

Evaluation of a solid-phase extraction system for determining pesticide residues in milk

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ABSTRACT

A simple and rapid procedure based on reversed solid-phase extraction with octadecylsilica was developed for determining chlorinated pesticide residues in milk. The need for an agent that breaks the fat globules was first investigated and the method variables were optimized on whole homogenized milk (3.6% fat content). Recovery experiments performed for 26 organochlorine pesticides at levels of 3–40 µg/l gave >80% recoveries for all the compounds. The method was validated and evaluated by comparison with two widely used liquid–liquid extraction methods. The performance was checked by analysis of a certified standard with natural low endogenous levels (CMR 187) and different kinds of milk (skimmed, 2%, powdered, evaporated and condensed) spiked with the 26 pesticides. The procedure was used to analyse 45 commercial milks in which the presence of organochlorine residues had been detected. The proposed method offers advantages such as low cost and simplicity and the fact that the extracts obtained do not require a purification step.

INTRODUCTION

Two off-line steps are usually necessary for isolating organochlorine pesticides (OCPs) from milk: (1) extraction of the organochlorine pesticides from interfering matrix components, which involves liquid–liquid partitioning with organic solvents [1–6] or solid-phase extraction [7–9]; and (2) separation of the pesticides from co-extracted matrix constituents by means of column chromatographic separation (*e.g.*, alumina [10], Florisil [11], gel permeation [12,13] or HPLC [14]) or with reagents such as sulphuric acid [15,16] or potassium hydroxide [17].

These traditional methods are time consuming and expensive because of the high cost of the solvents and adsorbents. In contrast to such conventional extraction procedures, on-line extraction and clean-up procedures have been described using normal solid-phase extraction [18], which allows an important decrease in the number of manual operations involved but has the disadvantage of requiring large amounts of solvents.

Reversed solid-phase extraction reduces the cost of the analysis, because it requires smaller volumes of solvents and the amounts of solid phase needed are small. The use of octadecylsilica to extract organochlorine pesticide residues in milk has only been partially investigated for homogenized milk (fat globules of diameter 1 µm) [19] and skimmed and 2% milk [20].

In order to enhance the advantages of reversed solid-phase extraction, we have developed a optimized method for the determination of organochlorine residues in different kinds of milk.

EXPERIMENTAL

Reagents

Dichloromethane, *n*-hexane, acetonitrile, 2-propanol, ethanol, isobutanol, methanol, toluene and light petroleum (b.p. 40–60°C) were of pesticide grade and sodium lauryl sulphate, Triton 100-X, cetrinide, sodium chloride, sulphuric acid, sodium oxalate and anhydrous sodium sulphate were analytical-reagent grade.

Preparative octadecylsilica (55–105 µm) was obtained from Waters–Millipore. A C₁₈ Empore disc

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(47 mm diameter and 8 μm particle size) was purchased from Analytichem International.

Organochlorine pesticide standards were purchased from Promochem, Riedel de Haën and Aldrich. A certified standard of powdered milk (CRM 187) was supplied by the EEC Community Bureau of Reference (BCR).

Apparatus

The GC analyses were carried out on a Konik 3000 chromatograph equipped with a ^{63}Ni electron-capture detector and two fused-silica columns. One was the primary column (30 m \times 0.25 mm I.D.), cross-linked with BP-5 (Scientific Glass Engineering), and the other was used as a confirmation column (30 m \times 0.24 mm I.D.), coated with DB-17 (J & W Scientific). In both columns, 3 μl of sample were injected in the splitless mode and the splitter was opened after 0.7 min.

The temperature programme was 0.8 min at

50°C, increased at 30°C min^{-1} to 140°C, which was held for 2 min, then increased at 5°C min^{-1} to 280°C, the final temperature being held for 10 min.

Procedure

A 1-g amount of octadecylsilica was transferred into a 100 mm \times 9 mm I.D. glass column fitted with a coarse frit (No. 3) and covered with a plug of silanized glass-wool. The microcolumn was treated with 10 ml of methanol and 10 ml of distilled water.

A 5-ml volume of milk plus 5 ml of water added of 10 ml of methanol were mixed by sonication in an erlenmeyer flask and passed through the microcolumn; a vacuum was applied. The microcolumn was washed twice with 10 ml of distilled water and the washings were discarded. The adsorbed residues were then eluted with 10 ml of organic solvent. The extract was concentrated at 45°C and 3 μl were injected into the gas chromatograph.

