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Sample Extraction Method Combining Micellar Extraction−SPME and HPLC for the Determination of Organochlorine Pesticides in Agricultural Soils

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A method for the determination of organochlorine pesticides in soil samples combining microwave assisted micellar extraction (MAME) with solid-phase microextraction (SPME) and high-performance liquid chromatography−UV has been developed. A mixture of two nonionic surfactants (polyoxyethylene 10 lauryl ether and polyoxyethylene 10 stearyl ether) was used for the extraction of pesticides from agricultural soils, and different types of SPME fibers were compared. The different parameters which affect extraction efficiency in the SPME procedure were optimized such as extraction time and temperature. The method developed involves extraction and preconcentration for the target analytes in soil samples. The analytical parameters were also studied and good recoveries obtained, RSD being lower than 10% and detection limits ranging between 36 and 164 ng g^{-1} for the pesticides studied. The proposed method was successfully applied to the determination of some organochlorine pesticides in several kinds of agricultural soil samples with different characteristics.

KEYWORDS: Organochlorine pesticides; micellar medium; extraction methods; microwave; solid-phase microextraction; soils; high-performance liquid chromatography.

INTRODUCTION

Sample preparation is a critical step in most analytical processes. The main problem encountered during the analysis is the separation of pollutants in a study from matrix components, which causes, by inefficient extractions, loss of analytes and low concentration levels in the extracts. The development of extraction and preconcentration steps prior to analytical determinations of trace level compounds has been explored in considerable depth over recent decades.

The methods usually used for the extraction of pollutants in solid samples are Soxhlet and ultrasonic extraction (*1*), which require high amounts or organic solvents and long analysis times. Other analysis methods have been developed, including pressurized liquid extraction (PLE) (*2*) and microwave assisted solvent extraction (MAE) (*3*).

Nowadays, MAE represents an interesting other option to the conventional techniques and exhibits many substantial improvements in analytical sample preparations, as it requires much lower volume of organic solvent, reduces extraction time, and lets multiple samples be prepared in one step (*4*−*6*). However, organic solvents are used as extractant in all of them. An alternative to these types of extractants would be the use of micellar systems. The extraction of organic compounds from solid samples using a micellar medium, so-called microwave assisted micellar extraction (MAME), offers advantages such as safety, low cost, and low toxicity (*7*, *8*).

However, a preconcentration step of the extract prior to the determination can be also required. It is at this stage that the potential for loss of analytes or contamination of samples is greatest.

Solid-phase microextraction (SPME) is a preconcentration technique that has been applied to the determination of several environmental pollutants in aqueous samples (*9*). Solid samples cannot be extracted directly using SPME, but can be coupled with other extraction methodologies, such as microwave extraction (*10*). For this reason, solid-phase microextraction can be an alternative to other preparation methods for soil samples prior to their analysis.

Normally the application of SPME has been performed in combination with gas chromatography; however, it is possible coupled with HPLC. Recently, many applications of SPME−HPLC have been published (*11*). The advantage of using HPLC is that compounds with low volatility or thermal labile compounds can be analyzed.

The aim of the present work was to investigate the capability of coupling micellar microwave assisted extraction and solid-phase microextraction to determine organochlorine pesticides in agricultural soil samples by HPLC−UV detection.

Organochlorine pesticides are lipophilic compounds which tend to associate with organic matter and organisms. Their hydrophobicity and low chemical and biological degradation rates have led to their accumulation in biological tissues and

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Table 1. Characteristics of Different Extraction Methods for the Analysis of Organochlorine Pesticides

extraction method	organic solvent	vol of solvent (mL)	time	toxicity	ref
Soxhlet	hexane, acetone, dichloromethane	30–100	6–24 h	high	*1, 6*
ultrasonic	hexane, acetone	10–50	1–3 h	high	*1, 2*
PLE[a]	hexane, acetone, dichloromethane	15–40	20–60 min	high	*2*
MAE[b]	hexane, acetone	10–30	5–20 min	av	*3–6*
MAME[c]	no	8	2–14 min	low	*7, 8*

[a] Pressurized liquid extraction. [b] Microwave assisted extraction. [c] Microwave assisted micellar extraction.

