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Short communication

Determination of organochlorine pesticides in skins and leather by gas chromatography

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Abstract

The simultaneous determination of residues of lindane (γ-HCH) and 10 other organochlorine pesticides (OCPs) in skins and leather was carried out by gas chromatography (GC) with electron-capture detection (ECD). GC with mass spectrometric detection was used to identity confirmation. Samples were extracted with hexane. The extracts were concentrated, and cleaned up on a Florisil column. Dibromooctafluorobiphenyl was added as internal standard. Hide fortifications of 0.5 and 5.0 ppm yielded average lindane recoveries of 98% and 96%, respectively. OCPs were determined in 57 samples of skins purchased from American, European and African countries in 1996–1997. OCPs were not detected in any of the American and European samples. Residues of lindane were found in 56% of African samples.

Keywords: Leather; Skins; Pesticides; Organochlorine compounds; Dibromooctafluorobiphenyl

1. Introduction

Several customer protection eco-labels for leather and leather goods have been established in Germany and other European countries [1]. Most of these labels include maximum allowable limits for aldrin, dieldrin, lindane, α-hexachlorocyclohexane (α-HCH), β-HCH, δ-HCH, heptachlor, heptachlor-epoxide, DDD, DDE and DDT.

Air drying of hides is one of the traditional methods of skin preservation. Drying is practised in areas with hot and dry climates, such as Africa. However, dried skins are susceptible to insect attack. The use of DDT and lindane to protect raw hides from insect damage was reported as early as 1954 [2]. Another organochlorine pesticide (OCP), dieldrin, was introduced to provide protection against ectoparasites [3]. Lindane was one of the most commonly employed insecticides for protecting hides and skins, at least until the 1990s [4,5]. However, most of the registered uses of DDT and other OCPs were banned in most countries since the 1970s because of widespread environmental contamination due to their persistence. The employ of DDT should be restricted to essential public health usage.

Very little is known about the residual contents of OCPs in skin and leather. Some workers have reported methods for the determination of HCH isomers mainly in effluents and solid wastes from the leather industry but also in hides. The gas chromatography–electron-capture detection (GC–ECD) technique was applied by Galassi et al. [6], Golob et

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al. [5], and Bugby et al. [8]. GC–mass spectrometry (MS) was used by Corning et al. [7]. However, no method for simultaneous determination of OCPs specified in eco-labels has been reported. For the world-wide trade with skins, leather and leather articles it is important to know which insecticides have been applied. Tanners are a passive receiver of residues of insecticides but they have to ensure compliance of finished leather with regulations such as customer protection eco-labels.

The objective of this paper is to describe a rapid and brief method for the simultaneous determination of OCPs in skins and leather in order to satisfy the requirements of customer protection eco-labels. This work deals with the application of well-known and easily available techniques for the analysis of skins and leather, samples which are very rarely studied.

2. Experimental

2.1. Instrumentation

(a) GC–ECD system: a Konik KNK-3000 fitted with a ^{63}Ni ECD system. A fused-silica capillary column, BPX-5 (30 m×0.22 mm I.D.) bonded phase, 0.25 μm film thickness, was used with hydrogen as carrier gas at 1.3 ml/min. Nitrogen at 70 ml/min was used as make-up gas. The oven temperature was held at 140°C for 1 min, programmed to 200°C at 6°C/min and then held for 3 min, followed by an increase at 5°C/min to 250°C, then an increase at 10°C/min to 280°C with a final hold at 280°C for 3 min. A 1-μl volume was injected splitless, with the split valve closed for 30 s. The injection port and detector temperatures were 250°C and 350°C, respectively.

(b) GC–MS system: Hewlett-Packard gas chromatograph HP G1801B GCD Plus equipped with an integrated electron ionization detector. A fused-silica capillary column, HP-5 (30 m×0.25 mm I.D.) bonded phase, 0.25 μm film thickness, was used with helium as carrier gas at 1.0 ml/min. The oven temperature was held at 140°C for 1 min and programmed to 280°C at 7°C/min with a final hold at 280°C for 6 min. A 1-μl volume was injected splitless, with the split valve closed for 1 min. The injection port was held at a temperature of 250°C and the MS interface was at 300°C.

