Clean-up of Chlorinated and Organophosphorus Pesticides Extracts Using Graphitized Carbon

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Introduction

Chlorinated and organophosphorus pesticides are sprayed on agricultural products and eventually migrate into the ground, thereby contaminating soil and groundwater or adhering to food and being consumed by humans. Many laboratories analyze field samples for chlorinated and organophosphorus pesticide residues. They also may test concentrations on agriculture products, both domestic and imported, prior to their going to market. Although agricultural and environmental industry samples are quite different, chemists face the same challenge in removing unwanted matrix interferences from the sample extract prior to analysis.

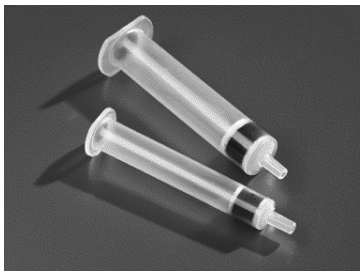
There are many types of matrix interference in gas chromatographic (GC) analysis of chlorinated pesticides, including nonvolatile (high molecular weight) compounds, acidic (polar) compounds, non-polar (hyrdrocarbon) compounds, and sulfur. There are various clean-up techniques to remove matrix interference compounds, however there is not one method that removes all classes of interference.

Recommended Clean-Up Procedures for Pesticides

- Gel Permeation Chromatography (GPC)
  - removes high molecular weight compounds and sulfur
  - size exclusion chromatography (SEC)
- Florisil®, silica gel SPE
  - removes polar organic compounds
  - normal phase chromatography

Project Scope

The scope of this work was to determine how graphitized carbon could be used in the clean-up process of pesticide extracts. Solid phase extraction (SPE) tubes containing CarboPrep™ 90 graphitized carbon were used for the testing. The surface area of the CarboPrep™ 90 carbon is 90m^2/gm, with a 250mg bed in a 3mL tube.



CarboPrep™ 90 SPE Tube
- 3mL tube
- 250mg bed
- 90m^2/gm

Project

1) The first step was to determine the solvent for eluting the chlorinated pesticides from the CarboPrep™ 90 SPE tubes, and for the recovery of the analytes.
2) The second step was to elute the organophosphorus compounds through the CarboPrep™ 90 SPE tube under the same conditions as the chlorinated pesticides.
3) The last step was to determine what compounds the CarboPrep™ 90 SPE tube removes from the extracts.

The compounds studied were selected from US Environmental Protection Agency (EPA) Method 8081A—Twenty-nine chlorinated pesticides including the surrogates tetrachloro-*m*-xylene (TCX) and decachlorobiphenyl (DCB); and US EPA Method 8141—48 organophosphorus pesticides including the surrogates tributyl phosphate (TBP) and triphenyl phosphate (TPP) were evaluated.

Project (contd.)

Chlorinated Pesticides

pk #	Analyte		pk #	Analyte
1	dibromochloropropane		15	g-chlordane
2	hexachlorocyclopentadiene		16	a-chlordane
3	terachloro-m-xylene (IS)		17	endosulfan I
4	cis-diallate		18	4,4' DDE
5	hexachlorobenzene		19	dieldrin
6	trans-diallate		20	endrin/chlorobenzilate
7	a-BHC		21	4,4' DDD
8	g-BHC		22	endo sulf II
9	b-BHC		23	4,4' DDT
10	d-BHC		24	endrin aldehyde
11	heptachlor		25	endosulfan sulfate
12	aldrin		26	methoxychlor
13	isodrin		27	endrin ketone
14	heptachlor epoxide		28	decachlorobiphenyl (IS)

Project (contd.)

