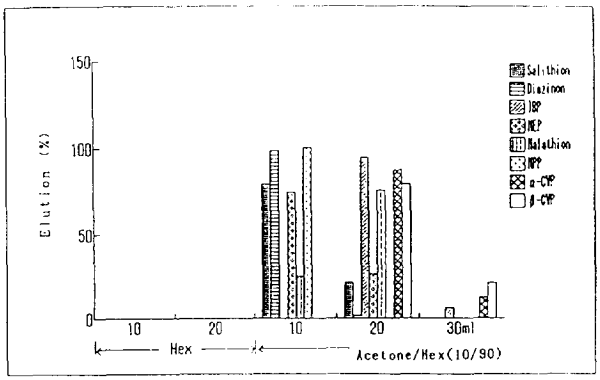
Compound	Capacity factor (k')[a]	Log k'	Calculated log P_{ow}	Reported log P_{ow}
IBP	9.16	0.96	3.19	3.34[b], 2.6 [7]
MEP	6.06	0.78	2.70	2.94[b], 2.2 [7]
Diazinon	11.31	1.05	3.43	1.92[b], 2.9 [7]
MPP	11.03	1.04	3.40	3.57[b], 3.0 [7]
EDDP	10.18	1.01	3.31	2.31[b], 2.6 [7]
Malathion	5.08	0.71	2.49	2.45[b], 1.9 [7]
Isoxathion	13.14	1.12	3.61	3.93[b], 2.9 [7]
EPN	17.88	1.25	3.97	2.00[b]
Methidathion	3.63	0.56	2.10	2.42[b], 2.5 [7]
Salithion	3.05	0.48	1.90	2.67[b], 2.3 [7]
Phosalone	13.70	1.14	3.66	4.30 [12], 3.0 [7]
Phosmet	3.75	0.57	2.14	2.83 [12], 1.8 [7]
α-CAVP	13.95	1.14	3.68	3.54[b]
β-CVP	11.45	1.06	3.45	2.7 [7]
Benzene	3.97	0.60		2.13 [11]
Bromobenzene	6.97	0.84		2.99 [11]
Biphenyl	15.61	1.19		3.76 [11]

[a] $k' = (t_R - t_0)/t_0$; $t_0 = 1.55$ min.
[b] From materials supplied by Japan Environmental Agency.

Table 3
Degradation tests for the pesticides at pH 5, 7 and 9

Compound	pH	Concentration (mg/l)	Residual (%)		
			After 1 h	After 5 days	
				Dark	Light
IBP	5	2.0	100	105	–
	7	2.0	100	101	103
	9	2.0	100	107	–
MEP	5	1.0	87	87	–
	7	1.0	84	84	80
	9	1.0	89	78	–
Diazinon	5	3.0	103	32	–
	7	3.0	95	86	84
	9	3.0	105	83	–
MPP	5	2.0	94	81	–
	7	2.0	95	70	30
	9	2.0	98	90	–
EDDP	5	2.0	99	67	–
	7	2.0	90	15	9
	9	2.0	10	0	–
Malathion	5	5.0	109	102	–
	7	5.0	107	71	52
	9	5.0	59	0	–
Isoxathion	5	2.0	89	81	–
	7	2.0	84	73	64
	9	2.0	87	72	–
EPN	5	2.0	87	31	–
	7	2.0	94	26	16
	9	2.0	105	16	–
Methidathion	5	3.0	102	86	–
	7	3.0	100	78	67
	9	3.0	99	46	–
Salithion	5	1.0	108	74	–
	7	1.0	84	0	0
	9	1.0	103	0	–
Phosalone	5	2.0	90	63	–
	7	2.0	97	57	51
	9	2.0	94	19	–
Phosmet	5	1.0	112	84	–
	7	1.0	63	0	0
	9	1.0	0	0	–
α-CVP	5	1.0	87	95	–
	7	1.0	98	98	95
	9	1.0	109	103	–
β-CVP	5	2.0	96	107	–
	7	2.0	97	95	94
	9	2.0	98	101	–

dard. An example is shown in Fig. 5. The concentration ratio of the OPs to the internal standards was determined from the peak-area ratio with the use of a calibration graph and then the detected amounts were calculated from the amounts of internal standards added. The con-



