RESTEK environmental

Applications note

CarboPrep™ SPE Cleanup of Method 8081A Chlorinated Pesticides

Many chlorinated pesticides have been banned for use because of their short- and long-term toxicity, carcinogenicity, and environmental persistence[1]. An expanded list of these chemicals, some of which are still actively applied in the field, has been included in the updated US Environmental Protection Agency (EPA) Method 8081A. Despite the fact that most of these chlorinated pesticides are now illegal to use, manufacture, and transport in the US, organochlorines are the eighth most common source of pesticide poisoning that results in reportable illness[2]. Although most of these chlorinated pesticides, insecticides, and herbicides have limited water solubility and mobility, they are found to bioaccumulate and persist in the environment. There is an ongoing risk for exposure from a number of sources, so it is still essential to test soils, wastewater, and sediments for their presence.

Many of the additional components included in the EPA Method 8081A update are difficult to analyze by gas chromatography (GC), especially the isomers of the carbamate herbicide diallate. However, these have been shown to separate well using the Rtx®-CLPesticides and Rtx®-CLPesticides2 column pair. For more details on EPA Method 8081A analysis using these columns, refer to Applications Note #59547.

Standard EPA methods for preparation and analysis of pesticide-containing hazardous wastes require initial liquid/liquid extraction with dichloromethane, gel permeation chromatography (GPC) fractionation of higher molecular weight interferences, and a final cleanup of polar contaminants with Florisil® columns or solid phase extraction (SPE) tubes, before analysis with GC-electron capture detection (ECD). Many labs have found that these cleanup precautions are not adequate and still produce high backgrounds in analytical samples, resulting in difficult quantitation and frequent GC/detector maintenance. The addition of a CarboPrep™ SPE tube, after the Florisil® cleanup, will remove additional mid- to non-polar contaminants without compromising the recovery of pesticides. Extracts will have lower backgrounds, producing better chromatograms with fewer interferences and extending the lifetime of inlet sleeves, guard columns, and reducing maintenance of sensitive ECD detectors. Results in Table I below show that recovery levels are excellent for this extended chlorinated pesticides list, when following the method described in Figure 1.

CarboPrep™ SPE tubes contain a nonporous, chromatographic grade, graphitized carbon, optimized for cleanup and concentration of environmental samples. Graphitized carbon has also been shown to be effective in the concentration and extraction of many environmentally significant analytes found in drinking and waste water, such as phenols and triazine herbicides[3,4]. This form of carbon has been useful in multi-residue fractionation of base/neutral compounds from acidic pesticides[5]. The high flow rates, which may be used with this material, allow rapid extraction of 1 to 4 liters of aqueous samples. The tubes have a low background level, especially suitable for pesticides. The high surface area provides maximum capacity with a minimum of bed weight, reducing the volume of solvent used during extraction. These same characteristics make CarboPrep™ SPE tubes an excellent choice for cleanup of solid waste samples.

References:

1. The 8th Report on Carcinogens - 1998, US Dept. of Health & Human Services, Public Health Service, www.ehis.niehs.nih.gov.
2. Recognition and Management of Pesticide Poisonings, US EPA, www.epa.gov.
3. "Trace Determination of Phenols in Natural Waters", A. DiCorcia, A. Bellioni, M. Madbouly, S. Marchese, *Journal of Chromatography A*, 1996, 733, 383-393.
4. "Ultratrace Determination of Atrazine and its Six Major Degradation Products in Water", A. DiCorcia, C. Crescenzi, E. Guerriero, R. Samperi, *ES&T*, 1997, 31, 1658-1663.
5. "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.

References not available from Restek.

Table I

Recovery of Chlorinated Pesticides from Solvent Extracts Using CarboPrep™ 90 SPE Cartridge

Analytes*	Percent Recovery	RSD n=6
dibromochloropropane	84.7	11.4
hexachlorocyclopentadiene	100.4	9.9
2,4,5,6 tetrachloro-*m*-xylene (surrogate)	90.6	8.1
cis-diallate	73.0	11.3
hexachlorobenzene	96.8	7.4
trans-diallate	93.0	10.3
α-BHC	93.7	9.7
γ-BHC	97.7	8.7
β-BHC	97.0	7.9
δ-BHC	106.7	6.4
heptachlor	111.6	8.0
aldrin	97.3	8.6
isodrin	98.5	7.8
heptachlor epoxide	101.6	7.0
γ-chlordane	91.2	11.3
α-chlordane	96.1	7.4
endosulfan I	97.0	7.5
4,4' DDE	100.1	6.7
dieldrin	104.9	4.1
endrin/chlorobenzilate	121.9	6.3
4,4' DDD	107.8	2.9
endosulfan II	108.8	4.9
4,4' DDT	103.5	6.5
endrin aldehyde	110.0	2.8
endosulfan sulfate	102.7	6.5
methoxychlor	119.1	6.1
endrin ketone	101.0	3.3
decachlorobiphenyl (surrogate)	96.8	3.5

*Analytes spiked at 80-160ng/mL in hexane.

