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Development of pressurized liquid extraction and cleanup procedures for determination of organochlorine pesticides in soils

E. Concha-Graña, M.I. Turnes-Carou, S. Muniategui-Lorenzo*, P. López-Mahía, E. Fernández-Fernández, D. Prada-Rodríguez

Department of Analytical Chemistry, Faculty of Sciences, University of A Coruña, Campus da Zapateira, E-15071 A Coruña, Spain

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Abstract

The scope of this work is the development of a rapid, reliable and sensitive method for the analysis of organochlorine pesticides from soils by pressurized liquid extraction (PLE). The effect of four parameters (temperature, pressure, static time and cell volume) on the extraction efficiency was studied. The great extracting power of the PLE causes the extraction of numerous interfering substances, so a more efficient purification of this extract was necessary. In this work several sorbents have also been assayed to carry out the purification of soil samples: Florisil, silica, alumina, carbon, as well as combinations of them. Finally, the proposed analytical method was validated using a certified reference soil material (CRM804-050) and the results were compared with those obtained by other extraction techniques (Soxhlet and microwave-assisted extraction).

Keywords: Pressurized liquid extraction; Extraction methods; Soil; Pesticides; Organochlorine compounds

1. Introduction

Pressurized liquid extraction (PLE; Dionex trade name ASE for accelerated solvent extraction) is an extraction technique developed by Richter in 1995 [1]. This technique is based on the use of a solvent or combination of solvents to extract organic pollutants at elevated pressure and temperature from a solid matrix. The high temperature favours the solubilization of the compounds by the solvent due to a change in their distribution coefficients, and the pressure improves the penetration of the solvent into the matrix [2].

PLE has some advantages above other extraction techniques such as shorter extraction time and lower consumption of solvents than Soxhlet and ultrasonic extraction; the universal use of solvents of different polarities opposite to microwave extraction; temperatures ranging from room temperature up to 200 °C and pressures in the range of 5–200 atm (1 atm = 101325 Pa), among others [3]. In the last years, PLE has been applied to the extraction of organochlorine pesticides from different matrices: solid wastes [4], soils [5,6], vegetation, fish [7], fruit, vegetables [8], etc. and it is used in the U.S. Environmental Protection Agency (EPA) method 3545 for the analysis of organic compounds in solid matrices.

In trace analysis of organic compounds in complex matrices like soils, the cleanup of the obtained extracts is as important as the extraction step. Moreover, the presence of interferences could impaired the limits of detection or even damage the chromatographic system. In this sense, when organochlorine pesticides are extracted from soil samples with hexane–acetone (1:1 v/v) by microwave energy or PLE, a coloured extract is often obtained. Due to the great extracting power of the solvents and the analytical methodology employed, this extract contains numerous interfering substances, which makes the purification of this extract mandatory.

The method of purification more commonly used is the solid-phase extraction with glass columns or commercial cartridges. There are a lot of sorbents that have been used for

* Corresponding author. Tel.: +34 981 167000; fax: +34 981 167065.
E-mail address: smuniat@udc.es (S. Muniategui-Lorenzo).

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the cleanup of extracts of soils, being the most commonly employed the alumina [9–11] and Florisil [6,12–14]. Another sorbents, such as silica or carbon, are less used, although sometimes they are employed combined with alumina or Florisil [8].

The aim of this work is the study of the factors which affect the efficiency of the PLE extraction (in preheat mode) of organochlorine pesticides from soils. Due to the low number of factors to study (some of them discrete factors), the application of experimental designs was not considered, and the study was carried out by an univariate procedure. In this work we assay more compounds, lower amount of sample (1 g; that reduces the amount of dispersing agent) and lower cell volume than in EPA 3545 method and in previous works [4,6]. The solvent selected to carry out the experiments was a mixture of hexane–acetone (1:1 v/v). The extraction variables studied are the following: temperature (50–150 °C), static time (5–10 min), solvents volume (the volume depends on the commercial cell size, so 5 and 11 mL cells were assayed) and pressure [between 1500 and 2000 p.s.i. (p.s.i. = 0.145 kPa)]. These ranges were selected according with the bibliography and the characteristics of the equipment. Furthermore, in this work several sorbents have been assayed to carry out the purification of soil samples: Florisil, silica, alumina, carbon as well as combinations of them.

Finally, the analytical recoveries and standard deviations of the whole method were calculated and it was also validated by the analysis of a certified reference soil material (CRM804-050). Although the pressurised solvent extraction of organochlorine pesticides was validated for some matrices like sediments (SRM 1944, SRM 1941) [15], urban dust (SRM 1649a), mussel tissue (SRM 2974) [16] and animal feed (BCR 115) [17], as far as we know, there are no references about validation with a soil reference material.

2. Experimental

2.1. Apparatus

The pressurized liquid extraction was made with a ASE 200 System (Dionex, Sunnyvale, CA, USA). A rotary evaporator Büchi R-3000 (Büchi Labortechnic, Postfach, Switzerland) was used in the evaporation step and a Visiprep vacuum distribution manifold from Supelco (Bellefonte, PA, USA) was employed in the purification.