Table 2. Organochlorine Pesticides Studied, Wavelengths, and Retention Times

no.	compound	abbrev	λ (nm)[a]	t_R (min)[b]
1	4,4'-dichlorodiphenyldichloroethane	4,4'-DDD	238	5.4
2	dieldrin	dieldrin	220	6.1
3	4,4'-dichlorodiphenyltrichloroethane	4,4'-DDT	238	8.7
4	2,4′-dichlorodiphenyltrichloroethane	2,4′-DDT	238	9.6
5	4,4'- dichlorodiphenyldichloroethylene	4,4'-DDE	238	10.9
6	aldrin	aldrin	220	11.9

[a] Detection wavelength. [b] Retention time.

subsequent magnification of concentrations in organisms progressing up the food chain (*12*). In addition they are also toxic compounds which can affect human health (*13*); for these reasons they are listed as U.S. Environmental Protection Agency (EPA) priority pollutants (*14*).

Organochlorine pesticides have been used during a half-century due to their effectiveness as insecticides. These compounds are banned in developed countries since the 1970s, but in underdeveloped countries they are still used especially for the control of vector-borne diseases such as malaria (*15*, *16*). Despite not being used by many countries for some years, they are present in the environment; in this way, the long-term persistence of DDT and its metabolites in soil has been reported (*17*−*20*).

The analysis of these kinds of compounds requires complex procedures involving several steps such as cleanup, extraction, and preconcentration prior to their quantification (*1*).

For this reason, the coupling of MAME and SPME can be a viable alternative for the determination of these analytes. This methodology offers advantages such as it is faster than other conventional extraction methods and does not require the use of potentially hazardous organic solvents, as we can observe in **Table 1**.

EXPERIMENTAL PROCEDURES

Reagents. Organochlorine pesticides were obtained from Cerilliant Corporation (provided by LGC Promochem, Barcelona, Spain) and prepared by dissolving appropriate amounts of the commercial products in methanol. The organochlorine pesticides are listed in **Table 2** (numbers and abbreviations identify the compounds in figures).

The nonionic surfactant used in this study, a mixture of polyoxyethylene 10 lauryl ether (POLE) and polyoxyethlylene 10 stearyl ether (stearyl, with a composition of 70% POLE and 30% stearyl), were obtained from Sigma-Aldrich (Madrid, Spain) and prepared in bidistilled water.

The 50 μm Carbowax-TPR 100 (CW-TPR), 75 μm Carboxen-polydimethylsiloxane (CX-PDMS), 100 μm polydimethylsiloxane (PDMS), 60 μm polydimethylsiloxane-divinylbenzene (PDMS-DVB), 65 μm PDMS-DVB, and 85 μm polyacrylate (PA) fibers of the SPME system were provided by SUPELCO (Madrid, Spain).

Table 3. Physicochemical Characteristics and Organic Matter Content of Soils Studied

soil	agricultural uses	particle size (%) 0.3 mm	0.2 mm	0.15 mm	≤0.1 mm	pH	OM (%)	conductivity (μS/cm)
Tafira	garden	44.4	17.2	14.6	23.8	8.3	4.8	292
Sta Brigida	pine forest	56.5	17.8	12.8	12.8	5.9	3.9	483
Valleseco I	potatoes	36.33	16.43	15.19	32.06	4.84	4.4	202
Valleseco II	potatoes	25.16	13.17	14.38	47.29	3.91	6.2	100

Methanol HPLC-grade was obtained from Panreac Química S.A. (Barcelona, Spain).

All solvents and analytes were filtered through a 0.45 μm cellulose acetate membrane filter, and ultrahigh-quality water obtained by a Milli-Q water purification system (Millipore, USA) was used throughout.

Apparatus. The chromatograph system consists of a Varian pump fitted with a Varian Autosampler 410 with a volume selector, a column valve module with an internal oven, and a Varian PDA detector. The system and the data management were controlled by Star software from Varian (Varian Inc., Madrid, Spain). The stationary-phase column was a Varian Microsorb-MV 100-5 C18, 150 × 4.6 mm, 4 μm particle diameter. The analytical column was inserted in the column module and thermostated at 30 ± 0.2 °C.