For milk powder, 1 g of the powder was reconsti-

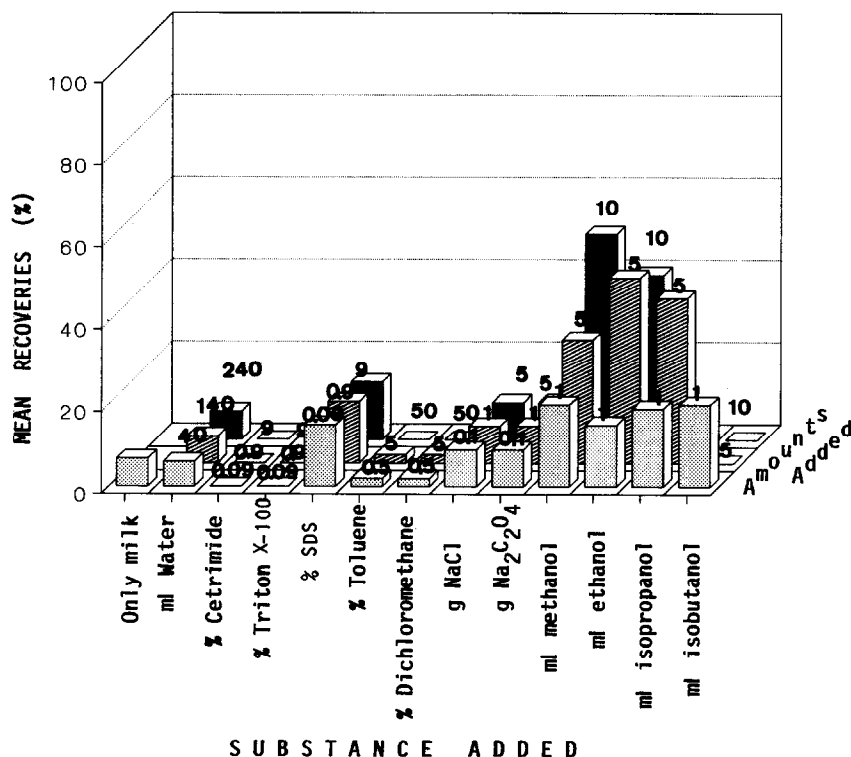


Fig. 1. Effect of different substances that can induce the rupture of fat globules. Experiments were performed using 10 ml of milk as sample, 0.5 g of C_{18} and eluting with *n*-hexane. SDS = Sodium dodecyl (lauryl) sulphate.

TABLE I

RECOVERY [MEAN \pm R.S.D. (%) ($n = 5$)] OF ORGANOCHLORINE PESTICIDES FROM 10 ml OF MILK USING 0.5 g OF C_{18} , DIFFERENT VOLUMES OF METHANOL AND 10 ml OF *n*-HEXANE

Compound	Concentration in milk ($\mu\text{g l}^{-1}$)	Volume of methanol (ml)						
		1	3	5	7	10	13	15
Aldrin	5	8 \pm 10	22 \pm 12	31 \pm 11	49 \pm 9	51 \pm 6	50 \pm 12	29 \pm 14
Captafol	14	13 \pm 13	18 \pm 14	29 \pm 8	54 \pm 9	50 \pm 5	49 \pm 8	40 \pm 10
Captan	7	14 \pm 12	30 \pm 11	36 \pm 11	37 \pm 10	35 \pm 9	35 \pm 4	14 \pm 12
<i>o,p'</i> -DDD	6	12 \pm 9	39 \pm 12	42 \pm 14	49 \pm 12	47 \pm 7	47 \pm 12	28 \pm 14
<i>p,p'</i> -DDD	9	10 \pm 13	25 \pm 12	38 \pm 11	42 \pm 12	42 \pm 7	43 \pm 14	33 \pm 12
<i>o,p'</i> -DDE	7	7 \pm 15	32 \pm 13	41 \pm 11	59 \pm 10	64 \pm 8	60 \pm 12	46 \pm 15
<i>p,p'</i> -DDE	7	5 \pm 12	14 \pm 10	23 \pm 10	34 \pm 11	33 \pm 7	32 \pm 9	19 \pm 12
<i>o,p'</i> -DDT	9	25 \pm 14	34 \pm 12	44 \pm 9	54 \pm 12	55 \pm 9	45 \pm 12	25 \pm 11
<i>p,p'</i> -DDT	9	12 \pm 13	25 \pm 10	34 \pm 9	42 \pm 16	59 \pm 8	50 \pm 9	35 \pm 9
Dicofol	40	5 \pm 10	12 \pm 14	25 \pm 16	44 \pm 12	54 \pm 8	53 \pm 11	33 \pm 10
Dieldrin	6	30 \pm 14	40 \pm 11	47 \pm 12	60 \pm 10	71 \pm 9	70 \pm 10	49 \pm 15
α -Endosulfan	15	17 \pm 14	30 \pm 15	40 \pm 12	47 \pm 11	48 \pm 10	48 \pm 13	33 \pm 13
β -Endosulfan	6	16 \pm 14	36 \pm 13	42 \pm 9	50 \pm 12	60 \pm 8	60 \pm 10	54 \pm 12
Endosulfan sulphate	11	7 \pm 9	26 \pm 12	40 \pm 11	49 \pm 13	51 \pm 7	42 \pm 9	39 \pm 12
Endrin	13	33 \pm 10	50 \pm 12	57 \pm 12	74 \pm 12	63 \pm 8	62 \pm 12	45 \pm 13
Heptachlor	5	21 \pm 12	25 \pm 11	30 \pm 10	35 \pm 9	38 \pm 9	39 \pm 13	35 \pm 12
Heptachlor epoxide	5	12 \pm 13	23 \pm 13	43 \pm 12	47 \pm 10	52 \pm 10	55 \pm 15	47 \pm 11
α -HCH	5	49 \pm 10	44 \pm 11	41 \pm 12	46 \pm 11	50 \pm 7	49 \pm 10	36 \pm 11
β -HCH	5	43 \pm 14	44 \pm 11	62 \pm 11	65 \pm 9	66 \pm 7	60 \pm 10	55 \pm 12
δ -HCH	5	42 \pm 12	46 \pm 13	49 \pm 11	49 \pm 10	49 \pm 8	49 \pm 10	45 \pm 12
γ -HCH	3	45 \pm 12	44 \pm 11	46 \pm 14	48 \pm 11	46 \pm 10	44 \pm 11	35 \pm 12
BHC	3	19 \pm 15	35 \pm 10	40 \pm 12	45 \pm 13	49 \pm 8	44 \pm 14	30 \pm 13
Isodrin	10	8 \pm 12	27 \pm 12	37 \pm 14	42 \pm 10	45 \pm 9	39 \pm 12	23 \pm 14
Metoxichlor	16	22 \pm 13	36 \pm 12	43 \pm 12	46 \pm 11	50 \pm 10	49 \pm 12	34 \pm 11
Mirex	8	12 \pm 14	18 \pm 15	21 \pm 11	40 \pm 15	50 \pm 8	29 \pm 10	12 \pm 9
Tetradifon	8	15 \pm 10	24 \pm 10	39 \pm 11	54 \pm 13	61 \pm 6	48 \pm 12	25 \pm 10

