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Comparative Studies on the Recovery of Organochlorine Pesticides Between Dry Column Chromatography and Acetonitrile Partitioning

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Environmental pollution with organochlorine pesticides is evident throughout the world, and a great number of quantitative analytical data have been reported. However, there is no standardized analytical method which is generally accepted; different institutes follow different methods. In the previous studies, we compared the dry column chromatography with the acetonitrile partitioning method regarding the recovery of pesticides in human milk (YAKUSHIJI et al. 1980, KUWABARA & KASHIMOTO 1981). We had recovery rates of more than 80% with α-, β-, γ-, δ-HCH, *p,p'*-DDE, DDD, DDT and dieldrin by using both methods. However, recovery of hexachlorobenzene (HCB) by acetonitrile partitioning was 66% while recovery by dry column chromatography was 83%. In this paper, we report the difference of these two methods in treating vegetable oil and animal lipid.

METHODS

Soybean oil as an example of vegetable oil and butter fat as an example of animal lipid are processed. Each lipid containing organochlorine pesticide mixtures of lower level, medium level or higher level is treated by either one of the following two procedures. One is Florisil dry column chromatography (partly modified; WAKIMOTO & TATSUKAWA 1972, YAKUSHIJI et al. 1979) and the other is acetonitrile partitioning (partly modified; JOHNSON 1965). Both use Florisil wet column chromatography for cleanup. The two procedures are compared regarding recovery for the pesticides from soybean oil and butter fat.

Figs. 1, 2 and 3 show the analytical methods. Pesticides added to 2 g of each of the lipids are listed in Table 1. In the table, added amount of low, medium and high level of these pesticides are listed in the upper, medium and lower column, respectively.

Materials: Butter available on the market; soybean oil, first class; n-hexane, acetonitrile, anhydrous sodium sulfate, diethyl ether and acetone; reagents for pesticide analysis; α-, β-, γ-, δ-HCH, dieldrin, *p,p'*-DDE, DDD, DDT, HCB, heptachlor epoxide manufactured by Wako Pure Chemical Industries, Ltd. Florisil by Floridin Co.

