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Determination of pesticides in water by capillary gas chromatography with splitless injection of large sample volumes

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ABSTRACT

A large-volume injection for a capillary gas chromatograph equipped with an electron-capture, nitrogen–phosphorus-selective (NPD) or flame photometric detector is proposed for the determination of pesticides. The cold-trap column, a deactivated fused-silica column (3 m × 0.53 mm I.D.), was attached to the analytical column (30 m) and the regulation column (3 cm), DB-5, both of 0.25 mm I.D. with film thickness 0.25 μm, with a dual-outlet splitter. The regulation column was connected with the solvent-diversion column, a deactivated fused-silica column (2 m × 0.53 mm I.D.), which was led out of the column oven and attached to an electromagnetic valve. By opening the valve in the splitless mode, the pesticides slowly injected in *n*-hexane in a volume from 25 to 150 μl were trapped in the cold-trap column, and a large volume of *n*-hexane was almost all diverted from the gas chromatograph through the diversion column. The trapped pesticides were introduced to the analytical column by closing the valve. Twenty-five pesticides, scattered on a golf course in Japan, were determined at concentrations from 1 to 100 ng/ml in *n*-hexane. The reproducibility of separation of the pesticides by the proposed method was similar to that of normal splitless (1-μl) injection. The proposed method was applied to the screening of the pesticides in groundwater after liquid–liquid extraction with dichloromethane; the pesticides could be determined at levels lower than 1 μg/l in a 20-ml water sample.

INTRODUCTION

Many contaminants in environmental waters that are thermally stable and volatile have been determined by capillary gas chromatography (GC) after sample enrichment by liquid–liquid [1–4] or solid-phase extraction [3–5]. If they contain a high-polarity group such as carboxyl or hydroxyl, they are determined by capillary GC after appropriate derivatization of those groups. The merits of capillary GC are high resolution, reasonable analysis times and sensitive and specific detection.

Various types of apparatus and techniques have been developed for the determination of the contaminants in water at trace levels, such as increasing the concentration factor from 500 to 1000 [1,2] and introduction of selected ion monitoring in GC–mass spectrometry [1,6]. In addition, injection of large sample volumes in capillary GC has been studied in the past decade. One of the major problems in this regard is the removal of the large volume of solvent from the capillary column and the quantitative retention of analyte compounds in the column. The injection techniques for large-volume sample injection are classified into several groups. In one of them, the separation of analytes from the solvent (*ca.* 100 μl) is performed in the capillary column, which is called on-column injection. This technique is mainly used in capillary GC coupled with liquid chromatography (LC–GC) [7–10]. In another, the separation of analytes from the solvent (*ca.* 200 μl) is performed before

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the capillary column using a programmed-temperature vaporizer [11], which is called a PTV injector, and a modified system [12,13]. These methods are mainly applied for the determination of alkanes [9–12] or polyaromatics [8]. Further, splitless injection for large sample volumes (*ca.* 30 μl) in capillary GC was recently reported [14]. In the method utilizing a splitless injector, complicated apparatus such as valve switching systems and remodelling of the GC set-up is unnecessary, and contamination in the capillary column by high-boiling compounds is less than that with on-column injection for large sample volumes.

The object of this work was the development of a large-volume (>100 μl) sample injection system for capillary GC to determine pesticides at the level of a few ng/ml. We designed a capillary GC system with splitless injection of large sample volumes and established the optimum conditions. The application of an analytical method involving this GC system coupled with liquid–liquid extraction could reduce the sample volume and organic solvent volume in the screening of the pesticides in groundwater.