2.2. Reagents and standards

Certified standard solutions of OCPs, and the internal standard 4,4′-dibromooctafluorobiphenyl (DBOFB), were obtained from Supelco. Florisil Sep-Pak classic cartridges with 1 g of packing material were supplied by Waters. The solvents *n*-hexane and diethyl ether were of residue analysis Panreac (Spain).

2.3. Samples

Seventeen dried skins and 15 semi-processed (crust and wet-blue) hides from 10 different African countries were analyzed. Seventeen European and eight American raw hides were also analyzed. Samples were collected at Spanish tannery factories within the period 1996–1997.

2.4. Procedure

Samples were left for 48 h in a conditioning room at 23°C and 50% relative humidity and then cut into small pieces. A 5-g sample was Soxhlet extracted for 4 h using *n*-hexane. The extract was concentrated to approximately 2 ml by a rotary evaporator under vacuum. A Florisil cartridge was prewashed with 10 ml hexane. Then, the concentrated residue was transferred to the cartridge. When this was eluted, the Soxhlet flask was rinsed twice with 2 ml hexane adding each rinse to the cartridge. Florisil was then eluted with 8 ml 6% diethyl ether in hexane. All eluates were collected in the same tube and DBOFB was added as internal standard. Each sample was then analyzed by GC–ECD. To confirm identification of a pesticide, some samples were also injected into the GC–MS system. The total ion chromatogram was recorded and the mass spectrum was matched versus the spectrum library for the pesticide.

3. Results and discussion

A recovery study was performed to determine

method quality. A sample of fresh European cowhide was analyzed to verify that it did not contain OCPs. This blank skin sample was cut into small pieces. Eight portions of 5 g were respectively transferred to eight filter paper thimbles and then were each spiked with 1 ml of a standard solution of OCPs in hexane. The spiked samples were covered with a thin layer of cotton wool to prevent losses of OCPs during solvent evaporation. The solvent was allowed to evaporate at 23°C for 24 h. The recovery study was performed at two levels: 0.5 and 5 mg/kg. These levels were selected because they covered the range of the main customer protection eco-labels.

The average recoveries were greater than 85% in all cases, except for DDT and δ-HCH for which the recoveries were 75% and 76%, respectively (Table 1).

The limits of detection (LODs) were calculated as the amount of analyte that would give a signal three times the baseline noise. The LODs determined with GC–ECD are reported in Table 1.

It is well known that some compounds other than chlorinated ones respond to ECD. Among these are the phthalate esters and the organic acids. Not cleaned hexane extracts of hides contain high amounts of natural fats and fatty acids that may obscure pesticide peaks. These potentially interfering substances are removed by Florisil clean-up. Fig. 1 shows a chromatogram of incurred pesticides in a cowhide from Africa. This real sample was chosen for illustration because it contained six of the 11 targeted OCPs. Although hides often have more than 3% of fats and similar substances that are soluble in hexane, it can be seen from Fig. 1 that the chromatogram of the sample treated with Florisil has a clean baseline and that the few peaks due to co-extractives do not interfere. The peak at 14.9 min was identified by GC–MS as chlorpyrifos, a non-forbidden phos-

Table 1
Limits of detection and recoveries of 11 OCPs added to a hide sample

Pesticide	LOD (ng/g)	% R.S.D. (n=4)	Added (μg/g)	Recovery (%)	% R.S.D. (n=4)
α-HCH	5	±6	0.5	95	±3
			5.0	96	±1
β-HCH	12	±6	0.5	94	±3
			5.0	94	±3
Lindane (γ-HCH)	5	±6	0.5	98	±4
			5.0	96	±2
δ-HCH	8	±6	0.5	78	±9
			5.0	74	±4
Aldrin	5	±13	0.5	87	±5
			5.0	96	±2
Heptachlor	10	±6	0.5	88	±4
			5.0	97	±4
Heptachlor-epoxide	7	±5	0.5	88	±3
			5.0	92	±2
Dieldrin	7	±3	0.5	86	±3
			5.0	85	±5
4,4′-DDT	19	±18	0.5	76	±5
			5.0	74	±9
4,4′-DDD	9	±4	0.5	92	±8
			5.0	94	±8
4,4′-DDE	6	±6	0.5	84	±5
			5.0	94	±3