tuted with distilled water (1:9). For evaporated milk, 2 ml of the milk were mixed with 6 ml of distilled water. For condensed milk, 7 g were reconstituted with 18 ml of distilled water.

For recovery experiments, 0.1 ml of an ethyl acetate solution containing OCPs was added to milk and the mixture was left to stand overnight at 4°C. The sample was equilibrated to room temperature before proceeding with the above procedure.

RESULTS AND DISCUSSION

In order to optimize the extraction conditions, we first tested the follow mechanisms that can produce the rupture of the fat globule membrane: addition of water to 40, 240 and 490 ml; addition of surfac-

tant, using different kinds of detergents, *viz.*, anionic (sodium lauryl sulphate), non-ionic (Triton 100-X) and cationic (cetrimide), and different concentrations in milk, *viz.*, 0.09, 0.9 and 9.9% (w/v); addition of different amounts (0.5, 5.0 and 50.0%, v/v) of non-polar organic solvents, such as toluene and dichloromethane, to milk; modification of the saline concentration, using different salts (NaCl and $\text{Na}_2\text{C}_2\text{O}_4$), and different concentrations (1, 10 and 50%, w/v) in milk; and addition of polar organic solvents, using methanol, ethanol, 2-propanol, isobutanol, acetonitrile, acetone and tetrahydrofuran, to different volumes (1, 5 and 10 ml).

Fig. 1 shows the results obtained as average recoveries of 26 organochlorine pesticides.

There are two mechanisms that do not provide

TABLE II
EFFECT OF SAMPLE SIZE ON RECOVERIES [MEAN \pm R.S.D. (%) ($n = 5$)] FROM 0.5 g OF C_{18} USING 10 ml OF METHANOL AND 10 ml OF *n*-HEXANE AS ELUENT

Compound	Milk sample (ml)		
	2.5	5	10
Aldrin	53 \pm 5	53 \pm 6	51 \pm 6
Captafol	42 \pm 4	43 \pm 6	40 \pm 5
Captan	50 \pm 6	42 \pm 2	45 \pm 9
<i>o,p'</i> -DDD	65 \pm 8	65 \pm 7	47 \pm 7
<i>p,p'</i> -DDD	60 \pm 10	55 \pm 8	42 \pm 7
<i>o,p'</i> -DDE	70 \pm 5	66 \pm 5	64 \pm 8
<i>p,p'</i> -DDE	60 \pm 8	56 \pm 6	33 \pm 7
<i>o,p'</i> -DDT	72 \pm 7	65 \pm 8	62 \pm 9
<i>p,p'</i> -DDT	68 \pm 10	69 \pm 7	59 \pm 8
Dicofol	90 \pm 9	78 \pm 10	62 \pm 8
Dieldrin	83 \pm 6	82 \pm 9	71 \pm 9
α -Endosulfan	78 \pm 8	69 \pm 9	48 \pm 10
β -Endosulfan	81 \pm 9	65 \pm 2	60 \pm 8
Endosulfan sulphate	72 \pm 6	64 \pm 7	51 \pm 7
Endrin	79 \pm 9	78 \pm 9	63 \pm 8
Heptachlor	52 \pm 8	46 \pm 9	38 \pm 9
Heptochlor epoxide	80 \pm 8	74 \pm 9	52 \pm 10
α -HCH	70 \pm 9	64 \pm 8	50 \pm 7
β -HCH	89 \pm 9	80 \pm 6	66 \pm 7
δ -HCH	78 \pm 10	70 \pm 9	49 \pm 8
γ -HCH	67 \pm 8	65 \pm 6	46 \pm 10
BHC	67 \pm 8	66 \pm 8	49 \pm 8
Isodrin	70 \pm 9	68 \pm 10	45 \pm 9
Metoxichlor	76 \pm 11	69 \pm 9	50 \pm 10
Mirex	74 \pm 9	68 \pm 8	50 \pm 8
Tetradifon	80 \pm 10	73 \pm 7	61 \pm 6

better recoveries than those obtained when milk alone is used: addition of water and modification of the saline concentration. The former probably does not give good recoveries because the dilution of milk with water does not alter the fat globule structure. The latter destroys the fat globules when the liquid-liquid extraction method [6] is used but, in our case, did not give good results.