Gas chromatography was performed with A Perkin-Elmer Autosystem XL chromatograph equipped with ^{63}Ni electron-capture detection (ECD) system, autosampler, PPC (programmed pneumatic control) and Totalchrom data processor. A methyl–phenyl–cyanopropyl silicone fused-silica capillary column of 30 m × 0.25 mm, 0.25 μm 007–608 Quadrex (New Haven, CT, USA), specific for pesticide analysis was employed.

GC–MS experiments were carried out by a Trace 2000 GC coupled to a Thermo Finnigan Polaris-Q (Austin, Texas, USA). The gas chromatograph was equipped with a programmed temperature vaporisation (PTV) injector. The capillary column 60 m × 0.25 mm, 0.25 μm was from J&W DB-XLB (Agilent Technologies, Palo Alto, CA, USA).

2.2. Materials

n-Hexane (95%), dichloromethane and acetone super purity solvents were purchased from Romil (Cambridge, UK). Ethyl acetate for residue analysis was from Panreac (Barcelona, Spain).

CLP Organochlorine Pesticide Mix, 2 mg mL^{-1} in toluene–hexane (1:1 v/v) was supplied by Supelco (Bellefonte, PA, USA). Isodrin Pestanal was from Riedel-de Haën (Seelze, Germany). Internal standard, 2,4,5,6-tetrachloro-*m*-xylene (TCMX) was also supplied by Supelco. Working standard solutions were prepared by dilution in *n*-hexane.

Certified reference material of pesticides on soil CRM804-050, was supplied by Resource Technology Corporation (Wyoming, USA). This material consists in a real contaminated soil from an agricultural region of the Western USA.

Diatomaceous earth acid washed not further calcined was from Sigma–Aldrich Chemie, Germany.

The sorbents employed in the study of the cleanup step were: Sep-Pak Plus Florisil cartridges (1 g), Sep-Pak Vac 20 cc (5 g) Florisil cartridges and Sep-Pak Plus Silica cartridges (1 g) were supplied by Waters (Mildford, MA, USA). Envi-Carb Packing, 12 mL (1 g), 100 m^2 g^{-1}, Envi-Carb C Packing 12 mL (1 g), 10 m^2 g^{-1}, Superclean Envi-Florisil SPE Tubes 6 mL (1 g) and LC-Alumina-N (1 g) were supplied by Supelco. Neutral alumina and silica gel (70–230 mesh), both for column chromatography, were from Sigma–Aldrich Chemie. Alumina, diatomaceous earth and silica were precleaned by Soxhlet extraction 12 h with dichloromethane–methanol (2:1 v/v) and 12 h with dichloromethane–hexane (30:70 v/v). Then alumina was activated at 550 °C 12 h, and silica at 130 °C 12 h, and both were deactivated with a 5% Milli-Q water.

2.3. Pressurized liquid extraction procedure

Prior to the extraction assays, and with the purpose of studying the PLE cell blanks, a 11 mL cell (with a cellulose filter) was extracted with hexane–acetone (1:1 v/v), in a cycle of 5 min of heating and 5 min of static extraction, at 2000 p.s.i. of pressure and 100 °C of temperature. The extract was concentrated, re-dissolved in 1 mL of hexane and injected in a GC–ECD system. The chromatograms obtained present many interfering peaks. These peaks were identified as silicones, organic acids and some ftalates when the extracts were injected in a GC–MS in the total ion current (TIC) mode. To eliminate these interfering peaks, the extraction cell and the filter were pre-cleaned by extracting them in the PLE with the hexane–acetone (1:1 v/v) at 125 °C and 2000 p.s.i. during 5 min, prior to their utilization.

The experimental PLE conditions were studied by extraction of spiked soil samples. One gram of dried soil sample was mixed with 0.25 g diatomaceous earth. Once introduced in the cell, the mix was spiked at 0.1 μg g^{-1} level, with 100 μL of 1 μg mL^{-1} standard pesticide solution. As extraction solvent, a mixture hexane–acetone 1:1 (v/v) was selected for all the experiments because its efficiency in the extraction of organochlorine pesticides has been demonstrated in previous works [4,12,18]. The ASE 200 extractor was operated in preheating mode (the cell is introduced in the heated oven before the solvent is introduced).

After extraction, samples were concentrated to a drop (approximately 0.2 mL) in rotary-evaporator and purified. The eluate was evaporated to a drop in rotary-evaporator and to dryness by means of nitrogen stream. Sample was redissolved in hexane, the internal standard was added and finally injected in a GC–ECD.

2.4. GC–ECD analysis

Helium (99.999%) was used as carrier gas, at 1 mL min^{-1}. GC conditions were as follows: initial column temperature 60 °C (1 min) increased from 25 to 220 °C min^{-1}, then increased from 6 to 300 °C min^{-1} and finally held for 5 min. The temperatures of the injector and the electron-capture detector were 300 and 350 °C, respectively. The detector auxiliary gas was nitrogen (99.999%).

3. Results and discussion

3.1. Study of the PLE conditions

The factors studied to achieve the best efficient extractions for 21 organochlorine pesticides from soils were the oven temperature, pressure (which must be high enough to maintain the solvent at liquid state), static time and volume of solvents. The latter parameter was studied by changing the cell size (5 and 11 mL).

