

Comparative Study of Extraction Methodologies for Carbamate and Organophosphorus Pesticides in Water at ppb Levels

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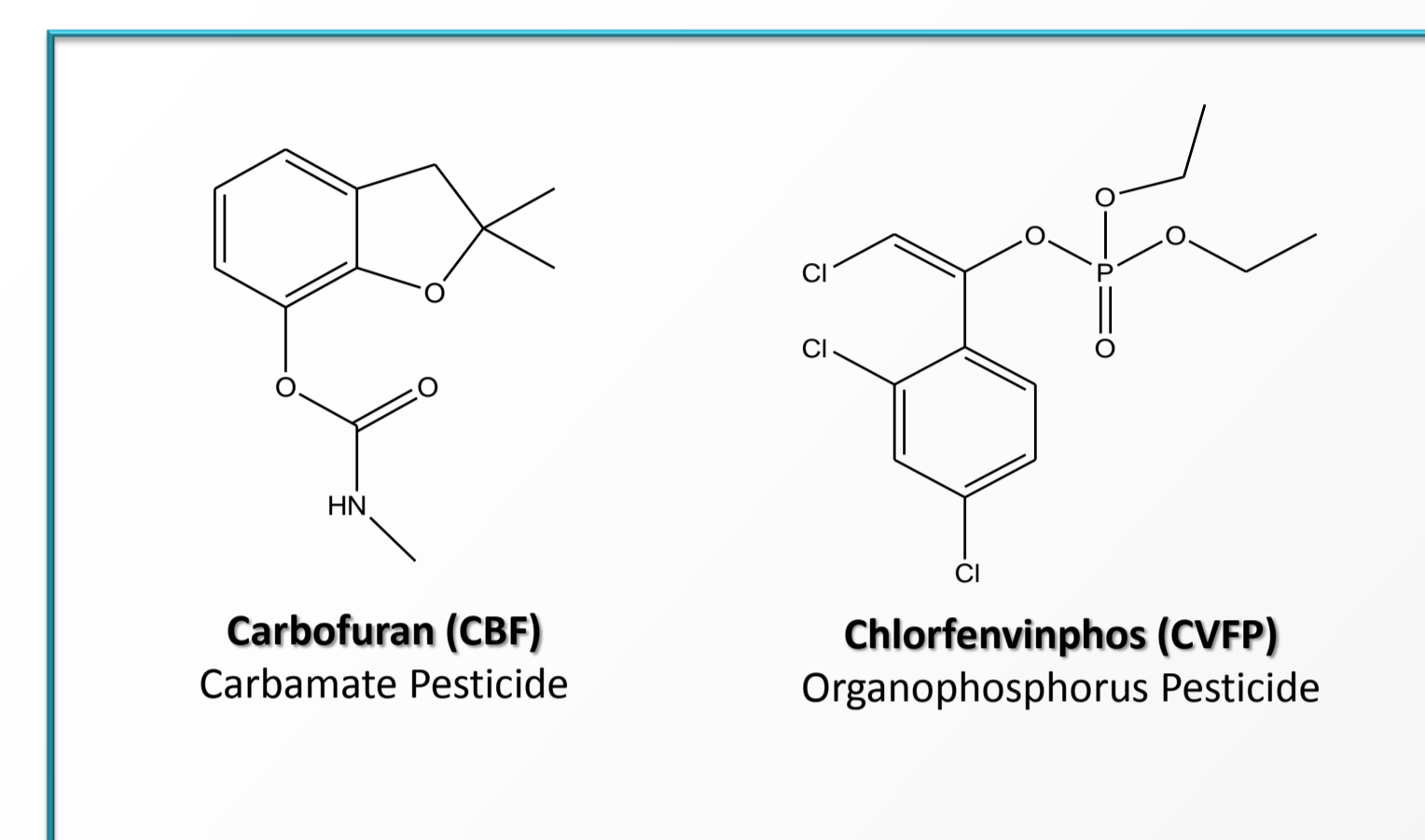
Introduction

Pesticides are types of well-known environmental contaminants. The use of pesticides provides benefits for increasing agricultural production. However, because of their highly persistent properties, their residues may appear in fruits and vegetables and can be distributed in aqueous environments by leaching and run-off from soil into ground and surface water.