EXPERIMENTAL

Apparatus

The GC system consisted of an HP 5890 gas chromatograph (Hewlett-Packard, Sunnyvale, CA, USA) equipped with a split–splitless injector and electron-capture (ECD), nitrogen–phosphorus-selective (NPD) or flame photometric detection (FPD) systems and a Shimadzu CR-4A integrator (Shimadzu, Kyoto, Japan). For the capillary inlet system, a glass insert of 1-ml volume was installed and the carrier gas was helium. The cold-trap column, a deactivated column (3 m × 0.53 mm I.D.) (GL Science, Tokyo, Japan) was connected to the analytical column (30 m) and the regulation column (3 cm), DB-5, both of 0.25 mm I.D. with film thickness 0.25 μm (J&W Scientific, Rancho Cordova, CA, USA), with a dual-outlet splitter (J&W Scientific) as shown in Fig. 1. The solvent diversion column, deactivated (2 m × 0.53 mm I.D.) (GL Science), was connected to the regulation column with a universal-type glass union

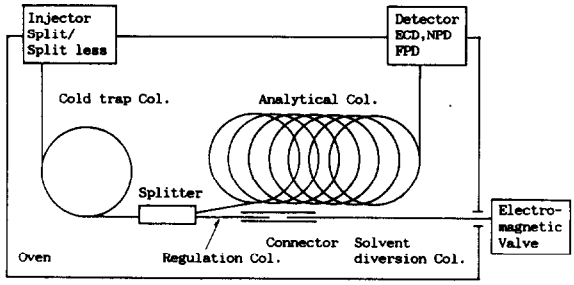

Fig. 1. Schematic diagram of the capillary GC system to divert large solvent volumes. Cold-trap column, deactivated fused-silica column, 3 m × 0.53 mm I.D.; analytical column, DB-5, 30 m × 0.25 mm I.D., film thickness 0.25 μm; solvent diversion column, deactivated fused-silica column, 2 m × 0.53 mm I.D.; splitter, dual-outlet type; connector, universal-type glass union.

(J&W Scientific) which was led out of column oven and connected to a three-way electromagnetic valve (GL Science) with a $\frac{1}{4}$-in. nut and graphite ferrule.

Chemicals

Butamifos, isoprothiolane, isoxathion and pyridaphenthion were purchased from GL Science and other pesticides from Hayashi Pure Chemical (Osaka, Japan), as listed in Table I. Organic solvents of pesticide grade were purchased from Wako (Osaka, Japan). Each of the 25 pesticides was dissolved in ethyl acetate–*n*-hexane (50:50, v/v) at a concentration of 1000 μg/ml, and then a pesticide mixture at a concentration of 10 μg/ml was diluted to ng/ml levels with *n*-hexane.

Chromatographic conditions

The oven temperature was always programmed as follows: held for 1 min at 40°C, increased from 40 to 180°C at 20°C/min and from 180 to 270°C at 4°C/min, and held for 2 min at 270°C. The injector was operated in the splitless mode with a splitless time of 1 min. The column head pressure was set at 100 kPa by the total mass flow controller of the gas chromatograph when the electromagnetic valve was closed. The injector temperature was set at 220°C. The temperatures for ECD, NPD and FPD were set at 300, 250, and 270°C, respectively. The septum purge flow-rate was 5 ml/min.

Injection procedures

The electromagnetic valve was set open and the head pressure was kept constant at the desired pressure by controlling the total mass flow controller of the gas chromatograph. Pesticide solution was slowly injected (manually) with a 250-μl gas-tight glass syringe in the splitless mode. The capillary GC and integrator operation were started when the electromagnetic valve had been closed after sample injection.

Sample preparation for groundwater

A 20-ml volume of groundwater spiked with pesticides standard was dispensed into a 30-ml separating funnel and 2 g of sodium chloride were added. The pesticides were extracted twice with 1 ml of dichloromethane, vigorously shaking for 1 min. The dichloromethane solution was dried with sodium sulphate and gradually evaporated off under a stream of nitrogen at room temperature. The extract obtained was dissolved in 1 ml of *n*-hexane.