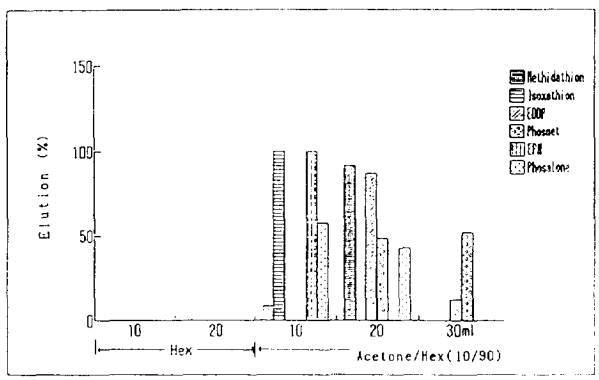


Fig. 4. Typical elution patterns of the OPs on the hydrated (100 + 5) silica column.

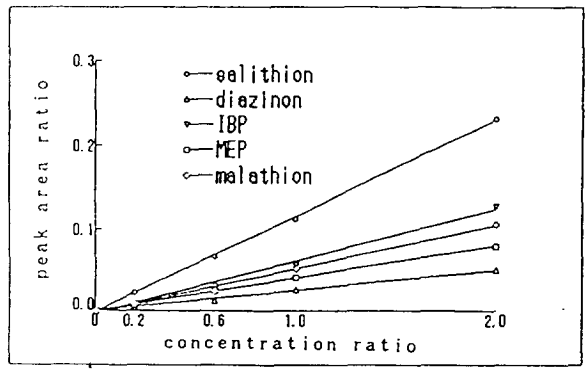
centration of OPs in environmental samples was calculated with the following equation:

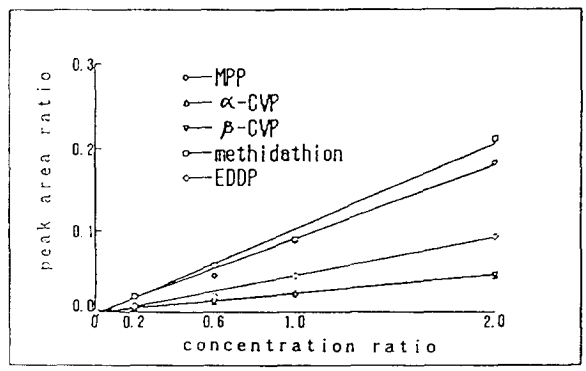
concentration (ng/ml or ng/g)

= amount detected (ng)/sample size (ml or g)

3.5. *Preservation in river water*

A 1000-ml river water sample spiked with 60–750 ng of the OPs was stored in a refrigerator and their concentrations were determined after 7 and 14 days. Fig. 6 shows stability of the OPs in river water. Phosmet was somewhat decomposed, but the other OPs virtually did not decompose in the river water when stored cool and in the dark place for 7–14 days. However, it is preferable that the analysis is carried out as soon as possible after sampling.





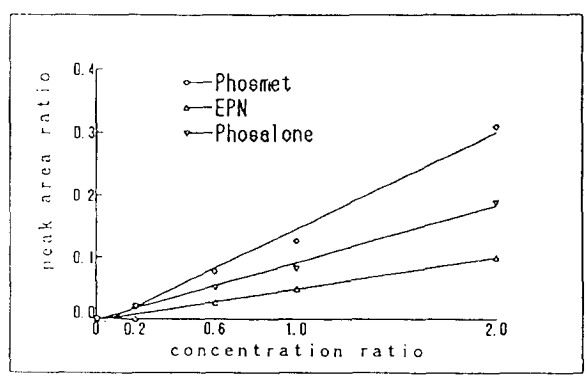


Fig. 5. Typical calibration graphs for the OPs.