Owing to the toxicity of pesticides, the European Directive 98/83/EC about the quality of water intended for human consumption establishes maximum concentrations of $0.1 \mu\text{g L}^{-1}$ for individual pesticides and $0.5 \mu\text{g L}^{-1}$ for the sum of all pesticides.

Two pesticides from different families were selected in this work – carbofuran (carbamate) and chlorfenvinphos (organophosphorus), in order to act as models to extend to other compounds of the same families.

The main objective was to develop an analytical methodology capable of detecting these pesticides at the legislated levels of concentration, but also suitable to be applied to cases in which there is a limitation of sample volume (e.g. from studies of pesticides degradation by advanced oxidation processes).



Experimental

Solid-Phase Extraction

Three types of SPE sorbents were tested, using different extraction methods according to the sorbent nature: LC-18 (non-polar silica based); HR-P (polymeric polystyrene-divinylbenzene resin based); Oasis HLB (copolymeric reversed-phase)

Method 1

Sorbent: LC-18; HR-P, Oasis HLB

Conditioning:

5 mL methanol
5 mL water

Sorption:

15 mL water sample

Elution:

5 mL methanol

Drying column

Evaporate to dryness with N_2

Re-dissolve in 0.5 mL methanol and 1 mL water

Method 2

Sorbent: LC-18; HR-P

Conditioning:

5 mL methanol
5 mL water

Sorption:

15 mL water sample

Elution:

5 mL methanol

Drying column

Evaporate to dryness with N_2

Re-dissolve in 1 mL ethyl acetate

Method 3

Sorbent: Oasis HLB

Conditioning:

5 mL ethyl acetate
5 mL methanol
5 mL water

Sorption:

15 mL water sample

Elution:

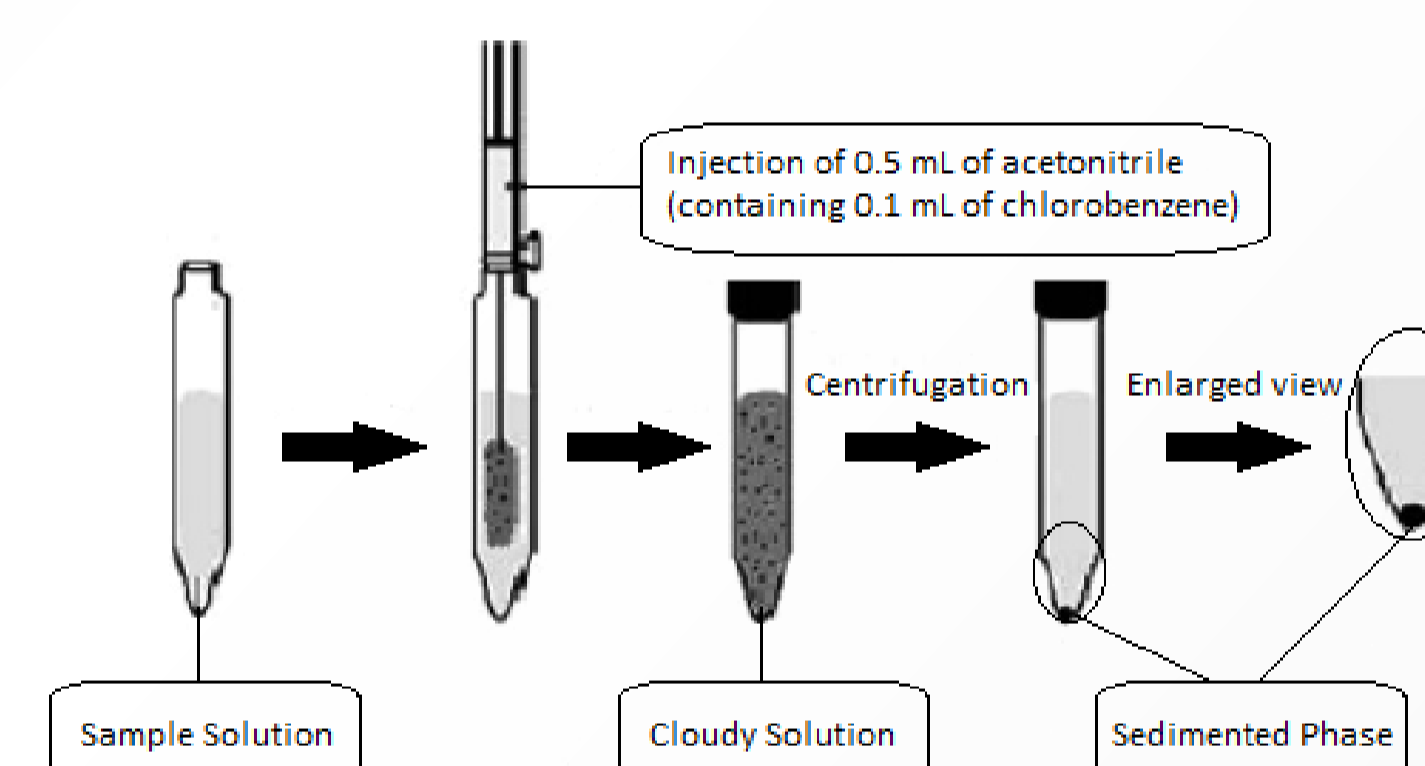
2x4 mL ethyl acetate

Drying column

Evaporate to dryness with N_2

Re-dissolve in 1 mL ethyl acetate

Dispersive Liquid-Liquid Microextraction



Extraction:

10 mL water sample

500 μL acetonitrile – dispersive solvent

100 μL chlorobenzene – extraction solvent

Gas Chromatography-Mass Spectrometry



GC-MS: Varian 4000 GC-MS, equipped with an ion trap mass detector

Column: DB-5MS (30 m x 0.25 mm i.d. x 0.25 μm film thickness column)

Temperatures: Injector: 290 °C; MS Transfer Line: 250 °C

Temperature Program: 130 °C for 2 min, 20 °C min^{-1} to 275 °C, and held for 1 min

Injection Volume: 1 μL (splitless injection)

Detection: SIM mode

Identification Ions: Carbofuran – 164, 149, 131

Chlorfenvinphos – 267, 269, 323

Results

Solid-Phase Extraction (SPE)

Method 1 (same extraction procedure)

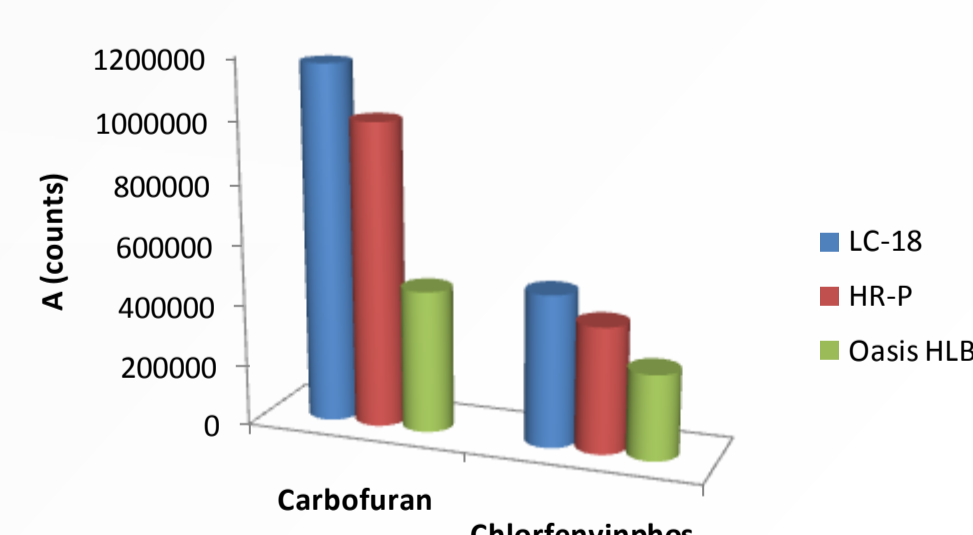


Figure 1. Comparative performance of 3 different sorbents used to extract a 1 mg.L^{-1} standard mixture, using Method 1.

