Silica Gel Chromatographic Cleanup Procedure for Organochlorine Pesticide Analysis with Capillary Gas Chromatography

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A reliable dry column procedure for organochlorine pesticides (heptachlor, dieldrin, and DDT) in meat is presented. Pesticides are extracted with 30% acetone in hexane from sample homogenates and purified with column chromatography using silica gel with 10% water. The pesticides are determined by capillary gas chromatography equipped with an electron capture detector. Recovery and reproducibility are adequate for regular monitoring. However, an interlaboratory study revealed that reproducible recovery of dieldrin was difficult to obtain by the initial method. Our studies established that changes in the chromatographic behavior were due to variations in the water content of the silica gel that can occur during equilibration and/or long-term storage.

INTRODUCTION

The use of most organochlorine pesticides is prohibited in Japan. To monitor organochlorine pesticides in foods imported from countries where these pesticides are used, a method including silica gel column chromatography for the residue analysis is employed (Suzuki et al., 1989; Sasaki et al., 1988). Many silica gel column methods have been described for organochlorine pesticide analysis in foods. These procedures are simple, effective, and rapid (Lee et al., 1991) when compared with the traditional method (Miyahara et al., 1992). Silica gel with 10% water has greater capacity to retain fat than Florisil (Smyth, 1972) or alumina (Steinwandter and Buss, 1975) columns that have been deactivated with 3–5% water. Unfortunately, extensive analytical experience and rare technical skill are required to obtain reproducible and reliable results with those methods that employ a dry silica gel procedure for cleanup. The elution behavior of the pesticides depends on many parameters. Even minor experimental variations can lead to different results. Despite the extensive use of silica gel in chromatography and many efforts to standardize silica gel itself and the procedures, some official methods employ those procedures for cleanup of organochlorine pesticides (FDA, 1991; MHW, 1987), but some do not (DFG, 1987; OVR, 1988; AOAC, 1990; USDA, 1988). Basically, the methods consist of extraction, cleanup with silica gel deactivated with 10% water, and GC determination with an electron capture detector (ECD). To obtain homogeneously deactivated silica gel, high-temperature activation over 400 °C and long-term equilibration (over 12 h in closed vessels) of the silica gel with added water (FDA, 1991) is prescribed. However, when silica gel is heated to 450 °C for 3 h, the silica gel is deactivated by a slow dehydration reaction (Scott, 1982). As a result, it is difficult to obtain homogeneous silica gel at temperatures in excess of 200 °C because of the irreversible dehydration. The change of silica gel properties during the equilibration process has not been clarified.

To evaluate the accuracy and precision of the original method (Suzuki et al., 1989), an initial interlaboratory comparison was conducted. The variance for dieldrin (CV% = 8.6) was significantly greater than that for each of the other pesticides (heptachlor CV% = 4.4; DDT CV% = 4.7). From this study and other observations, it became obvious that there are some problems with the method we employed. It was necessary to identify the parameters that caused the excessively high variance and to improve the reproducibility of method. Unfortunately, the chromatographic character of silica gel deactivated with water is not fully understood. Therefore, studies were undertaken by thermal analysis of the water bond to silica gel and by low-pressure chromatographic methods. This paper describes a method for reproducible silica gel chromatography and the effects of silica gel bound water on the chromatographic recovery of organochlorine pesticides as a part of a reliable method for monitoring pesticides in meats and oils.

