RESTEK environmental

Applications note

CarboPrep™ SPE Cleanup of Method 8141A Organophosphorous Pesticides and Herbicides

Organophosphorus pesticides (OPP) are widely applied in agriculture and home use. With the decline of organochlorine pesticides, OPPs have become the most widely used class of insecticides in the US. [1] Analysis of OPPs requires protection of prepared samples from thermal- and photodegradation and special detectors. In addition, the US EPA does not recommend GPC or Florisil® cleanup techniques for solvent-extracted samples. This makes gas chromatography (GC) analysis of low-level, complex matrices even more difficult. This Applications Note shows how CarboPrep™ 90 solid phase extraction (SPE) cartridges may be useful as an alternative in the cleanup of sample extracts containing OPP. Using Rtx®-CLPesticides columns also will help to improve GC analysis of these insecticides.

CarboPrep™ SPE cartridges contain a nonporous, chromatographic grade- graphitized carbon that is optimized for cleanup of environmental sample extracts. Graphitized carbon packings also have been effective in the concentration and extraction of a variety of pesticides in drinking water samples.[2] The high flow rates that can be used with this material allow rapid extraction of 1 to 4 liters of aqueous samples. The cartridges have a low background level, especially suitable for pesticides. The carbon surface provides maximum capacity with a minimum bed weight, reducing the volume of solvent used during extraction.

Studies using spiked solvent samples show that CarboPrep™ 90 SPE cartridges may be useful as an alternative in the cleanup of OPP insecticides before nitrogen phosphorus detection (NPD) or flame photometric detection (FPD) analysis. Previous studies at Restek have shown excellent performance in the recovery of organochlorine pesticides in sample extracts.[3] The same SPE cartridge and preparation method were used to extract the OPPs as in the previous studies (see procedure outlined in Figure 1).

Repetitive extracts show that 80% of the compounds tested exhibited greater than 80% recovery (Table 1). The average recovery range (n=5) was 42% for monocrotophos to 109% for merphos. CarboPrep™ 90 SPE cartridges also were shown to remove sample matrix interferences such as hydrocarbons and humic substances that cause chromatographic interference peaks and leave nonvolatile organic residue in the injection port. For fast, quantitative recovery of OPP compounds, CarboPrep™ 90 SPE cartridges offer a better alternative than GPC or Florisil® SPE.

Table I

Recovery of OPP from Solvent Extracts Using CarboPrep™ 90 SPE Cartridges

Analyte	% recovery avg. n=5	RSD
dichlorvos	91.6	5.8
mevinphos	90.7	8.9
ethoprop	103.1	8.7
phorate	101.7	10.2
naled	103.1	9.0
tributylphosphate (surrogate)	106.8	8.9
demeton-o	101.3	9.9
diazinon, demeton-s (coelution)	104.2	9.8
disulfoton	105.5	10.9
ronnel	101.9	10.1
merphos	109.3	8.9
chlorpyrifos	96.1	0.7
fenthion	103.6	9.8
parathion-methyl	103.1	10.1
trichloronate	101.6	14.7
tokuthion	98.8	11.1
stirofos	101.2	9.3
bolstar	98.1	7.9
fensulfothion	78.9	11.2
triphenylphosphate (surrogate)	92.9	9.1
azinphos-methyl	86.6	7.4
coumaphos	83.1	10.2
trichlorfon	55.0	12.9
thionazin	90.0	8.4
fonophos	94.6	8.1
dicrotophos	76.0	10.7
dichlorofenthion	95.3	9.1
chlorpyrifos methyl	101.8	9.9
aspon	91.9	7.9
fenitrothion	81.5	22.6
crotoxyphos	92.8	7.9
	avg. n=4	RSD
TEPP, sulfotepp (coelution)	84.7	0.4
dimethoate	82.3	17.4
monocrotophos	42.4	21.7
malathion	81.8	14.7
parathion-ethyl	80.3	13.9
EPN	64.4	14.7
terbufos	93.8	9.6
dioxathion	59.3	8.4
phosphamidon	68.7	10.0
chlorfenvinphos	80.4	10.5
carbophenothion	78.8	8.2
ethion	80.5	10.5
leptophos	91.3	1.7
famphur	78.5	7.1
phosmet	83.0	6.7
azinphos-ethyl	83.0	9.3

