- POSTERS -

OPTIMIZING THE DETERMINATION OF ORGANOCHLORINE PESTICIDES USING SOLID PHASE MICROEXTRACTION

Luminita Barbu, Emilia Teaca

SC APA NOVA SA, Bucharest, Romania

Abstract

In this paper we studied operating parameters to determine the optimal conditions for separation and concentration of organochlorine pesticides in aqueous samples using solid phase microextraction coupled with gas chromatography – mass spectrometry. Several parameters affecting extraction, viz. extraction mode, incubation time and temperature, stirring speed, extraction time, desorption time, bake out time and temperature, vial penetration were investigated. In our experiments we used polydimethylsiloxane 100 µm fibers at the extraction temperature of 85 °C for 10 minutes and desorption temperature of 250 °C for 3 minutes. Under these optimal conditions, the proposed solid phase microextraction method provided good linearity in the ranges of 0.5-1000 ng/mL organochlorine pesticides. The recoveries of pesticides in water samples exceeded 85%.

Introduction

Solid phase microextraction (SPME) was developed to address to need to facilitate rapid sample preparation in the laboratory. In the technique, a small amount of extracting phase that is dispersed on a solid support (fiber) is exposed to the sample for a well-defined period of time /1-9/. In one approach, a partitioning equilibrium between sample matrix and the extraction phase is reached. In this case, convection conditions do not affect the amount extracted. In a second approach that uses short time pre-equilibrium extraction, if convection or agitation or both are constant, then the amount of analyte extracted is related to time. Quantitation can then be performed based on time accumulation of analyte in the coating. SPME is considered to be complete when the analyte concentration has reached distribution equilibrium between the sample matrix and the fiber coating. In practice, this means that once equilibrium has been reached, the extracted amount is constant within the limits of experimental error and it is independent of further increases of extraction time /10-12/.
The distribution coefficient K_{fs} of the analyte between the fiber coating and sample matrix is defined as :

$$K_{fs} = \frac{C_f}{C_s} \qquad (1)$$

where C_f is the equilibrium concentration of analyte in the fiber and C_s is the equilibrium concentration of analyte in the sample.
The equilibrium conditions can be described by equation (2), according to the law of mass conservation :

$$C_0 * Vs = C_s * Vs + C_f * Vf \qquad (2)$$

where C_0 is the initial concentration of a given analyte in the sample, V_s is the sample volume, V_f is the fiber coating volume.

We can combine and rearrange equations (1) and (2) and finally, the number of moles of analyte *n* extracted by the coating can be calculated from equation (3):

$$n = C_f * Vf = Co * \frac{K_{fs} * Vs * Vf}{K_{fs} * Vf + Vs} \qquad (3)$$

Equation (3) indicates that the amount of analyte extracted onto the coating (*n*) is linearly proportional to the analyte concentration in the sample (C_0), which is the analytical basis for quantification using SPME /12/.

Materials and methods

Materials

Organochlorine pesticides mixture (2000ug/mL in acetone) and pentachloro nitro benzene (5000ug/mL in acetone) were obtained from Ultra Scientific Analytical Soluitions and 1 – WS organochlorine pesticide (certified reference material) was obtained from RTC – Fluka . All chemicals were of analytical grade with purity above 99 %. Fibers PDMS with coating thickness 100 µm, were purchased from Supelco.

Instrumentation

All experiments were performed on a GC (7890A, Agilent Technologies) with a micro electron capture detector and mass selective detector (5975C Agilent Technologies), a Multi Mode split/splitless inlet used in the splitless mode, and a MultiPurpose Sampler with SPME capability (MPS 2, Gerstel).

Gas chromatograph – The column was VF 1701 (60m x 0.25 mm I.D., 0.50 µm film thickness). The oven temperature was: initial 60 °C, held for 0.5 min, programmed to 150 °C at 50 °C/min, programmed to 275 °C at 8 °C/min and then held for 5 minutes. The carrier gas was helium maintained at a flow rate of 1.8 mL/min. The temperature of injector and detector were set at 250 °C and 300 °C, respectively.