The microwave oven used in this study was a Multiwave with a 6 EVAP rotor and 6 MF100 vessels (Anton Paar, Graz, Austria).

Procedures. *Soil Characteristics.* Different soils samples were collected from different agricultural locations of Gran Canaria (Canary Island, Spain): Tafira and Santa Brigida soils from the northeast of the island and Valleseco soils from the center. These soils did not show any signals of the pesticides studied in the chromatogram when a blank of them was done under our chromatographic conditions.

To determine the soil pH and conductivity, 5 g of each soil was mixed with 20 mL of bidistilled water; the slurry was stirred and then allowed to separate the supernatant, and the pH and conductivity were measured potentiometrically (*21*). The organic matter (OM) content was determined by the Sauerlandt method (organic matter oxidation by potassium dichromate and sulfuric acid) (*22*).

The physical−chemical characteristics of the soil samples are given in **Table 3**.

Preparation of Spiked Soils. The soil samples were air-dried at room temperature for more than 2 weeks and sifted through a sieve of 0.3 mm. Higher particles were thrown out. These samples were spiked as follows: 2 g of each soil was spiked with a solution of 4,4′-DDD; 4,4′-DDT; 2,4′-DDT; and 4,4′-DDE in methanol to obtain a final concentration of 0.8 μg g^{-1} of each analyte and with a volume of dieldrin solution to obtain a concentration of 1.6 μg g^{-1}. The samples were then stored in amber bottles at room temperature for 24 h before analysis, in order to obtain a dry and homogeneous sample.

Microwave Assisted Micellar Extraction. Once the soil sample was transferred to the vessel, the optimized volume and concentration of surfactant were added and the soil was subjected to the microwave assisted micellar extraction process (MAME) (*7*, *23*). The vessels were closed to avoid the loss of extract during the extraction process at microwave power and time optimized; after this, the vessels were allowed to cool first for 10 min with the microwave fan and then for another 5 min at room temperature outside the microwave oven before being opened. The extract solution was removed from the vessels, filtered with a 0.45 μm syringe-driven filter, and transferred to a glass tube.

There are different parameters that can influence the MAME process such as amount of soil, extractant volume and concentration, and irradiation time and power. Therefore it would be necessary to optimize these variables and their correlations to obtain satisfactory recovery percentages. Optimization of MAME conditions for these compounds

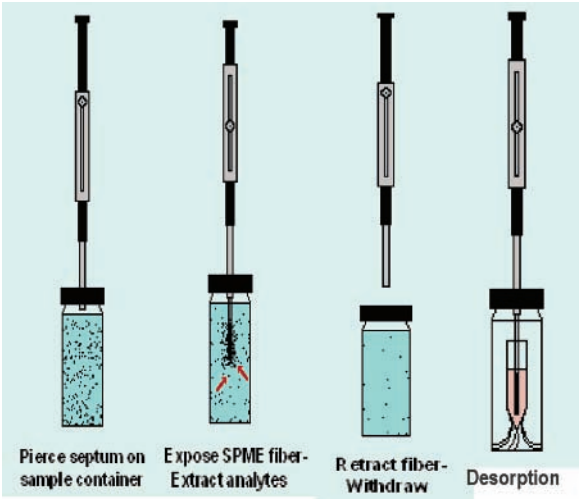

Figure 1. Scheme of MAME–SPME procedure.

has been reported in a previous study (*24*). We used a multivariable factorial design (*25*, *26*) and a central composite design (*3*) to find optimum conditions.

In this study, we have chosen 2 g of soil sample from Valleseco I with 4.4% organic matter and a pH of 4.8 and a concentration of 1.2 μg g^{-1} for 4,4′-DDD, 4,4′-DDT, 2,4′-DDT, and 4,4′-DDE and 2 μg g^{-1} for aldrin and dieldrin to carry out the extraction process. The optimum extraction conditions for the surfactant mixture under study are 8 mL of surfactant solution at 5% (v/v), 775 W of microwave power, and 8 min of microwave time (*24*).

Solid-Phase Microextraction (SPME) Process. The fibers were conditioning during at least 30 min in methanol before being used, according to the supplier's instructions.