Although the addition of non-polar solvents has been proposed for C_{18} extraction from homogenized milks by Barcarolo *et al.* [19], our assays showed that it actually decreases the recoveries. One explanation for this could be that the diameter of the fat globules is larger in our case than in the previous work and the organic solvents cannot

break them up, and moreover the residues are probably more soluble in the organic solvents than in octadecylsilica sorbent. With concentrations of 50% the mechanism cannot operate because two layers form.

Addition of surfactants yields the most variable results. With non-ionic and cationic surfactants, no organochlorine pesticides were recovered. With an anionic surfactant the recoveries were slightly better than without it.

The use of polar organic solvents has been reported for the selective extraction of OCPs from milk [1,9,20]. Acetone, acetonitrile and tetrahydrofuran are not suitable for solid-phase extraction because they yield a precipitate. Although alcohols increase the recoveries, the results are better when the

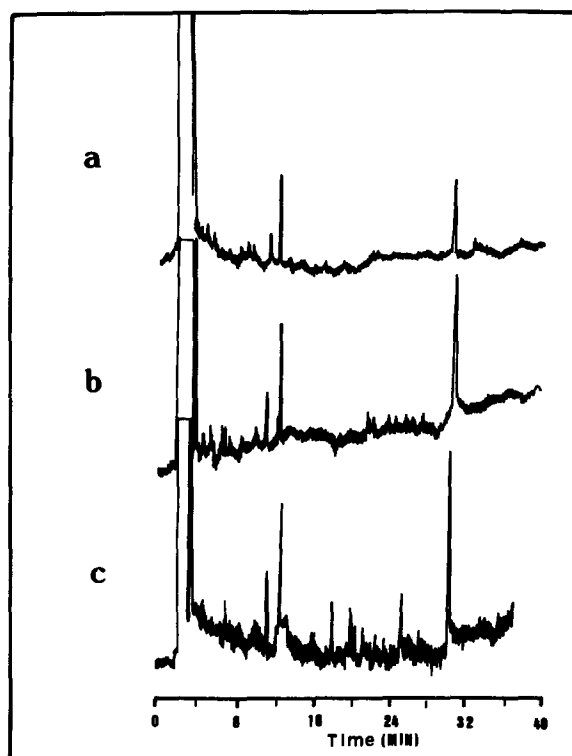


Fig. 2. Chromatograms of extracts obtained from unspiked milk with the eluents (a) *n*-hexane, (b) light petroleum and (c) *n*-hexane-light petroleum (1:1).

TABLE III

RECOVERY [MEAN \pm R.S.D. (%) ($n = 5$)] OF ORGANOCHLORINE PESTICIDES FROM 5 ml OF MILK PLUS 10 ml OF METHANOL WITH 10 ml OF *n*-HEXANE AS ELUENT USING DIFFERENT AMOUNTS OF C₁₈

Compound	Amount of octadecylsilica (g)					
	0.1	0.3	0.5	0.7	1.0	1.2
Aldrin	18 \pm 10	38 \pm 12	53 \pm 6	57 \pm 6	58 \pm 6	58 \pm 6
Captafol	23 \pm 14	28 \pm 14	33 \pm 6	45 \pm 6	49 \pm 5	48 \pm 5
Captan	17 \pm 10	36 \pm 10	42 \pm 2	43 \pm 8	45 \pm 9	44 \pm 8
<i>o,p'</i> -DDD	22 \pm 9	43 \pm 9	65 \pm 7	80 \pm 9	87 \pm 7	88 \pm 4
<i>p,p'</i> -DDD	32 \pm 12	45 \pm 10	55 \pm 8	82 \pm 9	92 \pm 7	93 \pm 6
<i>o,p'</i> -DDE	33 \pm 8	59 \pm 9	66 \pm 7	68 \pm 10	84 \pm 8	86 \pm 5
<i>p,p'</i> -DDE	25 \pm 12	44 \pm 10	56 \pm 6	74 \pm 11	74 \pm 7	78 \pm 9
<i>o,p'</i> -DDT	32 \pm 14	49 \pm 10	65 \pm 8	77 \pm 8	85 \pm 8	87 \pm 8
<i>p,p'</i> -DDT	35 \pm 13	56 \pm 10	69 \pm 7	83 \pm 8	88 \pm 7	90 \pm 9
Dicofol	44 \pm 12	62 \pm 10	68 \pm 10	72 \pm 10	74 \pm 7	75 \pm 6
Dieldrin	50 \pm 14	69 \pm 11	82 \pm 9	86 \pm 9	91 \pm 8	92 \pm 5
α -Endosulfan	27 \pm 10	55 \pm 10	69 \pm 9	87 \pm 8	98 \pm 9	99 \pm 3
β -Endosulfan	36 \pm 13	46 \pm 13	65 \pm 2	88 \pm 8	90 \pm 6	94 \pm 8
Endosulfan sulphate	22 \pm 9	52 \pm 12	64 \pm 7	87 \pm 6	91 \pm 6	92 \pm 7
Endrin	33 \pm 10	50 \pm 12	78 \pm 9	84 \pm 7	93 \pm 5	95 \pm 9
Heptachlor	21 \pm 12	35 \pm 11	46 \pm 9	65 \pm 9	78 \pm 6	72 \pm 6
Heptachlor epoxide	33 \pm 13	53 \pm 13	74 \pm 9	87 \pm 9	92 \pm 11	92 \pm 10
α -HCH	49 \pm 10	44 \pm 11	64 \pm 8	96 \pm 11	100 \pm 8	98 \pm 7
β -HCH	43 \pm 14	44 \pm 11	80 \pm 6	85 \pm 9	96 \pm 8	97 \pm 9
δ -HCH	42 \pm 12	46 \pm 13	70 \pm 9	82 \pm 9	99 \pm 7	99 \pm 6
γ -HCH	45 \pm 12	44 \pm 11	65 \pm 6	98 \pm 6	106 \pm 10	99 \pm 8
BHC	19 \pm 15	35 \pm 10	66 \pm 8	75 \pm 13	99 \pm 9	99 \pm 8
Isodrin	8 \pm 12	27 \pm 12	68 \pm 10	82 \pm 10	95 \pm 9	96 \pm 8
Metoxichlor	22 \pm 13	36 \pm 12	69 \pm 9	86 \pm 9	90 \pm 7	94 \pm 8
Mirex	32 \pm 14	58 \pm 15	68 \pm 8	69 \pm 10	70 \pm 9	72 \pm 9
Tetradifon	45 \pm 10	63 \pm 10	73 \pm 7	78 \pm 9	82 \pm 7	85 \pm 10