Mass spectrometer – The mass-spectrometer detector was operating under electron impact mode (70eV). The MS temperatures adopted were : source

230°C, quadrupole 150°C; the acquisition range 45–400 m/z in SIM mode. The whole analytical procedure was controlled with the program MSDChemStation (Agilent Technologies) and Maestro (Gerstel).

SPME procedure – The SPME fiber used was polydimethylsiloxane 100µm. According to the manufacturer recommendation, the fiber was conditioned at 270°C for 30 min in bakeout station before analysis. A single type fiber was used for this study. The spiked aqueous solution (15 mL, 4ng/mL analyte in water – methanol 1:1) was placed in a 20-mL headspace vial. The vial was sealed with a septum and aluminum cap. Then it was immersed in a thermostatic agitator at 85 °C and stirred at speed of 250rpm for 10 min. The fiber was then immersed in solution for 10 minutes and thermally desorbed in the GC injection port for 3 minutes.
The parameters that affect the SPME process such as extraction mode, incubation time and temperature, stirring speed, extraction time, desorption time, bake out time and temperature, vial penetration were evaluated and optimized.

Results and Discussion

Extraction mode and stirring – SPME sampling can be performed in two basic modes : direct extraction and headspace extraction. In the headspace mode, the analytes are extracted from the gas phase equilibrated with the sample. In the direct extraction mode the coated fiber is inserted into the sample and the analytes are transported directly from the sample matrix to the extracting phase. Figure 1 shows the results obtained by direct immersion and headspace. To facilitate rapid extraction, some level of agitation is required to transport analytes from the bulk of the solution to the vicinity of the fiber. For aqueous matrices, more efficient agitation techniques, such as stirring, are required These conditions are necessary to reduce the effect caused by the ''depletion zone'' produced close to the fiber as a result of fluid shielding and slow diffusion coefficients of analytes in liquid matrices /10/. The influence of stirring on efficiency of extraction is shown in figure 2.

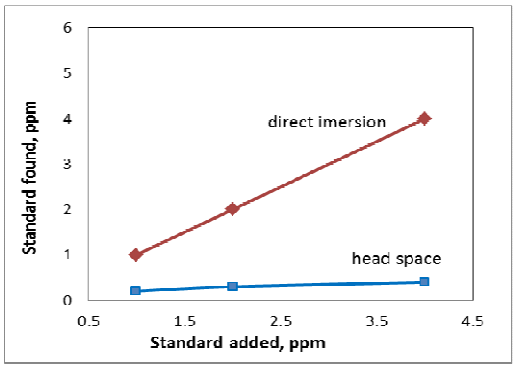


Figure 1
Effect of SPME sampling mode on extraction amount. Standard : 1–4 ng/mL of PCNB in methanol – water 1:1

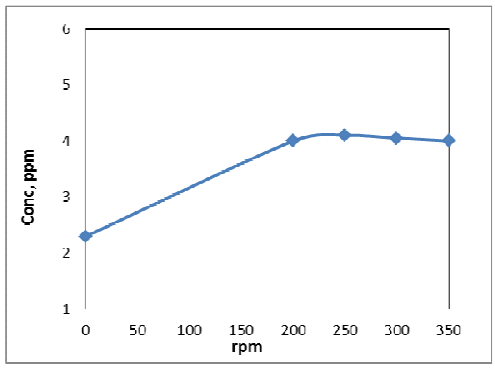


Figure 2
Effect of stirring on extraction amount by direct immersion.Standard : 4ng/mL of PCNB in methanol – water 1:1

In our experiments we use direct immersion and stirring 250 rpm.

Equilibration time and temperature – The effect of incubation temperature was investigated by varying in the range of 35-90 °C (figure 3) and incubation time in the range of 0-20min (figure 4). Efficiency of extraction increases with temperature and incubation time and in future experiments we use 85^{o}C for 10 min.

