Analysis of pesticide residues in water by DI-SPME-GC/MS/MS

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INTRODUCTION

Directive (EU) 2020/2184 on the quality of water intended for human consumption provides for maximum residue limits of 0.030µg/l for aldrin, dieldrin, heptachlor and heptachlor epoxide, 0.10µg/l for other pesticides (and pesticide metabolites) and a total pesticides limit of 0.50µg/l.
To achieve these sensitivities, sample preparation procedures are often long, complex and not free from possible errors.
ISO 27108:2010 standard method involves a simple preparation procedure using the SPME (Solid Phase Micro Extraction) technique by direct immersion, and analysis by gas chromatography and single quadrupole mass spectrometer.
ISO 27108:2010 standard method has been validated in the range of 0.05-0.30µg/l for about twenty analytes.
In this work we evaluated the use of this technique coupled to a gas chromatograph with triple quadruple mass spectrometer; the aim is to evaluate to extend the sensitivity up to 0.010µg/l and, at the same time, increase the number of analyzable pesticides.
In this work we tested 2 different SPME phases, the PA phase = Polyacrylamide, which is the one suggested by the ISO method and the PDMS-DVB-OC phase = polydimethylsiloxane – divinylbenzene (overcoated) which promises greater stability.

REAGENTS AND MATERIALS

The reagents used in this study were:
- Pesticide-free water (we used bottled mineral water)
- NaCl
- Pesticides mix 10-25-50-100-200 µg/l in acetonitrile

The materials used were:
- Headspace vials, 20ml, magnetic cap and silicone septum
- SPME fiber with holder (in this case smart type)

SAMPLE PREPARATION

10 ml of water sample is transferred to a vial for the headspace, 3 g of NaCl is added, the vial is closed and shaken until the salt is completely dissolved.

Standard preparation:
Standards are prepared from 10 ml of water (mineral water to simulate a saline content but not tap water which may contain residues in our city) and proceed as for the samples.
Then 10µl of pesticide mixture is added to the samples under the surface of the water.
5 mixtures were used with increasing concentrations starting from 10µg/l up to 200µg/l corresponding to 0.010-0.200µg/l in water.

Analysis:
Samples and standards are placed on the autosampler which performs all steps of conditioning, heating, stirring, extraction and desorption in the injector.
The instrumental method has not been modified from that usually used for the analysis of pesticides in food.
Only the injector liner was replaced with a “straight” one.

INSTRUMENT AND CONFIGURATION

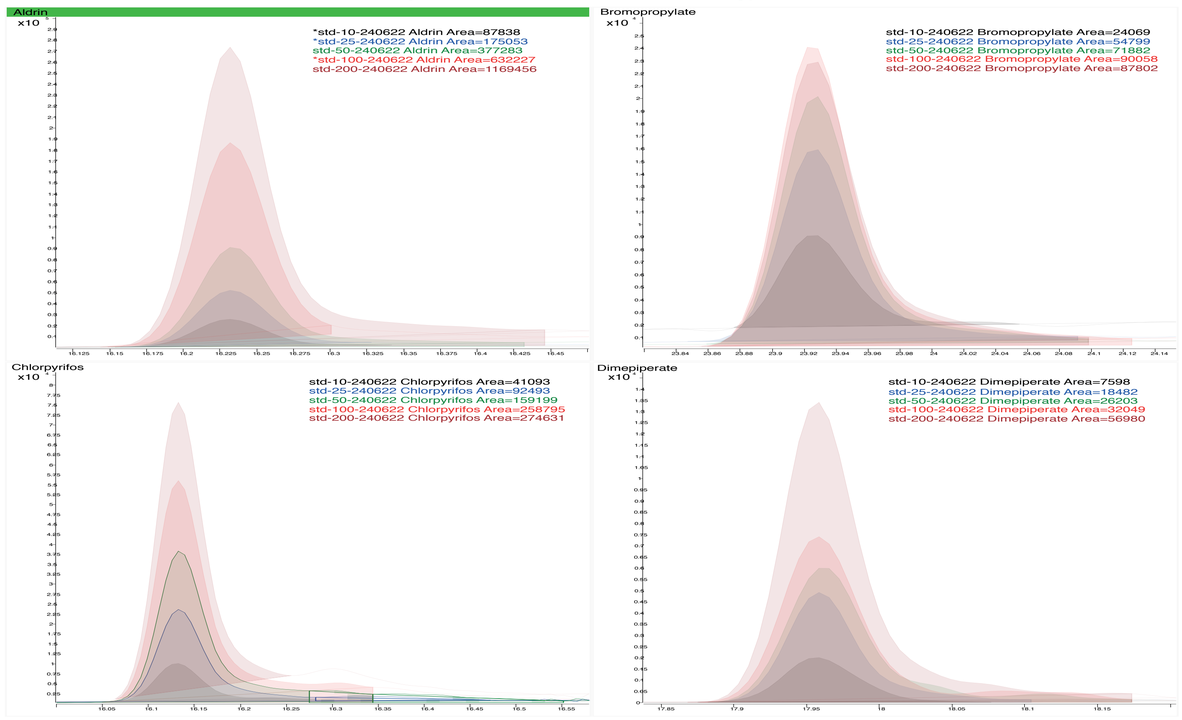
Instruments
- GC : Agilent 7890A
- MS : Agilent 7010
- Autosampler : PAL RTC 120
- Column : J&W DB5MS-UI 30m x 0,25mmID x 0,25µm film