3.6. *Detection limits and analytical precision*

Table 4 reports the detection limits and precision for the OPs. A blank test was performed with using 1000 ml of pure water and with other chemicals used in the analysis. No blank peaks corresponding to the OPs were observed in the chromatogram. Detection limits (DL) were

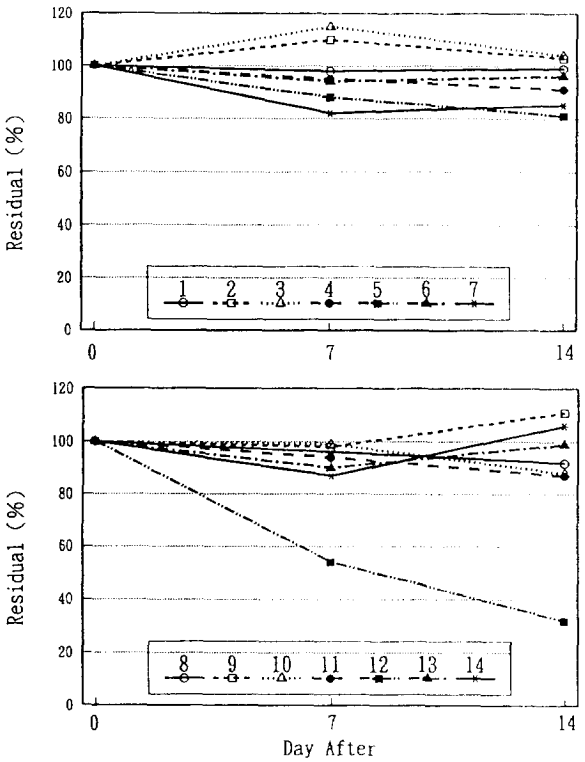


Fig. 6. Stability of the OPs in river water. Initial concentrations of the pesticides were as follows: (1) IBP 105; (2) MEP 150; (3) diazinon 90; (4) MPP 150; (5) EDDP 450; (6) malathion 300; (7) isoxathion 600; (8) EPN 750; (9) methidathion 450; (10) salithion 60; (11) phosalone 600; (12) phosmet 450; (13) α-CVP 150; (14) β-CVP 150 ng/l.

calculated from the sensitivity of the response estimating the standard deviation as follows:

$$D = t_{(n-1,0.05)}\,\sigma \,/\, \sqrt{n} \times \mathrm{d}C/\mathrm{d}R \qquad \mathrm{DL} = 3\bar{D}$$

where D is detection potential and $\bar{D}$ is the average value of D calculated using different concentrations (DL were defined as three times the detection potential), $t_{(n-1,0.05)}$ the t-distribution at 95% reliability, σ the standard deviation of the response, n the number of replicates, C the concentration of the pesticides and R the peak-area ratio of the analyte to the internal standard.

The pesticides (except for MPP) were determined with relative standard deviations (R.S.D.s) of 0.9–10.9% at levels in the range 0.035–0.750 ng/ml in water samples. The detection limits of the pesticides in water were calculated to be 0.013–0.120 ng/ml for 1000 ml of water. The detection limits of several OPs obtained using LC–MS–SIM [9,10] were reported to be 1–100 ng (signal-to-noise ratio 3–6) and those obtained using GC with nitrogen–phosphorus detection (NPD) [5] were 1 ng/l for 1000–4000 ml of water. Although they have been defined differently, comparison of the detection limits given by these methods showed that the values with GC–MS–SIM might be superior to those with LC–MS–SIM and inferior to those with GC–NPD. However, the detection limits in this work have been presented in order to assess the overall analytical procedure on the basis of statistical considerations with a view to using the method in an actual survey.

