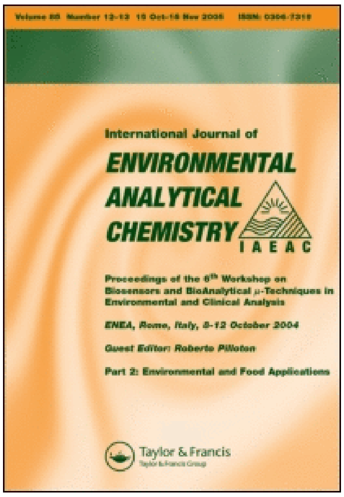

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Application of microwave-assisted micellar extraction combined with solid-phase microextraction and high-performance liquid chromatography with UV detection for the determination of organochlorine pesticides in different mud samples

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An analytical method combining microwave assisted micellar extraction (MAME) followed by solid-phase microextraction (SPME) and high-performance liquid chromatography–ultraviolet high-performance liquid chromatography with UV detection–detection is implemented for the determination of six organochlorine pesticides in different mud samples collected on Gran Canaria Island (Spain). This method allows detection limits to be reduced with respect to MAME extraction and also enables target organochlorine pesticides to be determined in complex matrices due to the clean-up procedure. Several new variables that affect the MAME–SPME process were introduced and optimized. A non-ionic surfactant, polyoxyethylene 10 lauryl ether, and a 60 μm polydimethylsiloxane-divinylbenzene fibre were used for this approach. After systematic investigations, the optimum experimental parameters were fixed. The optimized method provided satisfactory precision (relative standard deviation less than 10%), good recoveries (79.78–117.70%) and detection limits ranging between 28 and 136 $\mathrm{ng\,g^{-1}}$ for the pesticides studied. The proposed method was successfully applied to the determination of target organochlorine pesticides in several kinds of mud samples of different physico-chemical characteristics and areas. The MAME–SPME method was also validated and applied to a certified reference material.

Keywords: Microwave; Micellar solution; Solid-phase microextraction; Organochlorine pesticides; Mud samples

1. Introduction

Modern trends in analytical chemistry are moving towards the simplification and minimization of organic solvent on sample preparation. Traditional methods for extracting organic pollutants from solid samples are typically time-consuming, employ multistep procedures with high risk of losing analytes, and use large amounts of organic

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solvents [1]. Thus, there is a great need to develop comprehensive methods that integrate sampling, extraction, and concentration, and minimize the use of organic solvents, thus resulting in a high sample throughput such as supercritical fluid extraction and microwave extraction [2, 3].

Microwave-assisted extraction (MAE) is a rather new technique that has been used for the extraction of organic pollutants for solid samples. Compared with conventional extraction methods it is a fast method that uses a low volume of extraction solvent [4–6]. An alternative to organic solvents as extractants would be the use of micellar systems. The combination of MAE with micellar media as extractants (microwave-assisted micellar extraction, MAME) has been successfully used for the extraction of several kinds of organic compounds from solid samples [7–10]. However, the analysis of MAME extracts could require clean-up and preconcentration steps prior to the determination. Solid-phase microextraction (SPME) could be used for this purpose.

SPME was first described by Lord and Pawliszyn [11]. It is a technique whereby the analytes are adsorbed onto the surface of a coated silica fibre. Initially, SPME was mainly described for applications in environmental analysis of liquid samples using GC as the determination technique [12]. Recently, interest in the applications of this technique combined with LC has increased, and a number of applications have been developed [13].

In this work, MAME followed by solid-phase microextraction and high-performance liquid chromatography with UV detection (HPLC–UV) has been implemented for quantitative analysis of organochlorine pesticides in different mud samples of several coastal regions.

Organochlorine pesticides are known to show bioaccumulative behaviour due to their high lipophilicity and persistence [14], with subsequent risks to human health [15, 16]. In the aquatic environment, organochlorine pesticides are removed from the water and adsorbed on the particulate matter due to their high affinity with organic matter, and finally accumulated on mud, which may play a role as a secondary contamination source [17]. For these reasons, these compounds are listed as a US Environmental Protection Agency (EPA) priority pollutant [18].

The experimental parameters of the MAME–SPME procedure were studied, including traditional variables in SPME optimization such as absorption and desorption time, extraction temperature, and ionic strength, but also new variables like dilution of MAME extract, the influence of vibration in desorption process, or the desorption volume, which have not previously been studied. The method's precision, recoveries, and linearity were also investigated. To prove the method validity, it was applied to the determination of organochlorine pesticides in a certified material, and in different mud samples from different areas of Gran Canaria (Canary Islands, Spain).