RESULTS AND DISCUSSION

Diversion of solvent

We designed a solvent diversion system with splitless injection based on the difference in resistance (trapping efficiency) depending on the length of two DB-5 columns. When the electromagnetic valve was opened in the splitless mode with an injector temperature of 220°C and a column oven temperature of 40°C, the flow-rates of the carrier gas at the exits of the solvent diversion and analytical columns changed with the column head pressure, as shown in Fig. 2. The ratios of the flow-rate of the carrier gas in the analytical column to that in the diversion column were 1:200 and 1:240 at head pressures of 40 and 80 kPa, respectively. The total flow-rate which were fixed at the splitting ratio did not change during the injection of 100 μl of *n*-hexane at about 2.5 μl/s at any head pressure examined. The septum purge flow-rate, 5 ml/min, was also unchanged during injection of *n*-hexane in the splitless mode. Therefore, with the construction of the columns as shown in Fig. 1, the large amount of solvent vaporized in the injector could be passed through the cold-trap

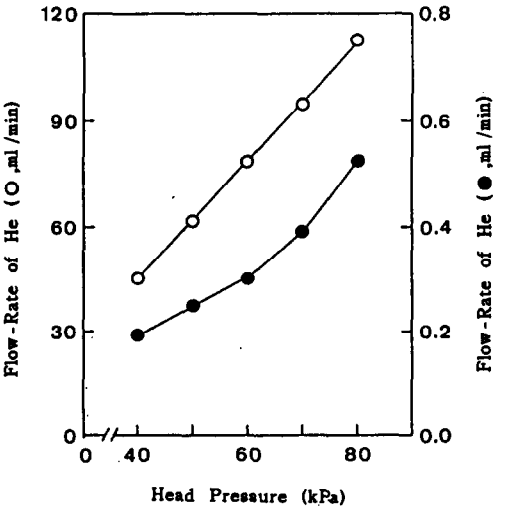

Fig. 2. Flow-rate of carrier gas at the exits of (●) analytical and (○) solvent diversion columns. Injection temperature, 220°C; oven temperature, 40°C; other conditions as in Fig. 1.

column and diverted from the analytical column through the solvent diversion column outside the gas chromatograph. In practice, the peak areas of the solvent on the FPD and NPD chromatograms with large-volume injection, as shown in Fig. 3B and C, respectively, corresponded to the peak areas from the splitless injection of about 3 μl of *n*-hexane.

Trapping of pesticides

The effect of the flow-rate of the carrier gas on the retention of analytes in the cold-trap column was examined. As shown in Fig. 4A, the retentions of dichlorvos, which is the most volatile of the pesticides examined (Table I), diazinone and butamifos decreased with increasing carrier gas flow-rate. The proposed method utilized recondensation of the analytes vaporized in the injector on the cold-trap column in the GC oven. When the flow-rate of the carrier gas in the column is high, the analytes may escape from the solvent diversion column. For trapping dichlorvos, the optimum flow-rate of the carrier gas, which was that of the solvent diversion column plus that of the analytical column, ranged from 40 to 60 ml/min.

The effect of varying the solvent diversion time on the retention of the analytes was examined. When the electric valve was opened for

