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Determination of 21 organochlorine pesticides in tree leaves using solid-phase extraction clean-up cartridges

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Abstract

A method to determine 21 organochlorine pesticides (OCPs) in tree leaves [chestnut (*Castanea sativa*), hazel (*Corylus avellana*), oak (*Quercus robur*) and walnut tree (*Juglans regia*)] based on microwave-assisted extraction (MAE) followed by solid-phase extraction (SPE) clean-up is described. After extraction with hexane:acetone (50:50), four different sorbents (Florisil®, tandem Florisil® + alumina, silica and ENVI™-Carb) were assayed for the clean-up step. Pesticides were eluted with 5 mL of hexane:ethyl acetate (80:20) and determined by gas chromatography and electron capture detection (GC–ECD). Carbon was the sorbent, which provided colourless eluates and chromatograms with less interferent compounds. Analytical recoveries obtained were ca. 100% for all the studied pesticides with this sorbent.

Keywords: Organochlorine pesticides; Tree leaves; Microwave-assisted extraction

1. Introduction

Organochlorine pesticides (OCPs) have been widely used in agriculture. They have been effective in the control of pests and diseases and due to their low biodegradability and persistence they have become an important group of contaminants in the environment. Moreover, these chemicals are very toxic, and they are known to induce cancer and be endocrine disrupters in several organisms, so they result to be a significant risk to natural ecosystems and human health [1]. Although the use of most organochlorine pesticides have been banned or restricted in industrialized countries, they are still detected in the environment [2,3] because of their former use and spill out, high persistence and low biodegradability.

Contaminant levels in vegetation samples can be used as indicators of environmental pollution as plants can suffer adhesion and absorption of compounds from soil and deposition and absorption of volatile compounds from atmosphere. Previous studies have shown that different organs of the plant present different accumulation pattern of pesticides, showing the following sequence of contamination levels: leaves > stalks > roots [4]. This can be attributed to the lipid content of the tissue and to atmospheric deposition [5]; furthermore as pesticides are semivolatile compounds, they volatilize from soil increasing their concentration in the atmosphere close to the plant [6]. Therefore, leaves can be used to biomonitor atmospheric contamination being possible studies overlong periods of time on global, regional or local levels [7].

In last years, new analytical procedures for the determination of pesticides are in use [8]. These new techniques have advantages over conventional methods with respect to solvent consumption, time of analysis, sample amount requirements and automation feasibilities. The analytical methods used to monitor pesticide residues require the extraction and isolation of pesticides from the studied matrix and a final determination with chromatographic procedures [9]. In the case of complex matrices, such as plant materials, the presence of interferences may obscure the analytical signal of the stud-

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ied compounds. Therefore, most sample pretreatments need clean-up steps to reduce the detection limits of the methods and to avoid inaccurate results in chromatographic determinations [10].

The clean-up is the most laborious step in most analytical procedures since OCPs have to be accurately separated from the bulk of the matrix. Solid-phase extraction (SPE) using cartridges filled with sorbents has been established as an important clean-up technique which compared other preparation procedures offers lower costs, reduced processing times, substantial solvents savings and simpler processing procedures [11]. Different type of sorbents, in particular Florisil® [7,12,13], silica [14–16] and alumina [17,18] have been used for separation of pesticides from biota co-extractives. Although silica is the most common material [19], in general it is not very efficient for the clean-up of vegetable extracts [9]. Florisil® have been often recommended for the purification of fruits and vegetables, but it has been seen that Florisil® cartridge clean up is not always adequate [20]. Florisil® can be replaced by alumina particularly for the analysis of fatty foods, but it has the disadvantage that some more polar pesticides are not quantitatively eluted from alumina columns [9]. Recently, increased attention is devoted to carbon systems [21–23].

In this work, tree leaves were extracted using MAE, which was followed by a clean-up step. The aim of this study was to compare four different SPE sorbents: Florisil®, a tandem of Florisil® and alumina, silica and carbon for the clean-up of OCPs in tree leaves. The analytical technique employed for the determination of OCPs was gas chromatography with electron capture detection (GC–ECD) due to the sensitivity and selectivity of ECD [24–26] followed by gas chromatography with mass spectrometry detector (GC–MS) for confirmation of the obtained results.