Two milliliters of the MAME extract and 2 mL of bidistilled water were introduced in a 4 mL vial for the SPME extraction under the optimized conditions. The desorption of the compounds was done in a 200 μL glass conic vial with 80 μL of methanol during 6 min. **Figure 1** represents a diagram explaining the extraction process.

Liquid Chromatography Analysis with UV Detection. The analysis of the extracted samples was carried out using high-performance liquid chromatography with UV detection (*11*, *27*, *28*). The separation and determination of the compounds under study were performed by injecting 50 μL of SPME extract into the liquid chromatograph, and the absorbance for each analyte, corresponding to the maximum wavelength, was then measured (**Table 2**). The mobile phase used for the separation of the six organochlorine pesticides mixture was methanol−water (84:16%,v/v), isocratic with a flow rate of 1 mL min^{-1}.

A linear relationship was obtained between peak areas and the analyte concentrations in the range of 50−500 μg L^{-1}, with high correlation coefficients ($\geq$0.990).

RESULTS AND DISCUSSION

Optimization of SPME Procedure. *Fiber Selection and Optimization of Extraction/Desorption Conditions.* SPME involves a diffusion process in which analytes partition between a sample phase and a polymeric stationary phase. The efficiency of analyte extraction by SPME can vary widely depending upon the matrix nature, the time period of absorption, desorption, temperature, and salt addition (*29*), but also these variables depend on the kind of fiber that is used (*30*).

One critical aspect of SPME optimization is the selection of the appropriate fiber for the extraction of the analytes. In order to choose the best fiber for the MAME−SPME process for the extraction of organochlorine pesticides, extraction efficiencies of six different fibers were investigated: 50 μm Carbowax-TPR 100 (CW-TPR); 75 μm Carboxen-polydimethylsiloxane (CX-PDMS); 100 μm polydimethylsiloxane (PDMS); 60 μm polydimethylsiloxane-divinylbenzene (PDMS-DVB); 65 μm PDMS-DVB, and 85 μm polyacrylate (PA) fibers.

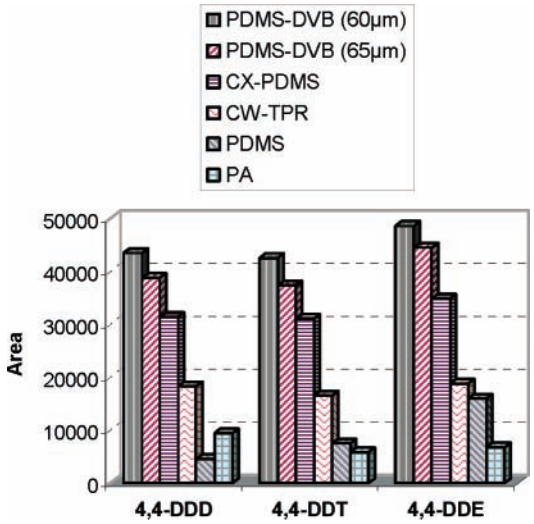

Figure 2. Peak areas obtained in the MAME–SPME extraction with six different fibers.

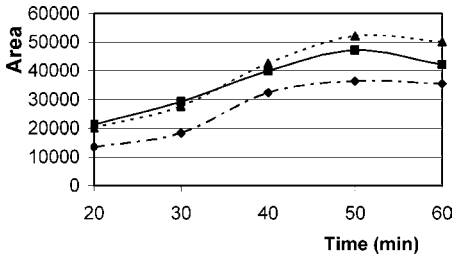

Figure 3. Absorption time optimization for SPME extraction using a nonionic surfactant mixture and PDMS-DVB fiber: 4,4′-DDT (◆), 4,4′-DDD (■), and 4,4′-DDE (▲).

With the aim of comparing the extraction efficiencies of these six commercial fibers, intermediate work conditions were used. These conditions for most cases are enough for the establishment of equilibrium between the solution and fiber (*31*). Selected conditions were 60 min of absorption time at room temperature and 10 min of desorption time. In all cases the desorption was done in 80 μL of methanol. The obtained results for the six fibers are showed in **Figure 2** for the compounds 4,4′-DDD, 4,4′-DDT, and 4,4′-DDE as representatives of the behavior of the studied organochlorine pesticides. It can be observed that the fiber which gives best results for MAME−SPME extraction of these pesticides is PDMS-DVB 60 μm, so we used this fiber for the optimization and analysis.

