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Recovery Studies of Organocholorine Insecticides in Fruits and Vegetables Using Cyclic Steam Distillation

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Environmental pollution with organochlorine pesticides is evident throughout the world, and the use of several of these pesticides has been banned in many countries for several years. In Chile, the use of DDT and its derivatives has been banned only since 1984 after its findings in milk, meat and vegetables. There are several methods for the routine analysis of organochlorine methods in fruits and vegetables (Sisson et al. 1968, Luke et al. 1975, Pesticide Analytical Manual 1982 a), but they exhibit significant disadvantages in time, cost, equipment and amount of coextractives, particularly waxes and colorants.

The purpose of this work was the development of rapid and efficient methods for the extraction, clean-up and determination of organochlorine pesticides in fruits and vegetables. We studied the feasibility of the application of cyclic steam distillation with and equipment similar to the Nielson - Kryger steam distillation apparatus (Veith and Kiwus 1977) but constructed in our laboratory (Albornoz and Ober 1980).

A continuous distillation-extraction apparatus which resembles the Nielsen-Kryger one was employed in the mid fifties for the determination of a herbicide residue in soil and plant tissue (Bleidner et al. 1954). Both apparatus resemble each other, but the Bleidner apparatus uses a larger extraction solvent volume and places it in a separate flask attached to the steam distillation-extraction head.

Cyclic steam extraction has been applied as a sample preparation method for pesticide residues by several authors (Cooke et al. 1979, Cooke et al. 1980, Chang and Sampath, 1984). During the last years we have been using steam extraction for pesticides in fish and water samples, and now we extend its application to fruits and vegetables. We studied the recovery of lindane, heptachlor, aldrin, dieldrin, o,p'- DDT and p,p'- DDT,

which are of common use in Chile, from apple, lettuce, cabbage, beet, potato, carrot and cauliflower. In the recovery studies additions were 0.01 and 0.10 ppm for lindane, heptachlor and aldrin, 0.015 and 0.15 ppm for dieldrin, and 0.025 and 0.25 ppm for o,p'- DDT and p,p'-DDT.

MATERIALS AND METHODS

All the solvent were residue analysis grade. All pesticides were analysis grade and were obtained from the Environmental Protection Agency (U.S.A.). The standard solutions were prepared in isooctane (Pesticide Analytical Manual 1982b).

50 g of minced sample were fortified with the pesticides at the levels prefixed and were blended with double-distilled water in a high-speed mixer. The macerated product was transfered into a 2ℓ round-bottomed flask with a liter of water and a steam distillation unit attached to the flask. Ten mℓ Isooctane was added to the solvent trap through the top of the column. The samples were boiled vigorously for 1 and 2 hrs. The pesticides are retained in the isooctane layer. The upper isooctane layer was collected with 2-5 mℓ isooctane rinses of the column. The organic extracts were dried with anhydrous sodium sulfate and this volume adjusted to 10 mℓ.

In lettuce and carrot we found interferences that were almost completely removed by a clean-up in a 14 x 200 mm chromatographic column packed with grade V alumina and Fuller's earth in approx 15:1 ratio. The pesticides were eluted from the column with 30 mℓ of hexane.

G.C. analyses were performed on a Perkin-Elmer Sigma 3B gas chromatograph equipped with a ^{63}Ni electron capture detector. Two 2m x 2 mm i.d. glass columns packed with 1.5% OV-17 + 1.95% QF-1 on 80/100 mesh Cromosorb W, AW DMDCS and 3% OV-225 on 100/120 mesh Cromosorb W HP were used. Injector, column and detector temperatures were 270, 185, and 270° C respectively. The carrier gas flow (argon + 5% methane), was 35 mℓ/min and purified after passing through an Oxitrap (Alltech Associates Inc, USA).

G.C. Analysis were also performed with SE-54 cross-linked glass capillary columns made in our laboratory (Santa María et al. 1985). Figure 1 shows the separation of the organochlorine pesticides recovered from a carrot sample in 12 m x 0,3 mm i.d. glass capillary column.

The quantification was made by comparison with standards. Peak areas were measured with a Perkin Elmer Sigma 15 data procesor.