Figure 1

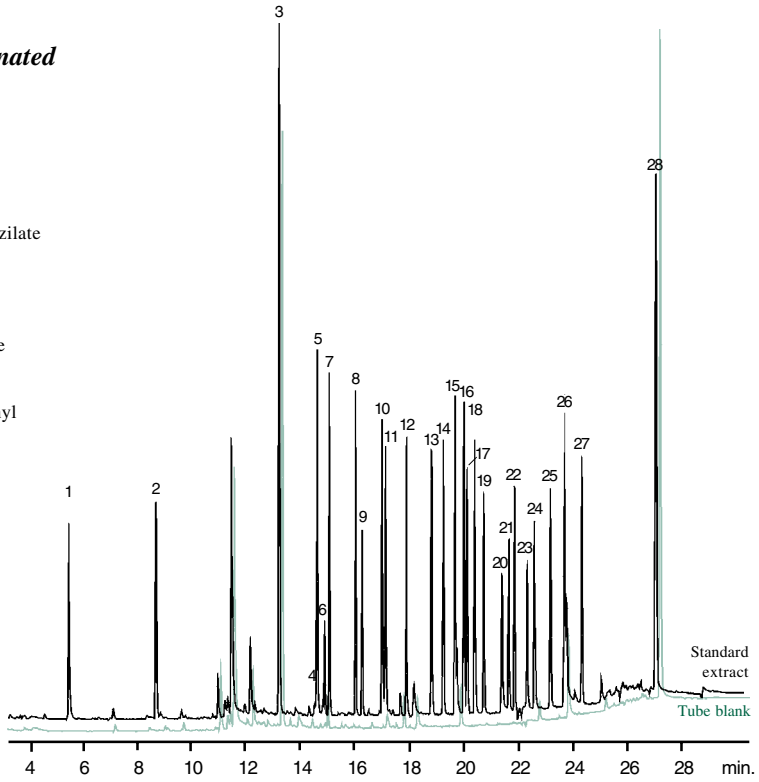
Cleanup method for chlorinated pesticides provides better separation.

Solvent Extracts of Method 8081A Chlorinated Pesticides Using CarboPrep™ 90

1. dibromochloropropane
2. hexachlorocyclopentadiene
3. tetrachloro-*m*-xylene
4. *cis*-diallate
5. hexachlorobenzene
6. *trans*-diallate
7. α-BHC
8. γ-BHC
9. β-BHC
10. δ-BHC
11. heptachlor
12. aldrin
13. isodrin
14. heptachlor epoxide
15. γ-chlordane
16. α-chlordane
17. endosulfan I
18. 4,4'-DDE
19. dieldrin
20. endrin/chlorobenzilate
21. 4,4'-DDD
22. endosulfan II
23. 4,4'-DDT
24. endrin aldehyde
25. endosulfan sulfate
26. methoxychlor
27. endrin ketone
28. decachlorobiphenyl

30m, 0.32mm ID, 0.25µm
Rtx® CLPesticides2 (cat.# 11324).

Oven temp.: 80°C (hold 1 min.) to 300°C @ 9°C/min. (hold 10 min.)
Inj.: 220°C direct injection using Uniliner® sleeve (cat.# 20335).
Det. temp.: ECD 310°C
Carrier gas: helium



Standards:	Organochlorine Pesticide Mix AB #1	cat# 32291
	Pesticide Surrogate Mix	cat# 32000
	Organochlorine Pesticide Mix C #1	cat# 32296
Column:	Rtx®-CLPesticides2, 30m x 0.32mmID, 0.25µm	cat# 11324
Sample:	0.5 - 1.0mL solvent extracted sample exchanged into hexane. Standards and surrogates were spiked into hexane.	
Tube:	3mL, 250mg CarboPrep™ 90	cat# 26091
Tube conditioning:	Apply 2mL CH_2Cl_2:hexane (20:80) and pass through tube.	
Extract clean-up:	Prepare collection rack with vials, place under each tube. Add 0.5-1.0mL of extracted sample to tube and collect all solutions passing through. Do not expose carbon bed to air. Add 20mL of CH_2Cl_2:hexane (20:80) to tube and allow it to elute using gravity feed.	
Extract concentration:	Solvent exchange extract to hexane. Do not allow extracts to dry completely. Concentrate extract to 0.5- 1.0mL. Sample is ready for analysis.	

Product Listing:

Description	cat. #
RTX®-CLPesticides2, 30m, 0.32mm ID, 0.25µm	11324
CarboPrep™ 90 cartridge 3mL, 250mg	26091
Pesticide Surrogate Mix	32000

Description	cat. #
Organochlorine Pesticide Mix AB #1	32291
Organochlorine Pesticide Mix C #1	32296