2. Experimental

2.1 *Reagents*

Organochlorine pesticides were obtained from Cerilliant Corporation (provided by LGC Promochem, Barcelona, Spain), prepared by dissolving appropriate amounts of

Table 1. Target organochlorine pesticides, wavelengths, and retention times.

No.	Compound	Abbreviation	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.

the commercial products in methanol to obtain a concentration of 1 gL^{-1}, and stored in amber bottles at 4°C. Working solutions were prepared by further diluting these concentrations. The organochlorine pesticides are listed in table 1 (numbers and abbreviations identify the compounds in figures).

The non-ionic surfactant used in this study, polyoxyethylene 10 lauryl ether (POLE), was obtained from Sigma-Aldrich (Madrid, Spain) and prepared in bidistilled water.

The 60 µm polydimethylsiloxane-divinylbenzene (PDMS-DVB) fibre of the SPME system was provided by SUPELCO (Madrid, Spain). Before use, the fibre was conditioning with methanol according to the supplier's instructions. Specifically, each day prior to analysis, the fibre was washed in water and conditioned in methanol. Finally, it was dried before extraction. HPLC-grade methanol was obtained from Panreac Química SA (Barcelona).

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

2.2 *Apparatus*

The liquid-chromatography system consisted 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 data management were controlled by Star software from Varian (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 (Anton Paar, Graz, Austria) with a 6 EVAP rotor and 6 MF100 vessels (Anton Paar, Graz, Austria).

2.3 *Procedures*

2.3.1 Mud characteristics. Different mud samples were collected from different coastal regions of Gran Canaria: Maspalomas, Las Palmas de G.C., La Aldea, Sardina del Norte, Taurito, and Hoya Pozuelo. The location of each mud sample is shown in figure 1. These samples did not show any signals in the chromatogram when a blank was analysed. The physico-chemical characteristics of the mud samples are listed in table 2. To determine the pH and conductivity, 5 g of each mud was mixed with

Figure 1. Representation of the different coastal regions of Gran Canaria (Spain) where the mud samples were collected.

Table 2. Mud characteristics.

	Particle size (%)						
Mud	0.3 mm	0.2 mm	0.15 mm	≤0.1 mm	pH	Organic matter (%)	Conductivity (mS cm^{-1})
Maspalomas	58.30	31.79	9.12	0.79	9.3	0.43	2.39
Las Palmas	2.15	22.66	68.87	6.31	8.8	0.65	0.30
La Aldea	34.60	15.15	17.62	32.63	8.6	3.36	1.93
Sardina	70.54	26.45	2.97	0.04	9.1	0.60	1.75
Taurito	64.68	21.75	7.60	5.95	9.3	0.69	0.88
Hoya Pozuelo	67.01	23.74	5.46	3.79	8.6	1.08	0.35
San Felipe	45.65	19.56	17.40	17.40	7.6	3.02	12.92
Salinetas	72.46	24.25	3.18	0.10	9.1	0.28	0.11
Agaete	70.99	20.23	7.09	1.67	9.7	0.27	0.69
Jinamar	56.43	29.58	9.99	3.99	9.8	0.15	0.16

20 mL of bidistilled water; the slurry was then stirred and the supernatant allowed to separate. The pH and conductivity were measured potentiometrically [19]. The organic matter content was determined by the Sauerlandt method (organic matter oxidation by potassium dichromate and sulfuric acid) [20].

2.3.2 Preparation of spiked mud. The mud samples were air-dried at room temperature for more than 2 weeks and sifted to a particle size of less than 0.3 mm. Spiked mud was prepared by mixing them with an organochlorine solution in acetone 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 concentration for Aldrin and Dieldrin of 1.6 μg g^{-1}. The sample was then stored in amber bottles at room temperature for 24 h before analysis to obtain dry and homogenous samples.

2.3.3 Microwave-assisted micellar extraction. Once the mud sample (2 g) was transferred to the vessel, the optimum volume (8 mL) and concentration of surfactant (5%, v/v) were added, and the sample was subjected to the MAME process at the optimum conditions. The vessels were then allowed to cool first for 10 min with the microwave fan and after another 5 min at room temperature before being opened. The extract solution was filtered with a 0.45 µm syringe-driven filter for the SPME process.