Three oven temperatures were assayed: 65, 100 and 150 °C. As it can be seen in Fig. 1, the best results were obtained at 100 °C. At 150 °C recoveries obtained were slightly lower than at 100 °C, especially for the most volatile compounds. Furthermore, many other interfering compounds were extracted, leading to dirty chromatograms (Fig. 2). Regarding the pressure (Fig. 3), no significant differences were observed in the recoveries, as has been demonstrated by comparison of the results using the Student's *t*-test for paired data at a 95% of significance. So, a pressure of 1500 p.s.i. was selected, since better precision was obtained. Later it was studied that the static time, and as Fig. 4 shows, the duplication of the time of extraction did not produce any improvement in the extraction efficiency. No statistical differences were obtained by application of the *t*-test (P = 95%) and then 5 min of static time was selected.

Finally, the solvent volume was evaluated. The volume depends on the size of the cell and on the degree of filling. In this case, the same amount of sample and dispersing agent was employed in all the experiences, and two sizes of cell were tested: 5 and 11 mL. No significant differences at 95% of significance were observed between the recoveries obtained with both sizes, thus, the cell size of 5 mL was selected due to the lower consumption of solvents. These results are presented in Fig. 5.

To summarize the results obtained, the extraction conditions selected were: 5 mL cell, temperature 100 °C, pressure 1500 p.s.i., heat time 5 min, static time 5 min, flush volume 60% and hexane–acetone 1:1 (v/v) as solvent.

Besides the compounds that appear in the figures, other pesticides were also studied (endrin, *p,p′*-DDT, β-HCH and

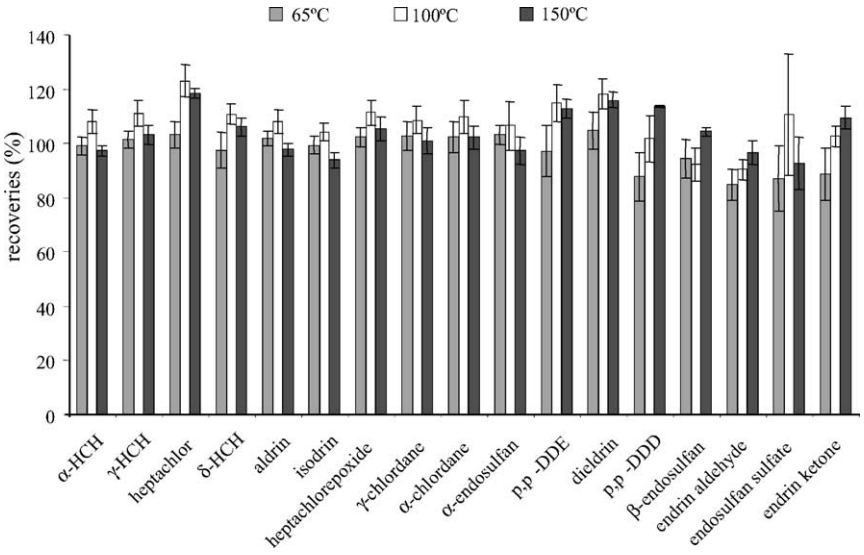

Fig. 1. Effect of the oven temperature in the efficiency of the extraction (n:3). Extraction conditions: pressure 1500 p.s.i., static time 5 min and PLE cell volume 5 mL.