molecular chain length is shorter because in this way the viscosity diminishes. For this reason, methanol was selected.

The effects of the volume of methanol, sample size, amount of C₁₈ and eluent were tested and the results are given in Tables I, II, III and IV, respectively. The concentration of organochlorine pesticides in milk was kept constant throughout the test (see Table I). The recoveries reported are the means of five analyses.

When *n*-hexane, light petroleum or a mixture of the two are used as the eluent, they provide very similar recoveries. Light petroleum increases the recoveries of HCH isomers slightly and *n*-hexane increases the recoveries of the DDT isomers; mixing

increases both. However, the difference is only about 5%. Fig. 2 shows chromatograms of unspiked milk obtained with each of the eluents.

The organic extract concentration was studied. The chromatograms obtained by injecting an extract of unspiked milk concentrated to different volumes are shown in Fig. 3.

The effect of the sample flow-rate though the C₁₈ column (1, 5 and 20 ml min⁻¹) was also checked. No differences in the recoveries were observed.

Therefore, the optimum conditions for maximum recoveries of pesticides were established as 5 ml of milk, 5 ml of water and 10 ml of methanol mixed by sonication and passed through a microcolumn containing 1 g of C₁₈. Pesticides are eluted with 10 ml

TABLE IV

EFFECT OF THE ELUENT ON ANALYTE RECOVERIES [MEAN \pm R.S.D. (%) ($n = 5$)] FROM C₁₈ USING THE CONDITIONS INDICATED IN THE PROCEDURE

Compound	<i>n</i> -Hexane	Light petroleum	<i>n</i> -Hexane–light petroleum (1:1)
Aldrin	58 \pm 6	68 \pm 10	67 \pm 8
Captafol	49 \pm 5	38 \pm 12	49 \pm 9
Captan	45 \pm 9	45 \pm 8	45 \pm 9
<i>o,p'</i> -DDD	87 \pm 7	92 \pm 8	90 \pm 7
<i>p,p'</i> -DDD	92 \pm 7	99 \pm 9	101 \pm 7
<i>o,p'</i> -DDE	84 \pm 8	78 \pm 5	85 \pm 10
<i>p,p'</i> -DDE	74 \pm 7	70 \pm 6	76 \pm 12
<i>o,p'</i> -DDT	85 \pm 8	77 \pm 8	87 \pm 9
<i>p,p'</i> -DDT	88 \pm 7	77 \pm 8	89 \pm 9
Dicofol	74 \pm 7	98 \pm 10	99 \pm 8
Dieldrin	91 \pm 8	89 \pm 6	92 \pm 7
α -Endosulfan	98 \pm 9	94 \pm 10	98 \pm 8
β -Endosulfan	90 \pm 6	86 \pm 10	91 \pm 5
Endosulfan sulphate	91 \pm 6	89 \pm 10	92 \pm 11
Endrin	93 \pm 5	104 \pm 6	95 \pm 6
Heptachlor	78 \pm 6	95 \pm 8	97 \pm 10
Heptachlor epoxide	92 \pm 11	94 \pm 9	93 \pm 11
α -HCH	100 \pm 8	99 \pm 8	102 \pm 7
β -HCH	96 \pm 8	101 \pm 10	102 \pm 9
δ -HCH	99 \pm 7	101 \pm 9	103 \pm 10
γ -HCH	106 \pm 10	102 \pm 9	104 \pm 10
BHC	99 \pm 9	104 \pm 7	102 \pm 6
Isodrin	95 \pm 9	96 \pm 8	95 \pm 9
Metoxichlor	90 \pm 7	98 \pm 8	99 \pm 8
Mirex	70 \pm 9	66 \pm 8	72 \pm 10
Tetradifon	82 \pm 7	72 \pm 7	85 \pm 10

of *n*-hexane and concentrated to a volume of 0.5 ml.