2. Material and methods

2.1. Samples

Leaves of four tree species, namely chestnut (*Castanea sativa*), hazel (*Corylus avellana*), oak (*Quercus robur*) and walnut tree (*Juglans regia*), were taken in a total surface of 5300 m^2 from A Coruña (NW Spain). Leaves were collected from approximately 1.6 m above the ground level. A sample (ca. 1 kg) was initially selected and subsequently reduced to 100 g following the quartering procedure. These units were cut into slices and then were lyophilised and ground. Finally samples were stored at room temperature in glass receptacles out of light exposure until their analysis, which was done within at least three months.

2.2. Reagents

2.2.1. Pesticide standards

A mix of organochlorine pesticides named "Appendix IX Organochlorine Pesticide Mix" (Supelco part number 46960U), containing: aldrin; α-HCH; β-HCH; δ-HCH; dieldrin; α-endosulfan; β-endosulfan; endosulfan sulfate; endrin; endrin aldehyde; γ-HCH; heptachlor; heptachlor epoxide (isomer B); methoxychlor; *p,p′*-DDD; *p,p′*-DDE and *p,p′*-DDT (2 mg mL^{-1} each one in toluene:hexane (1:1)), was obtained from Supelco (Bellefonte, PA, USA). Individual standards of endrin ketone, α-chlordane, γ-chlordane and 2,4,5,6-tetrachloro-*m*-xylene (TCMX) were also obtained from Supelco. Isodrin was purchased from ChemService (West Chester, PA, USA).

2.2.2. Solvents

Acetone, *n*-hexane 95%, dichloromethane and methanol 205 gradient quality were Super Purity Solvents from Romil (Cambridge, UK). Ethyl acetate (PAR) for instrumental analysis was from Panreac (Barcelona, Spain).

2.2.3. Sorbents

Superclean™ ENVI™ Florisil® SPE Tubes 6 mL (1 g), Superclean™ LC-Si SPE Tubes 6 mL (0.5 g), ENVI™-Carb of 100 m^2 g^{-1} packing 12 mL (1 g) were from Supelco. Alumina for column chromatography was from Sigma (St. Louis, MO, USA).

Alumina was pretreated before its use. Soxhlet extraction of alumina was performed with dichorometane:methanol (2:1) during 12 h and then another 12 h with dichloromethane:hexane (30:70). Once dried, alumina was activated at 350 °C for 12 h and further deactivated with Milli-Q water (5%).

2.3. Materials and apparatus

Soxhlet and thermostatic bath (Precis-Bat S-147-200) from JP Selecta (Abrera, Barcelona, Spain) were used. Microwave extraction was carried out using a laboratory microwave oven (Anton Paar Multiwave, Graz, Austria) equipped with a built-in magnetic stirrer, a fibre-optic temperature sensor, a pressure sensor and a basic six-position extraction rotor.

A rotary evaporator Büchi R-3000 (Büchi Labortechnic AG, Flawil, Switzerland) was used in the evaporation step. A Visiprep® vacuum distribution manifold from Supelco was employed in the purification step. An ultrasonic bath Branson 3200 (Energieweg, The Netherlands) was used.

The GC equipment consisted of a Perkin Elmer (Norwalk, CT. USA) Autosystem XL chromatograph equipped with a ^{63}Ni electron capture detector (ECD), an autosampler, split–splitless injector, programmed pneumatic control and a computer running Turbochrom 4 data processor. For separation a 35% diphenyl 65% dimethylsiloxane capillary column (30 m × 0.25 mm × 0.25 μm) DB-35MS (J&W Scientific, Folsom, CA, USA) was employed.

GC–MS was carried out by a Trace 2000 GC coupled to a Thermo Finnigan Polaris-Q (Austin, TX, USA). The gas

chromatograph is equipped with a programmed temperature vaporisation (PTV) injector. Separation was achieved with a J&W DB-XLB (Agilent Technologies, Palo Alto, USA) (60 m × 0.25 mm × 0.25 μm).