To optimize the extraction process, one of the most important steps is the determination of the time needed until it reaches equilibrium between the sample matrix and the coating of the fiber. **Figure 3** shows the extraction time profile obtained for three organochlorine pesticides (4,4′-DDT, 4,4′-DDD, and 4,4′-DDE) by increasing extraction time from 20 min to 60 min. As can be observed, the amounts of the three compounds extracted (presented as peak areas) increase greatly with extraction time up to 50 min. Increases of the extraction time beyond this point do not result in a proportional increase in the peak areas for these pesticides. The rest of the compounds gave similar results. To achieve enough sensitivity in analysis for all compounds, 50 min of extraction time was selected for the analysis of these samples, obtaining good reproducibility and an acceptable analysis time.

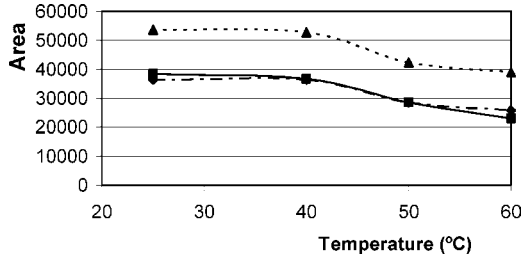

Figure 4. Temperature extraction optimization for SPME extraction: 4,4′-DDT (◆), 4,4′-DDD (■), and 4,4′-DDE (▲).

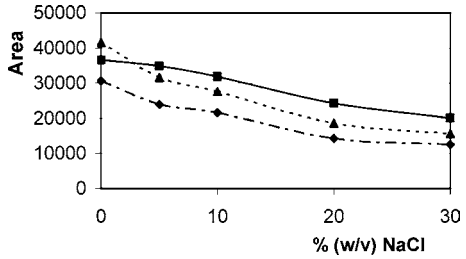

Figure 5. Optimization of the NaCl concentration in the SPME extraction: 4,4′-DDT (◆), 4,4′-DDD (■), and 4,4′-DDE (▲).

The following step in the optimization process was to select the optimum desorption time. It was determined by immersion of the PDMS-DVB fiber into 80 μL of methanol in the glass vial before injection into the HPLC system. The desorption time was studied in the range of 2−10 min. It was found that the peak area of analytes increases lightly with the desorption time up to 6 min; after this time the peak area remains constant, showing that desorption of the analytes has been produced. Then we chose 6 min as the optimum desorption time.

The temperature of extraction can play an important role in the absorption of analytes, because it influences the mass transfer rates and the partition coefficients of the analytes (*31*). Extraction temperature influence was studied in the range 25−60 °C for an extraction period of 50 min. Extraction temperatures higher than 40 °C produce a decrease in the peak area. It can be observed in **Figure 4** that at temperatures lower than 40 °C the amount absorbed is practically constant. It has been found that the amount of analyte absorbed can decrease with increasing temperature (*32*). Therefore we decided to carry out all the measurements at room temperature.

Another extraction parameter which can have an effect in the extraction procedure is the ionic strength of the sample. The salt normally produces an improvement in the extraction in the fiber but also in the surfactant, so that both effects are opposite, and the efficiency of the fiber can be reduced. To determine the effect of NaCl addition on the extraction efficiency for organochlorine pesticides, we used a NaCl concentration range between 0% and 30% (w/v). **Figure 5** shows the results obtained for three representative pesticides, obtaining similar results for the rest of the analytes. It was found that for these compounds salt addition produces a decrease of the peak area of the organochlorine pesticides studied. This can be due to the competition between the fiber and the surfactant; for this reason we did not add salt in MAME−SPME extraction.

Finally, according to the obtained results in these previous studies, the optimum extraction parameters for target of selected pesticides were 50 min for absorption time, 6 min for desorption time, room temperature, and nonaddition of salt.

Analytical Parameters. Figure 6 shows a blank and a typical chromatogram obtained after the application of the optimized MAME−SPME procedure to a soil spiked sample with six organochlorine pesticides with a final concentration of 0.8 μg g^{-1} for 4,4′-DDD, 4,4′-DDT, 2,4′-DDT, and 4,4′-DDE and 1.6 μg g^{-1} for aldrin and dieldrin. It can be observed that the optimized conditions allow a good separation of analytes and a short analysis time.