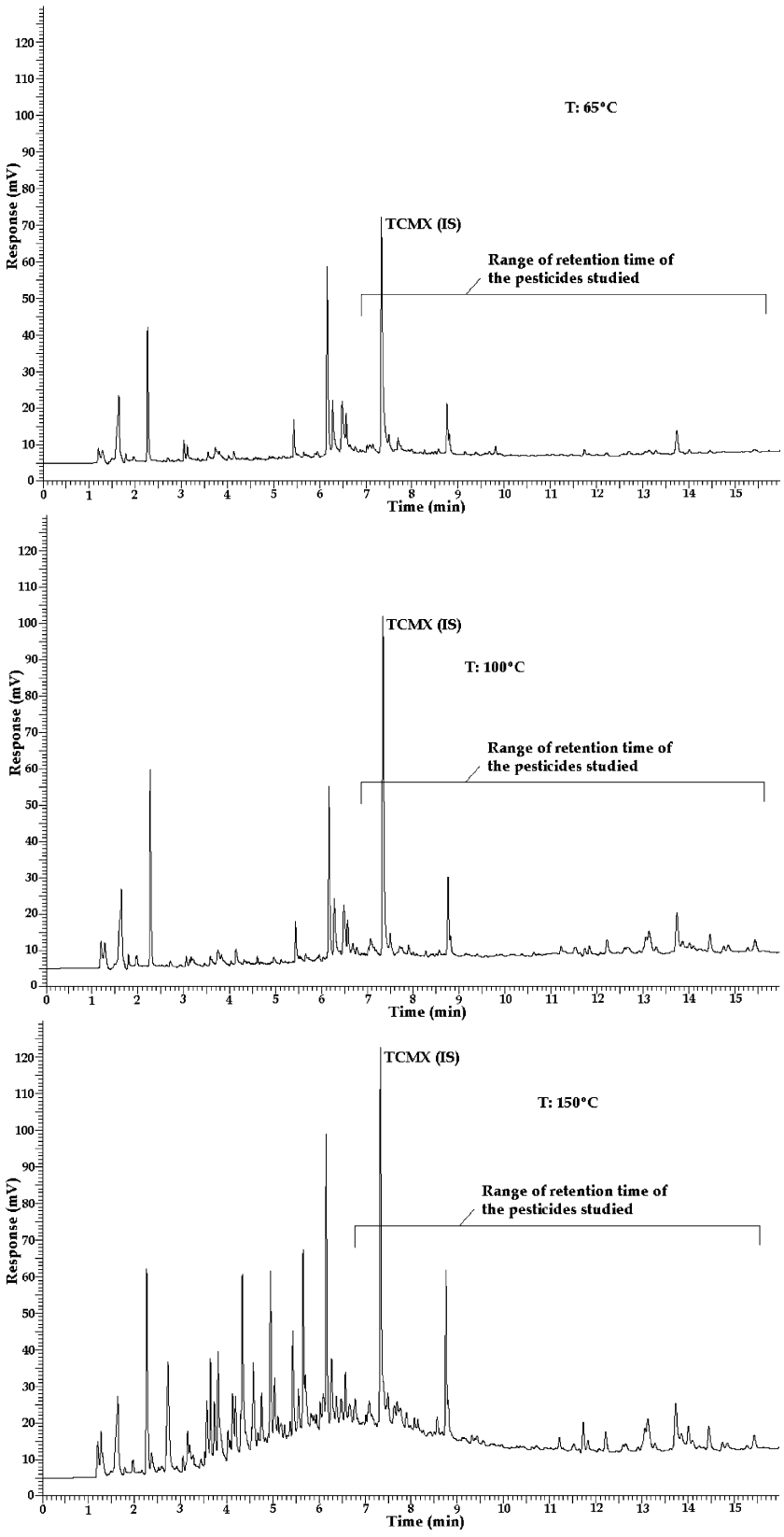

Fig. 2. Chromatograms obtained by PLE extraction of a soil sample at 65, 100 and 150 °C.

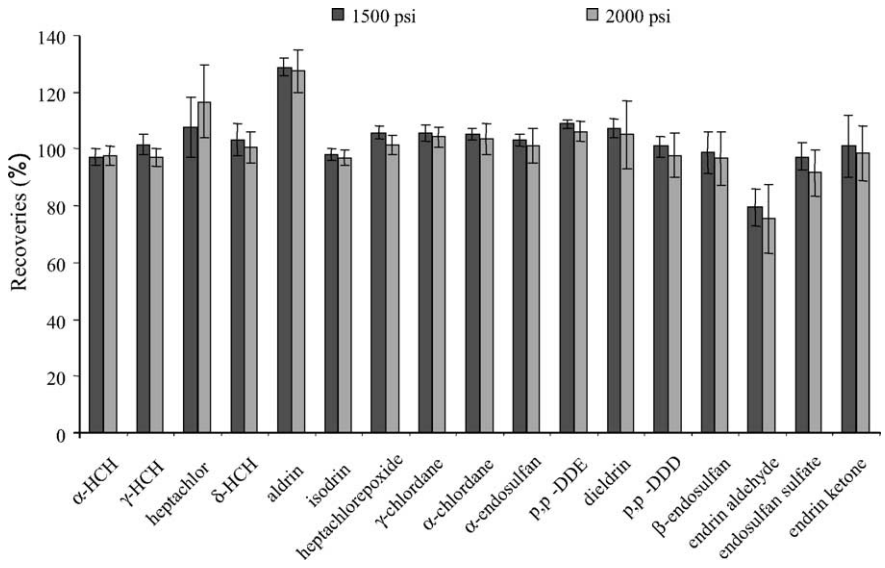

Fig. 3. Effect of the pressure in the efficiency of the extraction (n:3). Extraction conditions: oven temperature 100 °C, static time 5 min and PLE cell volume 5 mL.

methoxychlor). These pesticides were not included in the graphics because they have anomaly high recoveries (between 140 and 270%) due to problems with interfering peaks. These problems were partially corrected by the study of the cleanup step.

