Multiresidue Method for Some Pesticides in Lanolin by Capillary Gas Chromatography with Detection by Electron Capture, Flame Photometric, Mass Spectrometric, and Atomic Emission Techniques

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A method is described for the determination of pesticide residues in lanolin. Lanolin may be contaminated with pesticides due to treatment of sheep or storage of greasy wool in a warehouse. Residual pesticides were isolated by Florisil column chromatography and fractionated into two portions. Each fraction was injected into capillary gas chromatographs equipped with electron capture and flame photometric detectors. Results of recovery tests for organochlorine pesticides (BHC's, aldrin, dieldrin, and DDT's) and organophosphorus pesticides (diazinon and fenitrothion) ranged from 75% to 110% at two concentrations. Quantitation limits ranged from 0.01 to 0.05 ppm for organochlorine pesticides and 0.1 ppm for organophosphorus pesticides. Several lanolin samples were examined according to this method. An older lanolin sample was contaminated with several pesticides. A few unknown peaks were identified by the combination of capillary GC with mass spectrometry and atomic emission.

INTRODUCTION

There are many lanolin-containing cosmetics and over the counter (OTC) and prescription drugs. The FDA detected pesticide residues (FDA, 1988, 1989) in bulk lanolin supplies. The pesticides found included diazinon at 21 ppm, smaller amounts of DDE (a breakdown product of DDT), lindane, and other forms of hexachlorocyclohexane. To reduce the likelihood of contamination of the final products, it is necessary to monitor those residues in lanolin.

Lanolin is produced from sheep's wool grease. The presence of pesticides in lanolin may result from the following: sheep pesticide dips for control of parasitic infestations (Hirayama, 1982); pesticides sprayed on pastures for control of noxious insects; and application of insecticides for warehouse storage of greasy wool (Nagano Livestock Breeding Station, 1945). A multiresidue pesticide procedure is required because it is difficult to predict which pesticides will be found in imported lanolin.

Chromatographic methods for the determination of pesticides in vegetables or oily materials have been published (Martindale, 1988; Sapp, 1989). Selective detection by gas chromatography (GC) with electron capture detection (ECD) (Cessna, 1990) or flame photometric detection (FPD) (Miyahara, 1991) is currently used for pesticide analysis. A method was reported for a pesticide that is applied to cattle hair (Yeung, 1988). For pesticides in lanolin, a multiresidue method was proposed (Diserens, 1989), which includes solid-phase extraction and Sep-Pak C_{18} purification, but these methods are difficult to use when unknown contaminants are present, because pesticide identifications are limited to comparisons of retention times and responses with those of standards. Capillary GC with mass spectrometric detection (MSD) and atomic emission detection (AED) provides convenient identification of peaks in gas chromatography. Tentative identifications of the contaminants can be made with these detectors.

This paper describes a multiresidue method for pesticides in lanolin. The 10 structures of the pesticides chosen are illustrated in Figure 1. Residual pesticides were extracted with *n*-hexane, partitioned into acetonitrile, purified by Florisil column chromatography, and detected by capillary GC with AED, MSD, ECD, and FPD.

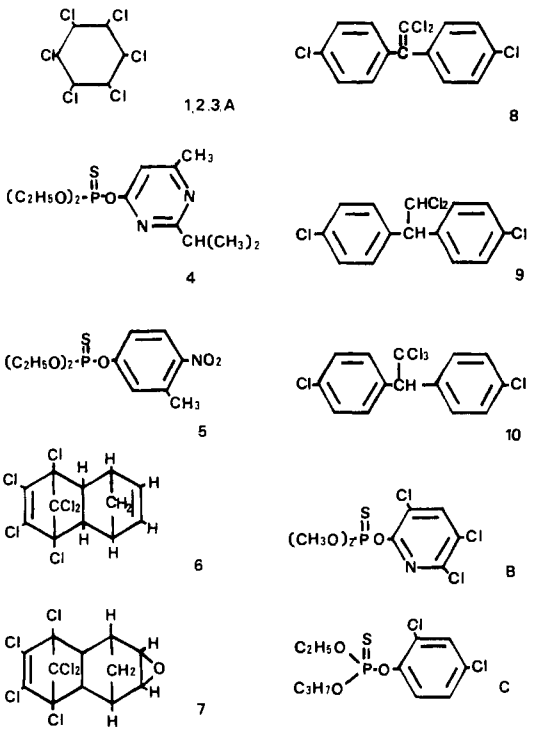

Figure 1. Structures of pesticides. 1, α-BHC; 2, β-BHC; 3, γ-BHC; A, δ-BHC; 4, diazinon; 5, fenitrothion; 6, aldrin; 7, dieldrin; 8, *p,p'*-DDE; 9, *p,p'*-DDD; 10, *p,p'*-DDT; B, chlorpyrifos; C, prothiofos.