Organophosphorus Pesticides

pk #	Analyte		pk #	Analyte		pk #	Analyte
1	dichlorvos		18	merphos oxone		35	sulfotepp
2	mevinphos		19	stirofos		36	dimethoate
3	ethoprop		20	bolstar		37	monocrotophos
4	phorate		21	fensulfothion		38	malathion
5	naled		22	TPP (surr.)		39	parathion-ethyl
6	TBP (surr.)		23	azinphos-methyl		40	EPN
7	demeton-o		24	coumaphos		41	terbufos
8	demeton-s		25	trichlorfon		42	dioxathion
9	diazinon		26	thionazin		43	phosphamidon
10	disulfoton		27	fonophos		44	chlorfenvinphos
11	ronnel		28	dicrotophos		45	carbophenothion
12	merphos		29	dichlorofenthion		46	ethion
13	chlorpyrifos		30	chlorpyrifos methyl		47	leptophos
14	fenthion		31	aspon		48	famphur
15	parathion-methyl		32	fenitrothion		49	phosmet
16	trichloronate		33	crotoxyphos		50	azinphos-ethyl
17	tokuthion		34	TEPP			

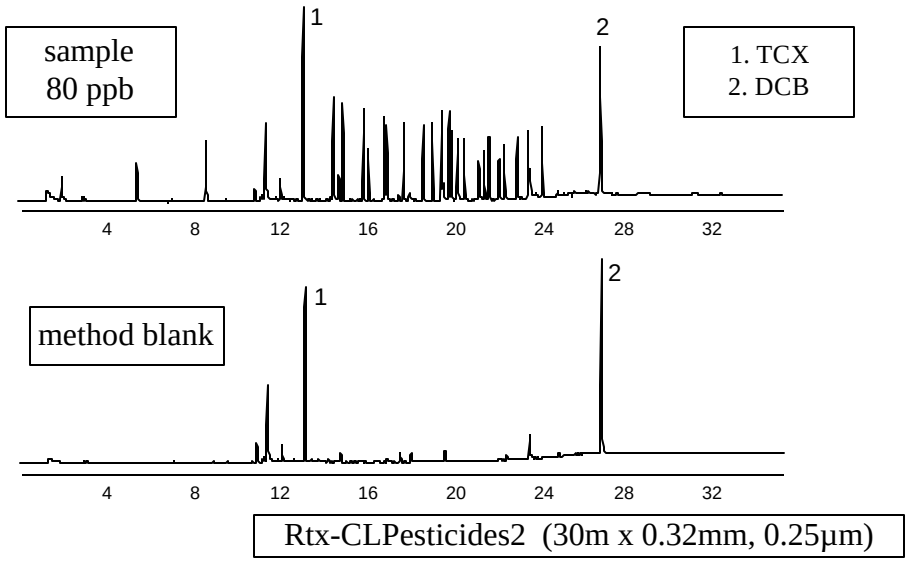
CarboPrep™ Clean-Up of Chlorinated Pesticides

The elution of chlorinated pesticides was determined using 250mg/3mL CarboPrep™ 90 tube.

The procedure is as follows:

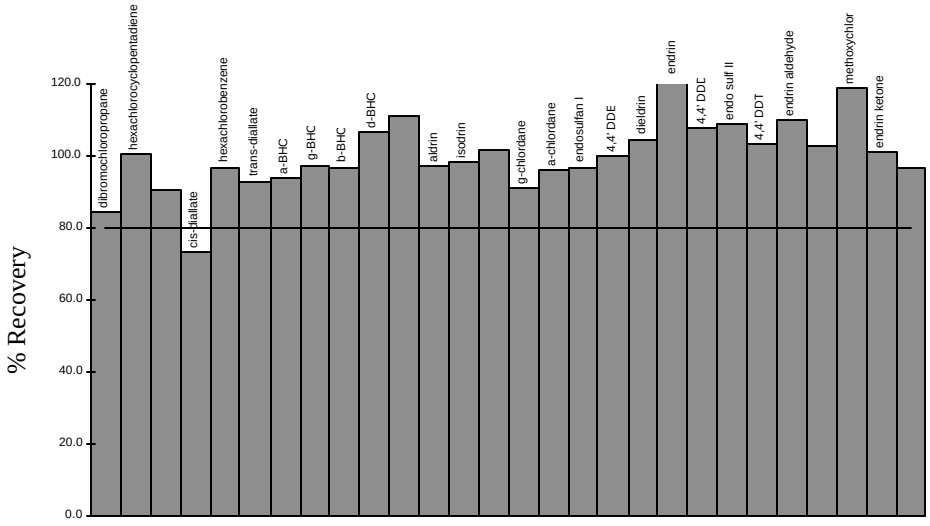
1) Condition tube with 3mL hexane. Not only is this done to condition the tube, but also to remove fines from the carbon bed. A second conditioning solvent system requires the tube to be rinsed with methylene chloride followed by hexane. This system removes a wider range of organic material from the carbon. From this point on, do not expose the carbon to air.
2) Transfer the 1mL sample extract to the tube, and elute to the top of tube bed.
3) Elute with 20mL methylene chloride/hexane (20:80).
4) Concentrate extract to 1mL.