3.2. Study of the cleanup step

In organic trace analysis it is very important to obtain clean extracts prior to the chromatographic analysis, due to the low limits established by the legislation for most compounds, as well as in order to protect the chromatographic system. Thus, the purification step must be carefully studied. In this work, Florisil, silica, alumina, carbon and combinations of these sorbents, were assayed to carry out the purification of soil extracts obtained by pressurized liquid extraction. The sorbents and the elution solvents employed in each experiment can be seen in Table 1. Two of the experiments included the presence of a silica inside the PLE cell as pre-cleanup (experiment 9) or cleanup (experiment 10), as proposed by some authors [6,19]. No experiments were undertaken adding with carbon inside the PLE cell due to the physical characteristics of the carbon, which could clog up the porous frit and contaminate the extraction system. The commercial devices (Sep-pack cartridges and tubes) were placed in a Visiprep vacuum distribution manifold. All the sorbents were pre-cleaned, by passing the elution solvent through them, and then dried by vacuum and nitrogen stream for 30 min. After the cleanup

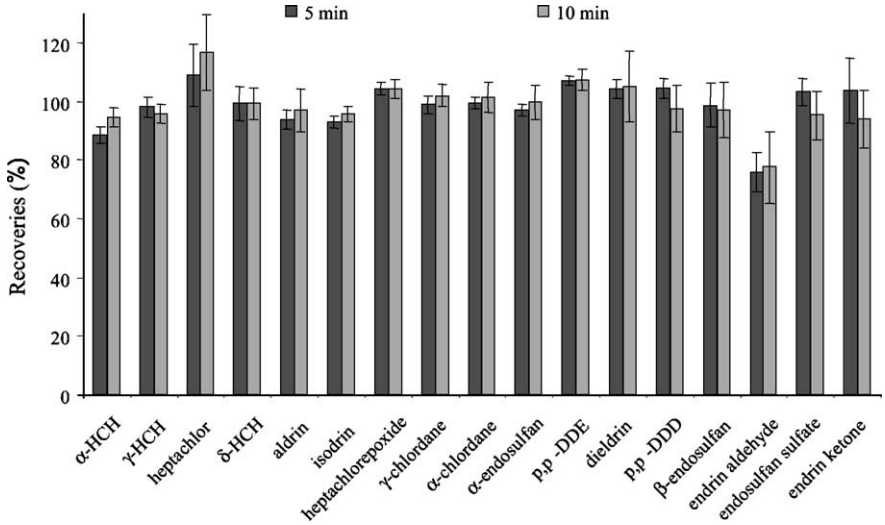

Fig. 4. Effect of the static time in the efficiency of the extraction (n:3). Extraction conditions: oven temperature 100 °C, pressure 1500 p.s.i. and PLE cell volume 5 mL.

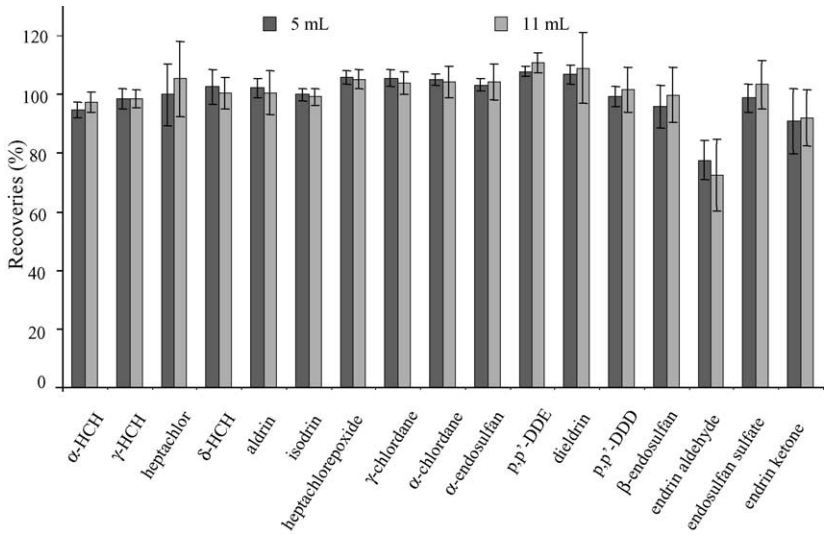

Fig. 5. Effect of the PLE cell volume (solvent volume) in the efficiency of the extraction (n:3). Extraction conditions: oven temperature 100 °C, pressure 1500 p.s.i. and static time 5 min.

step, the eluate was concentrated in the rotary evaporator and dried by nitrogen stream. Sample was re-dissolved in hexane and then injected in the gas chromatograph.

The PLE soil extract presents a dark yellow colour, and after the cleanup with Florisil, alumina or silica, the resulting eluate is pale yellow, whereas when carbon is used as sorbent, a colourless eluate is obtained.

By injecting the extracts in a GC–ECD system, it can be seen that the experiments 1, 2 and 3 give dirtier chromatograms, possibly due to the use of higher solvent volumes and the use of a laboratory prepared column (experiment 2) that involves more manipulation than with the commercial devices. For the remaining experiments the chromatograms registered were very similar and quite clear, because of the high selectivity of ECD. Fig. 6 shows some of the experiences as well as the chromatogram obtained by direct injection of the extract, without cleanup.

The same extracts were injected in an ion trap GC–MS (scanning between 50 and 450 amu) in order to identify the interfering compounds. Although these substances could not be detected by ECD, they are present in the eluates and can damage the chromatographic system. The chromatograms obtained showed important differences depending on the sorbent used (Fig. 7). When carbon is used in the cleanup (experiments 12 and 13) the chromatograms registered were very clear, whereas those obtained with the other sorbents, present peaks that corresponded to aliphatic and cyclic hydrocarbons. These peaks were also obtained when carbon $100\,m^2\,g^{-1}$ was eluted with 30 mL of solvent mixture (experiment 11). No differences were observed when comparing the assays with silica inside the PLE cell, or purifying with silica cartridges.