2.4. Sample preparation

Tree leaf samples (0.3 g) were weighed into an extraction vessel and extracted with 15 mL of hexane:acetone (50:50) with stirring using the following microwave program: 1 min ramp from 100 to 800 W, a 4 min hold at 800 W, 0 W for 2 min, 1 min ramp from 100 to 800 W, a 4 min hold at 800 W. After cooling, vessels content was filtered through 0.6 μm glass fibre filter MN GF-6 (Macherey Nagel, Düren, Germany) and the filtrate was concentrated to ca. 1 mL using a rotary evaporator.

SPE cartridges were connected to a Visiprep® vacuum distribution manifold. Previously to their use cartridges were washed with elution solvent and dried with nitrogen during 30 min. Then cartridges were loaded with concentrated extract and pesticides were eluted with 5 mL of hexane:ethyl acetate (80:20). Finally eluates were evaporated to a drop in rotary-evaporator and got to dryness by a gentle nitrogen stream. Once dissolved in hexane, the solution was filtered through a syringe filter PTFE of 0.45 μm (Lida, Manufacturing Corp, Kenosha, WI, USA) and pesticides were determined by gas chromatography and electron capture detection (GC–ECD).

2.5. Chromatographic procedure

Helium (99.999%) was used as carrier gas flowing at 1.2 mL min^{-1}. The oven temperature was programmed from 60 °C (1 min) to 220 °C at a rate of 25 °C min^{-1}, 220 to 300 °C at a rate of 6 °C min^{-1}. The temperature of the injector operating in splitless mode (volume injected 1 μL) was held at 300 °C and electron capture detector temperature was 350 °C. The detector auxiliary gas was nitrogen (99.999%). Quantification was performed using TCMX as internal standard. Fig. 1 shows a chromatogram of a standard solution containing of 0.1 mg L^{-1} of each pesticide injected under these chromatographic conditions.

GC–MS was operated scanning in Full Scan mode from 50 to 400 amu. Transfer line temperature 290 °C; ion source temperature 240 °C and multiplier voltage 1275 V. A PTV injector operating in solvent-split mode was employed. The volume injected was 8 μL, split flow 20 mL min^{-1}. Injector temperature programme: 80 °C increased at 3.3 °C s^{-1} to 300 °C (held for 15 min). Oven programme: initial column temperature 80 °C (1 min) increased at 30 °C min^{-1} to 180 °C (3 min), then increased at 3 °C min^{-1} to 220 °C (4 min), increased at 30 °C min^{-1} to 300 °C and finally held for 3 min. Fig. 2 shows a GC–MS chromatogram of a standard solution with 1 mg L^{-1} of OCPs.

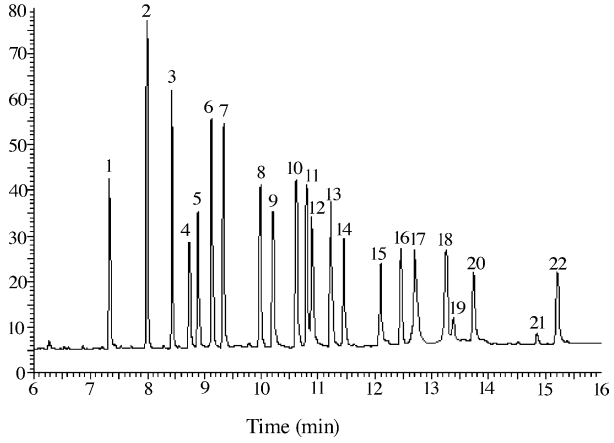

Fig. 1. GC–ECD chromatogram of a standard solution with 0.1 mg L^{-1} of OCPs. Target compounds are numbered as follows: (1) 2,4,5,6-tetrachloro-*m*-xylene (TCMX) (IS); (2) α-HCH; (3) γ-HCH; (4) β-HCH; (5) heptachlor; (6) δ-HCH; (7) aldrin; (8) isodrin; (9) heptachlor epoxide; (10) γ-chlordane; (11) α-chlordane; (12) α-endosulfan; (13) *p,p′*-DDE; (14) dieldrin; (15) endrin; (16) *p,p′*-DDD; (17) β-endosulfan; (18) *p,p′*-DDT; (19) endrin aldehyde; (20) endosulfan sulfate; (21) methoxychlor; (22) endrin ketone.