EXPERIMENTAL PROCEDURES

Materials. Pesticide standards (Table I) were purchased from Wako Pure Chemical Co. (Some of the pesticides are suspected carcinogens. Handle them with care.) All organic solvents were of pesticide grade.

Florisil PR was activated at 130 °C overnight.

Lanolin samples (Japan pharmacopeial grade, low pesticide grade, purified lanolin, and cosmetic decolorized grade) were donated by several lanolin suppliers. Technical and chemical grade lanolins were purchased from Wako Chemical Co. Old lanolin had been stored for many years in our laboratory.

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Table I. Pesticides

pesticides	chemical name	purity, %
α-BHC (1)	a,a,e,e,e,e-hexachlorocyclohexane	>99
β-BHC (2)	e,e,e,e,e,e-hexachlorocyclohexane	>99
γ-BHC (3)	a,a,a,e,e,e-hexachlorocyclohexane	>99
diazinon (4)	*O,O*-diethyl *O*-(2-isopropyl-4-methylpyrimid-6-yl)phosphorothioate	>99
fenitrothion (5)	*O,O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate	>97
aldrin (6)	(1*R*,4*S*,5*S*,8*R*)-1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene	>97
dieldrin (7)	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-*exo*-5,8-dimethanonaphthalene	>98
p,p'-DDE (8)	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene	>99
p,p'-DDD (9)	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane	>98
p,p'-DDT (10)	1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane	>99

Table II. Gas Chromatographic Conditions

condition	eluting pattern	ECD	FPD	AED	MSD
inlet temp, °C	290	250	250	250	250
injection mode[a]	spls	spls	whole	spls	spls
waiting time, min	1	1		1	1
injection vol, μL	2	1	1	2	1
column liquid phase	MS	DB-1	DB-5	DB-1	DB-1
length, m	25	30	15	25	30
diameter (i.d.), mm	0.32	0.32	0.53	0.32	0.32
film thickness, μm	0.25	0.25	1.0	0.25	0.25
carrier gas	He	He	He	He	He
flow rate, mL/min	3	3	30	3	3
oven temp program,[b] °C	50	40	250[c]	40	40
	(1)	(1)		(1)	(1)
	[20]	[20]		[20]	[20]
	180	150		150	150
	(0.5)	(1)		(1)	(1)
	[8]	[4]		[4]	[4]
	280	210		210	210
detector temp, °C	290	280	255	250	270

[a] Spls denotes splitless injection mode. Whole denotes an injection without split. [b] Holding time and program rate are shown in parentheses (minutes) and brackets [°C/minute], respectively. [c] Isothermal.

Extraction. Lanolin (0.5 g) was added to a separatory funnel (50 mL) and dissolved in 10 mL of *n*-hexane. For the recovery studies, lanolin was spiked at this step with eight organochlorine pesticides at levels of 0.2 and 1 ppm based on lanolin and with two organophosphorus pesticides at levels of 1 and 2 ppm. Acetonitrile (20 mL) saturated with *n*-hexane was added to the *n*-hexane solution in the separatory funnel. Pesticides were extracted from *n*-hexane solution with two 20-mL portions of hexane-saturated acetonitrile. The acetonitrile extracts were combined and poured into a 1-L separatory funnel that contained 400 mL of 5% sodium chloride aqueous solution and 100 mL of *n*-hexane. After the separatory funnel was shaken, the aqueous phase was discarded. The organic phase was washed twice with 100-mL portions of water and dried over anhydrous sodium sulfate. The organic solvent was evaporated to about 10 mL under reduced pressure below 40 °C.

Florisil Column Chromatography. A slurry of *n*-hexane and Florisil (20 g) was added to a column (22 mm i.d. × 300 mm), and 10 g of sodium sulfate was placed on top of the Florisil. The concentrated extracts in *n*-hexane were poured into the column. Initially, 200 mL of a mixture of *n*-hexane and ether (95:5) was passed through the column (fraction A). Fraction B was isolated by passing 200 mL of ether through the column (fraction B). Each fraction was concentrated under reduced pressure and brought to 5 mL with *n*-hexane.

Gas Chromatography. The GC conditions are shown in Table II.

Electron capture detection (ECD): gas chromatograph, Shimadzu Model 9A equipped with splitter (Shimadzu Model SPL9A); detector current, 0.5 nA; attenuation, 10.