Fig. 4 shows chromatograms of spiked milk, unspiked milk and blank analyses.

The proposed procedure was compared with a procedure using a C₁₈ disc, but the small particle size (8 μ m) was not appropriate for the sample, which could not pass through the pores.

To validate the method, whole milk and a certified standard of milk powder were analysed according to the present procedure and the results were compared with those obtained with the Suzuki *et al.* [1] and sulphuric acid–*n*-hexane [15] extraction methods. Table V gives the mean recoveries, relative standard deviations and detection limits obtained with whole milk. Although the recovery re-

sults are in general satisfactory, the sulphuric acid–hexane procedure destroys endosulfan isomers and metabolites, endrin and heptachlor epoxide, significantly diminishes the recovery of the HCH isomers and isodrin and provides the largest relative standard deviations. The Suzuki *et al.* [1] procedure provides the highest limit of detection, which may not be adequate for the low concentrations of these residues present in milk.

The results obtained with the certified standard are given in Table VI and corroborate the previous results.

To check the performance, the proposed method was applied to spiked samples of different kinds of milk. The results are presented in Table VII. The

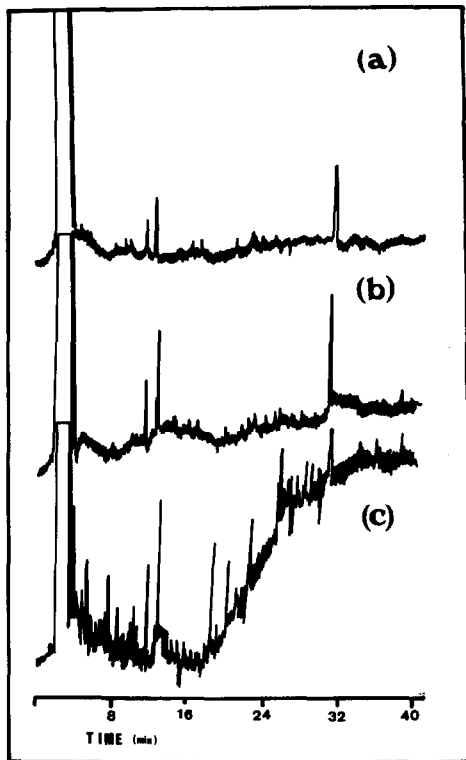


Fig. 3. Chromatograms obtained by injecting an extract of different unspiked milk concentrates: (a) 1 ml; (b) 0.5 ml; (c) 0.2 ml.

recoveries were similar for the different kinds of milk, except for condensed milk which, because of its high sugar content, yielded recoveries decreased by as much as 70%.

To verify the solid-phase extraction procedure, 45 commercial milk samples were analysed: 31 samples of sterilized milk (13 of whole milk, 9 of 2% milk and 4 of skimmed milk), 7 samples of powdered milk (3 of whole milk, 4 of skimmed milk), 5 samples of condensed milk and 2 samples of evaporated milk. Table VIII shows the contents of positive samples and Fig. 5 illustrates the chromatograms obtained from sample 4 in both chromato-

graphic columns. The concentrations found in milk were always lower than those established by the EEC [21].

In conclusion, solid-phase extraction with octadecylsilica can be used to determine organochlorine pesticides in milk. The recoveries obtained are similar to those reported with liquid-liquid extraction methods, and the traditional advantages of solid-phase extraction, *i.e.*, simplicity, speed and low cost, are maintained.

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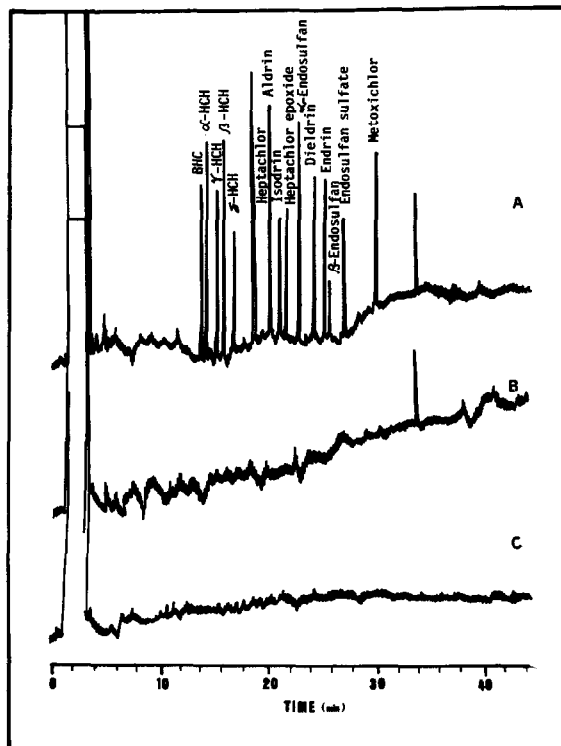


Fig. 4. Chromatograms of extracts obtained by the proposed method from (A) milk spiked with 15 OCPs, (B) unspiked milk and (C) blank.