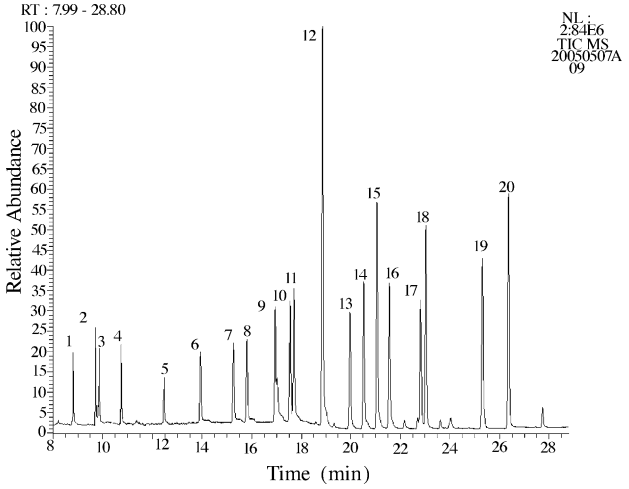

Fig. 2. GC–MS chromatogram of a standard solution with 1 mg L^{-1} of OCPs. Target compounds are numbered as follows: (1) α-HCH; (2) β-HCH; (3) γ-HCH; (4) δ-HCH; (5) heptachlor; (6) aldrin; (7) isodrin; (8) heptachlor epoxide; (9) γ-chlordane; (10) α-endosulfan; (11) α-chlordane; (12) *p,p′*-DDE + dieldrin; (13) endrin; (14) β-endosulfan; (15) *p,p′*-DDD; (16) endrin aldehyde; (17) endosulfan sulfate; (18) *p,p′*-DDT; (19) endrin ketone; (20) methoxychlor.

3. Results and discussion

MAE was carried out according to a method previously developed in our laboratory [18]. MAE was chosen as extraction method as this technique offers advantages such as be amenable to automation, require short extraction times, reduce organic solvent consumption and reduce costs of analysis. However, lipid compounds as well as other molecules present in the samples are coextracted with the analysed pesticides so a clean-up step is recommended to diminish the

presence of interferents in the final extract, which can damage the capillary column as well as resulting in a matrix enhancement effect [23]. Preliminary clean-up experiments were carried out in order to find the best sorbent for the solid-phase extraction. For this purpose the following systems were considered: Florisil® (1 g) commercial cartridges; Florisil® (1 g) commercial cartridges + 5% deactivated alúmina (0.5 g); silica (0.5 g) commercial cartridges; ENVI™-Carb (1 g) commercial cartridges.

The elution solvent should be of a low polarity (e.g. hexane) to eluting less polar residues and leaving more polar co-extractives in the column, although for more efficient elution of the more polar organochlorine pesticides, e.g. eldrin and dieldrin, a more polar solvent mixture should be chosen. Therefore, mixtures hexane:ethyl acetate at several ratios (80:20, 70:30, 60:40) were evaluated. Although good recoveries were obtained with the three mixtures, it was observed that the more the eluting solvent polarity is increased, the greater is the portion of interference substances and less effective is the clean-up; also the time required for the evaporation of the other two mixtures was longer. Therefore, the mixture hexane:ethyl acetate 80:20 was chosen as elution solvent.

The efficiency and precision of the SPE using different adsorbents was carried out by spiking the adsorbents with 1 mL of standard solution containing of 0.1 mg L^{-1} of each pesticide and then the elution system and analysis before described were applied. Three fractions of 5 mL of elution solvent each one was collected. The results obtained corresponding to the first fraction are shown in Table 1, which shows the analytical recoveries (mean ± standard deviation, $n = 4$). Satisfactory recoveries were obtained for all pesticides except for endrin aldehyde. The analysis of the second and the third fractions showed that an additional volume of elution solvent would be needed for endrin aldehyde when silica (5 mL, 88% recovery) or Florisil® + alumina (10 mL, 83% recovery) were used as adsorbents. The values of repeatability, in terms of relative standard deviation (R.S.D.), were quite low for all adsorbents, ranging between 1 and 7% when carbon was used as adsorbent.