CarboPrep™ Clean-Up of Chlorinated Pesticides (contd.)



Rtx-CLPesticides2 (30m x 0.32mm, 0.25µm)

CarboPrep™ Clean-Up of Chlorinated Pesticides (contd.)



CarboPrep™ Clean-Up of Chlorinated Pesticides (contd.)

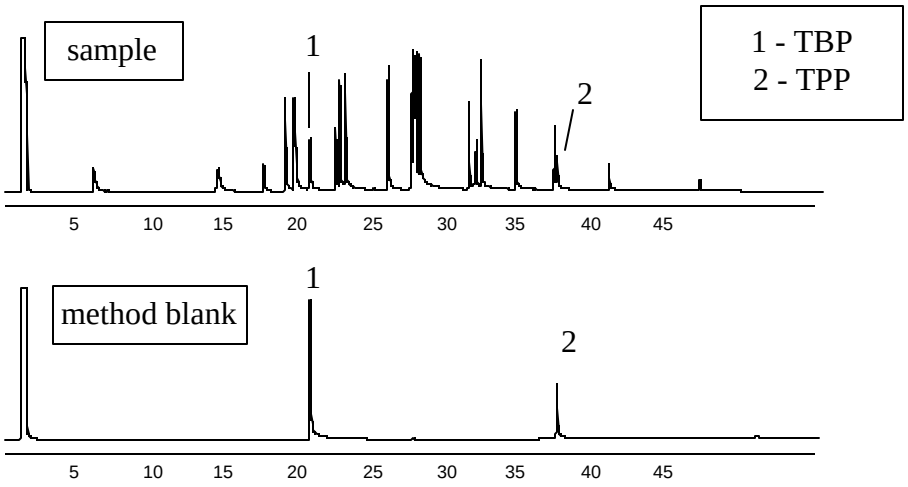
Average recovery range (n=6): 73% for *cis*-diallate to 122% for endrin/chlorobenzilate; 29 compounds tested

Compound	Rec
cis-diallate	73% (only rec <80%)
dibromochloropropane	85%
TCX	91%
α-BHC	94%
heptachlor	112%
4,4'-DDT	104%
endrin aldehyde	110%
endosulfan sulfate	103%
decachlorobiphenyl	97%