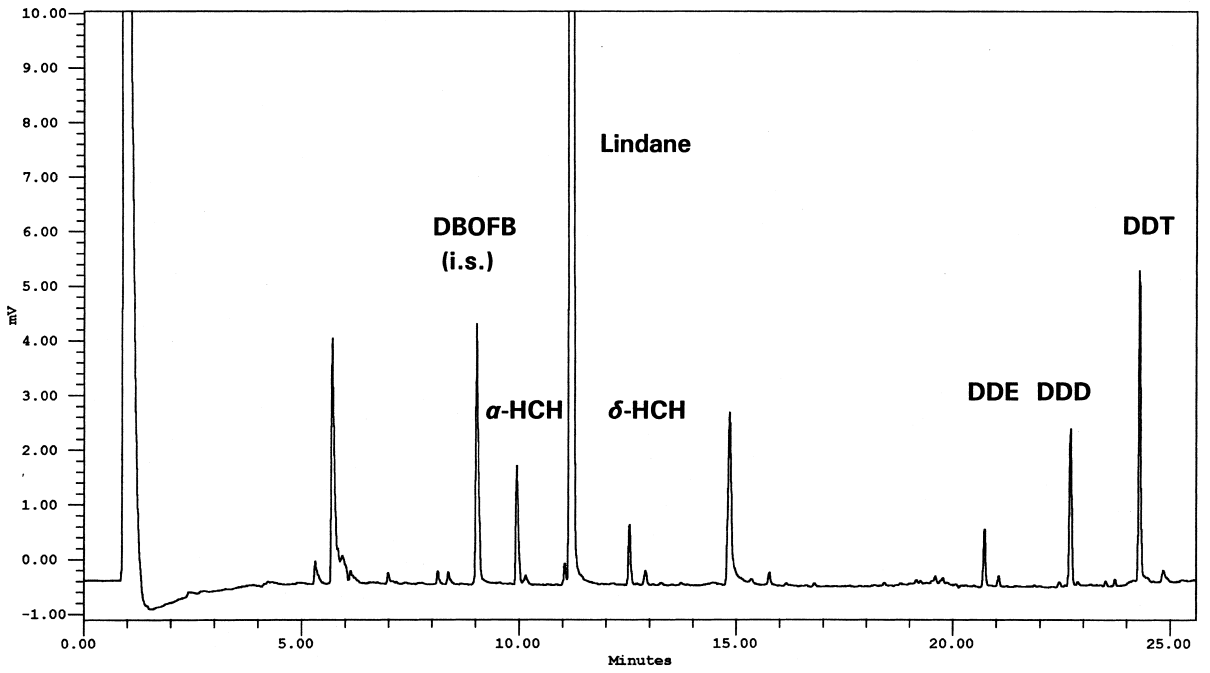

Fig. 1. GC–ECD chromatogram of a dried cow skin. For experimental conditions, see Section 2. α-HCH, 0.1 mg/kg; lindane, see Fig. 2; δ-HCH, 0.1 mg/kg; DDE, 0.04 mg/kg; DDD, 0.3 mg/kg; DDT, 0.8 mg/kg.

phoro-chlorinated insecticide. Fig. 2 shows a chromatogram of a duplicate of the same cowhide sample. An aliquot of the cleaned extract was diluted with hexane prior to the addition of DBOFB in order to adjust the area of the peak of lindane to the range of the calibration plots.

The 11 targeted OCPs were determined in 57 samples of skins purchased in 1996–1997 from European, American and African suppliers.

OCPs were not detected in any of the European and American samples. Most African samples (63%) contained residues of OCPs. Among pesticide residues identified, lindane was detected in 56% of African hides, α-HCH in 34%, DDT, DDD and DDE in 13%, β-HCH in 9%, and δ-HCH in 3%. In none of the samples did the total DDT content (DDT+DDD+DDE) reach the value of 1.5 mg/kg. The maximum level of lindane was 258 mg/kg. Eighteen percent of dried skins exceeded the 25 mg/kg level. These high amounts suggest that lindane is still used by some suppliers for protecting dried skins from insect attack during storage. Forty-four percent of African samples ranged from 0.5 to 10 mg/kg of total OCPs. These relatively low amounts could be attributed to residues from the insecticides used to control ectoparasites on the living animals [3].

