Optimization of SPME/GC-MS analytical method using Response Surface Methodology for pesticides monitoring in aqueous matrices

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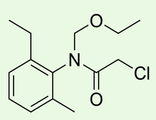
INTRODUCTION

Emerging pollutants are a type of contaminants that can occur in water sources. They can be defined as any synthetic or naturally occurring chemical or microorganism that is not usually monitored or regulated in the environment and have the potential to cause detrimental ecological and human health impacts. These compounds can be found in the environment in very low concentrations, at scales ranging from nanograms to micrograms per liter.[1]

Pesticides are an important group of emerging pollutants due to the continuous increase in their use in agricultural production process to control diseases, pests and weeds.[2]

MAIN OBJECTIVE

The main objective of this study is to develop an analytical method for monitoring six of the most used pesticides in the northeast of Portugal in water matrices.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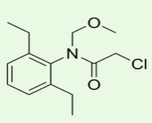
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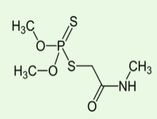
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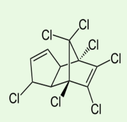
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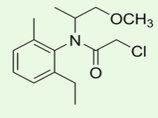
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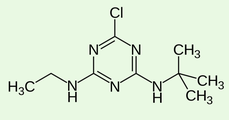
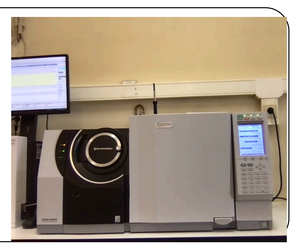

Terbuthylazine

EXPERIMENTAL METHODOLOGY

Optimization of solid phase microextraction (SPME), using a response surface methodology (RSM) based on an experimental planification defined using a Box-Behnken Design (BBD). Four parameters using three levels, considered: extraction time, pH value, ionic strength and extraction temperature.

Development of a methodology for detection and quantification by Gas Chromatography Mass Spectrometry (GC-MS).



Validation of the analytical method of extraction and quantification using real samples from three Northeast Portugal rivers: Onor, Sabor and Fervença.

RESULTS

Applying the design tool Box-Behnken to determine the most significant parameters and their respective values that allow obtaining the largest total area in the MS detector, using Full Scan Mode, the following results were obtained:

Significant parameters applying a quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	9,747E+14	14	6,962E+13	26,59	< 0,0001	significant
A-Extraction Temperature	2,619E+14	1	2,619E+14	100,03	< 0,0001	
B-Extraction Time	3,008E+14	1	3,008E+14	114,87	< 0,0001	
C-pH	9,590E+10	1	9,590E+10	0,0366	0,8525	
D-Addition of NaCl	3,119E+14	1	3,119E+14	119,12	< 0,0001	
AB	1,718E+13	1	1,718E+13	6,56	0,0306	
AC	5,786E+11	1	5,786E+11	0,2210	0,6495	
AD	1,509E+13	1	1,509E+13	5,76	0,0399	
BC	2,936E+12	1	2,936E+12	1,12	0,3173	
BD	1,720E+13	1	1,720E+13	6,57	0,0306	
CD	9,435E+12	1	9,435E+12	3,60	0,0901	
A^2	6,696E+12	1	6,696E+12	2,56	0,1443	
B^2	3,596E+13	1	3,596E+13	13,73	0,0049	
C^2	3,540E+13	1	3,540E+13	13,52	0,0051	
D^2	1,169E+12	1	1,169E+12	0,4462	0,5209	
Residual	2,357E+13	9	2,619E+12			
Lack of Fit	1,000E+13	7	1,429E+12	0,2106	0,9502	not significant
Pure Error	1,357E+13	2	6,783E+12			
Cor Total	9,983E+14	23				

Factor coding is **Coded**.
Sum of squares is **Type III - Partial**

The **Model F-value** of 26,59 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A, B, D, AB, AD, BD, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The **Lack of Fit F-value** of 0,21 implies the Lack of Fit is not significant relative to the pure error. There is a 95,02% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Figure 1. Determination of significant parameters using ANOVA .

Total area
4,22931E+06 — 2,90413E+07

X1= A: Extraction Temperature (°C)
X2= B: Extraction Time (min)

Actual Factors
C: pH=2
D: Addition of NaCl= 20%

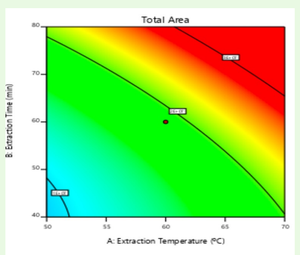


Figure 2. Contour plot

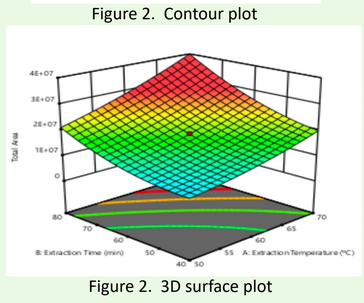


Figure 2. 3D surface plot

Once the optimal range values of the parameters mentioned above have been obtained, the method (SPME/GC-MS) has been validated, with samples collected from three rivers in Bragança region. Therefore, considering the following conditions (see Table 1), the following results were obtained:

Table 1. SPME optimized method.

Fiber coating	Polyacrylate (PA)
Extraction time	60 min
Extraction temperature	70°C
pH	2
NaCl	20%
Desorption time	4 min
Desorption temperature	250°C
Agitation	500 rpm

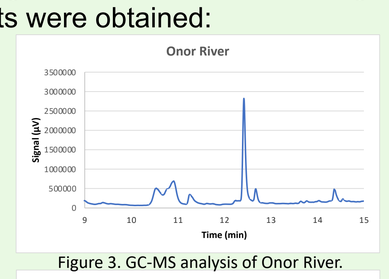


Figure 3. GC-MS analysis of Onor River.

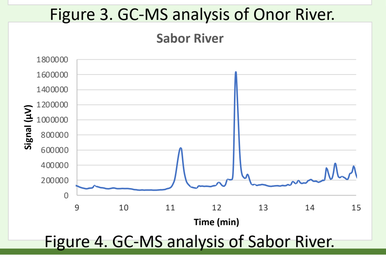


Figure 4. GC-MS analysis of Sabor River.

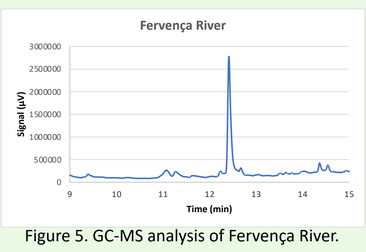


Figure 5. GC-MS analysis of Fervença River.

None of the pesticides under study were detected in the samples taken from the rivers. However, the highest peak is common among the three analysis and indicate that morpholine (fungicide) is present in all the three samples.

CONCLUSIONS AND FUTURE WORK

- Analyze the resulting areas of each compound separately, in order to identify the optimal conditions for each family of pesticides.
- Study the MS analysis using the Single Ion Monitoring (SIM) mode.
- Study other different types of fibers such as the CAR-PDMS or the PDMS/DVB.
- Extend the list of pesticides for better monitoring of the water quality in the northeast of Portugal.

ACKNOWLEDGEMENTS

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