Carbon $100\,m^2\,g^{-1}$ was selected as the more adequate sorbent to carry out the cleanup of the extracts. A study of the analytical recoveries of the cleanup step was done in order to determine whether 10 mL of solvents are sufficient to elute all the pesticides.

Table 1
Cleanup experiments

Experiment	Sorbent/device/amount	Elution
1	Florisil/cartridge/5 g	25 mL H–AE (80:20 v/v)
2	Silica + alumina/glass column/1 g + 1 g	10 mL H–AE (80:20 v/v)
3	Florisil/Sep-pack/1 g + alumina/cartridge/1 g	8 mL H–AE (80:20 v/v)
4	Florisil/cartridge/1 g + 1 g	5 mL H–AE (80:20 v/v)
5	Florisil/cartridge/1 g + 1 g	5 mL H–DCM (1:2 v/v)
6	Silica + florisil/cartridge/1 g + 1 g	5 mL H–AE (80:20 v/v)
7	Envi-florisil/cartridge/1 g	5 mL H–AE (80:20 v/v)
8	Florisil/cartridge/1 g	5 mL H–AE (80:20 v/v)
9	Silica in the cell/3 g + Florisil/cartridge/1 g	5 mL H–AE (80:20 v/v)
10	Silica in cell/3 g	5 mL H–AE (80:20 v/v)
11	Carbon $100\,m^2\,g^{-1}$/cartridge/1 g	30 mL H–AE (80:20 v/v)
12	Carbon $100\,m^2\,g^{-1}$/cartridge/1 g	10 mL H–AE (80:20 v/v)
13	Carbon $10\,m^2\,g^{-1}$/cartridge/1 g	30 mL H–AE (80:20 v/v)

H, hexane; EA, ethyl acetate; DCM, dichloromethane.