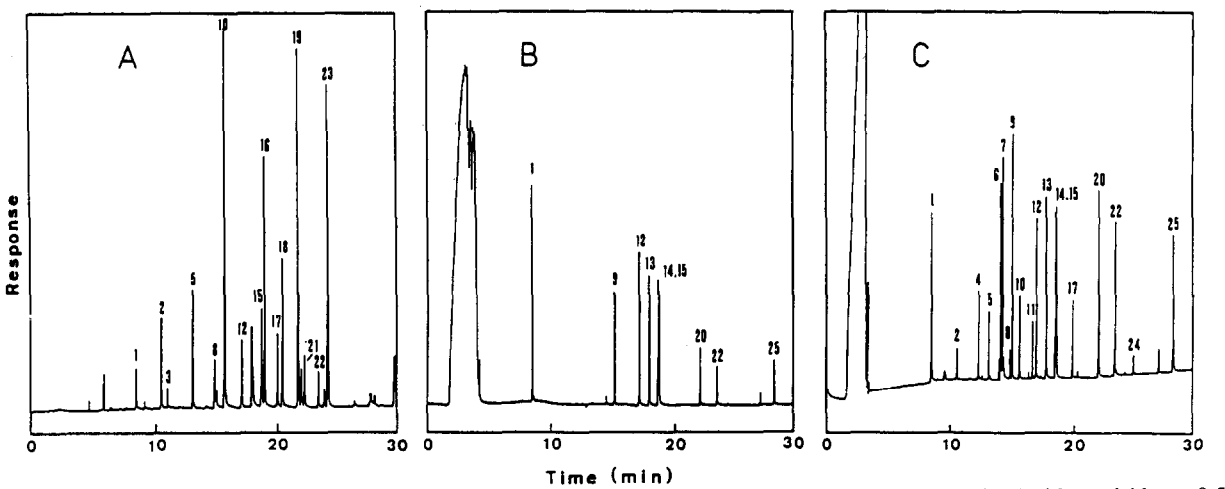

Fig. 3. Chromatograms obtained by large-volume injection of the extract from 20 ml of groundwater spiked with pesticides at 0.5 μg/l. Injection volume, 100 μl. (A) ECD; (B) FPD; (C) NPD. Injection conditions as in Fig. 5B. Numbers refer to Table I.

15 s after injection of 100 μl of the pesticide solution, dichlorvos was hardly detected (Fig. 4B). The retention of diazinon gradually decreased with increasing diversion time. Butamifos and pyridaphenthion were not affected by the diversion time. Hiller *et al.* [9] examined the effect of solvent diversion time with large-volume on-column injection, in which the optimum solvent diversion time was 0.25 min to trap hydrocarbons such as *n*-heptane and *n*-octane in