3.7. Recovery test

Analyte recoveries were investigated by using 1000 ml of river and sea water and 10 g of sediment and fish sample spiked with 120–1500 ng of the OPs. Table 5 gives the recoveries of the pesticides from these environmental samples. The OP recoveries were 101–145% from river and sea water with R.S.D.s of 0.9–8.2%. For sediment and fish samples, the recoveries were 93–166% (except for isoxathion) and 66–101% (except for phosmet), with R.S.D.s of 6.2–28.5% and 4.2–35.3%, respectively. Diazinon, MEP, malathion, β-CVP and phosalone could be detected at sub-ng/ml or -ng/g levels in the environment. Fig. 7 shows examples of their chromatograms for non-spiked and spiked samples of river water, sediment and fish.

4. Conclusions

The proposed method involving a column clean-up procedure and GC–MS–SIM determination may be useful for the routine analysis of environmental samples at low-ng/ml levels. Especially trace levels of the OPs in fish samples were successfully separated from interfering biota materials with the use of both normal- and

Table 4
Detection limits and analytical precision for the pesticides

Compound	Detection limit (ng/ml)	Analytical precision		
		Concentration (ng/ml)	Response[a]	R.S.D. (%)
IBP	0.027	0.035	117	7.7
		0.070	272	8.7
		0.105	387	5.3
MEP	0.032	0.05	108	10.9
		0.10	204	4.1
		0.15	306	3.7
Diazinon	0.013	0.03	116	2.9
		0.06	224	8.3
		0.09	306	2.1
MPP	0.120	0.05	58	31.4
		0.10	152	9.2
		0.15	222	25.7
EDDP	0.034	0.15	118	2.4
		0.30	252	3.6
		0.45	366	1.0
Malathion	0.044	0.10	108	7.1
		0.20	238	4.3
		0.30	348	4.3
Isoxathion	0.110	0.20	125	2.5
		0.40	274	7.6
		0.60	420	4.9
EPN	0.120	0.25	100	3.2
		0.50	206	6.1
		0.75	312	4.0
Methidathion	0.072	0.15	118	3.2
		0.30	246	7.4
		0.45	357	3.8
Salithion	0.013	0.02	111	0.9
		0.04	206	7.6
		0.06	258	6.5
Phosalone	0.073	0.20	109	5.8
		0.40	242	6.3
		0.60	363	1.4
Phosmet	0.048	0.15	123	3.0
		0.30	250	5.6
		0.45	384	1.3
α-CVP	0.023	0.05	121	7.8
		0.10	276	8.1
		0.15	402	1.2
β-CVP	0.024	0.05	123	4.1
		0.10	258	7.5
		0.15	372	3.0

[a] Average of four experiments.