High correlation coefficients (≥0.990) were obtained in all cases for the concentration range of 50 and 500 μg L^{-1} using the surfactant mixture at a concentration of 5% (v/v) and PDMS-DVB fiber under the optimum conditions.

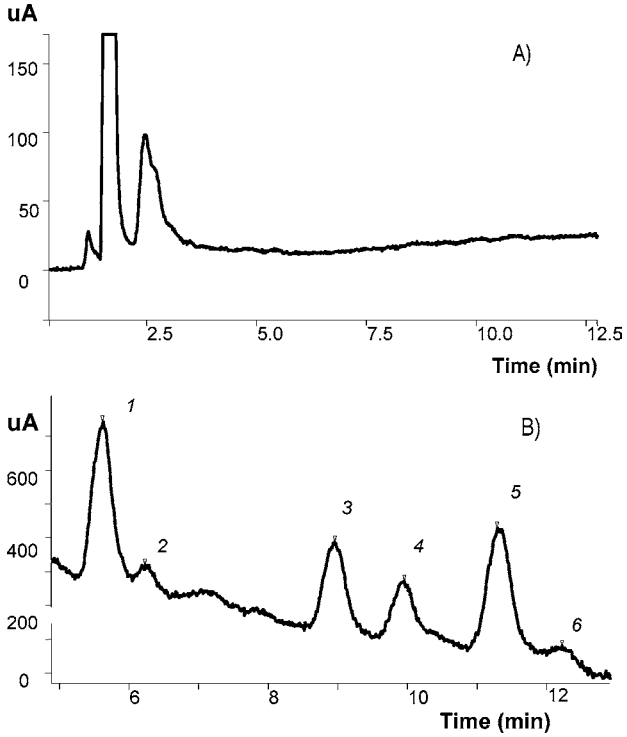

Figure 6. Chromatogram of an extract of a blank of Valleseco I soil sample after MAME−SPME procedure (**A**), and an extract of a spiked Valleseco I soil sample (**B**). Chromatographic conditions as described in the text. The numbering refers to **Table 2**.

Table 4. Analytical Parameters in the Determination of Studied Pesticides Using MAME−SPME[a]

compound	RSD (%)	LOD (ng g^{-1})
4,4′-DDD	5.3	64
dieldrin	9.5	124
4,4′-DDT	9.7	44
2,4′-DDT	9.6	100
4,4′-DDE	6.4	36
aldrin	10.1	164

[a] $n = 6$.

Table 5. Validation of MAME−SPME Extraction Method Coupled to HPLC Using a Certified Reference Material[a]

compound	ref value[b]	RSD (%)	confidence interval	concn found (MAME−SPME)
4,4′-DDD	1.531	0.476	1.294–1.767	1.576 ± 0.101
dieldrin	1.863	0.655	1.539–2.186	2.195 ± 0.114
4,4′-*DDT*	1.060	0.275	0.926–1.195	0.972 ± 0.095
4,4′-*DDE*	1.520	0.410	1.325–1.715	1.410 ± 0.171

[a] All values are expressed in μg g^{-1}. [b] The pesticide values in the sample were certified by USEPA SW846 (3rd ed.). Extraction Methods 3540A/3541 (Soxhlet), 3550 (sonication), and Analysis Method 8081.

Table 6. Recoveries Obtained after Application of MAME–SPME Procedure Coupled to HPLC to Four Different Soils

	4,4′-DDD	dieldrin	4,4′-DDT	2,4′-DDT	4,4′-DDE	aldrin
Tafira	85.7 ± 0.9	97.4 ± 8.6	90.2 ± 3.1	79.9 ± 3.8	81.5 ± 1.8	98.5 ± 2.7
Sta Brigida	75.5 ± 3.0	99.8 ± 9.1	92.6 ± 3.7	89.5 ± 6.8	86.0 ± 1.6	73.7 ± 6.0
Valleseco I	63.0 ± 2.3	98.8 ± 7.9	70.4 ± 4.2	77.5 ± 5.6	60.4 ± 3.2	59.1 ± 9.8
Valleseco II	96.2 ± 3.4	106.9 ± 9.4	83.4 ± 4.5	100.6 ± 4.2	93.5 ± 2.6	94.1 ± 10.0