2.3.4 Solid-phase microextraction (SPME) process. The SPME fibre used in the MAME–SPME procedure was 60 µm polydimethylsiloxane-divinylbenzene (PDMS-DVB) fibre for direct immersion. The fibre was conditioned and cleaned between extractions according to the supplier's instructions. Five millilitres of the MAME extract and 7.5 mL of bidistilled water were introduced in a 15-mL vial for the SPME extraction under the optimized conditions (60 min for absorption with stirring at a speed of 700 rpm, room temperature and non-addition of salt, and 8 min for desorption time). Desorption of the compounds was done in a 200-µL glass conical vial with 55 µL of methanol for 8 min.

2.3.5 Liquid chromatography analysis with UV detection. The extracted samples were analysed using high-performance liquid chromatography with UV detection [21], an easy, rapid, and economical detection method. The separation and determination of the compounds under study were performed by injecting 50 µL of extract into the liquid chromatograph, and the absorbance for each analyte, corresponding to the maximum wavelength, was then measured. The retention time and wavelength for each compound are listed in table 1. The eluent used for the separation of the six organochlorine pesticides mixture was methanol : water (84 : 16%,v/v) isocratic with a flow rate of $1\,\mathrm{mL\,min^{-1}}$.

The corresponding curve was calibrated under optimal MAME–SPME conditions, and the corresponding analyte concentrations ranged between 50 and $500\,\mu\mathrm{g\,L^{-1}}$ for 4,4′-DDD, 4,4′-DDT, 2,4′-DDT, and 4,4′-DDE, and between 100 and $1000\,\mu\mathrm{g\,L^{-1}}$ for Aldrin and Dieldrin. A linear relationship was obtained between the peak areas and the analyte concentrations, with high correlation coefficients ($\geq$0.994).

2.4 *Statistical analysis*

The experiment was designed using Statgraphics Plus software, version 5.1 (Manugistic, Rockville, MD), thus allowing several variables to be studied together without any interference from external or indirect variables.

3. Results and discussion

3.1 *Optimization of MAME methodology*

Optimization experiments were performed using a mud sample from Hoya Pozuelo (east of island) with 1.08% organic matter and pH 8.64 with POLE as extractant for the

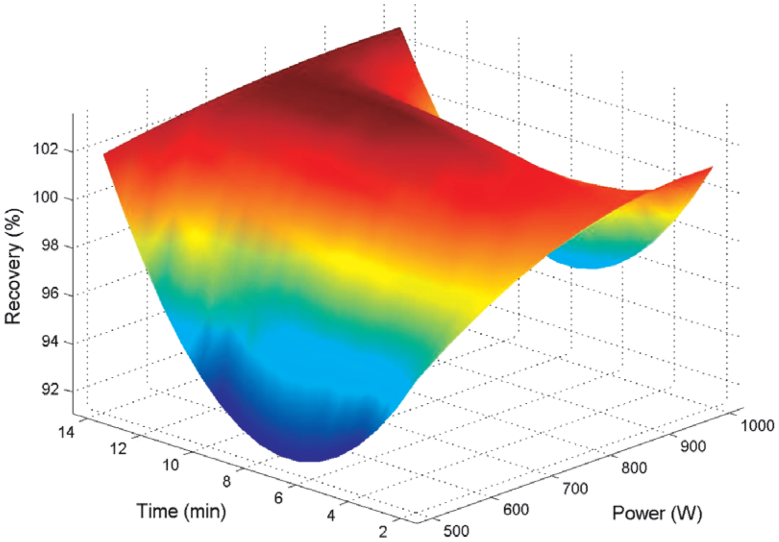

Figure 2. Response surface for the effect of power and time on the extraction of 4,4′-DDT.

mixture of six organochlorine pesticides under study. Parameters that can influence on MAME process are the amount of sample, extractant volume and concentration, irradiation time, and power.

In previous studies, the surfactant POLE was used for MAME procedure in soils samples, with an optimum surfactant volume of 8 mL and optimum surfactant concentration of 5% (v/v) [22]. Higher concentrations produce a decrease in peak area due to a higher viscosity in the solution. These values were fixed for the present study.