Methods 2 and 3 (different extraction procedures)

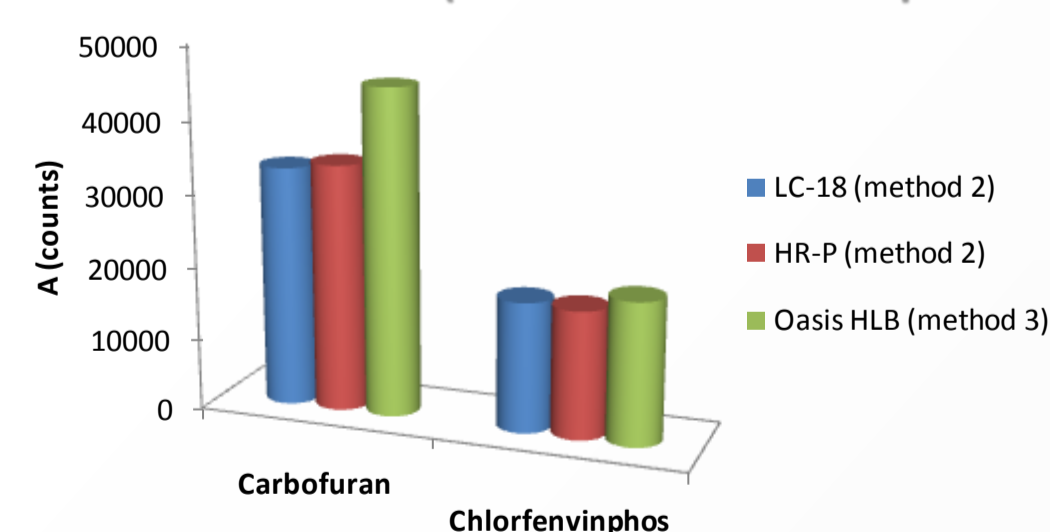


Figure 2. Comparative performance of 3 different sorbents used to extract a $10 \mu\text{g.L}^{-1}$ standard mixture, using Methods 2 and 3.

Table 1. Validation data for SPE (Methods 2 and 3).

Analyte	Carbofuran			Chlorfenvinphos		
	LC-18	HR-P	Oasis	LC-18	HR-P	Oasis
Extraction column	LC-18	HR-P	Oasis	LC-18	HR-P	Oasis
Linearity Range ($\mu\text{g.L}^{-1}$)	2 – 60			2 – 60		
LOD estimated ^a ($\mu\text{g.L}^{-1}$)	0.9	0.9	0.7	1.7	1.7	1.5
% R ^b	124	128	175	109	107	118

^a Limit of detection; ^b % R – recovery percentage of 2 independent extractions.

LC-18 column showed the best results (Method 1)

Quantification problems (by GC/MS) occurred due to the solvents used (methanol/water)

Lower LOD would be achievable using larger sample volume

Dispersive Liquid-Liquid Microextraction (DLLME)

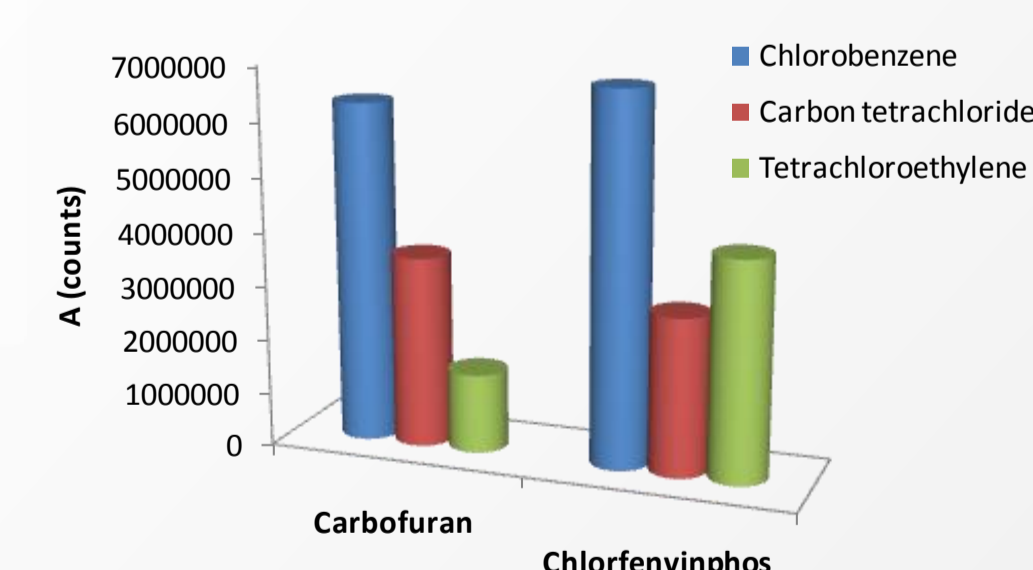


Figure 3. Comparative performance of 3 extraction solvents used in the extraction of a 1 mg.L^{-1} standard mixture of the selected pesticides.