Flame photometric detection (FPD): gas chromatograph, Shimadzu Model 15A equipped with splitter (Shimadzu Model SPL 9A); flame gas hydrogen flow, 60 mL/min; air flow, 60 mL/min; optical filter, 526 nm.

Mass spectrometric detection (MSD): gas chromatograph, Hewlett-Packard Model 5890A coupled to mass spectrometer (Hewlett-Packard Model 5990B); ion source voltage, 70 eV. The mass spectrometer was operated in full scan mode.

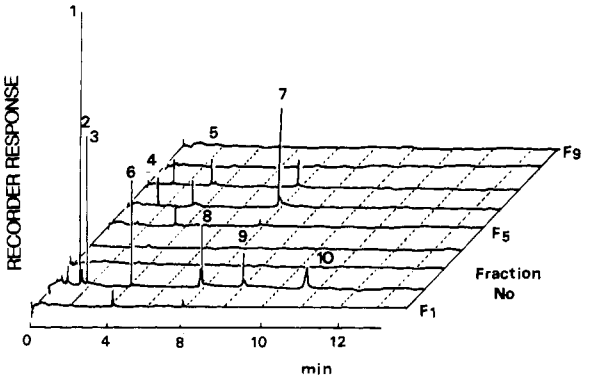

Figure 2. Eluting pattern of pesticides from Florisil column. 1, α-BHC; 2, β-BHC; 3, γ-BHC; 4, diazinon; 5, fenitrothion; 6, aldrin; 7, dieldrin; 8, *p,p'*-DDE; 9, *p,p'*-DDD; 10, *p,p'*-DDT.

Atomic emission detection (AED): gas chromatography, Hewlett-Packard Model 5890A coupled to atomic emission detector (Hewlett-Packard Model 5921A); cavity temperature, 250 °C.

Calibration. Standard solutions were prepared at four concentrations ranging from 0.001 to 5 μg/mL. Standard solutions suitable for the detector sensitivity were prepared. The external standard procedure was used. Calibration curves were obtained from the linear regressions of the concentrations of the three level standard solutions vs the peak areas. Calibration curves for the eight pesticides with the ECD were linear in the range 0.01–1 μg and those for the two pesticides determined by FPD were linear in the range 0.5–5 μg.

Eluting Pattern for Pesticides from Florisil Column. A mixture of 10 pesticides (2 μg of each) in *n*-hexane (2 mL) was deposited on the Florisil column according to the procedure described under Florisil Column Chromatography. To establish the procedure, 50-mL fractions were collected. The first eluent was *n*-hexane containing 5% diethyl ether (fractions 1–3). The second eluent was diethyl ether (fractions 4–8). The fractions were analyzed by GC with ECD. The cleanup procedure used for lanolin was a modification of the AOAC method (AOAC, 1990). The results are shown in Figure 2. BHC's (1–3), DDT (10) and its degraded compounds (8, 9), and aldrin (6) were found in fractions 1–3. Fractions 4–8 contained dieldrin (7), fenitrothion (5), and diazinon (4).

RESULTS AND DISCUSSION

Quantitative Analysis by GC with ECD. To evaluate the cleanup procedure, recovery tests were undertaken with GC/ECD. As shown in Table III, recoveries for eight pesticides at 0.2 and 1 ppm ranged from 75% to 99% with CV% of 5.4–10.1 and from 82% to 110% with CV% of 4.0–9.6, respectively. No significant differences were noted.

Typical gas chromatograms with ECD for eight pesticides are shown in Figure 3. Chromatogram c gave several unknown peaks. However, it is difficult to identify the peaks that appeared in chromatograms with ECD because it is responsive to many compound classes. From those

Table III. Overall Recovery[a] of Pesticides

	spiking level					
	0.2 ppm		1 ppm		2 ppm	
pesticide	recov, %	CV%	recov, %	CV%	recov, %	CV%
α-BHC	84	10.9	110	9.6		
β-BHC	78	6.6	88	5.2		
γ-BHC	89	8.3	102	7.7		
aldrin	77	8.4	97	6.8		
dieldrin	76	4.2	94	4.9		
p,p'-DDE	99	10.1	98	11.1		
p,p'-DDD	75	5.4	83	6.3		
p,p'-DDT	94	4.3	82	4.0		
diazinon			90	6.4	95	5.6
fenitrothion			93	5.5	98	5.1

[a] Values are means of three determinations.

