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SPME FOR THE SIMULTANEOUS DETERMINATION OF PHENOLIC, TRIAZINE AND ORGANOCHLORINE PESTICIDES BY GC/MS

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Introduction

Persistent organic pollutants, such as pesticides are worldwide distributed, causing a great social and scientific concern. As a result of this concern, EPA regulations established a maximum pesticide residue level, which for the particular case of water supplies is in the range of low parts-per-billion[1]. This work focuses in the determination of some groups of pesticides, such as organochlorine, triazine and phenols, including some alkylphenols, as octyl and nonylphenols which have been recently included into the endocrine-disrupting compounds, increasing their toxicological concern. Most pesticides occur in very limited quantities in the natural environment, which makes clearly demanding the search for sensitive analytical methodologies which in most cases also require the inclusion of preconcentration. Due to the drawbacks of conventional sample preparation procedures, regarding to their expensiveness, tediousness and time-consuming as well as for generally involving the use of highly toxic organic solvents, alternative sample preparation protocols are being required. With this aim in this work we show an example of application of Solid phase microextraction (SPME) as a solvent-free alternative to conventional sample preparation strategies. This technique involves important features such as simplicity, low cost, rapidity and sensitivity when is combined with appropriate detection modes[2,3]. An optimization of the SPME conditions for the simultaneous extraction of some compounds included into the three different groups of pesticides above mentioned is shown in this work.

Materials and Method

Chemicals. Lindane, endosulfan I and II, and atrazine were supplied by Riedel-de Häen (Seelze, Germany). Pentachlorophenol (PCP), 4-t-Octylphenol (OP) and 4-Nonylphenol (NP) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and 2,4-dichlorophenol (2,4-DCP) was obtained from Merck (Darmstadt, Germany). Stock standard solutions (200 mg/L) of each pesticide were prepared in methanol. Two separate group of mixtures were also prepared in methanol containing 2 mg/L of each individual pesticide. These solutions were stored in dark glass bottles at 4ºC. Working standard solutions of 20 µg/L were freshly prepared by dilution in Milli-Q water.

Equipment and SPME fibers. CG/MS analysis were carried out in a Hewlett Packard HP 6890 Series Gas Chromatograph coupled to a 5973 Mass Selective Detector.

The SPME device for manual extraction was purchased from Supelco (Bellefonte, PA, USA). SPME fibers, 60 µm PDMS-divinylbenzene (DVB), 65 µm PDMS-divinylbenzene (DVB), 65µm Carbowax-divinylbenzene (DVB) and 85 µm polyacrylate (PA) all supplied by Supelco, were conditioned in the hot injector of the gas chromatograph for 0.5-2 h at 250-320ºC according to instructions provided by the manufacturer.

Chromatographic separation. The separation was performed on a 30m x 0.25 mm HP 5MS column. Helium was used as carrier gas at a constant pressure of 13.3 atm. The temperature of the injection port was 250ºC. A 0.75 mm injection liner was used in splitless mode, with the split closed for 5 min. The column was held at 80ºC for 2 min, increased to 180ºC at a rate of 10ºC/min, and held for 5 min, followed by a rapid increase of temperature by 30ºC/min up to 250ºC, and held for 6 min. Electron impact mode at 70 eV has been used. Transfer line and ion source temperatures were set at 280ºC and 230ºC respectively. Selected ions for SIM mode operation were 162.00 (2, 4-DCP), 135 (4-t-OP), 181 (lindane), 200 (atrazine), 266 (PCP), 107 (NP), 195 (Endosulfan I and II) m/z, corresponding to the most sensitive ion fragment for each compound.
Solid-phase microextraction. SPME extractions were performed by placing 3 mL of standard solution in 4 mL amber vials. The SPME fiber was manually immersed into the solution for an appropriate time period for the complete absorption of the analyte into the stationary phase. Magnetic stirring was used for agitation and aluminum caps were used to seal the vials. After extraction, the fiber was thermally desorbed into the injector of the gas chromatograph at 250ºC for 5 min.

Results and discussion
SPME has been optimized for an optimal yield according to the following variables affecting to the absorption step.

