ESTABLISHMENT OF A GREEN METHOD COMBINING MICROWAVE ASSISTED MICELLAR EXTRACTION AND SPE FOR THE DETERMINATION OF ORGANOCHLORINE PESTICIDES IN SEAWEEDS

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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.

Sample preparation is a critical step in most analytical processes.
The development of extraction and preconcentration steps prior to analytical determinations of traces level compounds has been explored in considerable depth over recent decades.

Microwave assisted extraction of organic compounds from solid samples using micellar medium (MAME) represents an alternative to extraction with organic solvents. However, different components usually can be extracted together with target analytes and interfering on the determination. For this reason, it is necessary a clean-up step which eliminates these interferences and allows to preconcentrate the analytes. For this purpose solid phase extraction (SPE) can be used.

In this work a MAME-SPE procedure has been optimized for the extraction and preconcentration of six organochlorine pesticides in seaweed samples prior to their determination by HPLC-UV. The method's precision, recoveries and linearity were also investigated.
MAME-SPE procedure and traditional Soxhlet extraction method were compared in order to demonstrate the validity of proposed method. Finally it was applied to different kind of seaweeds from Canary Islands (Spain).

References

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EXPERIMENTAL

Seaweed samples were spiked with the pesticides mix. For the extraction was added to each 0.5 g of seaweed 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 SPE before being analysed in the HPLC/UV system.

5 ml of MAME extract and 20 ml of ultra-pure water were gone through Envirelut-Pesticide 500 mg SPE cartridge at 5 ml·min-1. After that, a wash step was done for reducing surfactant remains with 5 ml of ultra-pure water at the same flow rate. The retained analytes were eluted by 2 ml of methanol at a flow rate of 1 ml·min-1. Finally, 50 µl of extract were injected into chromatographic system.

Organochlorine Pesticides Mix

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

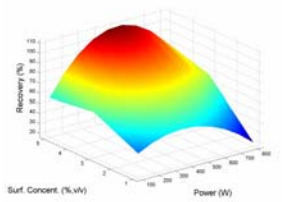
Gracilaria cornea seaweed

Ulva rigida seaweed

RESULTS AND DISCUSSION: MAME-SPE procedure

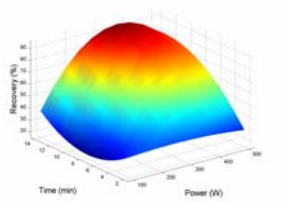
For MAME variables optimization was used a multiparametric analysis.

Surfactant Concentration

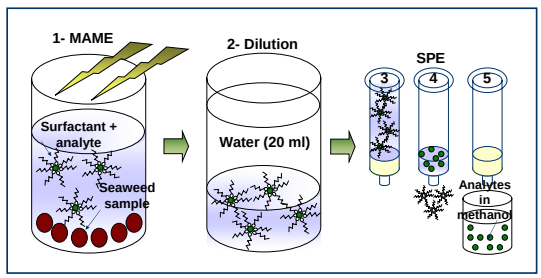


Response Surface Diagram where is represented the recovery of the compound 4,4'-DDT versus Power and Surfactant Concentration

Microwave's Power and Time



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

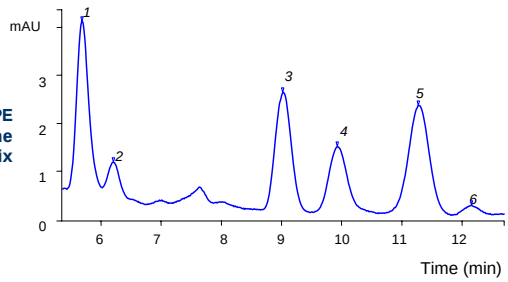


Optimum microwave conditions: 10 ml of POLE 5% (v/v) at 300 W during 14 min.

Optimum MAME-SPE conditions: Envirelut Pesticide cartridge. Absorption: 5 ml MAME extract + 20 ml water, 5 ml water for cleaning, Desorption: 2 ml methanol for desorption.

Analytical Parameters

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



Pesticides	Recovery (%)	R.S.D. (n=6)	Detection Limit (ng·g^{-1})
4,4'-DDD	92.9	3.5	12
Dieldrin	100.5	3.3	22
4,4'-DDT	92.6	2.8	2
2,4'-DDT	91.2	3.6	6
4,4'-DDE	107.7	5.3	2
Aldrin	78.8	4.6	38

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	92.9	100.5	92.6	91.2	107.8	78.8
Valonia	90.0	100.2	91.8	103.7	99.5	75.7
Coralina	81.3	84.9	86.6	83.0	86.5	73.9
Solieira	97.6	111.5	92.0	91.7	104.7	77.9
Gracilaria	90.6	97.9	81.4	86.5	83.1	83.4

CONCLUSIONS

The combination of microwave assisted micellar extraction (MAME) with SPE, provided sensitive and selective methods for the extraction of organochlorine pesticides residues in seaweed samples.

It can be successfully applied to the extraction and determination of these compounds in this kind of samples, using its coupling with HPLC-UV. Moreover, it presents significant advantages like simple handling, small solvent and sample amount needed and high sensitivity.

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