EXPERIMENTAL PROCEDURES

Analytical Procedure. *Reagents and Apparatus.* Pesticide standards, heptachlor (1) (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene >98%), dieldrin (2) (1,2,3,4,-10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-exo-5,8-dimethanonaphthalene >98%), and *p,p'*-DDT (3) [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane >99%), were purchased from Wako Pure Chemicals Co. All organic solvents were of pesticide residue analysis grade. (Some of the organic solvents are suspected carcinogens. Handle with care.) Silica gel used was silica gel 60, 70–230 mesh, Merck Art. 7734. A gas chromatograph with electron capture detector, Shimadzu Model 14A, with splitter (Shimadzu Model SPL14A) was used. Conditions: capillary column DB-1, 30 m × 0.32 mm i.d.; film thickness, 0.25 μm; carrier gas, helium, 3 mL/min; septum purge, helium, 3 mL/min; split ratio, 20; oven temperature program, initial 40 °C for 1 min, programmed to 150 °C at 20 °C/min, held at 150 °C for 1 min, followed by 4 °C/min to 210 °C, final 210 °C for 30 min; injector temperature, 250 °C; injection volume, 1 μL; injection mode, splitless; waiting time, 1 min; detector temperature, 280 °C; makeup gas, nitrogen, 50 mL/min; current, 0.5 nA; attenuation, 10^1. A Shimadzu Model 9A with splitter (Shimadzu Model SPL9A) was also used. Conditions: wide-bore capillary column CBP1, 12 m × 0.53 mm i.d.; film thickness, 1 μm; carrier gas, helium, 13 mL/min; oven temperature, 180 °C; injector temperature, 250 °C; injection volume, 1 μL; detector temperature, 280 °C; current, 0.5 nA; attenuation, 10^1; injection mode, whole. This injection was performed using a direct flash injection liner (Shimadzu, Part 221-29992-91), which consists of a glass tube with a tapered restriction at the bottom end. The taper automatically aligns and seals the wide-bore column for efficient sample transport and helps to prevent sample contact with the current ferrule. With this mode of injection, the sample is vaporized in the liner and swept onto the column.

Silica Gel with 10% Water Content. The silica gel was activated at 130 °C overnight and cooled in a desiccator and stored in a well-closed vessel after cool down to room temperature. To the activated silica gel was added sufficient distilled water

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Table I. Recovery[a] of Pesticides Added to Three Different Products at 0.02 and 0.01 ppm

product	spiking level, mg/g	heptachlor recovery, %	heptachlor CV%	dieldrin recovery, %	dieldrin CV%	p,p'-DDT recovery, %	p,p'-DDT CV%
beef	0.01	93	4.8	89	8.0	90	5.1
beef	0.02	96	4.1	92	6.8	103	4.6
pork	0.01	94	4.2	91	7.4	102	4.8
pork	0.02	98	5.0	95	6.9	98	5.3
chicken	0.01	97	4.6	90	7.6	99	4.7
chicken	0.02	95	4.3	93	6.7	100	4.5

[a] The values are means of three examinations.

to bring the final water content to 10% by weight. The silica gel in the sealed vessel was shaken by hand vigorously for 30 s and allowed to stand for 30 min with occasional shaking. After 30 min of shaking, the silica gel was ready for use. It cannot be stored for more than 6 h even in a well-closed glass container. Rapid equilibrium of water between silica gel and the atmosphere of the container gave heterogeneous silica gel. It must be used immediately because even storage in a well-closed glass container leads to significant changes. If it must be stored, it must be kept with a saturated $Na_2S_2O_3$ solution in a closed container.

Extraction. Sample (edible tissue, 50 g) was homogenized, and 150 mL of 30% acetone in hexane was added to the homogenates; the mixture was homogenized for 2 min. The homogenate was centrifuged at 2500 rpm for 10 min. The supernatant was transferred to a separatory funnel. The residue was extracted with two portions of 30% acetone in hexane, the mixture was homogenized for 2 min each time, and the homogenate was centrifuged at 2500 rpm for 10 min each time. The extracts were combined in a separatory funnel and washed with two 100-mL portions of water. The organic layer was dried over anhydrous sodium sulfate (ca. 20 g). The solvent was evaporated under reduced pressure. To complete evaporation, the temperature of the water bath was raised to 50 °C for 10 min at the final stage. The oily fat residue was subjected to silica gel column chromatography.

Silica Gel Column Chromatography. Silica gel deactivated with 10% water (15 g) was packed in a column (22 mm i.d. × 300 mm) with slight tapping. The concentrated residue (500 mg) was deposited on the top of the column and was eluted with 150 mL of a mixture of hexane and dichloromethane (80:20). The eluate was evaporated under reduced pressure and the residue dissolved in 5 mL of hexane.