In order to determine its reproducibility, the optimized extraction method was applied to six samples containing the mixture of the pesticides under study and analyzed under the established chromatographic conditions. The results obtained from relative standard deviation are listed in **Table 4**, where values are in the range of 5.3−10.1% in all cases. The limits of detection were also calculated for each analyte using a signal-to-noise ratio (s/n = 3) (*33*). The detection limits are in the range 36−164 ng g^{-1} (**Table 4**) for all compounds studied.

Validation with a Certified Soil. Recoveries obtained with spiked compounds may not be representative of those found with native compounds. Spiked analytes are generally lightly coated on the surface of the matrix whereas native ones can be strongly adsorbed inside the porous matrix. This can be explained by the diffusional and the kinetic limitations of the sorption process, and the several interactions which may have been simultaneously established between native analyte and the matrix (*34*).

The validity of the proposed MAME−SPME method coupled to HPLC was carried out applying it to a certified reference soil sample (CRM804-050) containing a mixture of pesticides 4,4′-DDD, 4,4′-DDT, 4,4′-DDE, and dieldrin.

The solubilization of target pesticides initially in the reference soil sample is achieved with the use of a mixture of two surfactants (polyoxyethylene 10 lauryl ether and polyoxyethylene 10 stearyl ether) in a microwave oven with the experimental conditions previously optimized (*26*). The extract obtained was subjected to SPME extraction with PDMS-DVB fiber under the conditions previously optimized in this work. **Table 5** shows the results obtained in this study, where we can observe that the recoveries obtained fal within the certified range for all compounds analyzed, so that the proposed extraction and determination procedure is suitable.

Applications. *Matrix Effect Study*. In order to study the influence of soil characteristics on the optimized MAME−SPME method, it was applied to the extraction and determination of pesticide mixtures in four different types of agricultural soils from different agricultural areas of Gran Canaria Island (Canary Island, Spain), with different levels of organic matter, pH, conductivity, and texture (**Table 3**). Blanks of these soil samples do not present peaks of organochlorine pesticides or interference in the chromatograms. These samples were then spiked with the mixture of pesticides to obtain a final concentration of 0.8 μg g^{-1} for 4,4′-DDD, 4,4′-DDT, 2,4′-DDT, and 4,4′-DDE and 1.6 μg g^{-1} for dieldrin and aldrin to investigate the matrix effect on this method. The selected concentration level for spiking was the one typical of acute pollution events that may occur in this kind of soil (*35*). The soil samples were stored in the dark at room temperature for 24 h before analysis.

Table 6 shows the recoveries obtained for the analytes under study in these different kinds of soils. In general, the extraction efficiency is satisfactory for all compounds, but it can be observed that recoveries vary depending on the soil characteristics. The texture of a soil is quite important in the sorption process (*36*). Clay is by far the most adsorbent of the three main soil textures (clay, silt, and sand) due to its small particle size, high surface area, and high surface charge (*37*). This has a relevant effect on the recovery; the higher clay percent a soil has, the lower the recovery is, so, in this case, the Valleseco II soil has a higher amount of particles with smaller size, and therefore, lower recoveries are obtained.

According to these results, we can conclude that the proposed MAME−SPME method coupled to HPLC is applicable to determine the target analytes in soil samples in the range of concentrations studied (200−2000 ng g^{-1}).

Conclusions. Microwave assisted extraction with surfactant as extractant combined with SPME and HPLC is a promising methodology for the determination of organochlorine pesticides in agricultural soil samples.

With this new method, the previous treatment in the analysis of organochlorine pesticides contained in solid samples could be reduced to a stage of solubilization of the pollutants in a micellar medium followed by a separation by SPME. This allows the analysis of these compounds in solid samples that cannot be extracted directly using SPME. Finally the organochlorine pesticides can be determined by HPLC−UV.

Some first results with this methodology are presented to show the suitability of this analytical process in the field of environmental control, and to illustrate the potential of the procedure.

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