TABLE V

RECOVERY [MEAN \pm R.S.D. (%) ($n = 6$)] AND DETECTION LIMITS (DL) ($\mu\text{g/l}$) OF 26 ORGANOCHLORINE PESTICIDES FROM FORTIFIED WHOLE MILK USING THE PROPOSED METHOD AND LIQUID-LIQUID EXTRACTION METHODS [1,15]

Compound	C_{18}		Suzuki <i>et al.</i> [1]		H_2SO_4 - <i>n</i> -hexane [15]	
	DL	Recovery	DL	Recovery	DL	Recovery
Aldrin	0.3	58 \pm 6	1.0	92 \pm 7	0.3	42 \pm 15
Captafol	2.3	49 \pm 5	9.1	52 \pm 6	3.0	34 \pm 12
Captan	2.3	45 \pm 9	9.5	45 \pm 12	5.0	36 \pm 13
<i>o,p'</i> -DDD	0.8	87 \pm 7	3.0	91 \pm 8	0.8	92 \pm 10
<i>p,p'</i> -DDD	0.5	92 \pm 7	1.8	97 \pm 7	0.5	94 \pm 10
<i>o,p'</i> -DDE	0.2	84 \pm 8	0.9	82 \pm 6	0.2	87 \pm 13
<i>p,p'</i> -DDE	0.4	74 \pm 7	1.3	71 \pm 6	0.3	83 \pm 9
<i>o,p'</i> -DDT	0.3	85 \pm 8	1.2	82 \pm 9	0.3	96 \pm 14
<i>p,p'</i> -DDT	0.4	88 \pm 7	1.6	91 \pm 6	0.5	90 \pm 10
Dicofol	6.4	74 \pm 7	25.4	82 \pm 3	7.1	78 \pm 15
Dieldrin	0.2	91 \pm 8	1.0	94 \pm 6	0.3	86 \pm 9
α -Endosulfan	0.3	98 \pm 9	1.1	92 \pm 7	—	—
β -Endosulfan	0.2	90 \pm 6	0.8	91 \pm 6	—	—
Endosulfan sulphate	0.3	91 \pm 6	1.3	91 \pm 8	—	—
Endrin	0.3	93 \pm 5	1.0	95 \pm 8	—	—
Heptachlor	0.3	78 \pm 6	1.0	90 \pm 6	0.3	83 \pm 11
Heptachlor epoxide	0.3	92 \pm 11	1.0	89 \pm 6	—	—
α -HCH	0.1	100 \pm 8	0.5	96 \pm 9	0.2	89 \pm 12
β -HCH	0.2	96 \pm 8	0.6	95 \pm 6	0.2	75 \pm 15
δ -HCH	0.3	99 \pm 7	1.1	94 \pm 10	0.4	73 \pm 12
γ -HCH	0.1	106 \pm 10	0.6	101 \pm 8	0.2	84 \pm 10
BHC	0.1	99 \pm 9	0.5	95 \pm 4	0.2	95 \pm 11
Isodrin	0.3	95 \pm 9	1.0	89 \pm 8	0.5	59 \pm 9
Metoxichlor	0.2	90 \pm 7	0.7	87 \pm 6	0.2	98 \pm 7
Mirex	0.7	70 \pm 9	2.6	60 \pm 8	0.7	97 \pm 9
Tetradifon	0.5	82 \pm 7	2.0	90 \pm 6	0.5	83 \pm 13

TABLE VI

CONCENTRATIONS OF ORGANOCHLORINE PESTICIDES IN A CERTIFIED STANDARD (CMR 187)

Compound	Concentration ($\mu\text{g/kg}$) ^a			
	Certified value	C_{18}	Suzuki <i>et al.</i> [1]	H_2SO_4 - <i>n</i> -hexane [15]
BHC	1.5 \pm 0.2	1.4 \pm 1.3	—	—
α -HCH	1.80 \pm 0.14	1.8 \pm 1.2	—	2.0 \pm 1.6
γ -HCH	5.7 \pm 0.7	6.0 \pm 2.4	5.2 \pm 1.6	6.5 \pm 2.4
β -HEPO ^b	(1.4) ^c	—	—	—
<i>p,p'</i> -DDE	6.6 \pm 0.6	5.6 \pm 0.9	—	6.4 \pm 4.9
Dieldrin	(2.3) ^c	—	—	—

^a Contents in dry mass.

^b β -HEPO = Heptachlor epoxide.

^c Values are not certified.