Calibration. Standard solutions were prepared at three different concentrations ranging from 0.001 to 0.1 μg/mL (hexane). Standard solutions were injected, and chromatographic peak response vs concentration was plotted. Linear least-squares regression analysis was used.

Interlaboratory Study. The samples were prepared by spiking 5.0 g of Benihana oil with three organochlorine pesticides at 0.50 ppm. The recoveries were calculated by comparing the peak areas of the residues with the calibration curve. The samples for interlaboratory study were prepared with an accuracy within 0.1% of the nominal concentration.

Each of nine laboratories received a sample solution. This sample was diluted with hexane to 250 mL. The solution (50 mL) was evaporated under reduced pressure.

Silica Gel Column Chromatography. Silica gel deactivated with 10% water (15 g) was packed in a column (22 mm i.d. × 300 mm) with slight tapping. The concentrated residue was deposited on the top of the column and was eluted with 150 mL of a mixture of hexane and dichloromethane (80:20). The eluate was evaporated under reduced pressure and the residue dissolved in 5 mL of hexane.

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Monitoring. Twelve samples including beef, pork, and chicken were obtained from Yokohama, Hakata, Nagoya, and Kobe Quarantine Offices. Those samples were imported from Ireland, Denmark, Australia, France, and Thailand in 1989. The samples were analyzed as described under Analytical Procedure. No residual pesticide was found in imported meats.

RESULTS AND DISCUSSION

Recovery Tests. To examine the performance of this method, recovery tests were conducted. Pesticides equivalent to 0.01 and 0.02 ppm were added to 20 g of homogenate samples. The samples were extracted and defatted with deactivated silica gel columns. The concentrated eluates were injected without further cleanup. Table I shows that satisfactory recoveries (89–103%) were obtained at 0.01 and 0.02 ppm. Those recoveries were comparable with those of 92–105% reported by Suzuki et al. (1989). CV% of heptachlor and DDT ranged from 4.1 to 5.3, and that of dieldrin ranged from 7.4 to 8.0. These values were also comparable with those of the initial study (CV% values of heptachlor, dieldrin, and DDT were 2.8, 6.3, and 2.9, respectively). As shown in Figure 2, the peaks of pesticides were almost free from interferences. The cleanup procedure may be adequate for the analysis of organochlorine pesticides in meat.

Results of Intra- and Interlaboratory Studies. To evaluate the reproducibility of the procedure, intra- and interlaboratory studies were conducted. The results of intralaboratory studies are shown as entries 1 and 2 in Table II. Study 1 shows it was difficult to obtain reproducible results without control of the water content. The yield of dieldrin ranged from 0 to 27% and CV% was 163.0. After the water content of the silica gel was specified, all statistical parameters of each pesticide were improved as shown in study 2. The results of interlaboratory studies are shown as studies 3 and 4. Study 3 was performed before it was realized that the ruggedness of the method was poor. The recoveries of heptachlor, dieldrin, and DDT ranged from 74 to 110%. Those were comparative with the recoveries of study 4. The variances of heptachlor and DDT were also comparable with those of study 4, but the variance of dieldrin (8.6) was greater than that of the other pesticides (4.4 and 4.7 for heptachlor and DDT, respectively.). Statistical analysis of the results (ranking test, Youden's plot chart, quality control chart) indicates that some laboratories reported results that statistically deviated significantly from the expected results (Youden and Steiner, 1975). In contrast, study 4 was performed carefully, and the variances for dieldrin were significantly (P = 0.1%) improved. For heptachlor and DDT there were no difference between studies 3 and 4. From those

Table II. Overall Recovery of Three Pesticides

study	n	heptachlor recovery, %	heptachlor range	heptachlor CV%	dieldrin recovery, %	dieldrin range	dieldrin CV%	p,p'-DDT recovery, %	p,p'-DDT range	p,p'-DDT CV%
1[a]	3	76	72–80	3.8	6.4	0–27	163.0	76	70–92	11.3
2	3	96	91–99	4.3	91	81–97	7.6	94	90–101	4.4
3	9	96	88–104	4.4	95	74–104	8.6	100	94–110	4.7
4	9	96	88–103	5.0	98	91–101	3.3	100	93–111	4.8

[a] Study 1 was the initial study, and study 2 was the run after the water content of the silica gel was specified. Study 3 is the first interlaboratory study, and study 4 is the second interlaboratory study.