0007-4861/82/0029-0347 $01.40

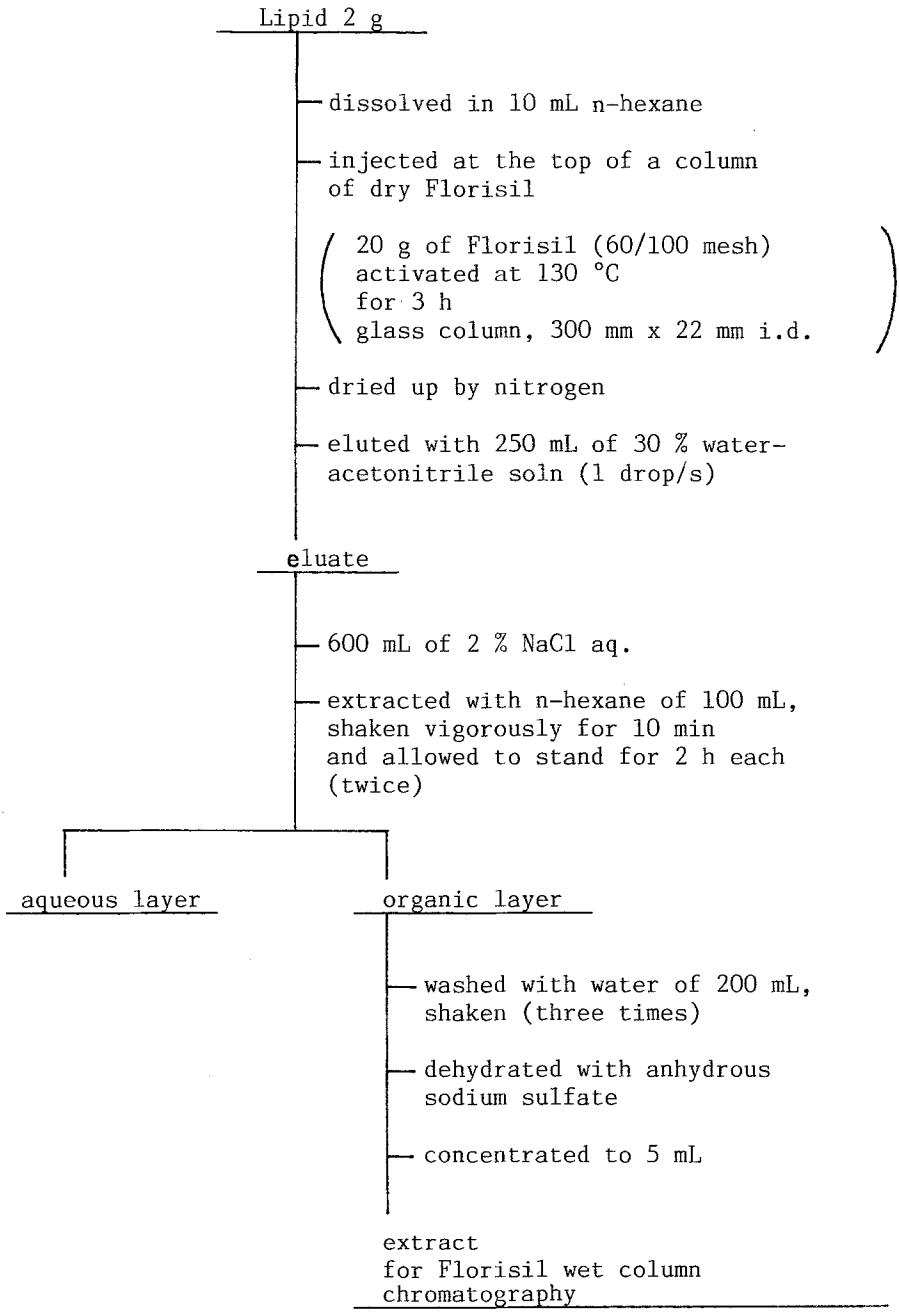

Fig.1. Florisil Dry Column Chromatography

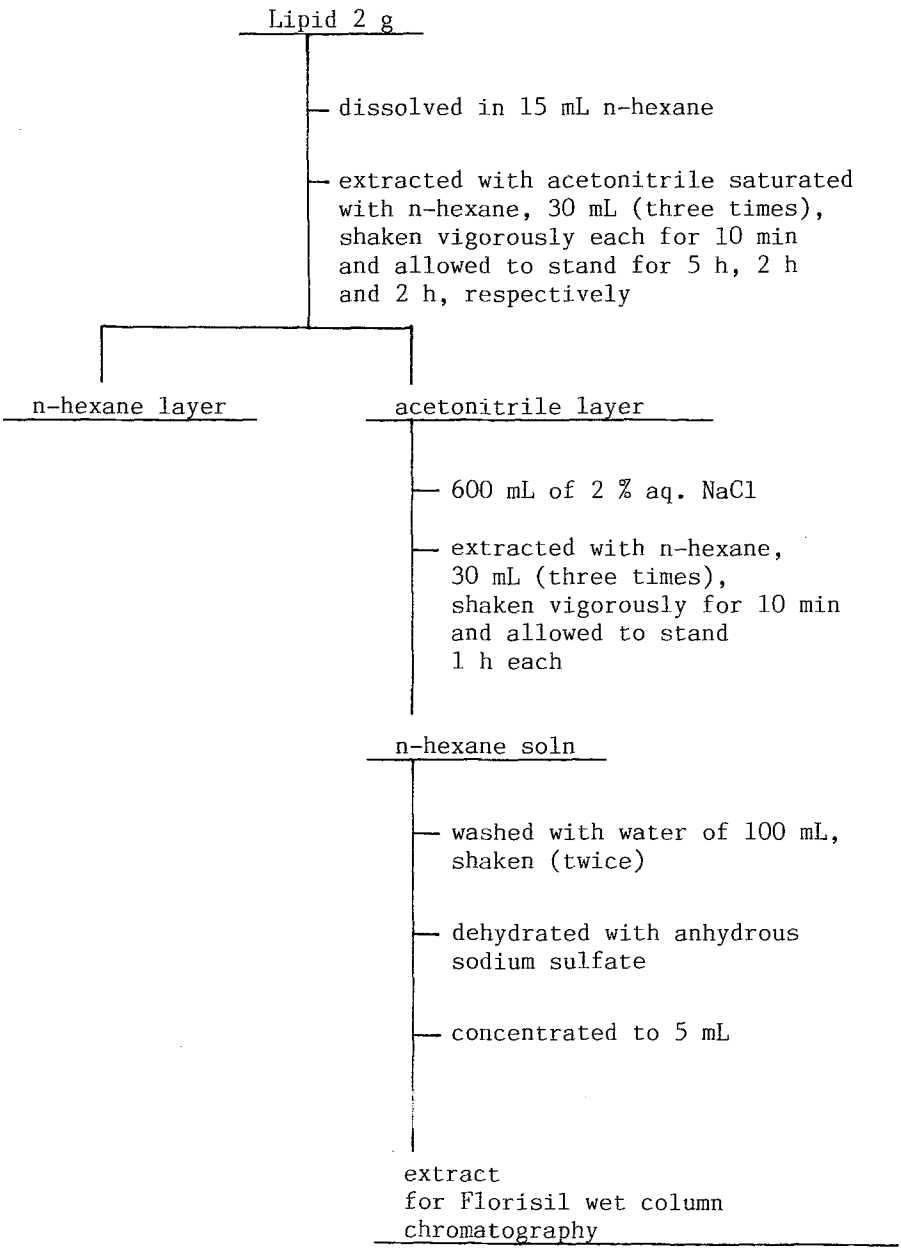

Fig.2. Acetonitrile Partitioning Method

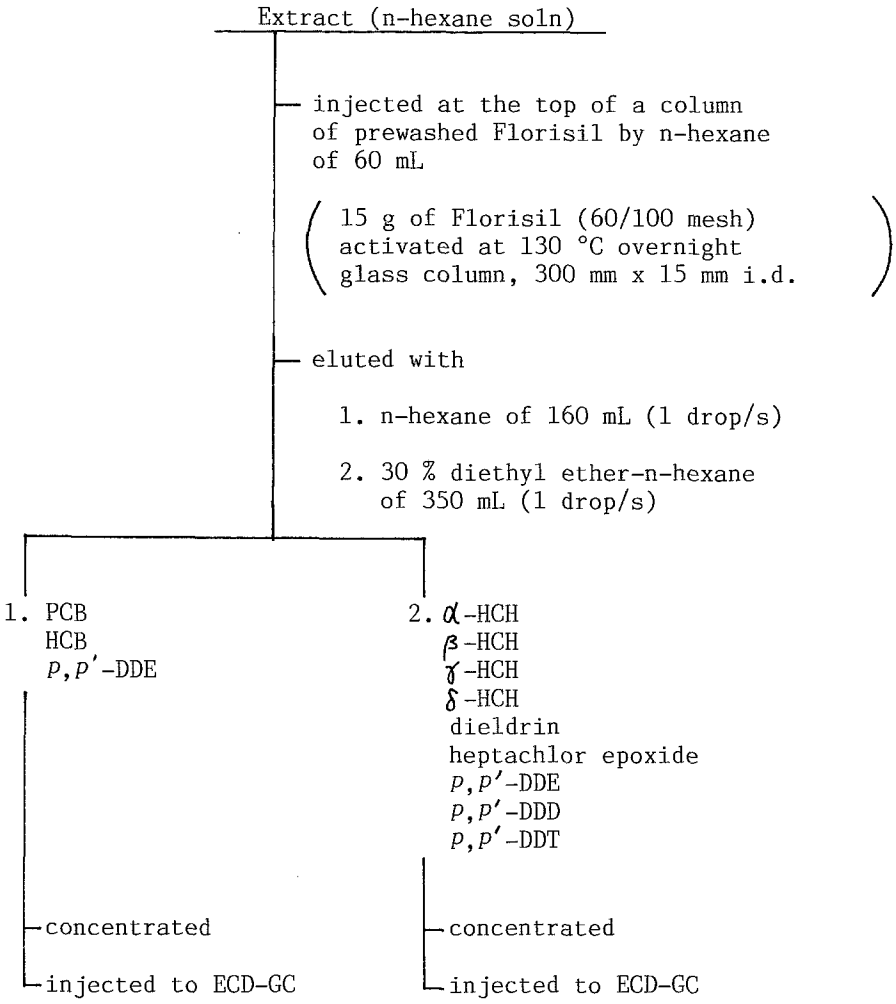

Fig.3. Florisil Wet Column Chromatography

RESULTS AND DISCUSSION

The levels of all the pesticides in untreated soybean were lower than the detection limits (α-, γ-, δ-HCH < 1; β-HCH, p,p'-DDE, heptachlor epoxide, dieldrin < 2; p,p'-DDD, DDT < 10 ppb). The level of α-HCH, p,p'-DDE, HCB and heptachlor epoxide in the butter fat is 36.2; 9.6; 8.7; and 4.8 ppb, respectively, whereas those of other compounds were lower than the detection limit (the same as soybean oil). Table 1 shows the result obtained by the above described methods after the portion of these natural pollutions have been excluded. Table 2 shows

