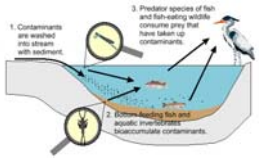
CLEAN-UP IN MICROWAVE ASSISTED MICELLAR EXTRACTION USING SPME FOR THE CHROMATOGRAPHIC ANALYSIS OF ORGANOCHLORINE PESTICIDES IN SEAWEEDS SAMPLES

D. Vega Moreno, Z. Sosa Ferrera, J.J. Santana Rodríguez.
Department of Chemistry, Faculty of Marine Sciences, University of Las Palmas de Gran Canaria, 35017, Las Palmas de Gran Canaria, Spain. Tel: +34 92845 44 25, Fax:+34 928 45 29 22, e-mail: jsantana@dqui.ulpgc.es
www.gi.ulpgc.es/aqma/

INTRODUCTION

The analysis of **organochlorine pesticides** residues has received an increasing attention in the last decades. These compounds tend to associate to particulate matter as seaweeds due to their hydrophobicity and persistence. It can produce a bioaccumulative effect through food chain with consequent for human health.



In this way, the continuous monitoring of pesticides residues in environmental samples has great importance and demands high efficiency, unique selectivity and high sensitivity techniques.

Microwave assisted micellar extraction (MAME) has been developed as an alternative for the extraction of different pollutants from solid matrices.

During the extraction step, many interfering components are co-extracted with target analytes. The main aim of clean-up stage is to remove substances that could interfere with the final determination and quantification of target analytes in HPLC-UV system. Removal of interfering substances can be made by **solid phase microextraction (SPME)**, producing also an intensification of the analytes signals by means of extract clean-up and preconcentration.

The aim of this work is evaluate the suitability of solid phase microextraction for the clean-up of MAME extracts before the final chromatographic determination of pesticides residues in seaweed samples.

EXPERIMENTAL

Seaweed samples were spiked with the pesticides mix. For the extraction was added to each 0.5 g of sample, 10 ml of POLE (Polyoxyethylene 10 lauryl ether) and irradiated at the optimized microwave conditions. Surfactant extracts were then removed, filtrated and clean-up by SPME before being analysed in the HPLC/UV system.

Organochlorine Pesticides Mix

1.- 4,4'-DDD
2.- dieldrin
3.- 4,4'-DDT
4.- 2,4'-DDT
5.- 4,4'-DDE
6.- aldrin

Gracilaria cornea seaweed

Ulva rigida seaweed

RESULTS AND DISCUSSION

Microwave Assisted Micellar Extraction (MAME)

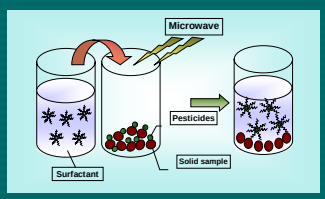
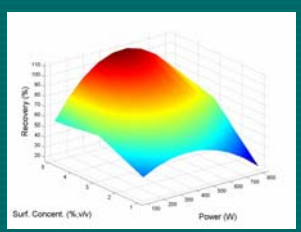


Diagram of MAME process

MAME has as advantages its simplicity, low cost, easy handling and non-toxic solvent use.

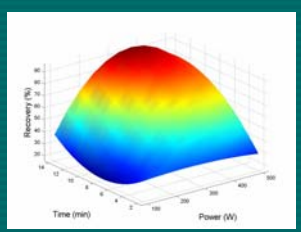
For the variables optimization was used a multiparametric analysis.

Surfactant Concentration



Response Surface Diagram where is represented the recovery of the compound 4,4'-DDT versus Power and Surfactant Concentration

Microwave's Power and Time



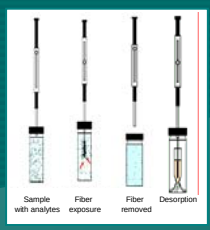
Response Surface Diagram where is represented the recoveryof the compound 4,4'-DDT versus Power and Time

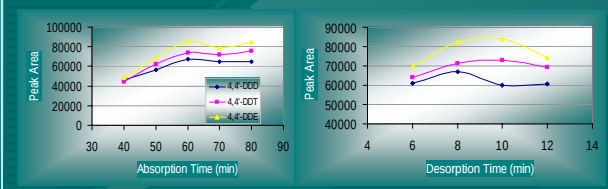
Optimum microwave conditions: 10 ml of POLE 5% (v/v) at 300 W during 14 min.

MAME-SPME procedure

As a second step, a 60 µm PDMS/DVB fiber was introduced in a solution with 5 ml of POLE with pesticides extract plus 7.5 ml of water in direct inmersion.

Desorption was done in a methanol volume of 55 µl with fiber's average stirring. The extract was analyzed in a HPLC-UV system.





Optimum MAME-SPME conditions: 60 min absorption time, 10 min desorption time at room temperature without salt addition.

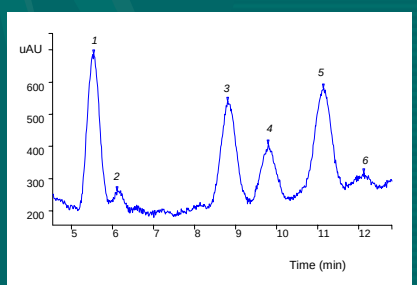
Analytical Parameters

Pesticides	Recovery (%)	R.S.D. (n=6)	Detection Limit ($ng \cdot g^{-1}$)
4,4'-DDD	89.5	8.4	148
Dieldrin	101.1	9.6	322
4,4'-DDT	91.5	6.9	164
2,4'-DDT	93.8	7.9	174
4,4'-DDE	90.2	8.8	138
Aldrin	87.4	10.3	348

Applications to different seaweed samples

Recoveries (%) obtained after MAME-SPME-HPLC-UV procedure in the determination of pesticides in different seaweeds

Seaweed	4,4'-DDD	Dieldrin	4,4'-DDT	2,4'-DDT	4,4'-DDE	Aldrin
Ulva	89.6	101.1	91.6	93.8	90.2	87.4
Valonia	103.8	104.0	94.3	101.9	99.5	91.7
Coralina	89.4	92.8	90.6	96.9	94.1	95.8
Solieira	84.4	104.3	92.8	90.3	80.5	101.6
Gracilaria	97.2	100.8	100.7	91.8	89.9	84.2



Chromatogram of an MAME-SPME extract of the mixture of six organochlorine pesticides

CONCLUSIONS

Microwave assisted extraction of pesticides using surfactant solutions coupled with SPME is a procedure with several advantages: is an efficient method, less time consuming and a green method with low cost.
The method has been applied to different types of seaweed samples with satisfactory results.

References

1. M. Maroni, C. Colosio, A. Ferioli, A. Fait. Toxicology 143 (2000) 61.
2. H. Mwevura, O. Othman and G.L. Mhehe, Mar. Poll. Bull. 45 (2002) 262.
3. M. Moreno Frías, A. Garrido Frenich, J. Martínez Vidal, M. Mateu Sánchez, F. Olea and N. Olea, J. Chromatog. B 760 (2001) 1.
4. Z. Sosa Ferrera, C. Padrón Sanz, C. Mahugo Santana and J.J. Santana Rodríguez, Trends Anal. Chem. 23(7) (2004) 469.
5. W. Ho, S. Hsieh, Anal. Chim. Acta 428 (2001) 111.

ACKNOWLEDGEMENTS

Spanish Ministry of for PhD Student Education and Science grant (FPU) of Daura Vega Moreno and for Research Project No. CTQ2006-06507/BQU.