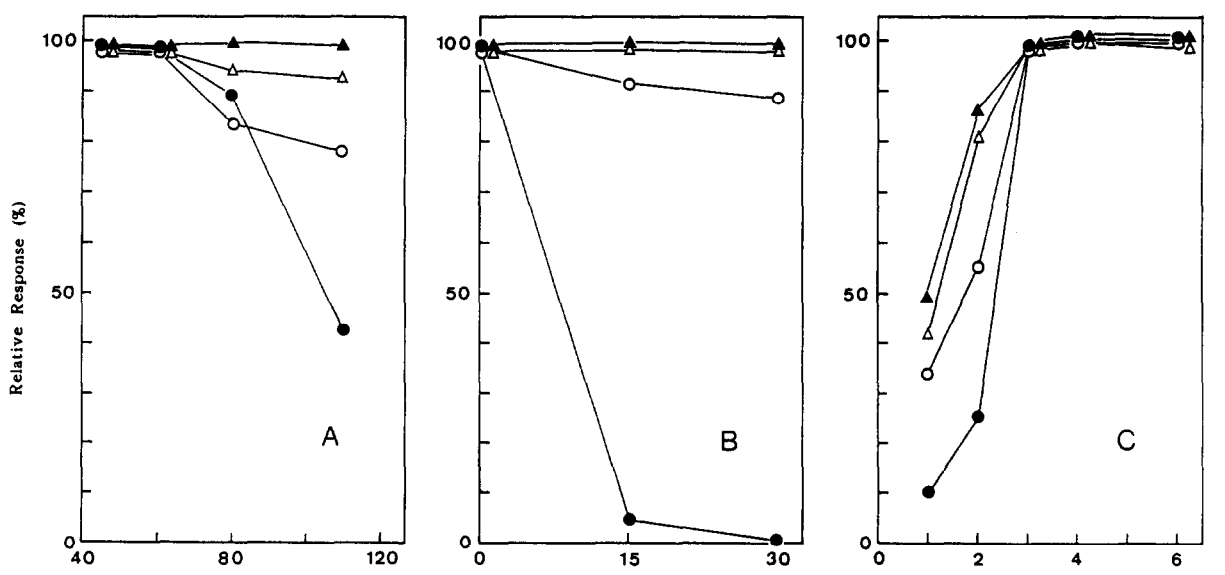

Fig. 4. Effects of flow-rate of carrier gas, diversion time and length of cold-trap column on retentions of pesticides. ● = Dichlorvos; ○ = diazinon; △ = butamifos; ▲ = pyridaphenthion. Injection temperature, 220°C; oven temperature, 40°C; injection volume, 100 μl; pesticide concentration, 10 ng/ml; injection speed, 2.5 μl/s; detection, FPD. (A) Cold-trap column, 3 m; diversion time, 0 s; (B) cold-trap column, 3 m; carrier gas flow-rate, 60 ml/min; (C) carrier gas flow-rate, 60 ml/min; diversion time, 0 s.

hexane [9]. With the splitless injection of large-volume samples reported by Tajima *et al.* [14], the optimum solvent diversion time was 0.3 min to trap *n*-dodecane in *n*-hexane. With the present method, to trap dichlorvos, etridiazole and chloroneb, it is necessary to close the valve immediately after sample injection.

The effect of the length of the cold trap column on the retentions of the analytes were examined. As shown in Fig. 4C, the retention of most of the pesticides examined was poor when using column lengths of 1 and 2 m. When the column length ranged from 3 to 6 m, trapping of the pesticides examined was not changed. In the splitless injection method of Tajima *et al.* [14] with the introduction of an SPB-1 precolumn (0.5 m × 0.53 mm I.D.; film thickness 0.5 μm) (Supelco, Bellefonte, PA, USA) to reconcentrate the analytes between the cold-trap and analytical columns, the optimum length of the cold-trap column was 2 m. For trapping low-volatility pesticides using only the cold-trap column, at least a 3-m length of deactivated fused-silica column is needed.

The effect of injection temperature on the retentions of the analytes was examined. An injector temperature of 180°C was insufficient to volatilize pyridaphenthion. With injector temperatures from 200 to 240°C, dichlorvos and pyridaphenthion, the first and last compounds on the chromatogram, respectively, were quantitatively recovered.

The effects of column oven temperature and injection speed on the trapping and separation of the pesticides are shown in Fig. 5. For trapping of the pesticides, the optimum oven temperature was 40°C (Fig. 5B). At 50°C, dichlorvos, etridiazole, chloroneb and benfluralin showed poor responses (Fig. 5C). When oven temperature was 30°C, the peak shape of each compound was distorted (Fig. 5A). Noy *et al.* [10] stated that this is due to recondensation of the solvent in the cold-trap column by means of a vaporizer as an LC–GC interface [10].

When the injection of a 100-μl sample was performed for 15 s (6.7 μl/s), the separation of each pesticide was incomplete, as shown in Fig. 5D. The optimum sample injection speed ranged from 2 to 3 μl/s under the conditions adopted.