GC Condition
- Oven : 50°C 0,1min
  : 100°C/min -> 70°C 2,2min
  : 40°C/min -> 150°C 0 min
  : 5°C/min ->240°C 0 min
  : 20°C/min -> 320°C 3,5 min
- Inlet : 60°C 0,1 min
  : 600°C/min -> 250°C 10min
  : 600°C/min -> 300°C
  : splitless
- Carrier : He 1ml/min

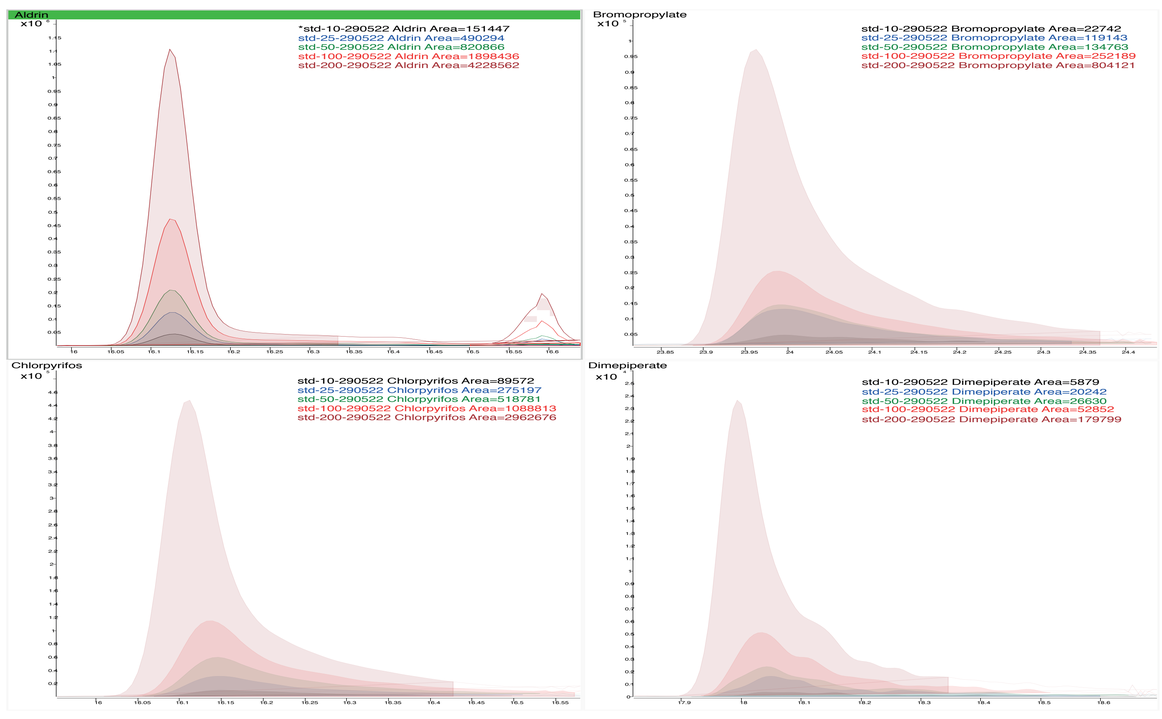
MS Condition
- Ionization mode : EI
- Analysis mode : MRM
- Collision gas : N_2 He
- Ion source : 280°C

SPME condition
- SPME fiber : PA 85µm
  : PDMS/DVB-OC 65µm+10µm
- Agitator : On
- xtract time : 40min / 50°C
- Desorb time: 10min
- Sample : 10ml + 3g NaCl