Table 1. Recovery of organochlorine pesticides from fortified samples*

Pesticide	Fortification Level (ppm)	% Recovery ± Std. deviation						
		Apple	Lettuce	Cabbage	Beet	Carrot	Potato	Cauliflower
Lindane	0.10	78 ± 3	79 ± 4	61 ± 3	68 ± 3	53 ± 3	84 ± 8	77 ± 11
	0.01	81 ± 8	96 ± 5	78 ± 5	62 ± 4	-	86 ± 4	87 ± 9
Heptachlor	0.10	40 ± 6	41 ± 4	33 ± 4	20 ± 4	26 ± 3	31 ± 7	50 ± 3
	0.01	15 ± 2	42 ± 9	26 ± 3	19 ± 3	-	28 ± 6	54 ± 3
Aldrin	0.10	93 ± 5	97 ± 8	95 ± 3	86 ± 3	66 ± 5	86 ± 8	80 ± 3
	0.01	77 ± 3	103 ±15	68 ± 2	71 ± 4	-	95 ± 4	98 ± 3
Dieldrin	0.15	102 ±10	-	95 ± 3	86 ± 4	71 ± 2	94 ± 5	80 ± 3
	0.015	83 ± 5	-	96 ± 7	78 ± 3	-	101 ± 2	86 ± 8
o,p'-DDT	0.25	95 ± 9	82 ± 7	76 ± 6	65 ± 5	38 ± 2	73 ± 6	62 ± 5
	0.025	79 ± 6	64 ± 5	76 ± 5	60 ± 5	-	63 ± 2	62 ± 4
p.p'-DDT	0.25	89 ±10	87 ± 6	64 ± 7	62 ± 4	31 ± 2	63 ± 4	47 ± 5
	0.025	74 ± 6	42 ± 9	58 ± 4	47 ± 4	-	65 ± 7	52 ± 4

* Mean of ten replicates S.D.

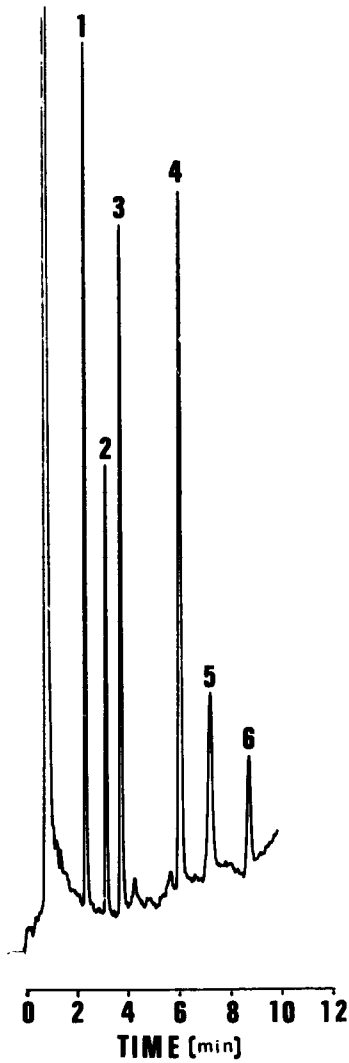

Figure 1. Separation of organochlorine pesticides on a 12 m x 0.3 mm i.d SE-54 cross-linked glass capillary column. Peaks: 1=lindane, 2=heptachlor, 3=aldrin, 4= dieldrin, 5=o,p'DDT, 6=p,p'DDT

RESULTS AND DISCUSSION

Table 1 presents the recoveries obtained for the pesticides studied. Variations in recoveries were found according to the vegetables samples studied and the pesticide considered. Low recoveries were obtained for heptachlor in all cases. This is an indication this pesticide is not extracted quantitatively by steam distillation. No significant increase in recovery was noted by increasing the distillation time from 1 to 2 hours. In lettuce it was imposible to eliminate totally one inter

ference that had the retention time of dieldrin. For this reason, this pesticide was not quantified in lettuce. With carrot the recovery was low for all pesticides, probably due to the clean-up treatment required for the elimination of impurities that interfere with the pesticide determination. Recovery for the low, addition level was not considered in this case. For o,p'-DDT and p,p'-DDT, recovery was not as good as for the rest, except for apple and lettuce for the highest addition level. With the capillary column a better separation and a shorter retention time compared to the packed column was obtained (Fig. 1).

The results indicate that cyclic steam distillation can be applied to routine analysis of organochlorine pesticides in fruits and vegetables with acceptable efficiency for the majority of the pesticides studied. This simple method of clean-up is a reduction in cost and time.

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