To optimize the microwave time and power, 2 g of sample was taken, and these variables were studied with a 3^2 factorial design where microwave power and time are represented against recovery. Temperature is a parameter that influences extraction but cannot be controlled directly. Figure 2 shows the response surface power *versus* time for the case of 4,4′DDT. The studies carried out for the rest of analytes show similar results for power and extraction time. The amount of analyte extracted increases with microwave power up to 800 W, with a resultant temperature of around 140°C. However, a decrease in efficiency extraction is observed at a higher power, probably due to volatilization or degradation of the analytes.

With respect to extraction time, the results obtained show that an intermediate time of 8 min is the most suitable. In agreement with the results obtained, we have choosen the following optimum conditions for the MAME procedure: 2 g of mud amount, 8 mL of surfactant volume, 5% (v/v) of surfactant concentration, 750 W of microwave power, and a microwave time of 8 min.

3.2 *Optimization of SPME procedure*

For the MAME–SPME procedure, it is necessary to study the amount and concentration of MAME extract, which will be used in the SPME step. To compare the extraction efficiencies with different vial compositions, at several percentages

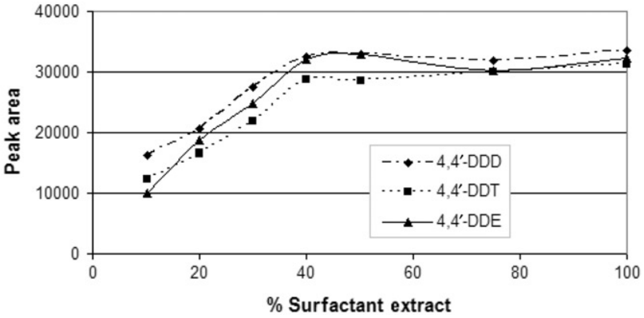

Figure 3. Peak areas obtained in the MAME–SPME extraction with different vials compositions (% surfactant extract and% water) for 4,4′-DDT (♦), 4,4′-DDD (■), and 4,4′-DDE (▲) compounds.

of POLE extract (with analyte concentrations of 0.2 $\mu g L^{-1}$ for 4,4′-DDD, 4,4′-DDT, 2,4′-DDT, and 4,4′-DDE, and 0.4 $\mu g L^{-1}$ for Aldrin and Dieldrin), intermediate working conditions were used [22]. Selected conditions were 40 min of absorption time at room temperature and 6 min of desorption time (desorption was done in 80 µL of methanol). The vials used were 15 mL vials, but they were filled with 12.5 mL of the selected surfactant extract solution. The solution composition was varied in this study between 10 and 100% (v/v) of surfactant, depending on the extract percentages used, that it is completed until 100% (12.5 mL) with bidistilled water. The results obtained for different vial compositions, depending on surfactant extract percentages, are shown in figure 3 for the compounds 4,4′-DDD, 4,4′-DDT and 4,4′-DDE, as representatives of the behaviour of the studied organochlorine pesticides. It can be seen that the vial composition where is obtained better results is for 40% of MAME extract and 60% of water. This represents a volume of 5 mL of MAME extract and 7.5 mL of water in a vial of 15 mL. Therefore, this vial composition was used for MAME–SPME optimization and analysis.

SPME involves a diffusion process in which analytes partition between the sample phase and the polymeric stationary phase [23]. The efficiency of analyte extraction by SPME can vary widely, depending on the values of the variables which affect this process, such as the period of absorption and desorption [24].

To optimize the extraction process, one of the most important steps is to determine the time needed until equilibrium is reached between the sample matrix and the coating of the fibre. Figure 4 shows the extraction time profile obtained for three organochlorine pesticides (4,4′-DDT, 4,4′-DDD, and 4,4′-DDE) by increasing the extraction time from 20 to 80 min. As can be seen, the amount extracted (presented as peak area) for the three compounds increases greatly with extraction time up to 60 min. The extraction yield did not improve significantly with longer extraction times. In subsequent studies, this time was selected as the extraction time. The rest of the compounds gave similar results.

The temperature of extraction and ionic strength of the sample can play an important role in analyte absorption [25], but in previous studies of the MAME–SPME procedure using POLE as an extractant and 60 µm PDMS-DVB fibre, it was proved that these two factors produced a decrease in the recoveries [22]. For this reason, in this study, these parameters have not been included.

