RESTEK environmental

Applications note

Improved Analysis of Organophosphorus Pesticides Using Rtx®-OPPesticides and Rtx®-OPPesticides2 Columns

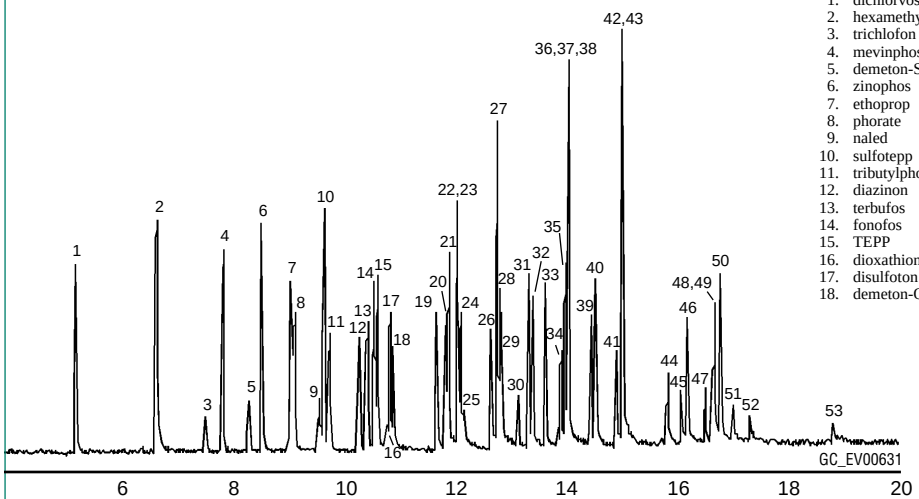
Organophosphorus pesticides (OPPs) are an important group of insect control agents used in agricultural and home settings. Although there are continuing concerns about their effects on health, their relatively low toxicity and short environmental fate have made them suitable replacements for banned organochlorine pesticides, especially in agricultural applications. Because of their widespread use, it is necessary to routinely monitor treated foods and surrounding soils and groundwater after OPP application, to ensure low residue levels.

Historically, the analysis of OPPs has presented challenges. US Environmental Protection Agency (EPA) Methods 8141 and 8141A were developed to help laboratories analyze soils, water, and solid wastes for OPPs. Method 8141A describes the many problems that can occur during capillary GC analysis. The OPP compounds represent a diverse group, many of which are photosensitive or easily degraded during routine standard preparation, storage, and analysis. In addition, individual analytes can be difficult to identify because of the large number of OPPs that might be present (e.g., a total of 49 possible analytes are listed in Method 8141A), and in the past GC/MS has not been sufficiently sensitive for routine use. Consequently, ion-specific detectors (e.g., a nitrogen phosphorus detector [NPD] or flame photometric detector [FPD] in the phosphorus mode) must be used to ensure sensitivity to detect low ppb levels of OPP compounds. This requires dual-column analysis for confirmation of analyte identities. Even the current EPA method states, "it is unlikely that all of them [OPPs] could be determined in a single analysis."[1]

Many capillary phases have been used for this dual-column analysis, but most present a large number of coelutions that make positive identifications difficult. For example, there are seven known pairs of coelutions on the 5% phenyl analytical column named in Method 8141A, and nine pairs of coelutions on the confirmation column. Until now, the Rtx®-OPPesticides column has given the best resolution of organophosphorus pesticides in the shortest time (Figure 1).

The Rtx®-OPPesticides column has advantages over other current technologies, but until now there has not been a confirmation column that has as few coelutions in as short an analysis time, to make it compatible with the Rtx®-OPPesticides column. To provide a good confirmation column to match the Rtx®-OPPesticides column, Restek chemists have developed a new polymer phase, the Rtx®-OPPesticides2 phase. In combination, these two columns will reduce the number of chromatographic coelutions and provide separations in less than 25 minutes.

Figure 1—The Rtx®-OPPesticides column provides good resolution and short analysis time for organophosphorus pesticides.



1. dichlorvos
2. hexamethylphosphoramide
3. trichlofon
4. mevinphos
5. demeton-S
6. zinophos
7. ethoprop
8. phorate
9. naled
10. sulfotepp
11. tributylphosphate (IS)
12. diazinon
13. terbufos
14. fonofos
15. TEPP
16. dioxathion
17. disulfoton
18. demeton-O
19. dichlorofenthion
20. chlorpyrifos methyl
21. dimethoate
22. dicrotophos
23. monocrotophos
24. ronnel
25. merphos
26. chlorpyrifos
27. aspon
28. fenthion
29. trichloronate
30. phosphamidon isomer (breakdown product)
31. methyl parathion
32. malathion
33. fenitrothion
34. tokuthion
35. phosphamidon
36. chlorfenvinphos
37. parathion
38. merphos oxone (merphos breakdown product)
39. stirophos
40. crotoxyphos
41. bolstar
42. carbophenthion
43. ethion
44. triphenylphosphate (IS)
45. leptophos
46. fensulfothion
47. tri-*o*-cresyl phosphate
48. phosmet
49. EPN
50. famfur
51. azinphos methyl
52. azinphos ethyl
53. coumaphos