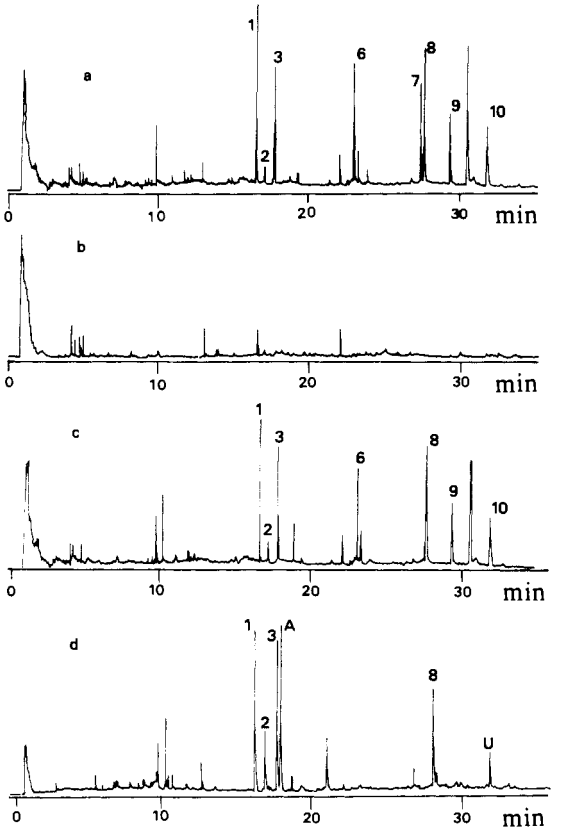

Figure 3. Typical chromatograms detected by GC with ECD of standards (a), control lanolin (fraction A) (b), fortified 0.2 ppm (fraction A) (c), and sample 1 (fraction A) (d). Numbers on top of peak refer to structures in Figure 1.

results, lower limits of quantitation (LOQ) for organochlorine pesticides were calculated as shown in Table IV.

Quantitative Analysis by GC with FPD. Recovery tests were performed with FPD to evaluate the procedure for fraction B. As shown in Table III, recoveries for two organophosphorus pesticides at 1 and 2 ppm ranged from 90% to 98% with CV% of 6.4 and 5.1, respectively. No significant differences were noted.

Typical gas chromatograms with FPD for two pesticides are shown in Figure 4. From those results, the LOQ for two organophosphorus pesticides (4, 5) in fraction B was 0.1 ppm (Table IV). This level is the same as that reported for other organophosphorus pesticides (Miyahara, 1991).

The combination of the selective FPD with the resolution of the fused capillary column was used to identify peaks in fraction B. The chromatogram (Figure 4d) of fraction B (sample 3) gave a peak that is tentatively identified as diazinon (4) because the retention time is identical to the

Table IV. LOD[a] and LOQ[b] (Nanograms) for ECD, FPD, AED, and MSD

	detector			
	ECD[c]	FPD[c]	AED[d]	MSD[d,e]
α-BHC	0.01		0.2[f]	0.6
β-BHC	0.05		2[f]	3
γ-BHC	0.01		0.4[f]	1
aldrin	0.01		0.8[f]	0.6
dieldrin	0.05		1[f]	0.5
p,p'-DDE	0.03		1[f]	1
p,p'-DDD	0.03		1[f]	0.6
p,p'-DDT	0.03		1[f]	1
diazinon		0.1	0.6,[g] 0.3[h]	0.6
fenitrothion		0.1	0.7,[g] 0.3[h]	2

[a] LOD is defined peak as 3 times the noise level. LOD can be calculated by dividing LOQ by 3. [b] LOQ is defined peak as 10 times the noise level. [c] LOQ. [d] LOD. [e] Operated in full scan mode. [f] Determined at 479 nm (chlorine monitor). [g] Determined at 178 nm (phosphorus monitor). [h] Determined at 181 nm (sulfur monitor).

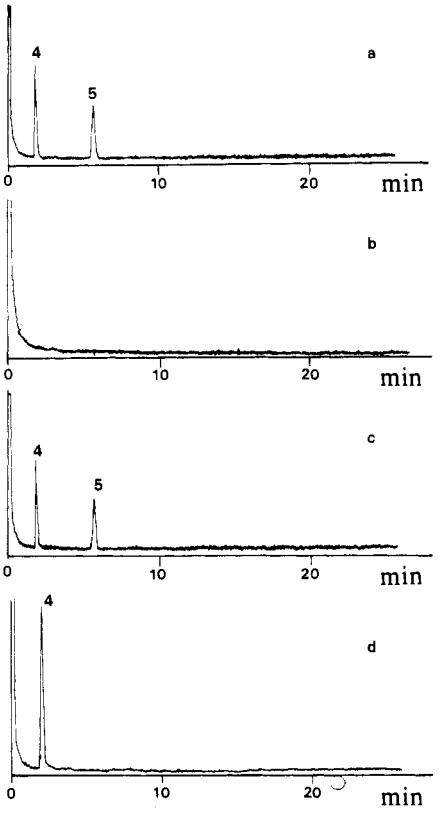

Figure 4. Typical chromatograms detected by GC with FPD of standards (a), control lanolin (fraction b) (b), lanolin spiked at 1 ppm (fraction b) (c), and sample 3 (fraction b) (d). Numbers on top of peak refer to structures in Figure 1.

