



# Determination of organophosphorus pesticide residues in oleaginous seeds by capillary gas chromatography with thermo-ionic detection

B. Bouchtane<sup>1</sup>, H. Khay<sup>1</sup>, M. Lafosse<sup>2</sup>, C. Elfakir<sup>2</sup>, A. Merrien<sup>1</sup>

<sup>1</sup> CETIOM, 270 avenue de la Pomme de Pin - 45160 Ardon - France ; bouchtane@cetiom.fr  
<sup>2</sup> Institut de Chimie Organique et Analytique, Université d'Orléans, UMR 6005, BP 6759, 45067 Orléans Cedex, France

A simple, fast and economical method has been developed for determination of organophosphorus pesticide residues as dichlorvos, diazinon, chlorpyrifos methyl, malathion, parathion methyl, pyrimiphos methyl and chlorpyrifos ethyl, in oleaginous seeds. The method uses a solid-liquid extraction with isooctane and a liquid-liquid extraction with acetonitrile (ACN) for pesticides extraction from oleaginous seeds. A further Solid Phase Extraction (SPE) clean up on C18 cartridge is optimized. The analysis of these 7 pesticides was realised using capillary gas chromatography with nitrogen/phosphorus detector ; their recoveries were in the range 100-110%.

## MATERIALS AND METHODS

9 steps for determination of organophosphorus pesticides residues in oleaginous seeds :

A crushed seed sample (10g) was spiked at a level of 200 µg/kg with dichlorvos, diazinon, chlorpyrifos methyl, malathion, parathion methyl, pyrimiphos methyl and chlorpyrifos ethyl and then analysed.

Step 1

### solid-liquid extraction with isooctane :

10 g of crushed seeds were extracted with 25 ml of isooctane in a 30 ml Teflon tube.

Step 2

the mixture was vortex mixed for 1 min, ultrasonicated for 15 min and then centrifuged for 5 min at 5000 x g. The supernatant was filtered on folded filter paper and collected in a 100 ml flask.

Step 3

Two further solid-liquid extractions with 2 x 20 mL of isooctane were operated.

Step 4

Combined supernatants were transferred in a graduated tube. The volume was adjusted, if necessary, to 65 mL with isooctane.

Step 5

A 10 mL volume of solution were rotary evaporated to 1 ml (T = 33°C and P = 75 mbar).

Step 6

the concentrated solution was transferred in a tube. The flask was rinsed with 5 mL of acetonitrile that were added into the tube

Step 7

The tube was vortex mixed for 1 min and then centrifuged for 5 min at 4 000 x g

Step 8

The acetonitrile phase was rotary evaporated to dryness (T = 33°C and P = 90 mbar)

Step 9

The residual material was dissolved in 1 ml of isooctane and then analysed by GC-NPD.

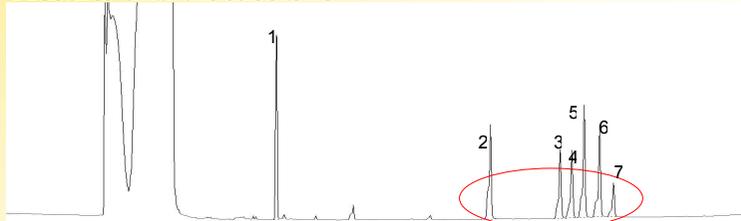
## GC analysis

A TR-5MS [5% phenyl (equiv) polysilphenylene siloxane] column (30 m x 0.25 mm I D x 0.25 µm), (Thermo electron, France) was employed. The sample was injected (1 µl) in splitless mode (48 s) and the oven temperature was programmed as follows : 50°C during 1 min, raised to 180°C (35°C/min), and to 280°C (6°C/min) and held for 2 min.

## CONCLUSION

A new analysis method of pesticide residues directly from oleaginous seeds is now available. Important objectives of this method were that it doesn't require oil extraction, it is simple, sensitive, fast, economic and respectful of the environment. Indeed this method appears very sensitive (LQ = 10 µg/Kg), easy to carry out, obtaining extracts requires approximately 1 hour if the extraction is carried out without purification on C18 cartridge and approximately 1 hour more if extracts are purified. Moreover, it is possible to carry out several analyses in series. The validation of the method showed that it was reliable and gave right results.

## Results and discussions



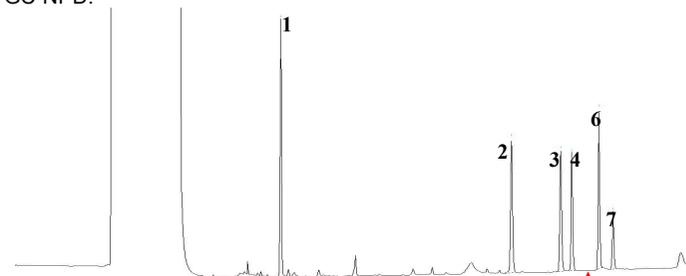
Chromatogram 1, 1 : Dichlorvos ; 2 : Diazinon ; 3 : Chlorpyrifos Methyl ; 4 : Malathion ; 5 : Parathion Methyl ; 6 : Pyrimiphos Methyl ; 7 : Chlorpyrifos Ethyl

### Clean up by SPE on C18 cartridges (this step takes the place of step 8 of the diagram describes on the left part of the poster)

To solve the problem of dissymmetric peaks, we added to the method a clean up by SPE on C18(1g,6ml) cartridges. The SPE clean up was realised on the acetonitrile layer.

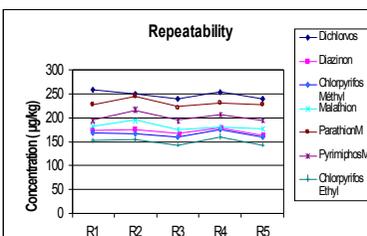
C18 cartridge was conditioned with 6 ml of MeOH, 6 ml of water and 6 ml of ACN. Then 5 ml partition acetonitrile extract were passed through the cartridge at an approximated speed of one drops per seconds.

An additional portion of 3 ml ACN passed for the complete organophosphorus elution. The acetonitrile extract was then evaporated to dryness under nitrogen stream. The residue is dissolved on 1 ml of isooctane and then analysed by GC-NPD.

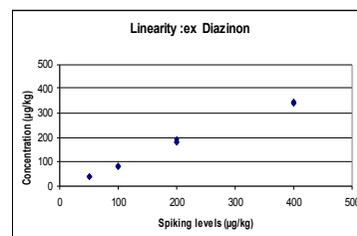


Peaks are symmetric but one of the 7 pesticides was lost, it was Parathion Methyl.

### Repeatability and linearity of the method without a clean up step



Coefficients of variation ranged from 3 to 5 % which it is very acceptable. The method is repeatable.



A good linearity was achieved in the range 50 - 400 µg/kg with correlation coefficients better than 0.99