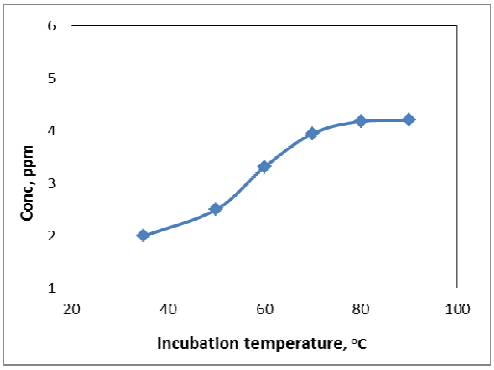


Figure 3
Effect of incubation temperature on extraction amount. Standard : 4ng/mL of PCNB in methanol – water 1:1

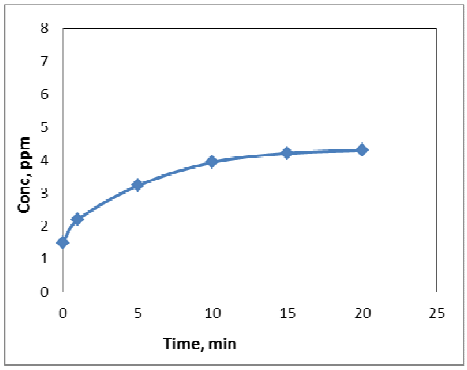


Figure 4
Effect of incubation time on extraction amount. Standard : 4ng/mL of PCNB in methanol – water 1:1

Extraction time – The extraction time was evaluated from 1 to 35 minutes. To achieve equilibrium between aqueous sample and coating fiber it takes more than 35 minutes and, in this case, it is possible to perform SPME without reaching equilibrium. In that instance, operator must ensure that the same SPME extraction time, incubation temperature and stirring are used for each sample. In our experiments, extraction time is fixed at 10 minutes (figure 5).

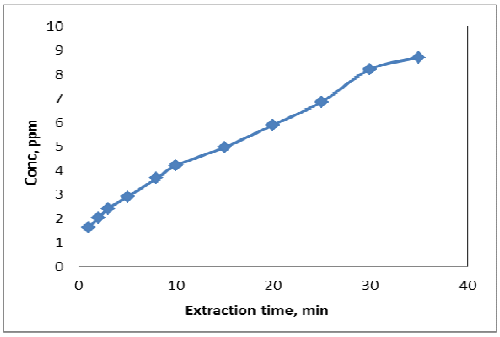


Figure 5
Effect of extraction time on extraction amount. Standard : 4ng/mL of PCNB in methanol – water 1:1

Desorption time and temperature – The desorption time was evaluated from 1 to 8 minutes at 250^{o}C (injection temperature). Into a GC capillary inlet system the SPME layer must be exposed to conditions that cause the absorbed solutes to desorb with as close to 100% efficiency as possible — and in a time that is short enough to be compatible with the chromatography mode in use. In our experiments, we operated with a desorption period of 3 minutes (figure 6).

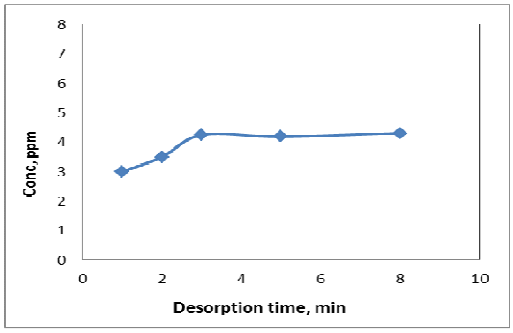


Figure 6
Effect of desorption time on extraction amount.
Standard : 4ng/mL of PCNB in methanol – water 1:1

SPME fiber conditioning – Due to carry-over we found very poor precision for SPME when working with desorption/bakeout times of 3 minutes and splitless desorption (figure 7).

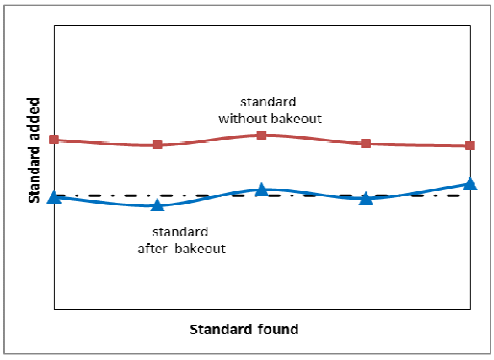


Figure 7
Effect of fiber conditioning on extraction amount.
Standard : 4ng/mL of PCNB in methanol – water 1:1

We therefore increased the bakeout time in the bakeout station to 15 min (figure 8), while the temperature is maintained at 250°C (figure 9) . This improved the precision for the analyte.