Table 5
Recovery of the pesticides from environmental samples

Compound	Sample	Sample amount	Added (ng)	Recovery (%)	Number of samples (*n*)	R.S.D. (%)
IBP	River water	1000 ml	210	123	4	5.4
	Sea water	1000 ml	210	127	4	6.9
	Sediment	10 g	1000	119	7	13.1
	Fish	10 g	1000	96	7	4.6
MEP	River water	1000 ml	300	116	4	1.2
	Sea water	1000 ml	300	115	4	5.4
	Sediment	10 g	1000	113	7	25.8
	Fish	10 g	1000	99	7	6.6
Diazinon	River water	1000 ml	180	122	4	2.3
	Sea water	1000 ml	180	115	4	5.4
	Sediment	10 g	1000	97	7	6.2
	Fish	10 g	1000	91	7	4.7
MPP	River water	1000 ml	300	112	4	1.1
	Sea water	1000 ml	300	108	4	5.3
	Sediment	10 g	1000	109	7	21.9
	Fish	10 g	1000	97	7	4.7
EDDP	River water	1000 ml	900	125	4	2.1
	Sea water	1000 ml	900	122	4	4.7
	Sediment	10 g	1000	112	7	28.5
	Fish	10 g	1000	67	7	9.8
Malathion	River water	1000 ml	600	126	4	3.5
	Sea water	1000 ml	600	125	4	5.7
	Sediment	10 g	1000	93	7	14.8
	Fish	10 g	1000	101	7	7.1
Isoxathion	River water	1000 ml	1200	128	4	3.4
	Sea water	1000 ml	1200	145	4	3.2
	Sediment	10 g	1000	–	7	–
	Fish	10 g	1000	66	7	35.3
EPN	River water	1000 ml	1500	101	4	2.6
	Sea water	1000 ml	1500	104	4	1.8
	Sediment	10 g	1000	125	7	11.7
	Fish	10 g	1000	91	7	10.8
Methidathion	River water	1000 ml	900	121	4	7.5
	Sea water	1000 ml	900	125	4	5.0
	Sediment	10 g	1000	133	7	20.4
	Fish	10 g	1000	94	7	5.0
Salithion	River water	1000 ml	120	101	4	3.3
	Sea water	1000 ml	120	121	4	5.7
	Sediment	10 g	1000	102	7	17.7
	Fish	10 g	1000	89	7	5.1
Phosalone	River water	1000 ml	1200	101	4	4.7
	Sea water	1000 ml	1200	103	4	0.9
	Sediment	10 g	1000	166	7	15.5
	Fish	10 g	1000	85	7	8.7
Phosmet	River water	1000 ml	900	132	4	3.7
	Sea water	1000 ml	900	119	4	3.2
	Sediment	10 g	10000	113	7	6.4
	Fish	10 g	1000	11	7	23.9
α-CVP	River water	1000 ml	300	128	4	8.0
	Sea water	1000 ml	300	135	4	8.2
	Sediment	10 g	1000	114	7	16.9
	Fish	10 g	1000	93	7	4.4
β-CVP	River water	1000 ml	300	125	4	7.2
	Sea water	1000 ml	300	128	4	5.8
	Sediment	10 g	1000	116	7	15.7
	Fish	10 g	1000	90	7	4.2