standard. Other results are shown in Figure 5. Chromatogram a of fraction A (sample 1) gave U, B, and C. Chromatogram b of fraction B (sample 1) gave peak 4, B, and C. From a comparison of the retention times with those of standard organophosphorus pesticides, peaks B and C were tentatively identified as chlorpyrifos (B) and prothiofos (C), respectively (FDA, 1991).

Qualitative Analysis by GC with AED. AED is a promising gas chromatographic detector for pesticide residues (Quimby and Sullivan, 1990). The AED system provides quantitative information about selected elements in the eluting compounds (Diserens, 1989). Since the molecular structures of pesticides contain a variety of elements, AED is convenient for compound identification (Sullivan and Quimby, 1990). Typical gas chromatograms for 10 pesticide analytical standards (3 ng) are shown in

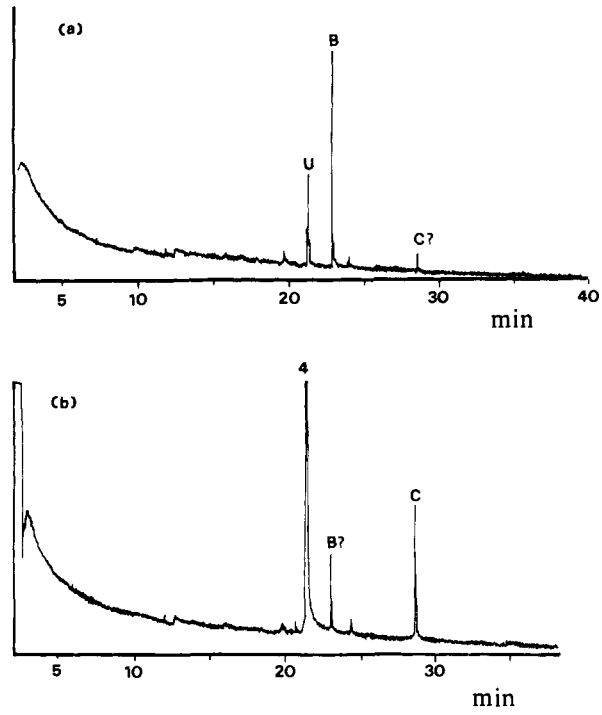

Figure 5. Gas chromatograms of samples by GC with FPD of sample 1 (fraction A) (a) and of sample 1 (fraction B) (b).

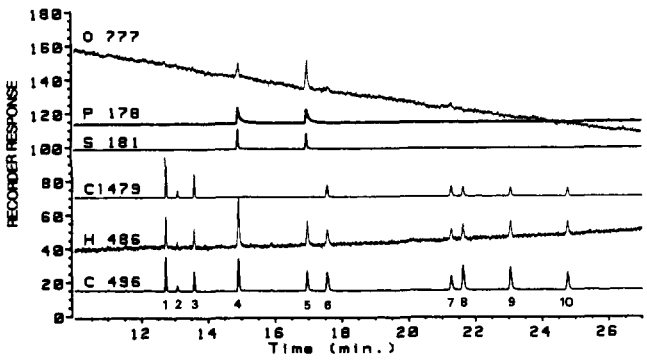

Figure 6. Set of chromatograms of standards detected by GC with AED. Chromatograms C, H, Cl, S, P, and O of standards (3 ng for each pesticide) were obtained at 496 (carbon monitor), 486 (hydrogen monitor), 478 (chlorine monitor), 181 (sulfur monitor), 178 (phosphorus monitor), and 777 nm (oxygen monitor), respectively. Numbers under peak refer to structures in Figure 1.

Figure 6. Many elements can be monitored by AED. In this study, chlorine, sulfur, and phosphorus were selected because elemental information can help characterize the compound in the peak. As shown in Figure 7, calibration curves are linear in the range 2–5 ng. The data indicate that sensitivities depend on the element selected (Abdillahi, 1990).