All the adsorbents assayed with standards were used to clean-up samples of chestnut leaves that were previously extracted following the procedure described in sample preparation section. Fig. 3 shows the GC–ECD chromatograms corresponding to chestnut leaf extracts purified with the sorbents considered. It can be seen that the efficiency of clean up was as follows: silica < Florisil® < Florisil® + alumina ≅ ENVI™-Carb. Moreover, carbon was the only one that gave colourless eluates. Thus, the use of carbon cartridges (EnviCarb®) has been selected as purification method with 5 mL of hexane:ethyl acetate (80:20) as elution solvent, and it was applied to the determination of OCPs in four species of tree leaves. Fig. 4 shows the full scan GC–MS chromatograms corresponding to chestnut leaf extracts purified with the sorbents considered; these chromatograms also show that carbon is the most efficient sorbent to remove other matrix compounds such as hydrocarbons, alcohols and esters, which though present are not detected by the selective electron capture detector, avoiding deterioration of the chromatographic column.

Regarding linearity, linear calibration curves for all pesticides over six calibration levels, from 0.005 to 0.100 mg L^{-1} were constructed using TCMX as internal standard. The calibration curves were linear over the whole concentration tested

Table 1
Analytical recoveries (%) of OCPs standard solution using different clean-up procedures ($n = 4$)

Pesticides	Florisil®		Florisil® + alumina		Silica		ENVI™-Carb	
	%*R*	%R.S.D.	%*R*	%R.S.D.	%*R*	%R.S.D.	%*R*	%R.S.D.
α-HCH	108	2	101	6	102	5	103	2
γ-HCH	108	2	104	5	103	4	104	2
β-HCH	118	3	113	4	106	5	122	6
Heptachlor	105	3	109	6	104	3	105	3
δ-HCH	109	3	104	4	103	3	101	1
Aldrin	108	4	105	5	102	4	104	1
Isodrin	106	4	105	6	103	1	104	1
Heptachlor epoxide	106	4	106	6	100	3	102	5
γ-Chlordane	106	5	108	5	103	2	104	1
α-Chlordane	105	5	108	5	105	3	106	1
α-Endosulfan	106	5	106	5	97	3	102	1
p,p′-DDE	101	6	106	5	100	4	104	5
Dieldrin	104	5	109	5	102	2	105	1
Endrin	96	6	112	4	106	4	108	3
p,p′-DDD	96	7	104	4	101	2	103	1
β-Endosulfan	103	6	106	4	103	2	105	2
p,p′-DDT	98	7	124	8	109	3	114	4
Endrin aldehyde	100	5	31	10	72	6	78	3
Endosulfan sulfate	99	6	104	4	103	4	99	5
Methoxychlor	87	13	115	3	110	4	107	7
Endrin ketone	99	6	103	5	99	2	101	2