TABLE 1. Fortification Level and Recovery of the Compounds

Compound	Fortification (μg)	Recovery (%)			
		Soybean Oil		Butter Fat	
		1)	2)	1)	2)
α-HCH	0.04	78.7	70.1	83.7	93.4
	0.20	82.8	84.0	79.2	73.5
	2.00	85.3	85.7	90.1	83.3
β-HCH	0.16	71.1	86.9	93.2	91.5
	0.80	81.8	85.1	80.8	80.5
	8.00	87.6	89.2	87.9	80.9
γ-HCH	0.04	79.6	90.0	85.4	93.0
	0.20	85.2	86.5	79.2	82.7
	2.00	87.1	88.7	88.0	80.7
δ-HCH	0.08	71.7	84.1	87.5	77.5
	0.40	85.7	86.4	87.3	86.0
	4.00	87.5	88.4	88.1	79.6
dieldrin	0.08	83.4	102.1	99.5	97.5
	0.40	89.0	87.1	93.8	88.1
	4.00	92.3	93.4	94.4	86.9
p,p'-DDE	0.08	86.6	90.7	79.6	81.8
	0.40	83.8	77.8	88.1	78.1
	4.00	83.5	87.5	92.6	79.1
p,p'-DDD	0.16	78.2	93.8	91.6	96.9
	0.80	91.9	91.0	96.0	91.2
	8.00	94.1	99.0	92.4	84.5
p,p'-DDT	0.16	83.3	97.8	100.0	95.2
	0.80	89.8	85.6	96.2	89.8
	8.00	83.2	89.8	86.4	77.0
HCB	0.016	63.8	49.3	56.6	51.3
	0.080	59.6	44.1	63.6	37.4
	0.800	52.5	48.1	66.2	45.4
heptachlor epoxide	0.08	75.7	94.8	99.6	97.2
	0.40	85.5	85.3	88.2	85.8
	4.00	90.7	93.9	95.0	87.9

1) Florisil dry column, 2) Acetonitrile partitioning.
Recovery (%) is indicated as duplicated analyses.

the summary of each data. In conclusion, all the added compounds except for HCB are recovered by more than 80 % by both of the methods. HCB, however, is recovered at a lower rate, especially by acetonitrile partitioning; 47.1 and 44.7 % in average from soybean oil and butter fat, respectively.