CarboPrep™ Clean-Up of Organophosphorus Pesticides

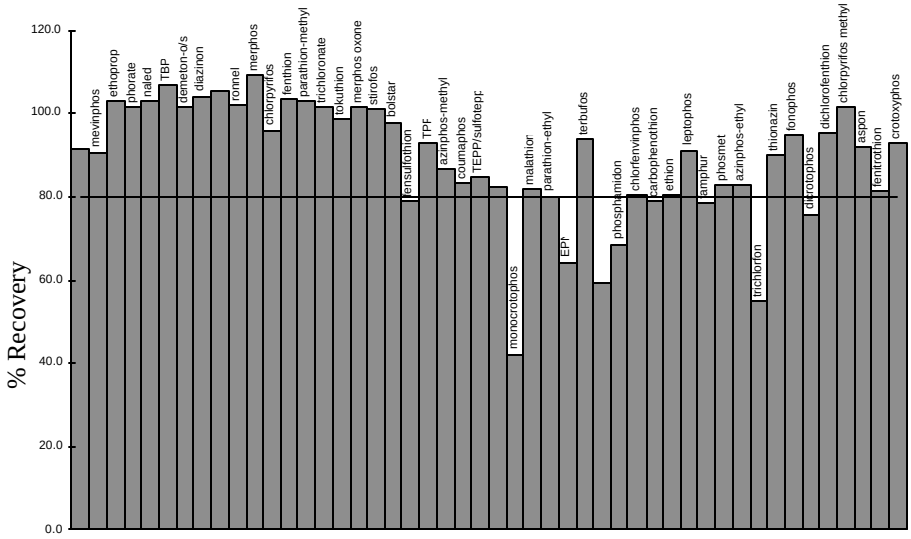
Organophosphorus pesticides eluted through CarboPrep™ 90 SPE tubes also exhibited good results for a majority of the compounds. The spiked extract was eluted using the CarboPrep™ 90 SPE tubes exactly as the chlorinated pesticides shown previously.

CarboPrep™ Clean-Up of Organophosphorus Pesticides (contd.)



Rtx-CLPesticides2 (30m x 0.32mm, 0.25µm)

CarboPrep™ Clean-Up of Organophosphorus Pesticides (contd.)



CarboPrep™ Clean-Up of Organophosphorus Pesticides (contd.)

- 80% of the compounds tested exhibited greater than 80% recovery
- Average recovery range (n=5): 42% for monocrotophos to 109% for merphos; 48 compounds
- Compounds exhibiting less than 80% recovery were:

Compound	Rec
fensulfothion	79%
monocrotophos	42%
EPN	64%
dioxathion	59%
phosphamidon	69%
carbophenothion	79%
famphur	78%
trichlorfon	55%
dicrotophos	76%

CaroPrep™ Clean-Up of Interferences, Discussion

The following tests were performed to help determine what type of matrix interferences the CarboPrep™ 90 tube removes from sample extracts. Two compound classes have been investigated—hydrocarbons and humic acids.

Hydrocarbons were tested because the normal clean-up steps for pesticides includes removal of high molecular weight compounds and polar compounds, but not nonpolar compounds like motor oil.

Humic acids are another common matrix interference found in soil samples that will cause chromatographic interference peaks and also will leave organic residue in the injection port, causing peak tailing and active sites.

CarboPrep™ Clean-Up of Hydrocarbon Interferences

The tests performed on the motor oil are as follows:

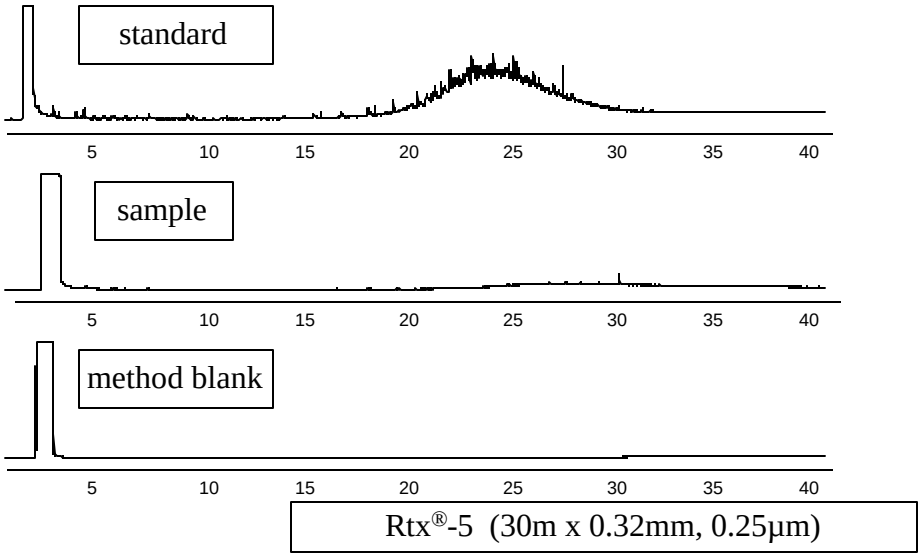
SPE Tube: CarboPrep™ 90 - 3mL, 250mg

Clean-up Method:

1) Condition tube with 3mL hexane
2) Apply 0.5mL CH_2Cl_2, containing 100µL of used motor oil solution standard
3) Elute with 20mL CH_2Cl_2:hexane (20:80)
4) Concentrate extract 0.5mL

As can be seen from the following chromatograms, a majority of the motor oil has been removed from the extract and the method blank is clean.

CarboPrep™ Clean-Up of Hydrocarbon Interferences (motor oil)



CarboPrep™ Clean-Up of Humic Substances

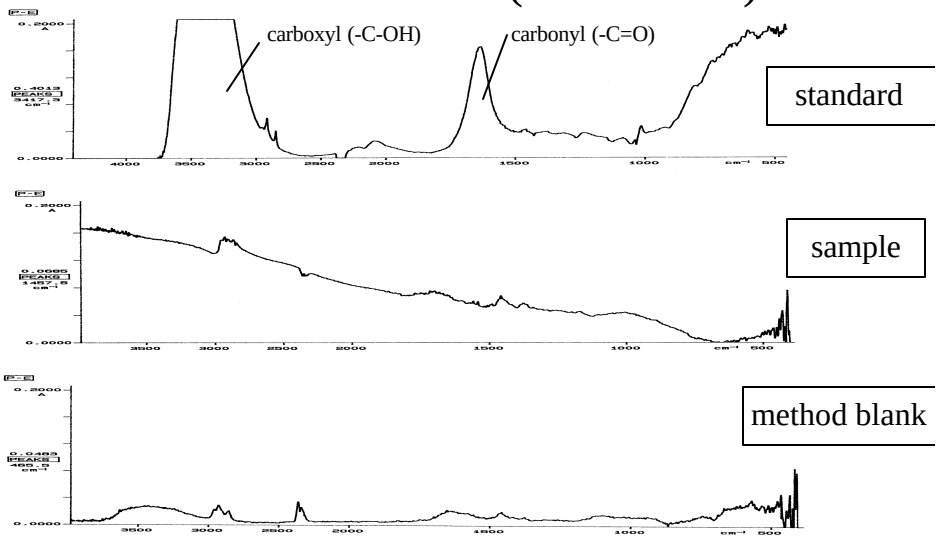
At this point of the investigation, the effect of CarboPrep™ 90 tube to remove humic acids from extracts was started. The initial test was to extract a known sample containing humic acids and elute this extract through the carbon tube. A sample of gascoyne leonardite (i.e., a humic substance standard reference material) was extracted with methylene chloride and this extract was used for testing.

The test determines if the humic acids were retained on the CarboPrep™ packing. We applied 1.0mL of the humic acid extract onto the packing and eluted it with hexane. The resulting extract was concentrated to 1.0mL.

Due to the non-volatility of the humic acids, FTIR was used for the analysis of eluted extracts through the tube. The results show that the humic acids are being retained by the CarboPrep™ packing.

Following is the standard, method blank, and sample scans produced from the FTIR analysis.

CarboPrep™ Clean-Up of Humic Substances (FTIR scans)



Conclusions

1.) Easy clean-up method:
fast, minimum solvent volumes

2.) Quantitative recovery of analytes

3.) Removes oils and humic substances

4.) Wide variety of uses:
organochlorines
organophosphorus

Future Work

1.) Additional compound classes for recovery:
PCBs
Base, neutral, acid semivolatiles
(US EPA Method 8270)
Chlorinated herbicides (US EPA Method 8151)

2.) Additional contaminant classes:
hydrocarbons
humic substances
sulfur

For More Information...

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