The next step in the optimization process was to select the optimum desorption time, which was determined in the static mode at room temperature by immersion of the

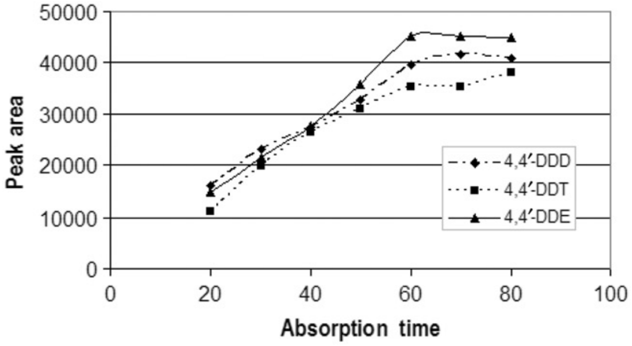

Figure 4. Absorption time (min) optimization for SPME extraction using POLE surfactant and PDMS-DVB fibre: 4,4′-DDT (♦), 4,4′-DDD (■), and 4,4′-DDE (▲).

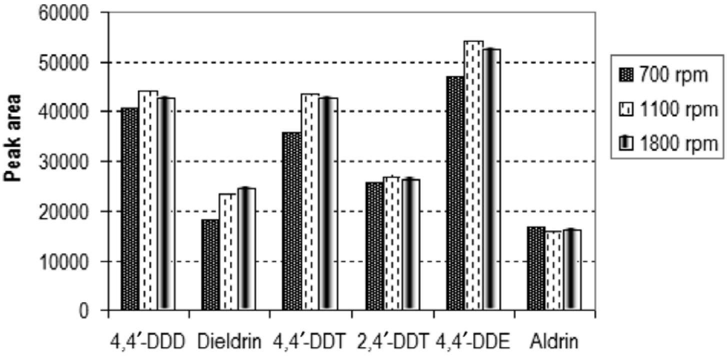

Figure 5. Peak areas obtained in the MAME–SPME extraction with different vibration levels on the desorption for the pesticides studied.

PDMS-DVB fibre into 80 μL of methanol in the glass vial before injection into the HPLC system. The desorption time was studied in the range of 4–12 min. It was found that peak areas of analytes increase with desorption time up to 8 min; after this time, the peak areas remain constant, thus showing that the analytes have been desorbed. We then chose 8 min as the optimum desorption time.

Other extraction parameters which can affect the SPME procedure and have not been studied before are the vibration on desorption and desorption volume. Stirring the solution improves mass transference between the fibre and the methanol phase, so the equilibrium can be achieved more efficiently by enhancing the diffusion of analytes from the fibre to the solution. To study the effect of vibration on the desorption, the SPME fibre metal support was submitted to different speeds: 700, 1100, and 1800 rpm. It was found that average vibrations (1100 rpm in the magnetic stirrer) produce the best peak areas for the organochlorine pesticides studied. Figure 5 shows the results obtained for the six pesticides. We chose 1100 rpm for the magnetic stirrer as the optimum value to carry out the desorption.

With these new conditions, the desorption volume was also studied. As shown earlier, 80 μL of methanol was used in the extraction optimization. However, lower volumes

Table 3. Peak areas obtained with different desorption volumes.

Compound	80 μL	70 μL	60 μL	55 μL
4,4′-DDD	44 129	49 310	57 597	64 606
Dieldrin	23 482	25 489	28 913	39 401
4,4′-DDT	43 403	48 103	60 087	66 718
2,4′-DDT	26 919	30 724	40 289	42 139
4,4′-DDE	54 074	60 684	80 986	84 090
Aldrin	15 947	22 240	30 195	42 301

produce an increment in the peak area. This was studied with four different volumes (table 3), and it can be seen that the peak area increases as desorption volume decreases for all studied analytes. According to these results, 55 μL of methanol was selected.

Finally, taking these previous results into account, the optimum extraction parameters for target pesticides were: 60 min for absorption time for direct SPME extraction, room temperature and non-addition of salt; 8 min for desorption time; and 1100 rpm for the magnetic stirrer for the desorption with a volume of 55 μL of methanol. Under these conditions, we checked that in our study the carryover effect would not be produced after the fibre washing process.

3.3 *Analytical parameters*

The samples were analysed using HPLC–UV. The chromatogram obtained for the mixture of pesticides (0.8 $\mu g\,g^{-1}$ for 4,4′-DDD, 4,4′-DDT, 2,4′-DDT, and 4,4′-DDE, and 1.6 $\mu g\,g^{-1}$ for Aldrin and Dieldrin) extracted from a spiked Hoya Pozuelo mud sample using MAME–SPME procedure is shown in figure 6. It can be seen that the mobile phase used (methanol : water, 84 : 16 v/v) allows a good separation of analytes and a short analysis time.