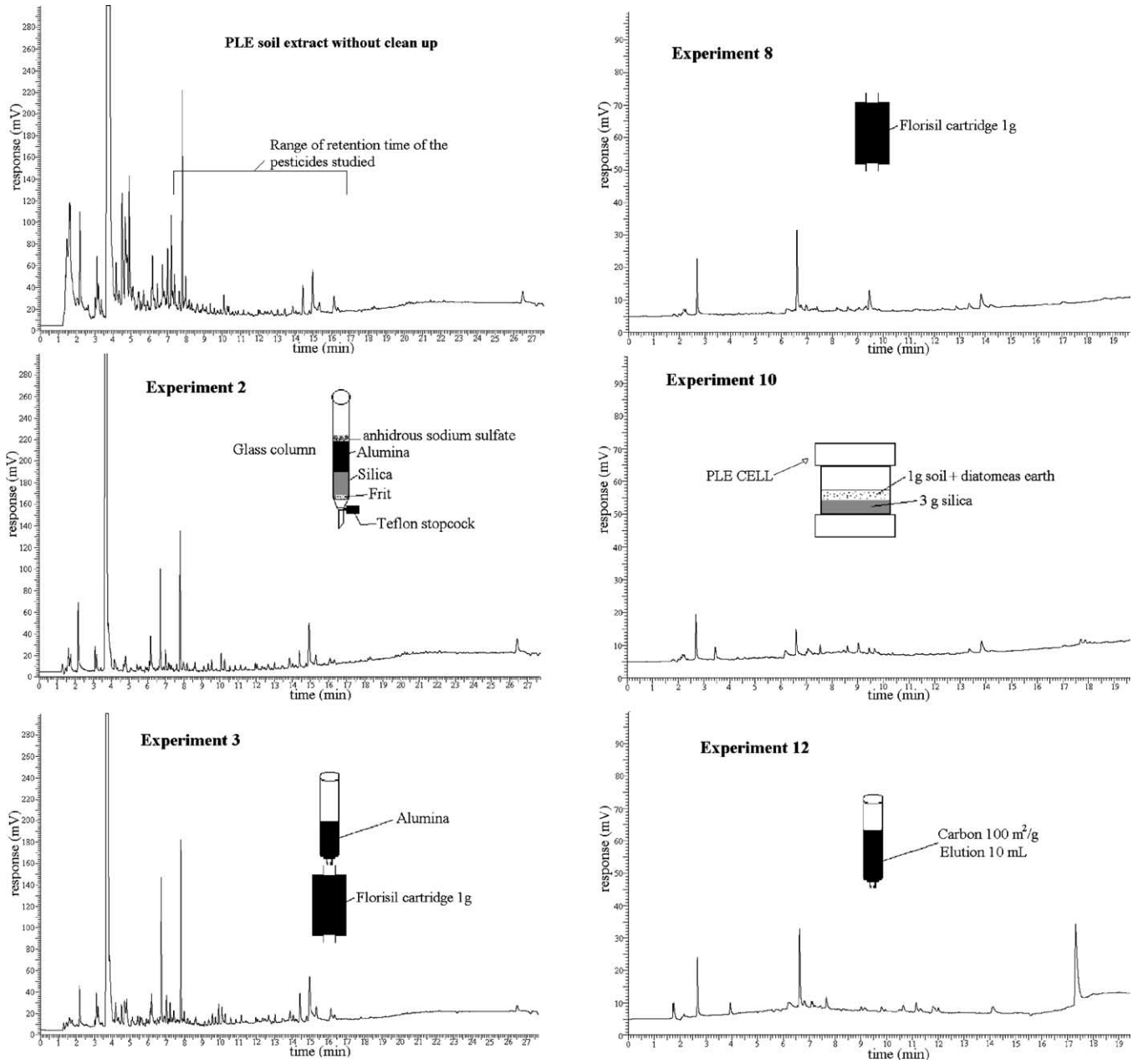

Fig. 6. GC–ECD chromatograms obtained without cleanup and in experiments 2,3,8,10 and 12.

The recoveries obtained by elution of five cartridges spiked with 1 mL of pesticide standard (0.1 μg mL^{-1}) were satisfactory for all the studied pesticides (between 90 and 109%, with RSD lower than 7%). The recoveries obtained for endrin, *p,p′*-DDT, β-HCH and methoxychlor were between 110 and 122%.

Finally, the cleanup conditions selected were: using the Visiprep cartridge of carbon (1 g, 100 m^2 g^{-1}) which was pre-cleaned by passing through it 20 mL of hexane–ethyl acetate (80:20 v/v), and then dried by vacuum and nitrogen stream during 30 min. The elution was done with 10 mL of hexane–ethyl acetate (80:20 v/v) passing drop by drop under gravity.

3.3. Method validation

The method developed was validated by extraction of a certified reference soil (CRM804-050). This material is a real-world waste sample, and then it is affected by the same preparation problems, analytical interferences, etc. as is typical for similar matrices received in the laboratory for analysis. The results obtained have confidence intervals that overlap or include the confidence interval of the certified material, except for γ-HCH and especially for α-endosulfan whose concentrations obtained are lower than the certified contents (Table 2). Similar values were obtained for these compounds, and for the others when the same material was extracted by