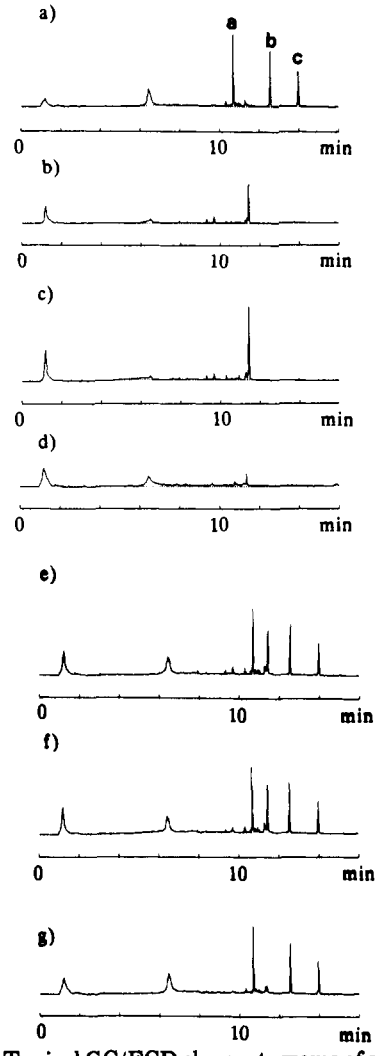

Figure 1. Typical GC/ECD chromatograms of sample extracts: (a) standards, (b) control beef, (c) pork, (d) chicken; extracts of (e) spiked beef, (f) pork, (g) chicken.

results it is concluded that, carefully done, the method could be adequate. It is necessary to note that the water control of silica gel is essential for this method.

Gas Chromatographic Conditions. Different types of gas chromatographic columns were considered for the analysis. A nonpolar wide-bore capillary column with whole injection mode provides good sensitivity with conveniently rapid separations. However, as shown in Figure 1, the peak widths are rather broad and the retention times are short; therefore, the peaks are subject to interferences by coextractives. A medium-bore capillary column with splitless injection mode gave comparable sensitivity and good separation from interfering peaks (Figure 1). However, chromatography with the medium-bore column took 3 times longer than that with the wide-bore chromatography. Sample analysis time with the medium-bore column was further increased because of the cool-down time necessary for the temperature program procedure. In contrast, chromatography with the wide-bore column was isothermal. Therefore, the wide-bore capillary was selected for routine use in this study. ECD was chosen rather than a mass spectrometric detector (MSD). ECD is more sensitive for these organochlorine pesticides than MSD and is readily available for organic pesticide analysis in Japan. Fortunately, cleanup for ECD is compatible with that for MSD.

Fat-Removing Effects. To improve recovery of dieldrin, either the water content of the silica gel or the

Table III. Effect of Water Content on Fat[a] Elution

column	mobile phase[b] water content, %	weight, mg 0	2.5	5	10	20
silica gel[c]	20% D–H	0	30	30	40	220
	20% A–H	240	390	370	380	400
Florisil[d]	20% D–H	0	0	0	330	390

[a] The values are means of duplicate examinations. [b] Abbreviations: D, dichloromethane; A, acetone; H, hexane. [c] The column for this test was prepared and treated as described in Table IV. Benihana oil (500 mg) was applied to the top of the column. The eluted oil was determined gravimetrically. [d] A slurry of silica gel or Florisil (15 g) in hexane was poured into the chromatographic glass column (22 mm i.d. × 300 mm).