To obtain the calibration curves, MAME–SPME followed by HPLC–UV analysis of the working solutions ranged from 50 to 1000 $\mu g\,L^{-1}$ was performed. A linear relationship was obtained between peak areas and the analyte concentrations, with high correlation coefficients ($\geq$0.994) and the range of yield of extraction between 91.18 and 108.34% (table 4). The relative standard deviations of the method calculated using six samples are listed in table 4. These results indicate standard deviation values between 2.43 and 10.11%, which show that the proposed method has an acceptable precision. The detection limits of each compound [26] were calculated as three times the noise for each pesticide and vary between 28 and 136 $ng\,g^{-1}$ for all compounds studied.

3.4 *Validation with a certified soil*

Spiked analytes are generally lightly coated on the surface of the matrix, whereas native analytes can be strongly adsorbed inside the porous matrix. Recoveries obtained with spiked compounds may not be representative of those found with native compounds, due to the several interactions which may have been simultaneously established between the native analyte and the matrix with time [27]. For this reason, the extraction procedure needs to validated with certified reference matrices. For this purpose, we used a certified reference sandy soil sample, from a region of the Western United States (CRM804-050) that contained four of the studied pesticides. The proposed extraction-determination procedure was carried out using 2 g of this soil under optimum conditions. Table 5 lists the pesticides present in the certified sample and corresponding certified values, the confidence intervals, and the concentration of each analyte obtained using the proposed MAME–SPME procedure. The concentrations obtained

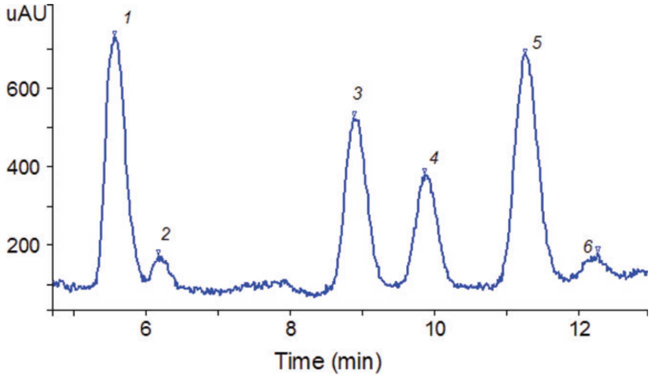

Figure 6. Chromatogram of an extract of a spiked Hoya Pozuelo mud sample after MAME–SPME procedure. Chromatographic conditions as described in the text, $\lambda = 238$ nm. Numbering refers to table 1.

Table 4. Analytical parameters in the method for the determination of pesticides studied using MAME–SPME–HPLC–UV.

Compound	Recovery (%)	RSD (%)[a]	LOD ($ng\,g^{-1}$)[b]
4,4′-DDD	104.5	2.4	44
Dieldrin	91.1	8.4	104
4,4′-DDT	108.3	3.8	40
2,4′-DDT	98.1	2.7	84
4,4′-DDE	105.7	4.3	28
Aldrin	98.9	10.1	136

[a] Relative standard deviation ($n = 6$).
[b] Limit of detection.

Table 5. Extraction and determination of pesticides using MAME–SPME procedure followed by HPLC–UV in a certified reference material.

Compound	Reference value[a]	Relative standard deviation	Confidence interval	Amount found[b]
4,4′-DDD	1.531	0.476	1.294–1.767	1.333 ± 0.052
Dieldrin	1.863	0.655	1.539–2.186	2.112 ± 0.119
4,4′-DDT	1.060	0.275	0.926–1.195	0.933 ± 0.028
4,4′-DDE	1.520	0.410	1.325–1.715	1.396 ± 0.167

[a] The pesticides values in the sample were certified by US EPA SW846 (3rd ed.). Extraction Methods 3540A/3541 (soxhlet), 3550 (sonication) and Analysis Method 8081.
[b] Mean of three determinations. All values are expresed in $\mu g\,g^{-1}$.

fall within the certified range for all compounds analysed, indicating that the proposed extraction procedure is suitable for this kind of matrix.