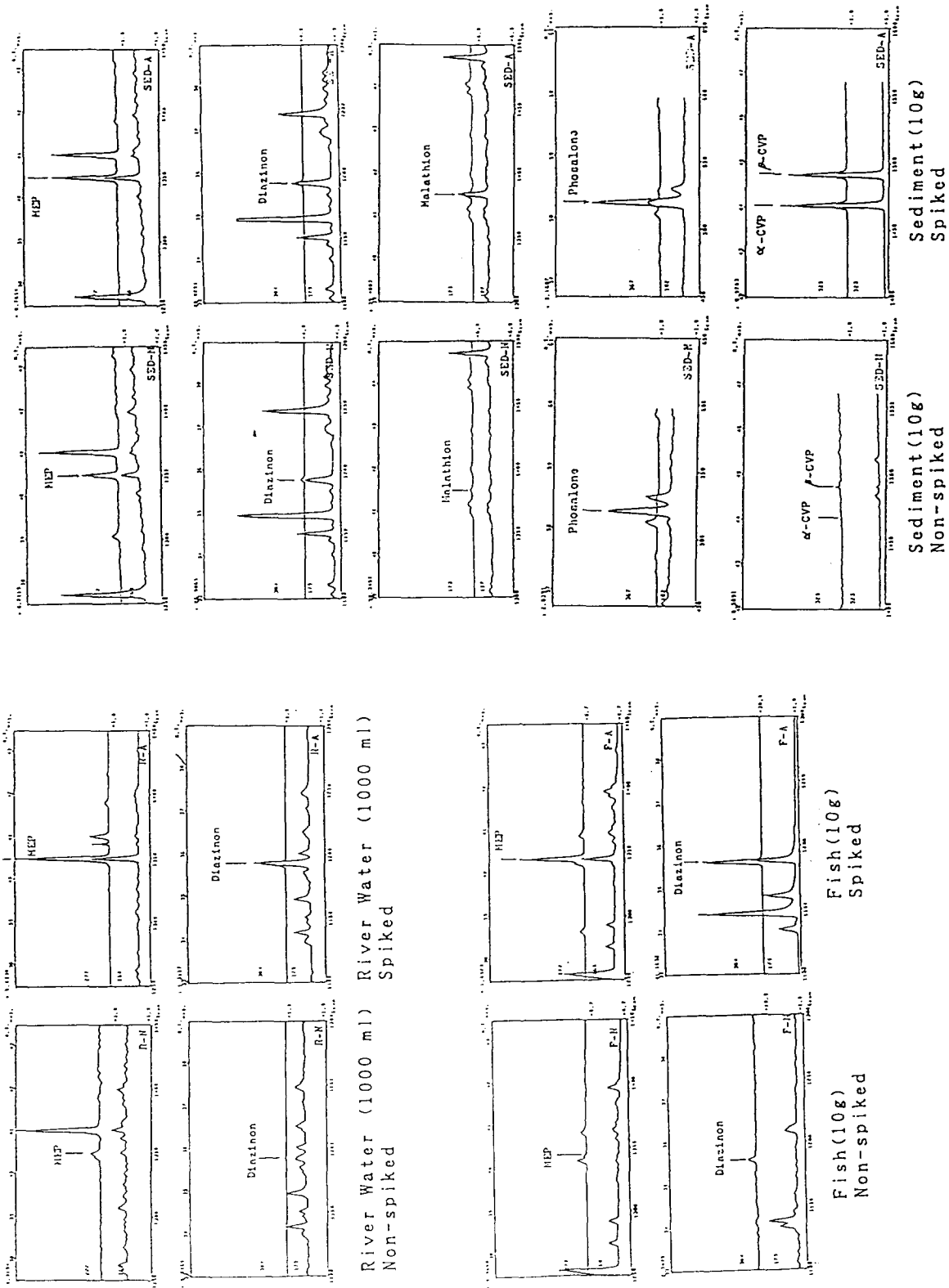


Fig. 7. Determination of the OPs in normal and spiked river water, sediment and fish samples.

reversed-phase column chromatography. Determination of the OPs with this method could probably be applicable to many other kinds of chemicals in environmental samples.

Acknowledgement

This work was supported by the Office of Health Studies, Environmental Health Department, Japan Environmental Agency (Project for Development of Analytical Method).

References

[1] S. Onodera, S. Wakabayashi, N. Furukawa, T. Ogawa, Y. Matsuura, K. Manabe, S. Suzuki, S. Ishikura and S. Suzuki, J. Environ. Chem., 2 (1992) 547.
[2] P.R. Loconto and A.K. Gaind, J. Chromatogr. Sci., 27 (1989) 569.
[3] M. Matsumoto, Shokuhin Eiseigaku Zasshi., 25 (1984) 410.
[4] A. Neicheva, D. Karageorgiev and T. Konstantinova, Sci. Total Environ., 123/124 (1992) 29.
[5] M. Mansour, D. Barcelo and J. Albaiges, Sci. Total Environ., 123/124 (1992) 45.
[6] K. Nishio and Y. Hayakawa, J. Jpn. Soc. Water Environ., 16 (1993) 55.
[7] T. Okumura and K. Imamura, Jpn. J. Water Pollut. Res., 14 (1991) 109.
[8] D. Barcelo and J. Albaiges, J. Chromatogr., 474 (1989) 163.
[9] D. Barcelo, G. Durand, R.J. Vreeken, G.J. Jong and U.A.Th. Brinkman, Anal. Chem., 62 (1990) 1696.
[10] S. Kawasaki, H. Ueda, H. Itoh and J. Tadano, J. Chromatogr., 595 (1992) 193.
[11] G.D. Veith, N.M. Austin and R.T. Morris, Water Res., 13 (1979) 43.
[12] C.T. Chiou, V.H. Freed, D.W. Schmedding and R.L. Kohnert, Environ. Sci. Technol., 11 (1977) 475.