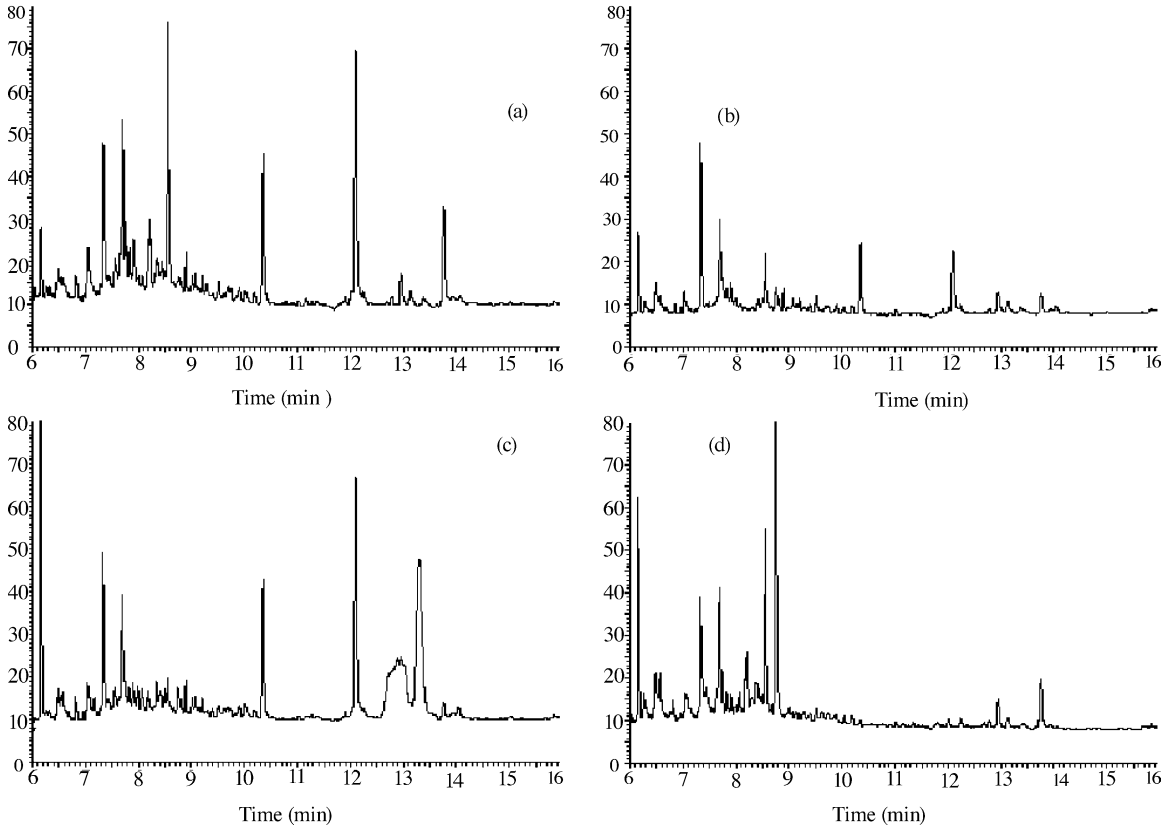

Fig. 3. GC–ECD chromatogram of chestnut leaf extracts purified with: (a) Florisil®, (b) Florisil® and alumina, (c) silica, (d) carbon.

for all the OCPs with correlation coefficients (R^2) ranging between 0.9926 for methoxychlor and 0.9968 for *p,p′*-DDE.

Limit of detection (LOD) and limit of quantitation (LOQ) were calculated at 3 and 10 times the standard deviation above the blank signal. Table 2 shows these values in ng g^{-1} of freeze dried samples calculated with blank chestnut tree extracts. Limits of detection ranged from 16 to 253 ng g^{-1} and LOQ ranged from 80 to 693 ng g^{-1}.

Recovery experiments were carried out with samples, which did not contain pesticide residues at detectable concentrations. For this purpose, 0.3 g of four different tree leaf samples were weighed into an extraction vessel and spiked with 1 mL of a standard solution with the organochlorine pesticides studied in a concentration of 0.1 mg L^{-1}. Samples were sonicated for 3 min and let stay 17 min. Each sample (0.3 g) was spiked three times and then analysed in duplicate following the procedure described in the experimental section. The analytical recoveries expressed as % as well as the R.S.D. obtained with spiked samples (0.33 mg kg^{-1} in freeze dried sample) with the proposed method of purification are shown in Table 3. Analytical recoveries were close to 100% in most cases and there were not many differences between different species of trees. As it can be seen, the analytical recovery is below 70% for endrin aldehyde in chestnut tree samples, which means that an interaction of this compound with the matrix occurs. In some cases recoveries of endrin and *p,p′*-DDT were over 120% which can be attributed to the presence of these pesticides in the blank sample, although the direct analysis of these compounds in the sample gave values under the detection limit and for this reason, this attempt

Table 2
LOD and LOQ in ng g^{-1} of freeze dried chestnut tree sample

Pesticides	LOD (ng g^{-1})	LOQ (ng g^{-1})
α-HCH	30	80
γ-HCH	35	90
β-HCH	69	178
Heptachlor	57	152
δ-HCH	39	98
Aldrin	33	84
Isodrin	42	106
Heptachlor epoxide	41	103
γ-Chlordane	40	101
α-Chlordane	39	105
α-Endosulfan	42	108
p,p′-DDE	39	107
Dieldrin	40	105
Endrin	69	182
p,p′-DDD	63	167
β-Endosulfan	16	104
p,p′-DDT	90	248
Endrin aldehyde	60	160
Endosulfan sulfate	37	135
Methoxychlor	253	693
Endrin ketone	43	120