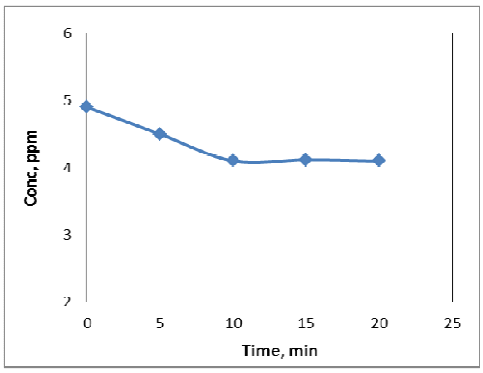


Figure 8
Effect of time bakeout on extraction amount. Standard : 4ng/mL of PCNB in methanol – water 1:1

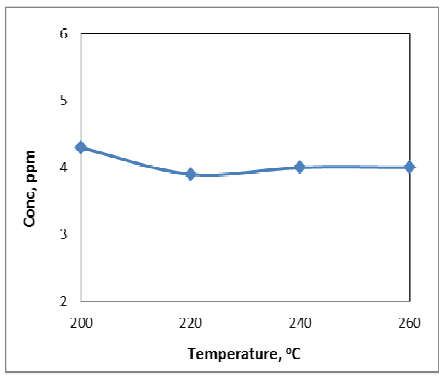


Figure 9
Effect of temperature bakeout on extraction amount. Standard : 4ng/mL of PCNB in methanol – water 1:1

Vial penetration – Vial penetration which determines how far the fiber extends into the vial was tested also. At 27 mm depth of the fiber in the vial were identified 15 compounds, while in the case of 33 mm, the number was higher (17 compounds). Figure10 also shows that the abundance of organochlorine pesticides presented is higher in the case of 33 mm vial penetration.

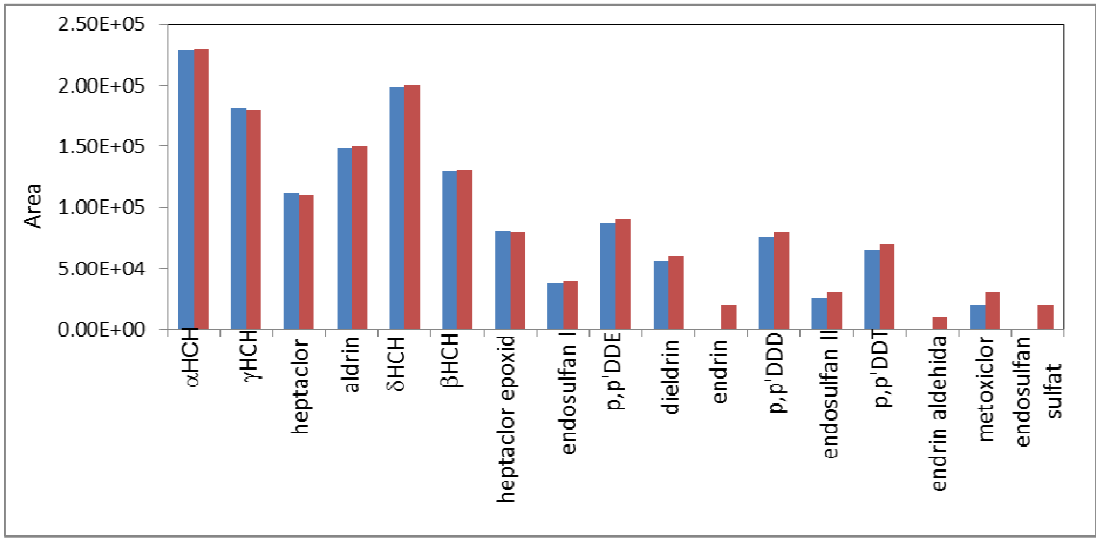
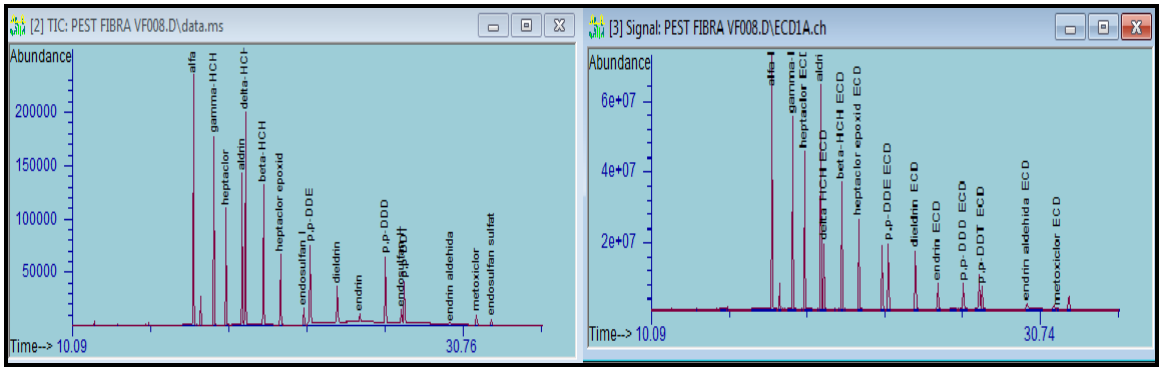