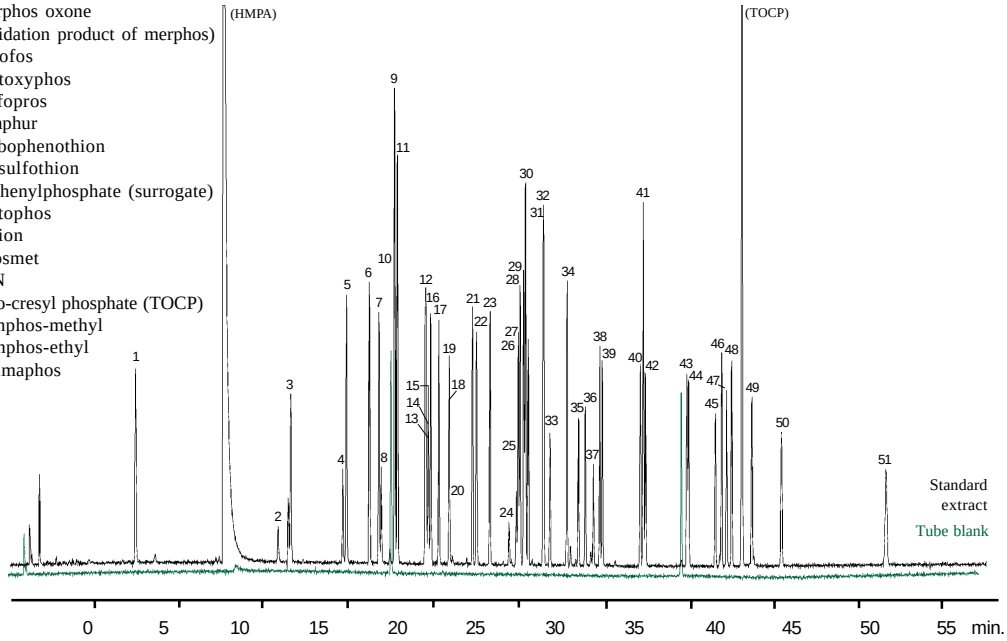
References:

1. "Recognition and Management of Pesticides Poisonings". http://www.epa.gov/oppfead1/safety/healthcare/handbook/handbook.htm, p.34
2. "Development of a Multiresidue Method for Analyzing Pesticide Traces in Water," C. Crescenzi, A. DiCorcia , E. Guerriero, R. Samperi, ES&T, 1997, 31 479-488.
3. "CarboPrep™ SPE Cleanup of Method 8081A Chlorinated Pesticides" Restek Application Note #59110.

Figure 1

CarboPrep™ 90 SPE Cleanup for Method 8141A OPPs Provides Quantitation-Level Accuracy

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



Rtx®-CLPesticides - 30m, 0.32mmID, 0.50µm cat.# 11139

Oven temp: 120°C (hold 10 min.) to 250°C (hold 15 min.) @ 4°C/min.
Inj.: 220°C, split/splitless sleeve
Det.: 295°C, Agilent (HP) 5890 FPD
Carrier gas: helium
Standards: OP Pesticide Calibration Mix A cat.# 32277, OP Pesticide Calibration Mix B cat.# 32278, OP Pesticide Mix C & D custom, Tributylphosphate surrogate standard cat.# 32280 Triphenylphosphate surrogate standard, cat.# 32281
Sample: 1.0mL hexane. Standards were spiked at 0.20µg/mL, injection volume 1µL.
Cartridge: 3mL, 250mg CarboPrep™ 90, cat.# 26091
Cartridge conditioning: Apply 3mL of hexane and pass through cartridge.
Extract clean-up: Prepare collection rack with vials, place under each cartridge. Add 1.0mL of extracted sample to cartridge and collect all solutions passing through. Add 20mL of CH_2Cl_2:hexane (20:80) to cartridge and allow it to elute using gravity feed.
Extract concentration: Solvent exchange extract to hexane. Do not allow extracts to dry completely. Concentrate extracts to 1.0mL. Sample is ready for analysis.

Product Listing:

Description	cat. #
Rtx®-CLPesticides, 30m, 0.32mm ID, 0.50µm	11139
Rtx®-OPPesticides, 30m, 0.32mm ID, 0.50µm	11239 ☆
CarboPrep™ 90 cartridge 3mL, 250mg	26091
Triphenylphosphate Standard	32281

Description	cat. #
Tributylphosphate Standard	32280
OP Pesticide Calibration Mix A	32277
OP Pesticide Calibration Mix B	32278

☆ Restek Recommended