Sensitivity for chlorine was the lowest of the three elements chosen. LODs were determined as shown in Table IV. LODs for the organochlorine compounds detected by AED were 100-fold lower than those for ECD. The sensitivities of AED and ECD depend upon the structure of the compound. The AED response for α-BHC (1) is greater than the response from an equal quantity of p,p'-DDT (10) in this study. The order of sensitivity detected by AED was the same as that of the ECD. LODs for BHC isomers differ from each other. This means that response factors for those chlorine compounds were not constant, in contrast to the results obtained for carbon, hydrogen, nitrogen, and oxygen (Sullivan and Quimby, 1989).

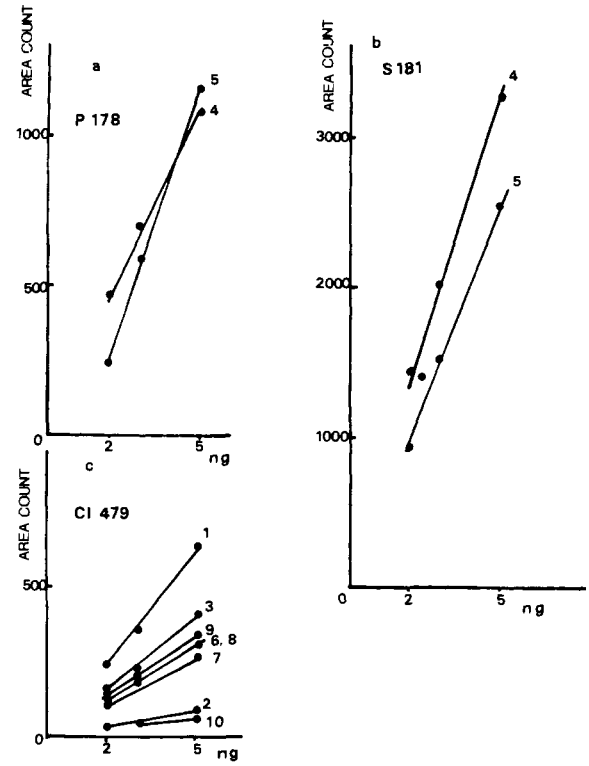

Figure 7. Calibration curves of pesticides detected by GC with AED: (a) calibration of diazinon (4) and fenitrothion (5) detected at 178 nm (phosphorus monitor); (b) calibration of diazinon (4) and fenitrothion (5) at 181 nm (sulfur monitor); (c) calibration of eight organochlorine pesticides (1, α-BHC; 2, β-BHC; 3, γ-BHC; 6, aldrin; 7, dieldrin; 8, p,p'-DDE; 9, p,p'-DDD; 10, p,p'-DDT) at 478 nm (chlorine monitor).

As shown in Table IV, LODs for diazinon (4) and fenitrothion (5) at 178 nm (phosphorus monitor) are 0.6 and 0.7 ng, respectively. Thus, the sensitivity of the phosphorus monitor was slightly lower than that of FPD.

The sensitivity of the sulfur monitor at 181 nm was the highest of the three elements compared in this study. The LOD for diazinon (4) and fenitrothion (5) was 0.3 ng. It is well-known that a relationship between the response of the sulfur mode FPD and the concentration of the sulfur-containing compound is nonlinear. However, the response of the AED sulfur monitor at 181 nm was linear. This result is consistent with the work done with sulfur compounds in fossil fuels (Skelton et al., 1989). The AED can be used as a gas chromatographic detector for qualitative analysis.

A gas chromatogram of sample 1 (fraction A) is shown in Figure 8 with chlorine detection at 479 nm. Peaks 1, 2, 3, and 8 were identified as α-, β-, γ-BHC (1, 2, 3), and p,p'-DDE (8), respectively. Chromatographic identifications were obscured in the chromatograms obtained with carbon detection at 496 nm and hydrogen detection at 486 nm because coextractives interfered with the peaks. Peaks A, B, and U were unknowns. Peak A, which is tentatively identified as δ-BHC by GC with ECD, contained chlorine, but no sulfur or phosphorus. Peak B, which was tentatively identified as chlorpyrifos, contained chlorine, sulfur, and phosphorus. Those results agree with the conclusions based upon other detectors.

Qualitative Analysis by GC with MSD. Identification by MSD is now a standard and powerful procedure. This procedure provides mass spectrometric information (base ion peak, molecular ion peak, and molecular weight) about the compound. Suitable cleanup procedures are needed to obtain low backgrounds. If those conditions