Table IV. Effect of Water Content in Silica Gel on Recovery[a,b]

mobile phase[c]	pesticide water content, %	recovery, % 0	2.5	5	10	20
5% D–H	heptachlor	106	82	83	93	91
	dieldrin	0	0	0	0	0
	p,p'-DDT	109	112	108	96	91
20% D–H	heptachlor	87	84	83	83	84
	dieldrin	0	23	66	70	81
	p,p'-DDT	87	83	83	80	80
50% D–H	heptachlor	99	79	83	97	102
	dieldrin	93	94	93	109	90
	p,p'-DDT	110	70	81	108	102

[a] Means of duplicate determination. [b] *Recovery test*: Performed at 30 min after water addition. Silica gel (15 g) was packed in a column (22 mm i.d. × 300 mm). Two milliliters of 2.5 ppm standard solution was added on top of the column. The elution volume was 150 mL, and the eluted pesticides were determined gas chromatographically. *Measurement of water content in silica gel*: Silica gel sample (2.5 g) was heated in a 150 °C oven for 20 h. The loss of weight was measured after cool-down in a desiccator.

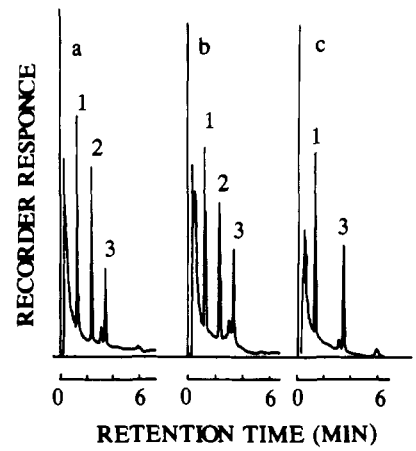

Figure 2. Typical chromatograms of elution from a silica gel column detected by GC with ECD: (a) standards; (b) elution from a silica gel column stored in sealed glass tube for 4 h after water addition at room temperature; (c) elution from a silica gel column for 12 h after water addition.

percentage of the polar components in the mobile phase had to be increased. The effects of these factors on the fat-removing ability of the column were examined. As shown in the Table III, the fat-retentive ability of column was reduced with water content in excess of 10%. The combination of 20% dichloromethane in hexane and 10% water in silica gel is necessary to effectively remove fat from the extract. It was also noted that the combination of 20% dichloromethane in hexane with a Florisil column resulted in poor resolution between the pesticides and the fat. Apparently, under these conditions, silica gel has more capacity for fat than Florisil (Smyth, 1972). Silica gel deactivated with 10% water and an eluting solvent of 20% dichloromethane in hexane was chosen for further study.

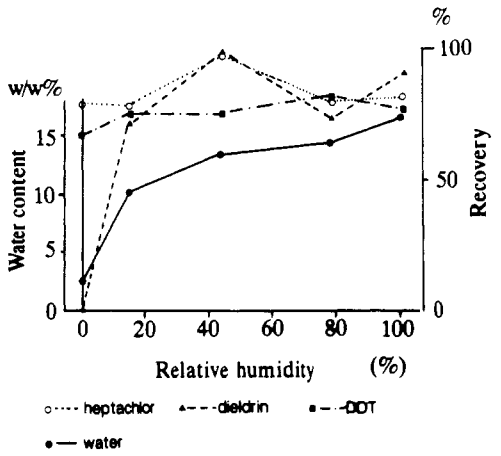

Figure 3. Changes of water content in silica gel during storage at various relative humidities and recoveries from chromatography. Silica gel deactivated with 10% water in 100-g amounts was stored in flasks with atmospheres of several different relative humidities (0, 15, 43, 78, 100%) for 1 week at 20 °C. The constant humidities were established with saturated salt solutions (LiCl for 15%, K_2CO_3 for 43%, Na_2SO_3 for 78%). In addition, silica gel was also stored with no other source of water vapor and with water at 20 °C to approximate 0 and 100% humidities, respectively. Using these silica gel samples, pesticides recovery tests were conducted as described in Table IV.