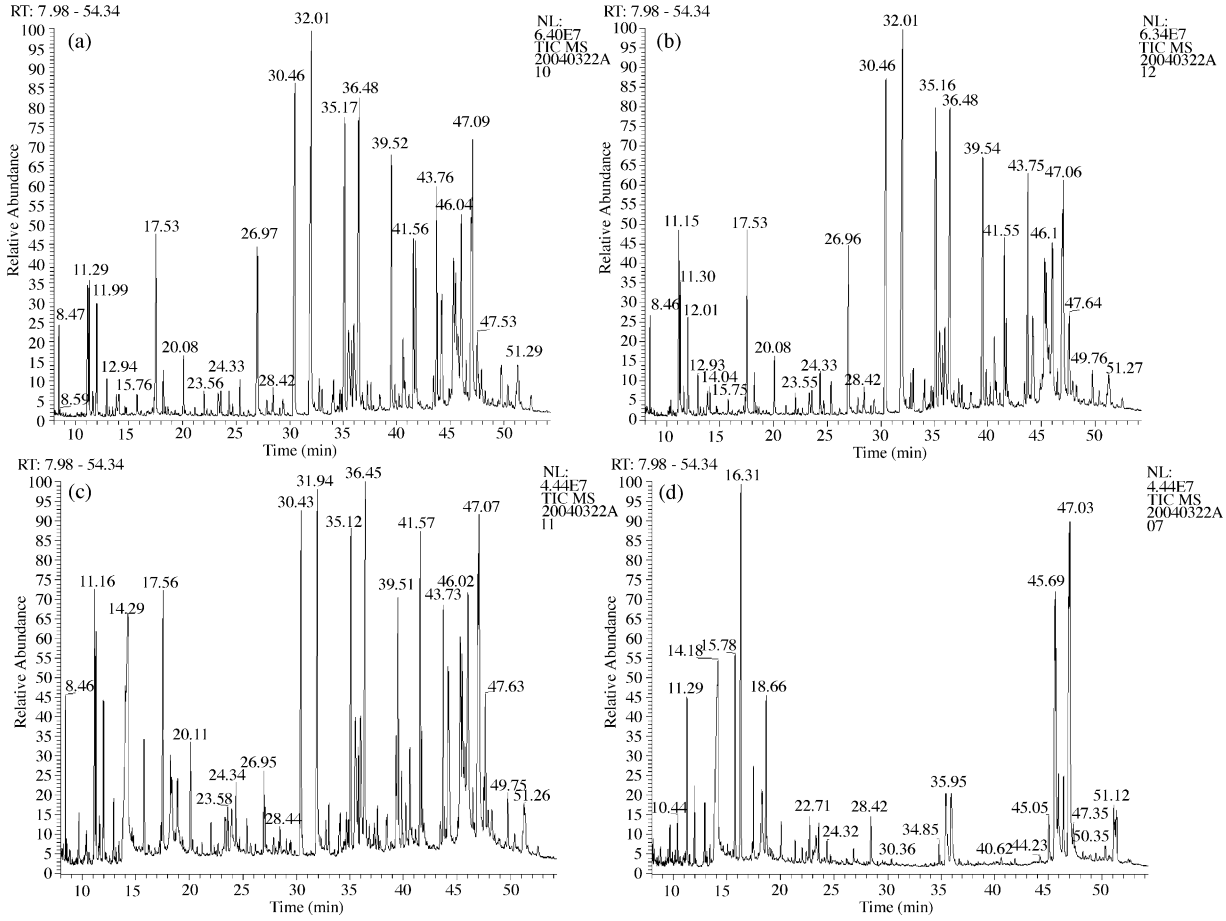

Fig. 4. GC–MS chromatogram of chestnut tree leaf extracts purified with: (a) Florisil®, (b) Florisil® and alumina, (c) silica, (d) carbon.