Chlorobenzene was the chosen extraction solvent

Preliminary assays showed that acetonitrile was the best dispersive solvent

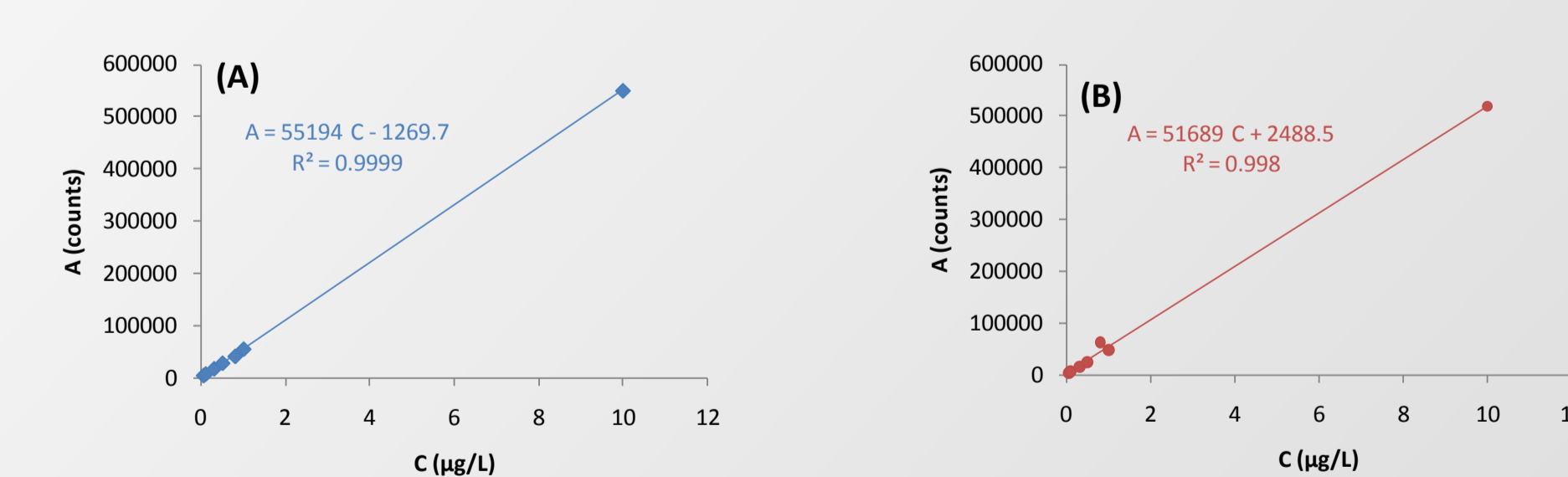


Figure 4. Calibration curve for extracted standards of (A) carbofuran, (B) chlorfenvinphos.

Table 2. Calibration curve for extracted standards of carbofuran and chlorfenvinphos.

Analyte	Carbofuran	Chlorfenvinphos
Linearity Range ($\mu\text{g.L}^{-1}$)	0.05 – 10	0.05 – 10
LOD ^a ($\mu\text{g.L}^{-1}$)	0.01	0.01
	1 $\mu\text{g.L}^{-1}$	10 $\mu\text{g.L}^{-1}$
Precision (% CV) ^b	14.5	7.9
% R ^c	69.5	74.3

^a S/N=3; ^b CV – coefficient of variation from 3 independent extractions; ^c % R – recovery percentage of 3 independent extractions.

Conclusions

- This study showed that SPE and DLLME are both suitable extraction methods for the pesticides studied.
- In comparison, DLLME is more simple and requires lower sample and solvent volumes. SPE method using LC-18 column yielded better results regarding recovery percentage, but LODs were higher than DLLME for similar sample volume.
- DLLME showed lower detection limits ($0.01 \mu\text{g.L}^{-1}$), simplicity and proved more suitable if sample volume is a limitation. However SPE cannot be excluded as a suitable analytical method even for extremely low concentrations, but in that case higher sample volume (up to 1 L) has to be used.