Aldrin, dieldrin, heptachlor and heptachlor-epoxide were not detected in any sample.

4. Conclusions

GC–ECD provides a rapid, sensitive and highly specific method for determining OCPs in raw hides and leather. Sample preparation is as simple as extraction, Florisil clean-up and internal standard addition. GC–MS allows the reliable confirmation of analyte identity.

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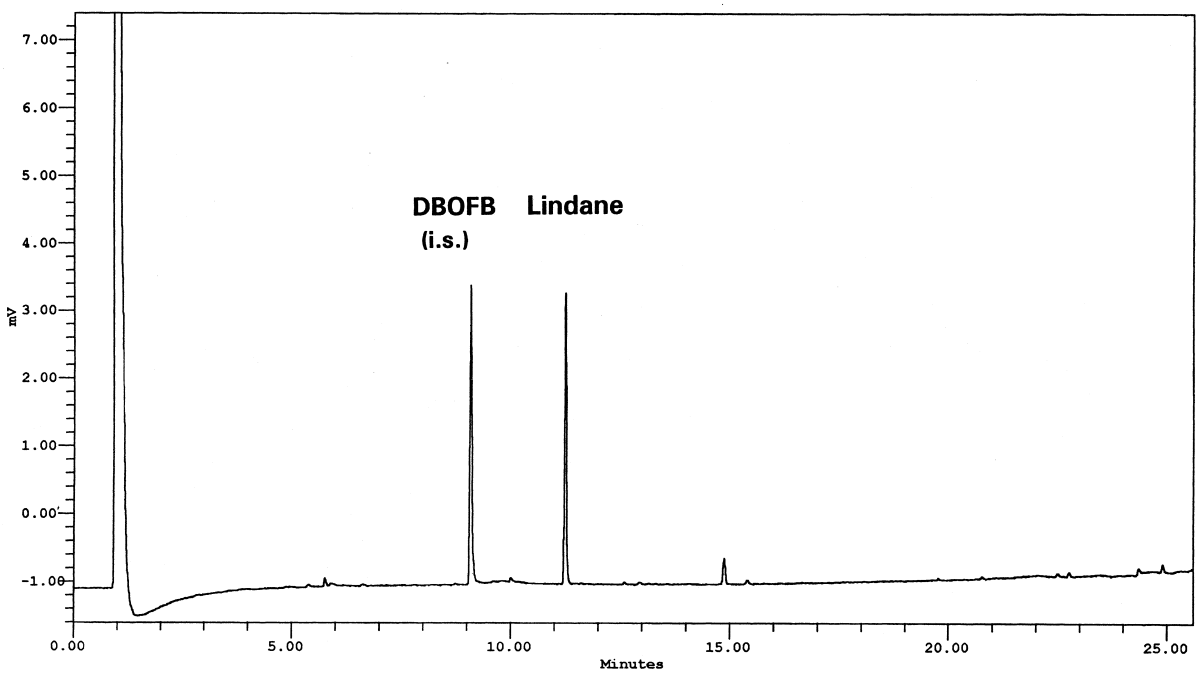

Fig. 2. GC–ECD chromatogram of the same sample of Fig. 1, diluted with *n*-hexane before DBOFB addition. For experimental conditions, see Section 2. Lindane, 8.5 mg/kg.

References

[1] G. Nickolaus, Proceedings of the XXIII IULTCS Congress, Friedrichshafen, 1995.
[2] R.L. Sykes, J. Am. Leather Chem. Assoc. 50 (1955) 312.
[3] R.G.H. Elliot, FAO Agricultural Services Bulletin, No. 67, FAO, Rome, 1985.
[4] J.H. Sharphouse, Leather Technician's Handbook, Leather Producers' Association, Northampton, 1989, pp. 16–17.
[5] P. Golob, F.V. Robinson, S. Gutu, J. Soc. Leather Tech. Ch. 76 (1992) 83.
[6] S. Galassi, A. De Paolis, R. Marchetti, Acqua Aria 6 (1983) 601.
[7] D.R. Corning, N.J. Cory, R.L. Sykes, J. Soc. Leather. Tech. Ch. 77 (1993) 3.
[8] A. Bugby, C. Parbery, R.L. Sykes, C.D. Taylor, J. Soc. Leather Tech. Ch. 74 (1990) 134.