Cleanup Procedure. The recoveries of the pesticides from silica gel columns with differing water contents are shown in Table IV. The recoveries of dieldrin from silica gel columns with 20% dichloromethane in hexane ranged from undetectable to 81% depending upon the water content. However, the recoveries of heptachlor and DDT ranged from 80 to 86% and were not affected by the water content of the silica gel.

The recoveries of dieldrin from a silica gel column were also affected by the polarity of the mobile phase. Changing the content of dichloromethane in hexane as well as the water content of the silica gel gave the dieldrin recoveries in Table IV. With 5% dichloromethane in hexane as the eluting solvent, dieldrin was not recovered from any of the deactivated silica gels. With 20% dichloromethane in hexane as the eluting solvent, the recoveries were improved as the water content in the silica gel increased. With 50% dichloromethane the recoveries were 79–110% and were not affected by the water content of the silica gel. The recoveries of other pesticides were not changed by the content of the silica gel or the dichloromethane in the hexane. Those results also suggest that the dieldrin molecule is strongly adsorbed on silica gel but is displaced by 50% dichloromethane in hexane is less strongly adsorbed by silica gel with 10 and 20% water; therefore, 20% dichloromethane is adequate. This means that equilibration of the dieldrin between the dichloromethane layer and the water layer on the silica gel is an important aspect of the recovery of dieldrin from the silica gel column.

Effect of Deactivated Silica Gel Storage Humidity and Temperature on Pesticide Recoveries. The variabilities of the recoveries due to the silica gel chromatography were examined. The recovery of dieldrin from the silica gel changes after prolonged storage. As shown in Figure 2, dieldrin was not recovered after 6 h. The effects of storage temperature on recoveries of pesticides were examined. The silica gel used in this test was prepared 12 h before use and was stored at 5, 20, and 30 °C. The results are shown in Table V. At 5, 20, and 30 °C, the recovery of dieldrin was 30, 0, and 0%, respectively. On the other hand, the recoveries of heptachlor and DDT were consistently in the range 85–102%.

The effects of storage humidity of the silica gel on the water content and recovery were examined. The water content of silica gel changed as shown Figure 3. Apparently the water on the surface of silica gel equilibrates readily with the atmosphere, and this can lead to a change in the "activity" of the silica gel. It is necessary to prepare the silica gel with 10% water immediately before use.