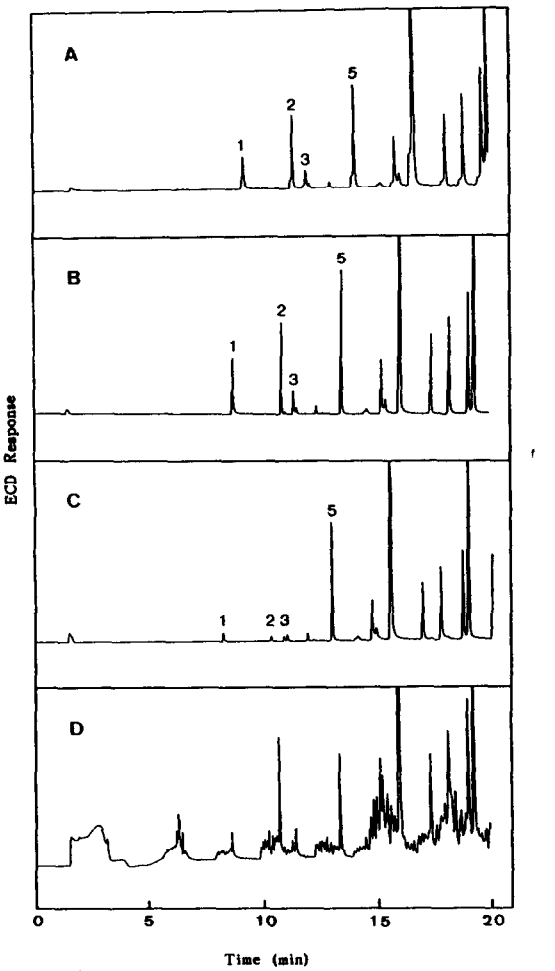

Fig. 5. Separation of pesticides by large-volume injection at altered GC oven temperature and injection speed. Cold trap column, 3 m; injection temperature, 220°C; injection volume, 100 μl; pesticide concentration, 10 ng/ml; carrier gas flow-rate, 60 ml/min; injection speed, 2.5 μl/s except for (D) 6.7 μl/s; diversion time, 0 s; detection, ECD. Oven temperature: (A) 30; (B) 40; (C) 50; (D) 40°C. Numbers refer to Table I.

Reproducibility of separation

The optimum conditions with large-volume injection to determine the pesticides were set as follow: injection temperature, 220°C; oven temperature, 40°C; cold-trap column length, 3 m; carrier gas (helium) flow-rate, 60 ml/min; valve close time, immediately after sample injection; and injection speed, *ca.* 2.5 μl/s. Under these conditions, the reproducibility of the separation of the pesticides was as reported in Table I. The

TABLE I

REPRODUCIBILITY OF SEPARATION OF PESTICIDES BY THE LARGE-VOLUME INJECTION METHOD COMPARED WITH THAT FROM THE SPLITLESS INJECTION METHOD[a]

No.	Pesticide[b]	Large-volume injection[d]			Splitless injection[e]		
		t_R (s)	$A \times 10^3$	$N \times 10^3$	t_R (s)	$A \times 10^3$	$N \times 10^3$
1	Dichlorvos	517.3(0.09)	21.7(9.8)	119	531.6(0.09)	42.0(2.0)	125
2	Etridiazole	642.0(0.05)	3.7(15.5)	226	659.6(0.20)	7.3(5.5)	239
3	Chloroneb[c]	675.1(0.05)	19.1(16.5)	202	686.0(0.09)	24.6(2.2)	200
4	Propoxur	749.0(0.02)	10.7(12.6)	249	768.5(0.12)	10.7(5.4)	262
5	Benfluralin	799.5(0.03)	8.4(8.6)	315	820.9(0.12)	10.4(5.8)	331
6	Simazine	860.1(0.02)	31.2(5.5)	327	881.5(0.12)	30.5(5.2)	344
7	Atrazine	869.2(0.02)	32.8(4.3)	336	890.8(0.12)	30.9(6.2)	352
8	Propyzamide	905.3(0.02)	4.3(7.4)	364	928.1(0.12)	3.2(6.3)	382
9	Diazinon	916.9(0.01)	34.3(6.1)	374	940.9(0.12)	41.3(3.9)	392
10	Chlorothalonil	953.4(0.01)	14.2(5.0)	404	977.0(0.11)	12.6(6.1)	423
11	Terbucarb	1017.0(0.02)	8.6(5.3)	460	1042.4(0.11)	8.0(4.5)	482
12	Tolclophosmethyl	1035.3(0.02)	26.2(4.9)	305	1061.0(0.11)	34.3(3.8)	320
13	Fenitrothion	1083.0(0.01)	31.5(5.3)	231	1108.9(0.10)	37.2(4.0)	242
14	Fenthion	1126.8(0.02)	27.9(3.2)	361	1153.4(0.09)	36.0(4.5)	378
15	Chlorpyrifos	1132.2(0.01)	28.3(5.3)	365	1159.5(0.09)	32.2(3.8)	382
16	Dactal[c]	1146.8(0.03)	220.0(5.2)	191	1173.0(0.05)	227.8(1.4)	195
17	Pendimethalin	1210.5(0.02)	13.7(6.3)	417	1238.1(0.09)	12.2(4.2)	435
18	Captan[c]	1236.2(0.03)	138.0(5.3)	302	1263.8(0.05)	77.8(5.8)	444
19	α-Endosulfan[c]	1313.9(0.03)	351.1(4.6)	192	1343.8(0.05)	358.0(2.0)	256
20	Butamifos	1330.4(0.01)	37.2(5.9)	350	1359.6(0.08)	40.1(4.8)	364
21	Isoprothiorane[c]	1345.3(0.03)	49.9(6.2)	357	1374.9(0.05)	43.0(1.8)	365
22	Isoxathion	1411.7(0.01)	29.7(6.6)	394	1441.6(0.07)	14.9(13.1)	410
23	β-Endosulfan[c]	1458.2(0.03)	325.9(4.5)	236	1489.9(0.05)	306.0(1.8)	242
24	Mepronil	1503.2(0.03)	3.2(8.0)	446	1532.2(0.07)	2.7(8.8)	463
25	Pyridaphenthion	1691.5(0.03)	26.8(6.2)	318	1721.6(0.06)	24.1(11.0)	329