Column: Rtx®-OPPesticides 30m, 0.32mm ID, 0.50µm (cat.# 11239)
Sample: 1.0µL of custom OP pesticides mix described in Figure 3 (GC_EV00602)
Concentration: 100ppb
Inj.: direct injection, Uniliner® DI liner (cat.# 20335)
Oven temp.: 100°C to 180°C @ 10°C/min. (hold 2 min.), to 300°C @ 18°C/min. (hold 2min.)
Inj. & Det. temp.: 250°C
Detector: FPD
Flow rate: 5cc/min., helium

environmental

Restek's proprietary computer-assisted stationary phase development (CASPD) modeling software was used to develop the new phase. This software predicts GC polymer phase selectivity based on the retention of key analytes under controlled GC conditions. The stationary phase selectivity can be optimized, often resulting in the design of a completely new phase. In this case the new phase, Rtx®-OPPesticides2, achieves much better resolution of the OPPs than traditionally used columns, with only two coeluting pairs. This makes the new column an ideal primary column, even exceeding the performance of the Rtx®-OPPesticides column, for analyses of organophosphorus pesticides (Figure 2).

The Rtx®-OPPesticides2 column has quickly become a workhorse column for laboratories analyzing organophosphorus pesticides.

GC/MS Analysis

In some methods, such as in food analysis, low-level detection of organophosphorus pesticides is not as important as the positive identification of the pesticides. In these cases a GC/MS analysis is the best approach. The Rtx®-OPPesticides2 column is an excellent choice for GC/MS because the column exhibits low bleed and maximizes resolution of the organophosphorus pesticides. Figure 3 shows a typical GC/MS analysis.

Effect of Carrier Gas Flow

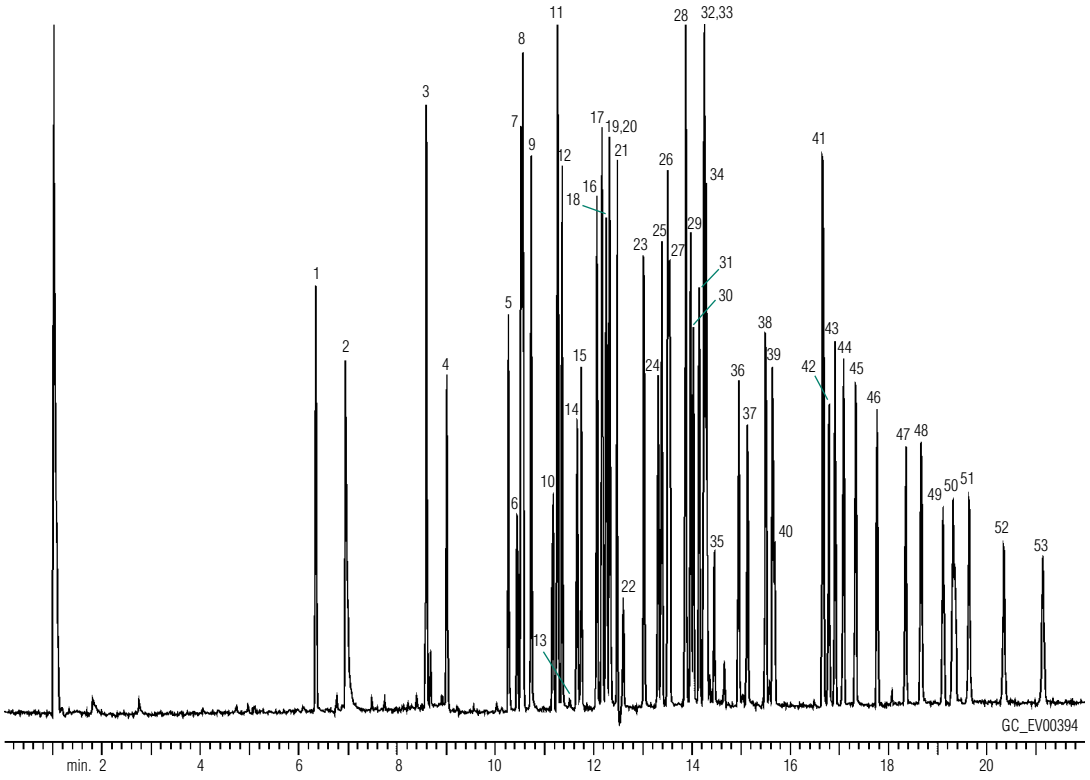
Flow conditions are extremely important to achieving the desired resolutions of OPPs. The chromatograms in Figure 4 are results from a flow rate study on the Rtx®-OPPesticides2 column. Flow can be used to enhance resolution and affect elution order. Because of the close elutions of so many of these compounds, it is critical to measure analytical velocity as either flow rate through the column or as dead time of an unretained analyte. Note that retention times and resolution (and, potentially, elution order) can shift with relatively small changes in dead time. In this analysis, we recommend using a slightly lower flow rate (longer dead time) to achieve the best overall separation.