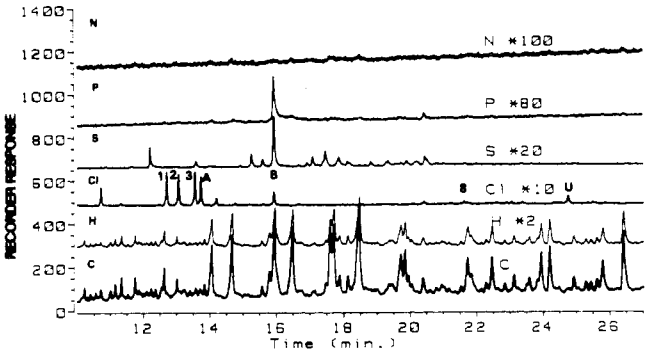

Figure 8. Set of chromatograms of sample detected by GC with AED. Chromatograms C, H, Cl, S, P, and N of sample 1 (fraction A) were obtained by the monitors at the same wavelength as in Figure 6 and by nitrogen monitor at 174 nm. Numbers beside element symbols indicate multiplier factor for recording sensitivity. Numbers at the peak tops of chromatogram Cl refer to structures in Figure 1. Peak U is an unknown peak.

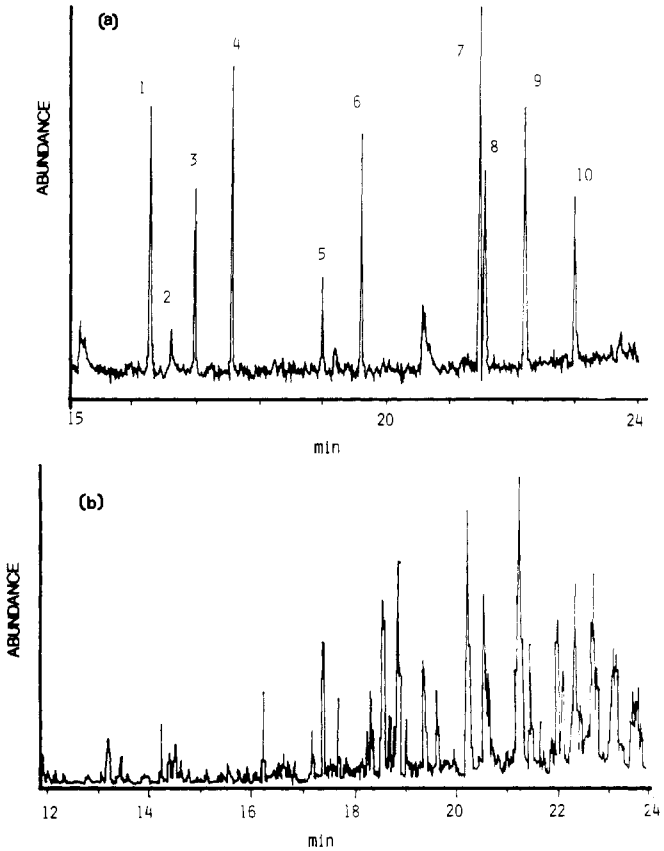

Figure 9. Chromatograms of standards and sample detected by GC with MSD: (a) chromatogram of 10 standards (3 ng for each pesticide 1–10); (b) chromatogram of sample 1 (fraction A). Numbers at the peak tops of chromatogram a refer to structures in Figure 1.

are fulfilled, this procedure is appropriate for identification of eluting substances.

MSD was performed to identify the peaks obtained by ECD, AED, and FPD. The total ion monitoring chromatograms of the analytical standards and the extract from lanolin are shown in Figure 9. Chromatogram a is essentially the same as that obtained by ECD. Peaks for all pesticides could be observed. On the contrary, the total ion chromatogram b obtained for the lanolin extract did not yield information about the pesticides in the sample. The procedure we employed was not suitable for detection by total ion monitoring. Therefore, selected ion chromatograms were utilized. Chromatography with ECD