Figure 10
Effect of vial penetration on extraction amount. Standard : 4ng/mL of organochlorine pesticide in methanol – water 1:1

- Vial penetration 33 mm
- Vial penetration 27 mm

Figure 11 shows a SPME-GC/MS chromatogram obtained from the standard organochlorine pesticides sample studied (TIC and µECD signals).



a b

Figure 11
SPME-GC/MS chromatogram. Standard : 4ng/mL of organochlorine pesticide in methanol – water 1:1; a – MSD signal, b – µECD signal

Figure 12 shows calibration curves for some analytes from standard mixture of organochlorine pesticides. Linear standard curves over the range 0.5-1000 ng/mL were obtained with a correlation coefficient of 0.996 or greater (table 1).

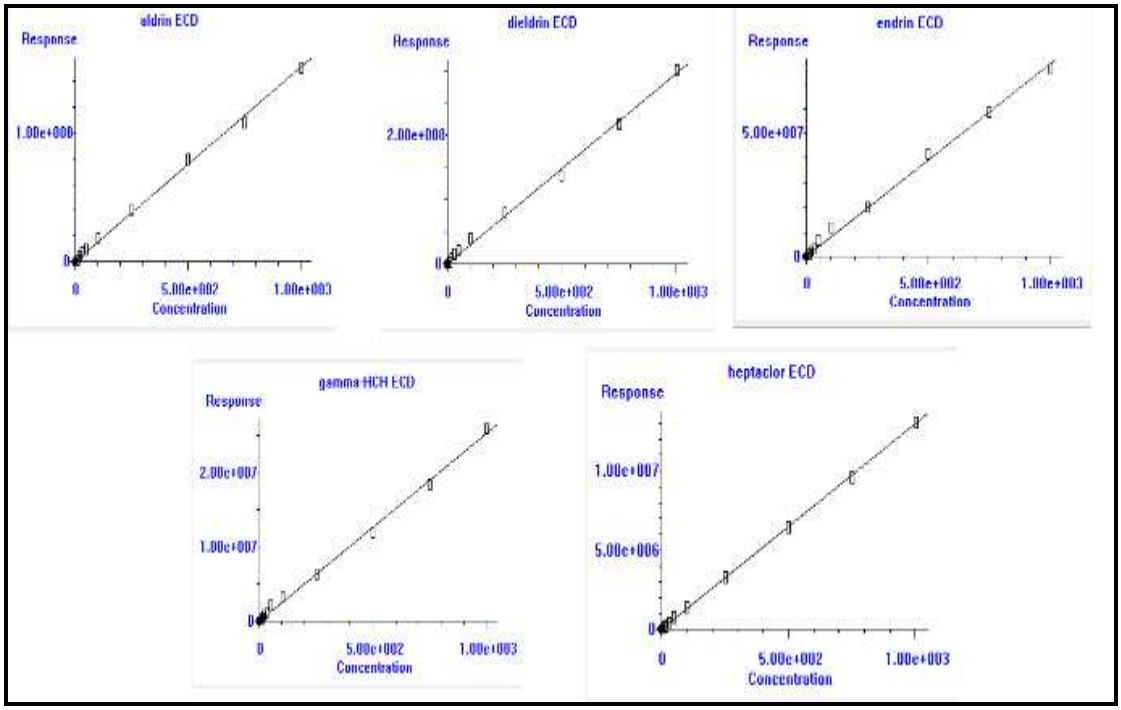


Figure 12
Calibration curves for some analytes from standard mixture of organochlorine pesticides