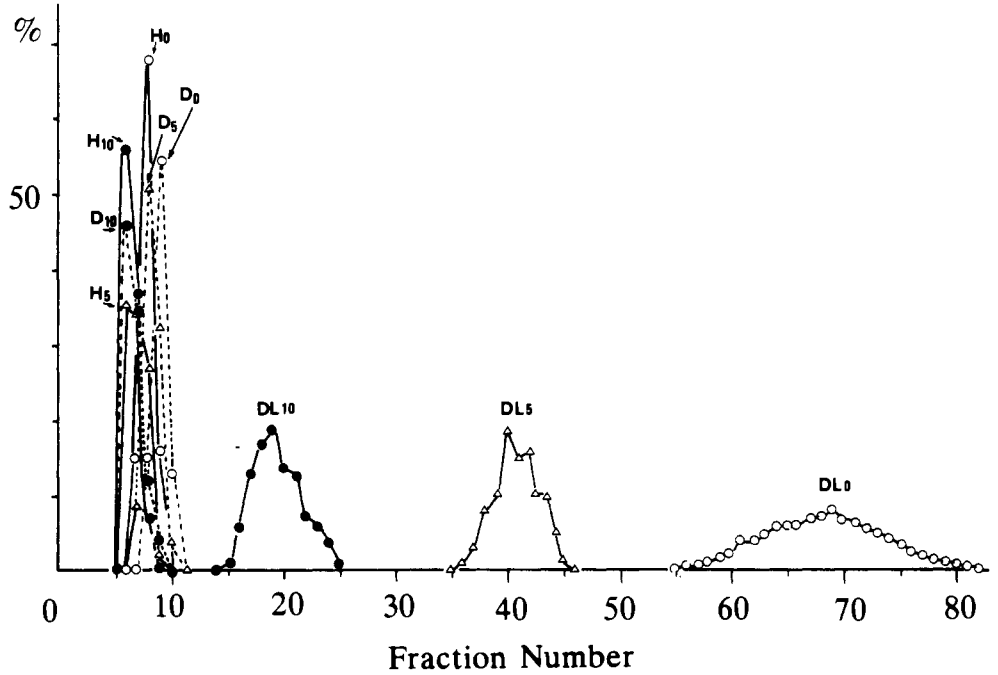

Figure 4. Eluting pattern of organochlorine pesticides. Abbreviations: H, heptachlor; D, DDT; DL, dieldrin. Suffixes of 0, 5, and 10 indicate water content in silica gel. Data were obtained under the following conditions. Silica gel was packed with slight tapping in a column (10 mm i.d. × 300 mm) for low-pressure chromatography. The mobile phase consisted of dichloromethane and hexane (1:4), which was pumped with a Shimadzu LC6A. The flow rate was 2 mL/min. A hexane solution of pesticides (2.5 ppm) was introduced on a Rheodyne LC injector equipped with a 2-mL loop. The eluate was collected as 4-mL fractions. The pesticides in each fraction were determined by ECD-GC as described under Analytical Procedure.

Table V. Effects of Silica Gel Storage Temperature on Recovery[a]

temp, °C	recovery, % heptachlor	dieldrin	p,p'-DDT
5	85.2	30.3	98.7
20	90.9	ND	102.7
30	90.5	ND	96.3

[a] Silica gel deactivated with 10% water (100 g) in sealed flasks was stored at 5, 20, and 30 °C for 12 h. Using these silica gel samples, pesticide recovery tests were conducted as described in Table IV.

Table VI. Effects of Water Content on Chromatographic Parameters for Low-Pressure Liquid Column Chromatography with Silica Gel

pesticide	water content, %	parameter[a] V_R, mL	k'	W, mL	N	H, cm
heptachlor	0	32	0.78	9.1	199	0.15
	5	28	0.56	10.3	125	0.24
	10	24	0.33	9.1	114	0.26
dieldrin	0	276	14.3	75.9	211	0.14
	5	164	8.11	28.9	511	0.05
	10	76	3.22	26.3	137	0.21
p,p'-DDT	0	36	1.00	8.1	324	0.09
	5	32	0.78	9.1	202	0.15
	10	24	0.33	10.1	92	0.32

[a] V_R, retention volume; k', capacity factor; W, peak width; N, theoretical plate; H, height equivalent to a theoretical plate.

The recoveries from silica gel columns that were stored at constant relative humidity at 20 °C are shown in Figure 3. Recoveries of dieldrin from silica gel stored in 43 and 78% relative humidity ranged from 73 to 99%. The water contents of the two silica gels were 10 and 12%. As the water content in the silica gel changed, the recovery of dieldrin changed.

Thus, after several days of storage, the results of silica gel column chromatography will be variable, and reproducible results will be difficult to obtain.

Change of Chromatographic Parameters. The effects of water content in silica gel on chromatographic parameters for the silica gel column were examined using a low-pressure liquid chromatographic system. The elution pattern for dieldrin was strongly influenced by the water content. In contrast, as shown in Figure 4, retention volumes (V_R) for heptachlor and DDT were independent of the water content. From the elution pattern, several parameters were calculated and are given in Table VI. Capacity factors (k') of the solid phase for three pesticides decreased as adsorbed water increased because the pesticides have little solubility in water. This indicates that the separation mode is normal phase rather than reversed phase. The theoretical plates (N) for heptachlor and DDT do not change as the water content of silica gel is increased. On the other hand, the N for dieldrin is increased. The change of the chromatographic parameters for dieldrin affect the recovery in the cleanup procedure. Separation of the three pesticides is given in Table VII. To eliminate interferences from crop extracts and minimize the separation time, silica gel with 10% water is desirable.