TABLE 2. Recovery of the Compounds by the Two Methods

Compound	Soybean Oil		Butter Fat	
	Dry Colm.[1]	Part.[2]	Dry Colm.[1]	Part.[2]
α-HCH	82.2± 4.4	79.9± 10.2	84.3± 5.5	83.4± 12.1
	74.1- 87.4	*59.7- 87.9*	*76.3- 91.9*	*62.7- 98.9*
β-HCH	80.1± 7.7	87.0± 9.5	87.3± 6.2	84.3± 8.1
	71.1- 90.1	*72.3-101.5*	*79.3- 96.9*	*77.6-100.0*
γ-HCH	83.9± 4.5	88.4± 8.7	84.2± 4.9	85.5± 9.1
	77.3- 90.9	*76.7-103.3*	*78.3- 90.2*	*77.0-102.3*
δ-HCH	81.6± 8.6	86.3± 3.2	87.6± 2.3	81.0± 7.5
	68.3- 92.5	*80.3- 89.6*	*84.2- 90.3*	*68.3- 88.1*
dieldrin	88.2± 4.9	94.2± 8.2	95.9± 3.1	90.8± 7.5
	81.0- 95.8	*86.7-108.3*	*91.7-100.0*	*83.7-105.0*
p,p'-DDE	84.6± 6.1	85.3± 6.3	86.7± 6.2	79.7± 2.9
	74.4- 92.6	*77.1- 90.7*	*77.3- 94.2*	*75.5- 82.6*
p,p'-DDD	88.0± 8.6	94.6± 7.1	93.3± 12.6	90.9± 6.1
	75.0- 99.0	*85.0-103.0*	*72.0-111.1*	*81.9-100.0*
p,p'-DDT	85.4± 7.2	91.0± 5.9	94.2± 6.4	87.3± 17.0
	73.8- 93.2	*84.7-100.0*	*84.4-100.0*	*72.2-118.2*
HCB	58.6± 7.2	47.1± 3.7	62.1± 5.5	44.7± 8.0
	45.1- 66.7	*43.3- 53.5*	*52.6- 69.1*	*35.2- 57.9*
heptachlor epoxide	83.9± 8.2	91.3± 6.0	94.3± 6.1	90.3± 8.1
	71.4- 96.4	*84.2-100.0*	*86.3-104.1*	*84.0-105.7*

1) Florisil dry column chromatography
2) Acetonitrile partitioning method

Each datum is shown as six samples' experiments.
Upper :mean± standard deviation (%)
Lower :*min.-max.* of the range (%)

Therefore, we suggest that caution should be exercised in interpreting the analytical result of HCB provided by these methods in field study. On the other hand, other organochlorine compounds allow satisfactory recoveries by these methods, provided a column chromatograph is thoroughly checked in advance and sufficiently eluted with solvent.

REFERENCES

JOHNSON, L. Y.: J. Assoc. Off. Anal. Chem. 48, 668 (1965).

KUWABARA, K. & T. KASHIMOTO: Proc. Osaka Pref. Inst. Publ. Health, Ed. Food Chem. (in Japanese) 12, 35 (1981).

WAKIMOTO, T. & R. TATSUKAWA: Japanese J. Water and Waste (in Japanese) 14, 1125 (1972).

YAKUSHIJI, T., I. WATANABE, K. KUWABARA, S. YOSHIDA, S. HORI, S. FUKUSHIMA, T. KASHIMOTO, K. KOYAMA, & N. KUNITA: Arch. Environm. Contam. Toxicol. 8, 59 (1979).

YAKUSHIJI, T., I. WATANABE, S. YOSHIDA, R. TANAKA, T. KASHIMOTO, & N. KUNITA: Proc. Osaka Pref. Inst. Publ. Health, Ed. Food Chem. (in Japanese) 11, 87 (1980).

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