Table 1. Linearity, detection limit and quantitation limit of the developed method (1 – WS organochlorine pesticide CRM)

Compound	Range of linearity (ng/mL)	Correlation coefficient (r^2)	Limit of detection (ng/L)	Limit of quantitation (ng/L)
Aldrin	0.5 – 1000	0,9973	6.95	22.94
γHCH	0.5 – 1000	0,9972	6.20	20.46
Dieldrin	0.5 – 1000	0,9968	9.52	31.42
Endrin	20 – 1000	0,9967	21.31	70.32
Heptaclor	0.5 – 1000	0,9997	7.82	25.81

Using CRM, the results demonstrated that the developed DI-SPME-GC method provides good recovery in the range of 84-98% as shown in Table 2. The intra-day and inter-day RSD values ranged from 4,2-6,8% and 5,9-10.8%, respectively (Table 2). Results are in agreement with the performance requirements of current legislation and so the developed DI-SPME-GC method can be applied to the analysis of water samples (surface water, river water, treated water, drinking water) for control and monitoring of environmental pollution.

Table 2. Recovery and relative standard deviation of the method – intra-day and inter-day analysis (1 – WS organochlorine pesticide CRM)

Compound	Concentration ng/mL	Recovery		RSD %	
		ng/mL	%	Intra-day (n =5)	Inter-day (n = 5)
Aldrin	0,87	0,74	85,05	6,8	10,8
γHCH	1,33	1,30	97,74	4,5	5,9
Dieldrin	2,00	1,89	94,50	4,2	7,1
Endrin	1,44	1,21	84,02	5,1	7,4
Heptaclor	1,69	1,54	91.12	4,9	8,2

Conclusion

The effects of various conditions were studied in order to optimize the technique.
Direct immersion SPME coupled with GC-MS is a rapid and simple method for extraction and quantitative analysis of organochlorine pesticides from water. In this study, the PDMS fiber was found to give high extraction efficiency. Under the proposed method, the results were obtained with low limits of detection, good precision, linearity dynamic ranges, and interference minimization. In view of the simplicity, sensitivity and selectivity, the present method is recommendable for control and monitoring of environmental pollution.

References

1. Shahtaheri, S. J., Heidari, H. R., Golbabaei, F., Alimohammadi,M., Rahimi Froshani, A., Iran. J. Environ. Health. Sci. Eng, **3**, 3, 2006, p. 169
2. VAS, G., VEKEY, K., J. Mass Spectrom., **39**, 2004, p.233
3. YAZDI, A.S., AMIRI, A.,Trends in Analytical Chemistry, **29**, 1, 2010, p. 1
4. Djurovic,R., Markovic, M. – J Serb Chem Soc, **72**, 8-9, 2007, p. 879
5. Flórez Menéndez, J.C., Fernández Sánchez , M.L., Sánchez Urıa, J.E., Fernández Martınez, E., Sanz-Medel, A., Analytica Chimica Acta **415**, 2000, p. 9
6. Quanlong Li, Xiaoxia Maa, Dongxing Yuana, Jinsheng Chenb, Journal of Chromatography A, **1217**, 2010, p. 2191
7. Wangkarn, S., Wutiadirek, W., Mj. Int. J. Sci. Tech., **1,** 2, 2007, p. 145
8. Cai, L., Xing, J., Dong, L., Wu, C., Journal of Chromatography A, **1015**, 2003, p. 11
9. Andreu, V., Pic, Y., Trends in Analytical Chemistry, **23**, 2004, p. 10
10. Lord, H., Pawliszyn, J., Journal of Chromatography A, **885**, 2000, p. 153
11. Magdic, S., Pawliszyn, J., Journal of Chromatography A, **723**, 1996, p. 111
12. Pawliszyn, J., Journal of Chromatographic Science , **38**, 2000, p. 270