Overlay of a calibration set with PA fiber type



Overlay of a calibration set with PDMS-DVB-OC fiber type



RESULTS

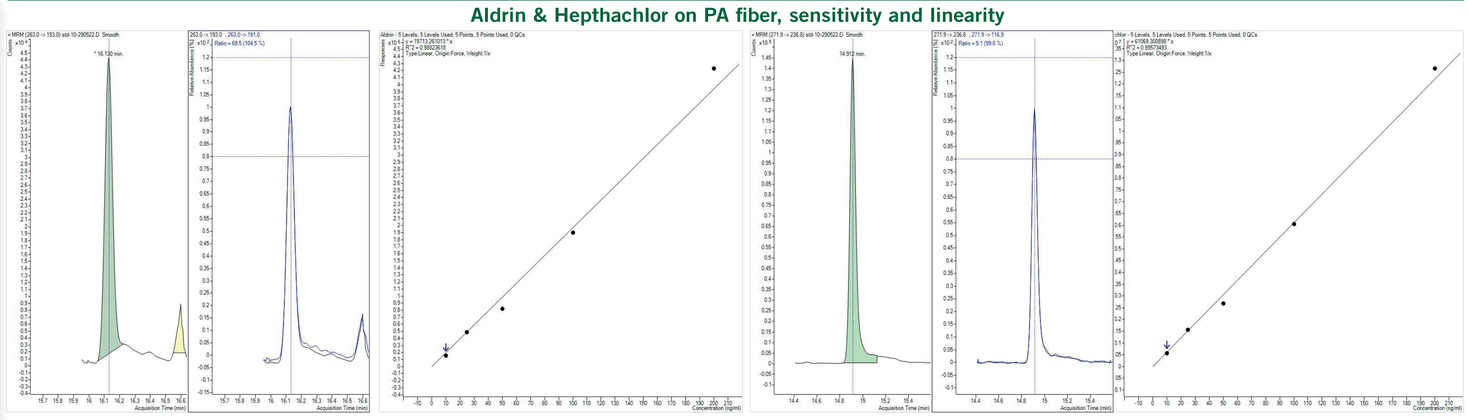
A pesticide mix consisting of around 300 components was used for this study.
From the tests carried out on the use of SPME these positive and negative aspects emerged:

PROs / CONs

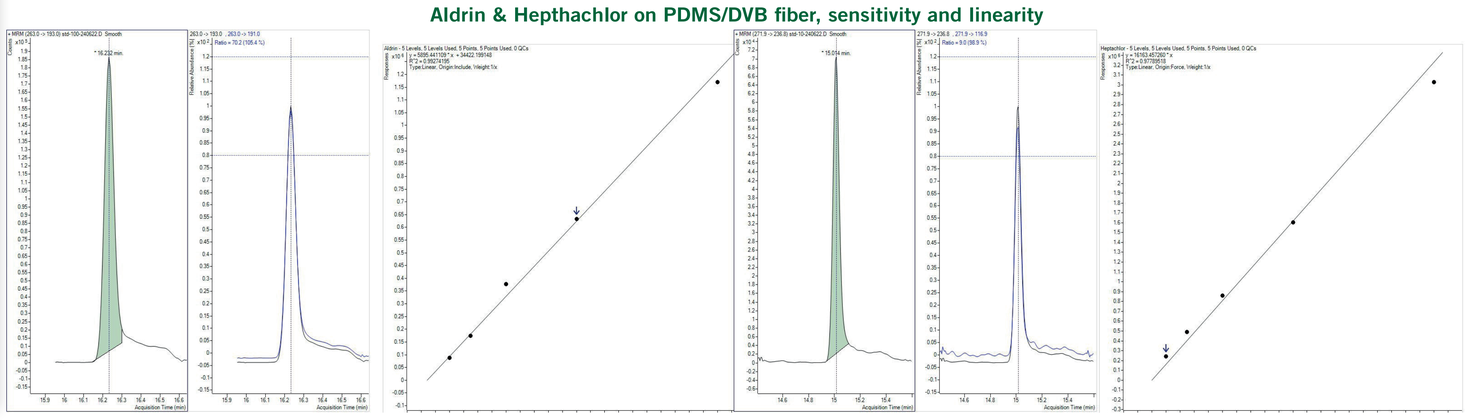
- The technique is extremely sensitive; the 4 organochlorine pesticides listed in the EU directive are sensitive and linear on both types of fibers tested.
- For this analysis a minimum volume of sample is required (only 10ml) and the preparation is very simple and fast.
- The 2 types of fibers allow the analysis of different pesticides but none of them is able to analyse all the tested pesticides.
- The PA fiber allows the analysis of about 230 pesticides, the PDMS / DVB fiber allows the analysis of about 160 pesticides.

The study found that the shape of the peak, the sensitivity and the linearity is conditioned by the type of fiber used.
PA fiber is better for sensitivity (peak area) but with reduced linearity to around 100ppt, PDMS / DVB fiber exhibits better linearity over the entire tested range 10-200ppt, but typically a lower response.
From the tests it was found that the 2 types of fibers have a different stability.
PA fiber seems particularly sensitive and requires more attention, degrades quickly and needs to be replaced frequently.
Attempts were made to improve the stability of the PA fiber by using milder extraction conditions and testing two types of injector.
Overall, the PDMS / DVB fiber appears to exhibit better stability.

Aldrin & Hepthachlor on PA fiber, sensitivity and linearity



Aldrin & Hepthachlor on PDMS/DVB fiber, sensitivity and linearity



CONCLUSIONS

The technique looks very promising, but the results obtained do not yet allow the use of SPME for quantitative analysis.
Now the method can be used as a screening analysis as the remarkable sensitivity and speed of preparation allow rapid discrimination between polluted and clean samples.
Despite the guidelines provided by the ISO 27108: 2010 standard method, the development of a multiresidual method on water with the DI-SPME-GC/MS/MS technique will require a further fine-tune work.

CONTATTI

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