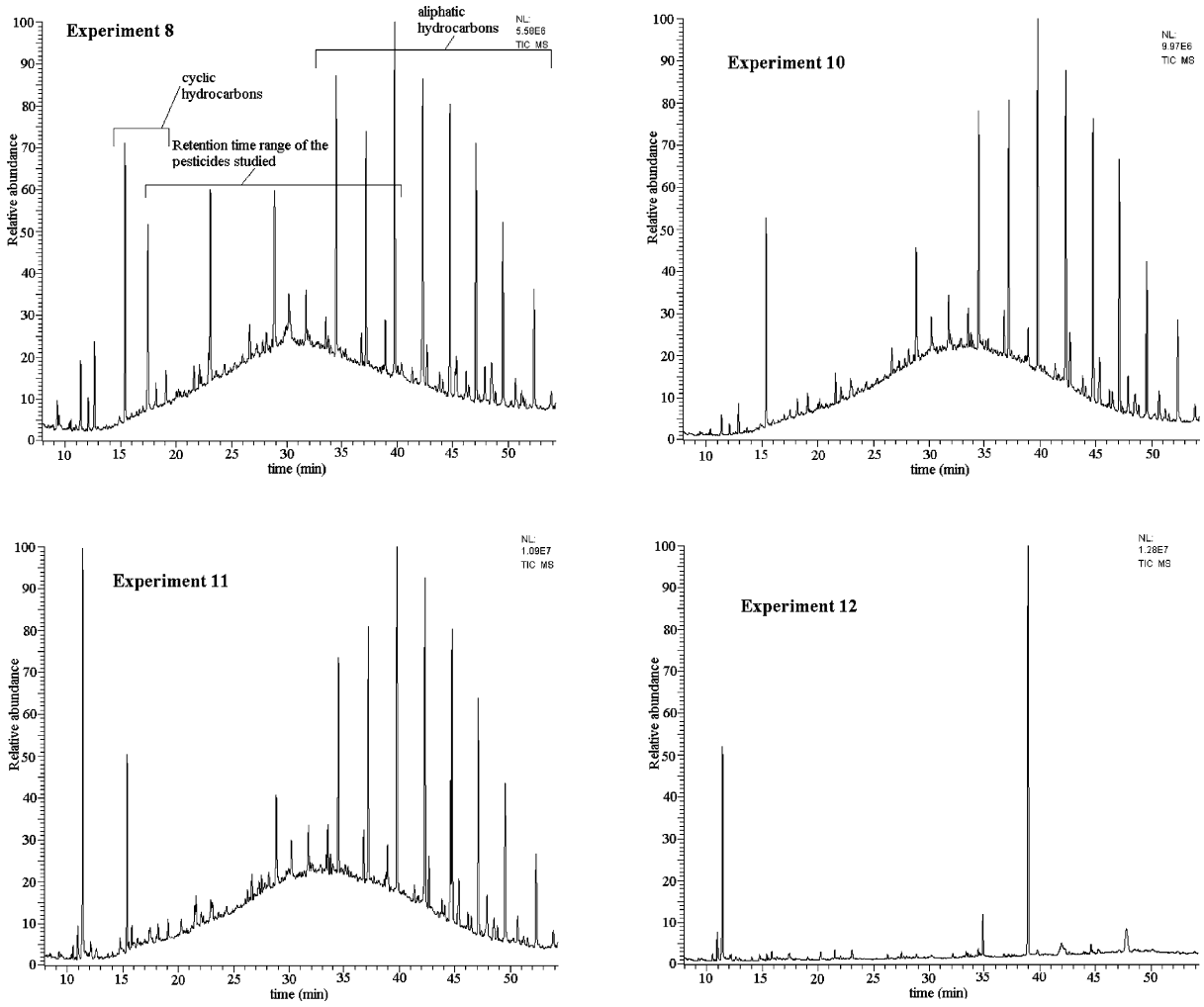

Fig. 7. GC–MS chromatograms obtained in experiments 8,10, 11 and 12.

microwave-assisted extraction [1 g, 100–800 W in 2 min, and then 8 min at 800 W; 10 mL hexane–acetone (1:1 v/v)] and by Soxhlet [1 g, 20 h, hexane–acetone (1:1 v/v)] [18] (Table 2). The standard deviations of the method are satisfactory (RSD lower than 10% for all the pesticides except aldrin).

For those organochlorine pesticides that are not certified in the reference material, the analytical recoveries were evaluated. The recoveries obtained and the precision of the proposed method ($n = 3$) for a soil spiked at 0.1 μg g^{-1} (100 μL of 1 μg mL^{-1} pesticide standard solution) were satisfactory for all the pesticides analysed (Table 3). Recoveries for endrin, *p,p′*-DDT, β-HCH and methoxychlor were considerably reduced regarding with the values obtained in the preliminary studies (140–270%), however, they are still slightly

Table 2
Certified values of the reference material and concentration obtained by the proposed method (μg kg^{-1}), by microwave-assisted extraction and by Soxhlet extraction

Pesticide	Certified value	PLE value	Microwave value	Soxhlet value
γ-HCH	491 (128)	299 (32)	320 (20)	498 (55)
Aldrin	18 (8.9)	14.1 (3.9)	14.6 (1.6)	25 (0.5)
α-Endosulfan	1464 (427)	456 (39)	485 (8.2)	554 (34)
p,p′-DDE	1520 (410)	1406 (110)	1671 (72)	1656 (70)
Dieldrin	1863 (655)	1582 (127)	1702 (47)	1907 (92)
Endrin	62.2 (8.6)	61.7 (4.3)	71.2 (1.4)	133 (10)
p,p′-DDD	1531 (476)	1384 (95)	1895 (89)	1655.3 (63)
β-Endosulfan	1128 (408)	771 (73)	854 (48)	872 (50)
p,p′-DDT	1060 (275)	1101 (26)	937 (160)	1317 (237)

Standard deviations in parenthesis.

Table 3
Analytical recoveries (%) and standard deviations (S.D.) obtained with the proposed method

Compound	Analytical recoveries (%)	S.D.
α-HCH	97.1	4.0
γ-HCH	95.9	3.5
β-HCH	129.5	20.1
Heptachlor	109.7	3.2
δ-HCH	102.9	3.8
Aldrin	96.6	3.7
Isodrin	97.5	4.4
Heptachlor epoxide	101.0	3.8
γ-Chlordane	100.2	4.2
α-Chlordane	99.9	4.0
α-Endosulfan	98.1	3.8
p,p′-DDE	100.7	4.6
Dieldrin	102.7	4.3
Endrin	116.4	8.2
p,p′-DDD	103.4	6.1
β-Endosulfan	92.8	4.4
p,p′-DDT	130.9	15.0
Endrin aldehyde	83.3	7.4
Endosulfan sulfate	96.5	8.2
Metoxychlor	141.7	28.0
Endrin ketone	96.3	6.2

high, which could be partially due to the carbon, as it is suggested by the recoveries obtained for these compounds in the cleanup step study.

4. Conclusions

An extraction method of organochlorine pesticides in soils by pressurized liquid extraction was developed. Four parameters affecting the efficiency of the extraction were investigated: temperature (100 °C), pressure (1500 p.s.i.), static time (5 min) and cell volume (5 mL).

The cleanup step was also studied by testing different common sorbents: Florisil, silica, alumina, carbon as well as combinations of them. The use of carbon cartridges of 100 $m^2\ g^{-1}$ was chosen as purification method, because this sorbent was the only one that gave clean GC–MS chromatograms. Moreover, colourless eluates were obtained, minimising the damage in the chromatographic system. The elution was done with a mixture of 10 mL of hexane–ethyl acetate (80:20 v/v).

The whole method of analysis was validated by study of the analytical recoveries as well as by extraction of the certified reference material CRM804-050, and by comparison of the values obtained with those obtained by Soxhlet and microwave-assisted extraction. The results obtained and the standard deviations were satisfactory, and then the method developed has demonstrated to be suitable for the extraction of organochlorine pesticides in soil samples.

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