Fiber type selection. The sensitivity of an SPME method strongly depends on the correct selection of the fiber coating and thickness. In this study, four commercially available SPME fibers were evaluated for the simultaneous extraction of the target pesticides: 65 um PDMS/DVB, 60 μm PDMS/DVB, 85 μm PA and 65 μm CW/DVB. These fibers were selected regarding to the structure of the analytes. Figure 1 shows the comparison of the efficiency of different SPME coatings for the extraction of the studied compounds from water samples. This efficiency is evaluated in terms of recoveries. PA coating, was expected to have greater affinity for phenolic compounds, but it was only observed for PCP. In general, for the other compounds, both 60 and 65 μm PDMS/DVB fibers which are mixed phases that extract compounds via adsorption, obtained the best global performance due its intermediate polarity properties which allow the extraction of analytes of a wide range of polarity. 60 μm PDMS/DVB phase, which is mostly recommended for HPLC, has resulted in the suitable coating for an efficient simultaneous extraction of the target compounds, the larger volume of PDMS/DVB stationary phase contained in this fiber may explain its improved adsorption capacity for the named compounds. Despite of being for HPLC use, it can be also used for GC analysis with thermal desorption with no damage over a large number of injections. This fiber was then selected for further optimization.

Sample agitation. Agitation facilitates mass transport between the aqueous sample and the fiber, contributing to a faster equilibration. Different stirring rates were selected and improved extraction efficiency was obtained for an increased agitation speed. 900 r.p.m. was then selected with this aim.

Sample pH. The extraction efficiency at different pH values in the matrix, in the range of 4-10, has been evaluated and no significant differences were observed in the adsorption efficiency of the target compounds in this pH range when using 60 μm PDMS/DVB fiber.

Extraction temperature. Extraction is limited by mass transfer achieved higher efficiency when the temperature is increased, but adsorption is an exothermic process, so there is an overall negative effect above certain temperature. Extraction temperatures between 25 and 75ºC were tested in order to compare the effect of this parameter on extraction yields. The results obtained show that temperatures around 60ºC were adequate for an optimal extraction yield. For lindane, DCP and PCP, the amount extracted decreases above this temperature. Different behavior was observed for atrazine which requires temperatures higher than 60ºC for an optimal extraction yield, while the optimal temperature for a higher extraction yield of alkylphenols was 65ºC, whereas not improved extraction was observed when using higher temperatures, from these results it can be established that 60ºC is the recommended temperature to carry out the simultaneous extraction of the selected pesticides.

Ionic strength. An increase of the ionic strength could be related with an improvement of the extraction efficiency. The effect of the ionic strength over the extraction with PDMS/DVB fiber, has been evaluated using different percentages of NaCl added to standard solutions. Figure 2 shows the results of the extraction yields obtained for the selected compounds. While the extraction yields of the most polar compounds, specially atrazine were improved by 2 to 5 times to a concentration of 30% NaCl, the extraction yield for less polar pesticides was clearly reduced even at low NaCl concentrations. This behavior could be explained by a decrease on the mobility towards the fiber coating , specially for non polar molecules. From the results obtained it can be concluded that the improved extraction efficiency for polar compounds whit salt addition is not significant compared with the efficiency decrease for the rest of compounds, furthermore salt addition can damage the fiber coating shorting its life time, consequently salt addition is not recommended for improving the extraction efficiency of the selected compounds.

Extraction time. The optimal extraction time has been evaluated exposing the selected fiber to standard solutions of the target compounds at 60ºC for times ranging from 30 to 120 min.
Fig 3 shows the optimal equilibration time of 60 min for most studied pesticides, except for PCP which reached the equilibrium at 30 min and for lindane and atrazine that have shown a tendency to equilibrium state around 90 min. Extraction times larger than 60 min are not reasonable for a suitable application and consequently, as a compromise between short overall analysis time and acceptable detection limit, 60 min was selected to carry out the experiments.
Once optimizated, the method was evaluated in terms of sensitivity, repeatibility, linearity and recovery and the data are shown in Table I.