Table 3
Analytical recoveries (%) of OCPs extracted from leaves of different tree species ($n = 3$)

Pesticides	Chestnut tree (*C. sativa*)		Hazel tree (*C. avellana*)		Oak tree (*Q. robur*)		Walnut tree (*J. regia*)	
	%*R*	%R.S.D.	%*R*	%R.S.D.	%*R*	%R.S.D.	%*R*	%R.S.D.
α-HCH	103	2	93	8	95	9	81	5
γ-HCH	93	2	108	6	91	5	95	2
β-HCH	100	12	123	9	136	8	104	15
Heptachlor	107	3	108	7	100	6	115	4
δ-HCH	81	9	88	6	92	9	111	7
Aldrin	96	8	95	2	95	5	81	1
Isodrin	81	9	85	5	88	7	94	7
Heptachlor epoxide	90	4	94	7	100	8	99	8
γ-Chlordane	88	5	93	6	92	9	95	8
α-Chlordane	86	5	90	11	91	9	99	8
α-Endosulfan	84	4	86	10	87	8	83	5
p,p′-DDE	94	4	90	6	98	7	114	11
Dieldrin	98	6	92	7	99	7	105	9
Endrin	107	2	109	5	126	6	147	9
p,p′-DDD	89	10	91	4	97	8	122	14
β-Endosulfan	81	6	87	7	92	9	114	11
p,p′-DDT	116	4	122	2	129	9	137	15
Endrin aldehyde	58	5	85	2	79	4	77	5
Endosulfan sulfate	96	5	86	7	83	12	114	11
Endrin ketone	81	4	84	4	93	10	99	10

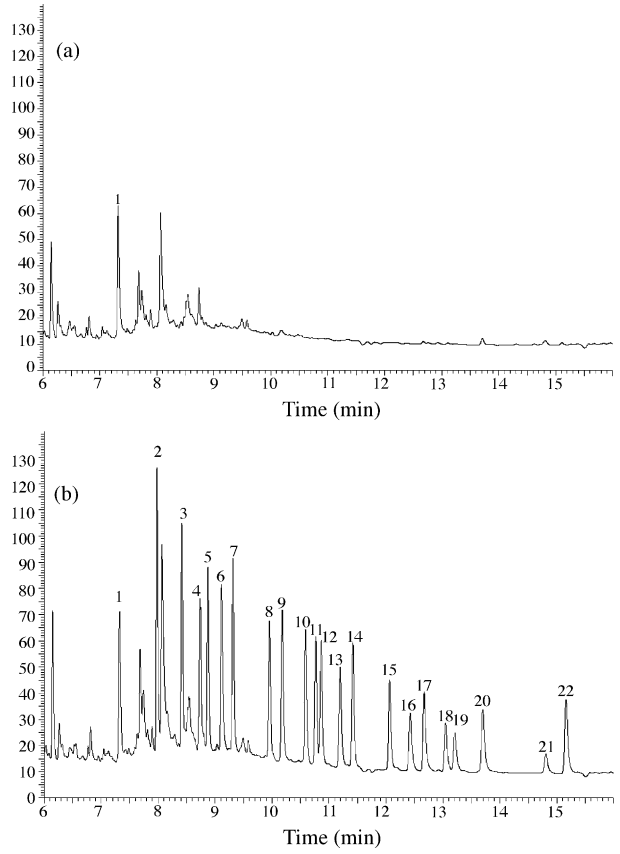

Fig. 5. GC–ECD chromatogram of walnut leaf extracts: (a) unspiked sample, (b) spiked sample.

could be not confirmed. These results show that the sample matrix affects the behaviour of these OCPs in the extraction and clean-up procedures used.

By way of an example Fig. 5 shows the GC–ECD chromatogram for walnut tree leaf unfortified and fortified with the OCPs listed.

4. Conclusions

A carbon cartridge eluted with 5 mL of hexane:ethyl acetate (80:20) was the most efficient clean-up procedure for tree leaf extracts in the determination of OCPs capable of eliminating the matrix interference and providing colourless eluates.

Recoveries obtained were satisfactory for both standard solution and spiked leaf extracts in the different species of trees studied.

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