[a] t_R = Retention time; A = peak area; N = plate number. Values in parentheses are relative standard deviations (%) ($n = 4$).
[b] Data from NPD ($n = 4$), except where indicated otherwise.
[c] Data from ECD ($n = 4$).
[d] 100 μl of 10 ng/ml solution in *n*-hexane.
[e] 1 μl of 1000 ng/ml solution in *n*-hexane.

theoretical plate number (N) and the relative standard deviation (R.S.D.) of the retention time (t_R) of each pesticide examined were similar to those using normal splitless (1 μl) injection. For the peak areas with large-volume injection, the R.S.D.s for dichlorvos, etridiazole, chloroneb, propoxur and benfluralin ranged from 9 to 17%, which is a poorer reproducibility than with the splitless method. In this experiment, injection of the sample and valve closing were performed manually; if these processes are carried out automatically, the R.S.D.s could be improved. The resolutions of simazine and atrazine for large-volume and splitless injection were 1.05 and 1.03, respectively, and those of fenthion and chlorpyrifos were 0.71 and 0.74, respectively.

The effect of injection volume on the retentions of the analytes was examined. Each plot of injection volume against peak area for each pesticide was linear from 25 to 150 μl at pesticides concentrations of 10 ng/ml ($r = 0.991$–0.999). Tajima *et al.* [14] reported that the maximum injection volume in the splitless mode was 30 μl when the sample was injected automatically at high speed and with a carrier gas flow-rate of 20 ml/min. Owing to the decrease of sample injection speed, the maximum injection volume in the proposed method is improved.

The present model is useful for injecting more than 100 μl of sample without a decrease in plate number and resolution of the pesticides, although the R.S.D.s of the retention of low-volatility pesticides such as dichlorvos, etridiazole, chloroneb and propoxur were more than 10%.

Screening of pesticides in groundwater

The application of the large-volume injection method to the determination of pesticides in groundwater samples was examined. The recovery data are reported in Table II. The recoveries of the pesticides were more than 73% at any pesticide concentration. The R.S.D.s of the recoveries of dichlorvos, etridiazole, chloroneb and propoxur ranged from 10 to 19% at 0.1 and 1.0 μg/l. Fig. 3 shows typical chromatograms obtained by injection of 100 μl of the extract from groundwater spiked with pesticides at a concentration of 0.5 μg/l. The chromatograms of the extracts were similar to those from pesticides standard solutions with respect to the plate number and retention time for each pesticide.