Compound	R^2 (Linear range: 0.3-30 ng)	C.V. % (6ng, n =5)	% Recovery (0.3ng)	L.O.D. (ng)
2, 4 -Dichlorophenol	0.998	7.6	31	0.06
4-tert – Octylphenol	0.997	4.4	112	0.02
Atrazine	0.998	6.0	21	0.06
Pentachlorophenol	0.997	11.7	88	0.03
Lindane	0.995	8.5	108	0.02
4 -Nonylphenol	0.999	10.6	77	0.02
Endosulfan I	0.996	16.7	95	0.03
Endosulfan II	0.995	24.3	97	0.04

Table I. Repeatibility, recovery, linear range and detection limits.

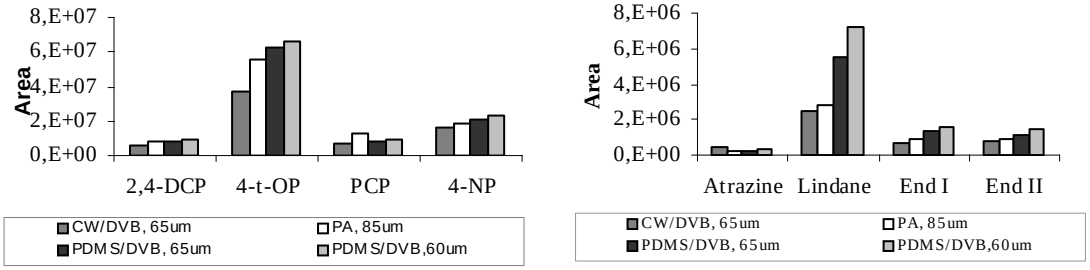

Figure 1. Comparison of extraction efficiency using four different SPME fibers.

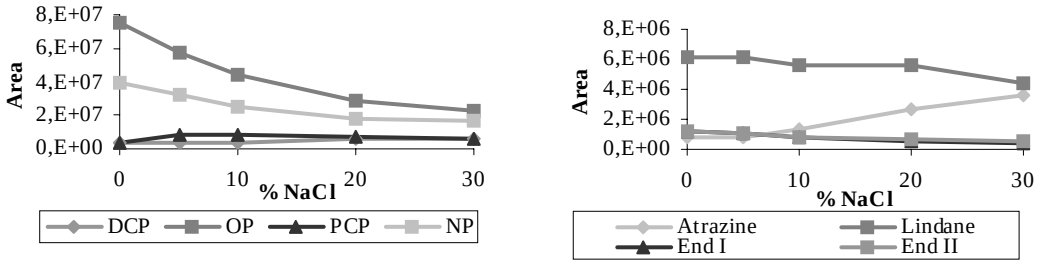

Figure 2. Influence of ionic strength on extraction efficiency.

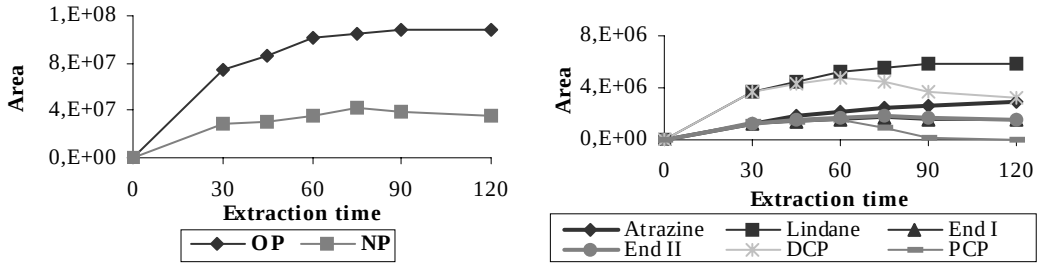

Figure 3. Extraction time profiles.

References

1. EC Drinking Water Guideline, 98/83/CE, Brussels, November 1998.
2. Alpendurada, M.F. (2000) J. Chromatogr.A. 889, 3.
3. Beltran, J., López, F.J. and Hernández, F. (2000) J. Chromatogr.A. 885, 389.