Elucidation of the type of water on the silica gel surface is important for greater understanding of the cleanup with silica gel (Klein, 1962; Scott and Kucera, 1978; Scott, 1982); therefore, thermal analyses were conducted using a thermal balance. The weight loss for silica gel deactivated with 10% water is shown in Figure 5 (top). The water in silica gel with 10% water was rapidly lost as the temperature increased. The differential water loss curve shows two maxima at room temperature and at 70 °C [Figure 5 (bottom)]. On the other hand, silica gel with 3% water gave only one peak at 85 °C in the differential weight loss curve. The silica gel with 10% water has a layer of water that is weakly bound to the silica gel surface. The water content of the silica gel was measured with a thermal balance, and the recovery tests were performed with 150 mL of 20% dichloromethane in hexane. No dieldrin was recovered from the column packed with silica gel with 3% water, but heptachlor and DDT were quantitatively recovered. On the other hand, all pesticides were recovered from a column packed with silica gel with 10% water that had been eluted with 150 mL of 20% dichloromethane in

Table VII. Resolutions and Capacity Factors

pesticide	water content, %	parameter[a] α	R_S
heptachlor/dieldrin	0	0.054	2.19
	5	0.068	2.99
	10	0.103	1.13
p,p'-DDT/dieldrin	0	0.070	2.15
	5	0.96	2.61
	10	0.103	1.13

[a] α, separation factor; R_S, resolution.

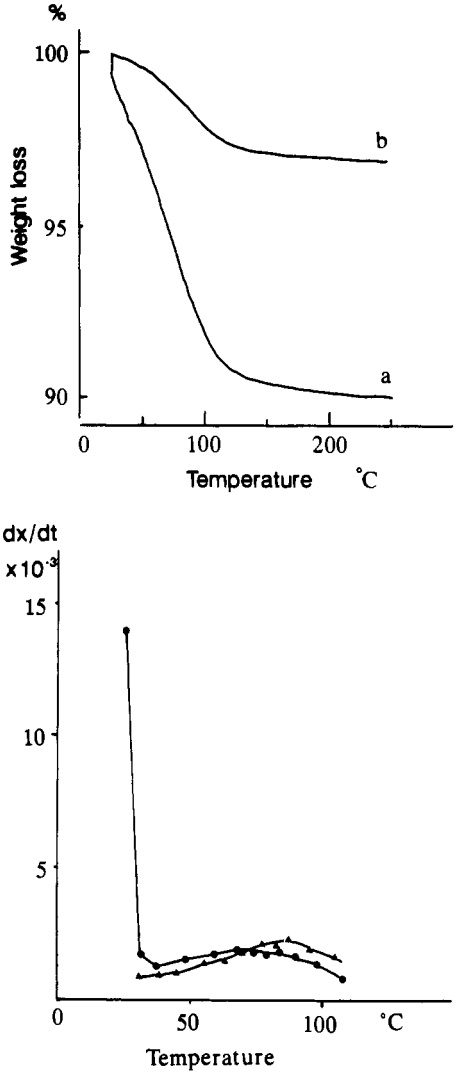

Figure 5. (Top) Weight loss graph of silica gel graph for 10% water containing silica gel (a) and for 3% water containing gel (b). Data were obtained under the following conditions. A Shimadzu thermal balance was used. The temperature was raised from 25 to 200 °C at 10 °C/min. Weights of samples were 10–12 mg. (Bottom) Differential curve of the weight loss.

hexane. Thus, the characteristic layer of water on the silica gel is important for the recovery of dieldrin from a column.

Conclusion. This procedure is suitable for analysis of nonpolar organochlorine pesticides (heptachlor, DDT, PCB, etc.) but may not be satisfactory for polar organochlorine pesticides (dieldrin, endrin, etc.). The recoveries of polar pesticides are dependent upon the water content in silica gel. Water content in silica gel can change during storage in closed containers. It is necessary to control the water content of silica gel, especially when polar materials such as dieldrin are to be analyzed. Changes in silica gel water content from 0 to 10% result in changes in the properties of the silica gel column (N, k') for polar pesticides. From the results of the thermal analysis, silica gel bound water which is lost at 25–50 °C is necessary to recover dieldrin from the column.

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