3.5 *Applications*

3.5.1 Matrix effect study. In order to study the influence of mud characteristics on the extraction, the optimized method was used to determine the studied mixture of organochlorine pesticides in 10 mud spiked samples with different levels of organic matter, pH, texture, and conductivity of different regions of Gran Canaria (figure 1). The selected concentration level for spiking ($0.8\,\mu g\,g^{-1}$ for 4,4′-DDD, 4,4′-DDT, 2,4′-DDT, and 4,4′-DDE and $1.6\,\mu g\,g^{-1}$ for Aldrin and Dieldrin) was typical of the acute pollution events that occur in this kind of sample [28]. The mud samples were spiked and stored in the dark at room temperature for 24 h before analysis. The results obtained are shown in table 6, and it can be seen that recoveries do not vary significantly depending on the mud characteristics. In all cases, the recoveries obtained were equal to or higher than 80%. This shows that the proposed method can be applied to different kinds of mud for the extraction of organochlorine pesticides with very satisfactory results.

3.5.2 Influence of ageing time. Decreasing recoveries resulting from ageing of matrices are a well-known phenomenon [29, 30]. The analytes present in recent samples are more easily extracted than those that have had a longer contact time. This can be explained as being dependent on whether the analytes are incorporated by adsorption (short periods) and sequestration (long periods) [31]. The former phenomenon occurs in the early stages of sorption, where H-bonding and Van der Waals forces prevail. On the other hand, sequestration involves sorption at remote microsites within the matrix [32].

In order to study the ageing effect, we used the MAME–SPME procedure for different ageing times after sample conditioning. The mud samples were spiked with the mixture of pesticides and stored at room temperature in the dark for 24 h, 1 week, 2 weeks, and 1 month before extraction. Figure 7 shows the recoveries obtained for the different pesticides in the case of the Hoya Pozuelo mud sample with ageing time.

Table 6. Recoveries (%) obtained after MAME–SPME–HPLC–UV procedure for the pesticides in 10 different mud samples[a].

Mud samples	4,4′-DDD	Dieldrin	4,4′-DDT	2,4′-DDT	4,4′-DDE	Aldrin
Maspalomas	101.1	79.7	96.1	83.91	100.1	105.6
Las Palmas	105.1	99.5	109.9	103.9	117.7	93.3
Hoya Pozuelo	104.6	91.1	108.3	98.1	105.8	98.9
La Aldea	100.0	89.8	109.4	94.8	108.9	84.4
Sardina	87.4	81.9	89.9	82.2	87.9	83.3
Taurito	105.6	89.9	100.1	95.0	110.5	95.2
Agaete	93.8	102.4	95.2	83.9	96.1	82.3
Jinamar	106.2	93.8	103.6	93.7	102.0	91.5
Salinetas	101.6	94.6	102.8	96.3	104.8	93.2
San Felipe	95.2	89.4	94.3	85.8	100.5	81.8

[a] Mean of three determinations.

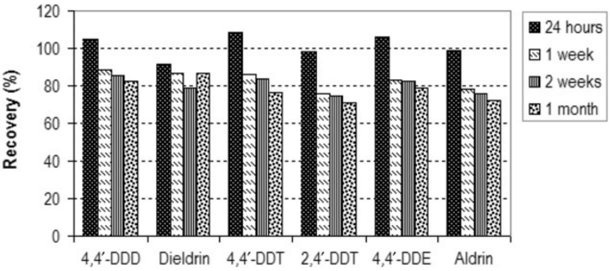

Figure 7. Recoveries (%) obtained after the MAME–SPME procedure for the pesticides at four different aging times for the Hoya Pozuelo mud sample.

In general, it can be seen that the recoveries decrease after the first day for all compounds, which could be explained as being due to the sorption process. After this time, the recoveries practically do not vary, with values always remaining above 70% in all cases. Moreover, none of the metabolites of DDT increases with the time, so we presume that the degradation processes did not occur with these ageing times. These results indicate that the developed method allows to determine the presence of pesticides in aged mud samples and show the viability of the method as an alternative to the conventional ones.

4. Conclusions

MAME–SPME followed by HPLC–UV was successfully implemented and applied for extraction and determination of organochlorine pesticides in several mud samples with different characteristics and areas of origin. Several new variables which affecting the MAME–SPME process were also investigated. The method is simple and economical, and does not require the use of an organic solvent.

MAME–SPME-HPLC provides recoveries higher than 80% with a relative standard deviation lower than 10% and detection limit of 28–136 ng g^{-1} for the organochlorine pesticides studied. Therefore, the experimental results show that the method developed is an alternative method for determination of pesticides in mud samples.

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