As environmental pollution by chemicals, including organic solvents, is of great public concern, it is preferable to be able to reduce the amounts of organic solvents used in laboratories when screening for levels of contaminants. With the normal splitless injection of a few microlites of sample, to determine pesticides at concen-

TABLE II

RECOVERY OF PESTICIDES (%) IN 20 ml OF GROUNDWATER BY THE LARGE-VOLUME INJECTION METHOD AFTER LIQUID–LIQUID EXTRACTION WITH DICHLOROMETHANE[a]

No.	Pesticide[b]	Fortification level (μg/l)		
		0.1	1.0	10.0
1	Dichlorvos	77.3 ± 16.4	85.4 ± 14.0	83.1 ± 5.2
2	Etridiazole	79.2 ± 18.9	76.7 ± 13.3	92.3 ± 1.9
3	Chloroneb[c]	90.2 ± 16.8	90.2 ± 17.1	100 ± 3.4
4	Propoxur	86.7 ± 11.5	83.4 ± 10.0	96.9 ± 1.2
5	Benfluralin	84.8 ± 10.3	87.0 ± 5.3	95.4 ± 3.9
6	Simazine	81.7 ± 10.4	86.1 ± 6.0	96.4 ± 2.1
7	Atrazine	84.1 ± 12.2	88.5 ± 5.2	92.1 ± 1.4
8	Propyzamide	73.3 ± 11.5	82.5 ± 9.2	98.2 ± 1.3
9	Diazinon	85.7 ± 10.0	90.9 ± 6.7	92.0 ± 3.9
10	Chlorothalonil	85.8 ± 9.4	91.0 ± 5.1	94.4 ± 4.9
11	Terbucarb	91.7 ± 14.4	91.1 ± 5.3	91.1 ± 1.4
12	Toluclophosmethyl	85.7 ± 7.2	92.8 ± 6.3	101 ± 2.4
13	Fenitrothion	82.4 ± 8.9	90.4 ± 4.2	94.2 ± 1.3
14	Fenthion	85.9 ± 11.0	93.5 ± 4.3	94.8 ± 1.6
15	Chlorpyrifos	85.9 ± 8.0	91.8 ± 4.3	92.9 ± 4.1
16	Dactal[c]	97.2 ± 2.9	91.9 ± 1.9	96.3 ± 1.5
17	Pendimethalin	90.0 ± 10.0	90.1 ± 6.4	99.5 ± 1.8
18	Captan[c]	87.2 ± 7.8	96.4 ± 4.9	102 ± 2.6
19	α-Endosulfan[c]	99.8 ± 3.0	89.3 ± 1.3	99.5 ± 1.7
20	Butamifos	93.0 ± 10.0	89.0 ± 3.6	96.1 ± 1.4
21	Isoprothiolane[c]	85.0 ± 6.4	98.0 ± 5.9	94.0 ± 3.0
22	Isoxathion	87.5 ± 16.0	87.8 ± 4.1	92.4 ± 1.6
23	β-Endosulfan[c]	89.4 ± 5.8	90.7 ± 4.0	102 ± 4.3
24	Mepronil	88.9 ± 9.6	86.9 ± 3.0	98.9 ± 3.5
25	Pyridaphenthion	93.8 ± 6.3	89.2 ± 8.0	89.8 ± 2.4

[a] Values are means ± S.D. ($n = 4$).
[b] Data from NPD, except where indicated otherwise.
[c] Data from ECD.

trations of 0.1 μg/l, a concentration factor from 500 to 1000 by liquid–liquid extraction with dichloromethane is needed. The injection of 100 μl of the extract from a water sample permits pesticide determinations at concentrations of 0.1 μg/l with a concentration factor of 20. In addition, this system is efficient with a capillary GC system equipped simply with a split–splitless injector without the need for complicated apparatus.

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