TABLE VII

RECOVERY [MEAN + R.S.D. (%) ($n = 6$)] OF 26 ORGANOCHLORINE PESTICIDES ADDED TO DIFFERENT KINDS OF MILK

Compound	Type of milk					
	Whole	2%	Skimmed	Powdered	Evaporated	Condensed
Aldrin	58 ± 6	68 ± 10	69 ± 9	79 ± 9	80 ± 6	65 ± 5
Captafol	49 ± 5	50 ± 9	54 ± 9	38 ± 5	39 ± 8	39 ± 10
Captan	45 ± 9	44 ± 10	37 ± 10	35 ± 9	37 ± 10	44 ± 12
<i>o,p'</i> -DDD	87 ± 7	85 ± 6	89 ± 7	85 ± 8	87 ± 9	79 ± 10
<i>p,p'</i> -DDD	92 ± 7	90 ± 6	92 ± 7	99 ± 5	98 ± 6	78 ± 10
<i>o,p'</i> -DDE	84 ± 8	88 ± 10	89 ± 8	82 ± 9	80 ± 12	92 ± 4
<i>p,p'</i> -DDE	74 ± 7	90 ± 10	84 ± 9	77 ± 9	82 ± 9	84 ± 5
<i>o,p'</i> -DDT	85 ± 8	80 ± 6	82 ± 8	101 ± 9	85 ± 10	80 ± 9
<i>p,p'</i> -DDT	88 ± 7	89 ± 6	90 ± 9	90 ± 9	81 ± 9	84 ± 6
Dicofol	74 ± 7	84 ± 9	80 ± 8	67 ± 6	73 ± 8	77 ± 10
Dieldrin	91 ± 8	91 ± 8	90 ± 10	95 ± 9	90 ± 10	79 ± 8
α -Endosulfan	98 ± 9	89 ± 9	92 ± 6	99 ± 10	88 ± 9	76 ± 8
β -Endosulfan	90 ± 6	87 ± 10	90 ± 9	99 ± 8	90 ± 10	74 ± 4
Endosulfan sulphate	91 ± 6	90 ± 8	94 ± 7	91 ± 7	92 ± 9	85 ± 7
Endrin	93 ± 5	93 ± 5	94 ± 5	91 ± 8	89 ± 6	76 ± 8
Heptachlor	78 ± 6	80 ± 7	85 ± 9	89 ± 8	80 ± 13	70 ± 7
Heptachlor epoxide	92 ± 11	88 ± 6	87 ± 7	102 ± 10	85 ± 5	78 ± 5
α -HCH	100 ± 8	97 ± 9	99 ± 8	94 ± 8	95 ± 9	73 ± 6
β -HCH	96 ± 8	92 ± 5	95 ± 9	114 ± 7	96 ± 8	102 ± 6
δ -HCH	99 ± 7	96 ± 6	99 ± 10	92 ± 8	93 ± 9	80 ± 9
γ -HCH	106 ± 10	100 ± 7	100 ± 6	110 ± 10	94 ± 9	85 ± 6
BHC	99 ± 9	97 ± 7	98 ± 7	95 ± 5	90 ± 9	84 ± 8
Isodrin	95 ± 9	97 ± 6	92 ± 7	85 ± 9	89 ± 12	89 ± 9
Metoxichlor	90 ± 7	90 ± 7	93 ± 9	97 ± 10	89 ± 12	86 ± 7
Mirex	70 ± 9	74 ± 8	76 ± 9	69 ± 8	69 ± 10	51 ± 9
Tetradifon	82 ± 7	80 ± 9	84 ± 6	83 ± 6	78 ± 9	80 ± 6

TABLE VIII

CONTENT OF ORGANOCHLORINE PESTICIDES IN COMMERCIAL MILK

Sample No.	Type of milk	OCP	Concentration ($\mu\text{g}/\text{kg}$) ^a
2	Sterilized whole milk	γ -HCH	2.8 ± 1.0
4	Sterilized whole milk	α -HCH	0.5 ± 0.1
		β -HCH	0.4 ± 0.2
		γ -HCH	0.4 ± 0.2
5	Sterilized whole milk	γ -HCH	1.6 ± 0.6
6	Sterilized whole milk	β -HCH	10.2 ± 2.8
11	Sterilized whole milk	γ -HCH	6.5 ± 2.6
18	Sterilized 2% milk	<i>p,p'</i> -DDE	23.3 ± 6.5
25	Sterilized skimmed milk	<i>p,p'</i> -DDE	12.2 ± 2.1
32	Powdered whole milk	Aldrin	2.0 ± 0.8
38	Powdered whole milk	Aldrin	7.3 ± 1.3

^a Mean ± standard deviation ($n = 4$).

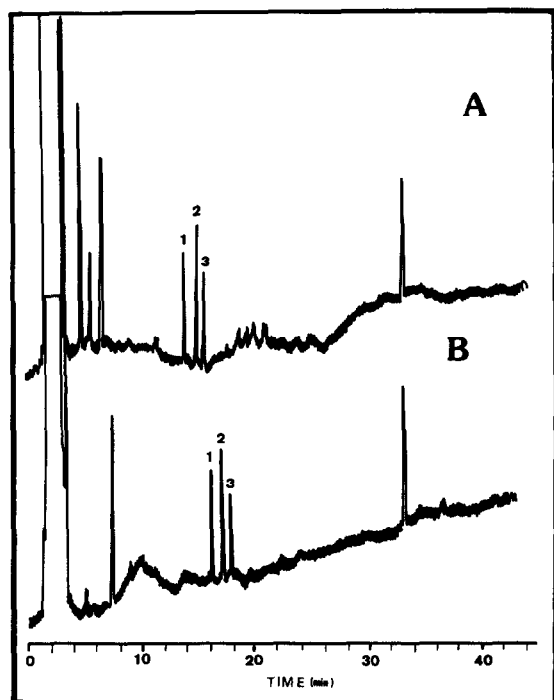


Fig. 5. Chromatograms obtained for sample 4 using two different capillary columns: (A) BP-5 and (B) DB-17. Peaks: 1 = α -HCH; 2 = γ -HCH; 3 = β -HCH.

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