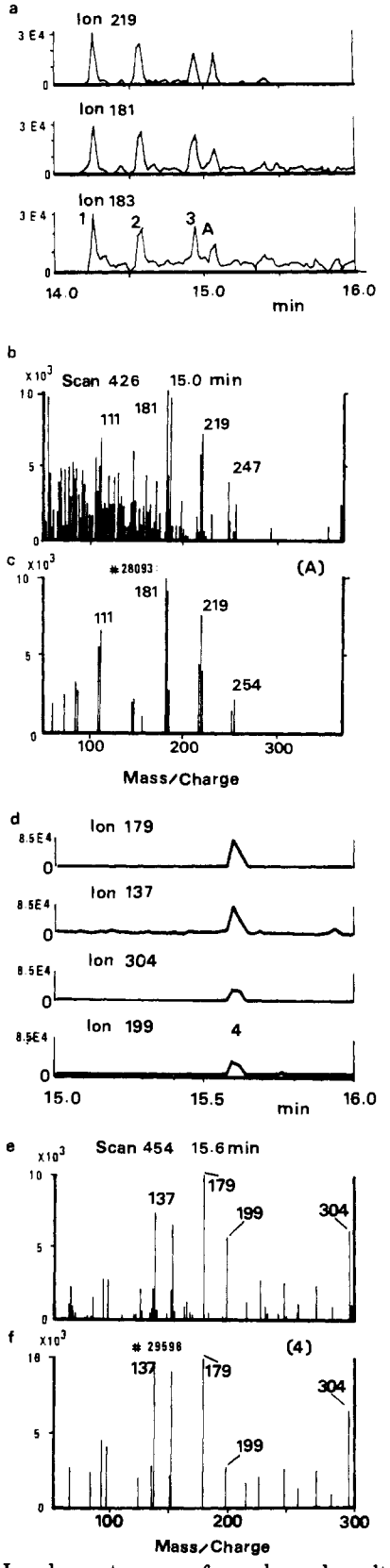

Figure 10. Ion chromatograms of samples and results of library search: (a) set of ion chromatograms at ion (m/z) 219, 181, and 183 of sample 1 (fraction A); (b) mass spectrum of sample 1 (fraction A) at 15.0 min; (c) mass spectrum of δ-BHC(A) in NBS library; (d) set of ion chromatograms at ion (m/z) 179, 137, 304, and 199 of sample 1 (fraction B); (e) mass spectrum of sample 3 (fraction B) at 15.6 min; (f) mass spectrum of diazinon (4) in NBS library.

or AED indicated that this sample contained some BHC's (1, 2, 3). Monitoring ions were chosen on the basis of

spectra in the NBS mass libarary for GC mass detection. Four main peaks, which are shown in Figure 10a, were observed in every ion chromatogram and corresponded to those in chromatograms obtained by AED and ECD. Peaks 1, 2, and 3 were confirmed as α-, β-, and γ-BHC (1, 2, 3) by comparing their mass spectra with those of standards. The mass spectrum of peak A, which is shown in Figure 10b, along with the retention time indicated that this compound was δ-BHC (A).

Peak 4 (fraction B of sample 3) in the ion chromatogram (Figure 10d) was identified as diazinon (4) by GC with mass spectrometric detection. The ion chromatograms for e/z 179, 137, 304, and 199 gave main peaks at the retention time of 15.6 min. The mass spectrum of the peak at 15.6 min is shown in Figure 10e with that of the standard diazinon (Figure 10f).

Cleanup Procedure for Detection. Initially, we tried a cleanup procedure based upon the Florisil column chromatography with a 15% ether and 85% *n*-hexane eluent. This procedure was not adequate for the determination of residual pesticides by ECD because the eluent contained many coextractives and nonvolatile materials. These extracts caused contamination of the gas chromatograph, and reproducible results were difficult to obtain after several injections without daily cleaning of the gas chromatograph (Szelewski, 1989).

A cleanup procedure that included charcoal column chromatography was not suitable for AED. Strong emission by carbon interferes with observation of less responsive elements. The high background resulted in appearance peaks due to the strong emission of carbon. At this point, further study is required.

Contamination of Pesticides in Lanolin. Ten samples were examined. The old lanolin was contaminated with organochlorine and phosphorus pesticides at low levels (BHC's, 0.8–1.9 ppm; organophosphorus pesticides, 0.63–2.6 ppm). The chemical grade lanolin, technical grade lanolin, some purified lanolin samples, and some low pesticide grade lanolin samples contained low levels of organophosphorus pesticides (2–6 ppm). The contamination levels in Japan were less than those in Switzerland (Diserens, 1989) and the United States (FDA, 1988). All pharmacopeial lanolins, cosmetic decolorized grade lanolin, and some low pesticide grade lanolin, which were recently produced, were free of pesticides.

CONCLUSION

The modified AOAC cleanup method for pesticides in fatty food (AOAC, 1990) was employed for detection and quantitation of residual pesticides in lanolin by ECD or FPD. LOQs were 0.01–0.05 ppm for organochlorine pesticides and 0.1–0.5 ppm for organophosphorus pesticides. It is possible to tentatively identify unknown peaks by AED, which provides information on the elemental content of the peaks. This information along with retention time data aids in identification. The chlorine monitor at 479 nm (AED) exhibited sensitivity differences among the BHC isomers. The order of LOD for the detectors was as follows: ECD < FPD < AED < MSD.

Identification of unknown peaks by MSD cannot be done because of excessive coextractives. In our attempts to detect a wide variety of pesticides, it was inevitable that various polar substances would also be isolated; therefore, the MSD could not be used. However, in the case of low background or high levels of pesticides, definitive identification was possible.

ACKNOWLEDGMENT

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