Conclusion

Organophosphorus pesticides analyses can present many challenges to the analyst, but the Rtx®-OPPesticides2 and Rtx®-OPPesticides column pair ensures quick analysis, exceptional resolution, and confirmation for more than 48 OPP analytes and their degradation products in a single, dual-column run.

1. US EPA Method 8141A Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique.

Figure 2—The Rtx®-OPPesticides2 column is an ideal primary column for fast, sensitive analyses of organophosphorus pesticides.



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

Column:	Rtx®-OPPesticides2, 30m, 0.32mm ID, 0.32µm (cat.# 11241)
Inj.:	1µL splitless injection of 100ng/mL custom OP pesticides mix described in Figure 3 (GC_EV00602)
Oven temp.:	80°C (hold 0.5min.) to 280°C @ 12°C/min. (hold 10 min.)
Injector:	200°C
Inlet liner:	4mm Siltek™ single gooseneck (cat.# 20798)
Detector:	FPD @ 250°C;
Dead time:	1.03 min. @ 80°C
Splitless hold:	1 min.

Figure 3—Low bleed and fast analysis times make the Rtx®-OPPesticides2 column an excellent choice for GC/MS analysis of organophosphorus pesticides.

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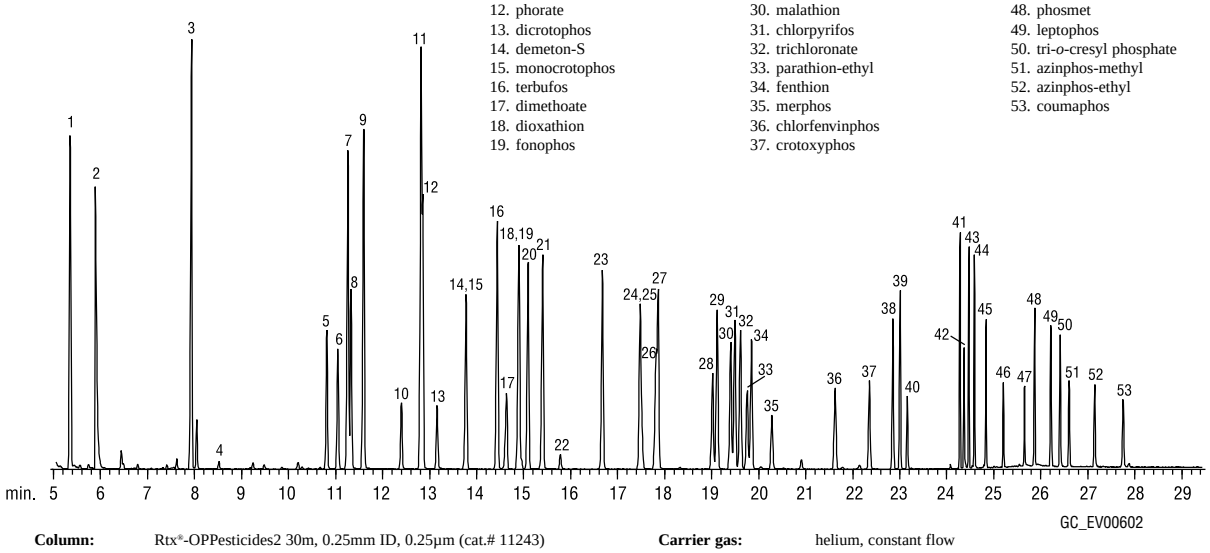
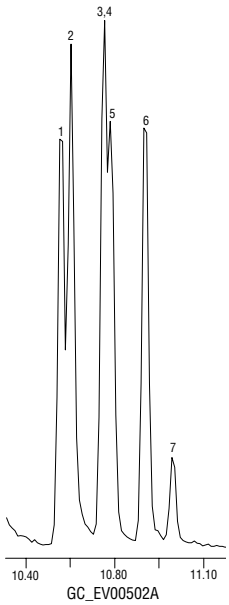
48. phosmet
49. leptophos
50. tri-*o*-cresyl phosphate
51. azinphos-methyl
52. azinphos-ethyl
53. coumaphos

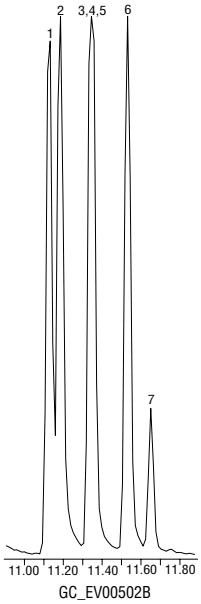


Column: Rtx®-OPPesticides2 30m, 0.25mm ID, 0.25µm (cat.# 11243)
Sample: Custom Mix, plus:
8140/8141 OP Pesticides Calibration Mix A (cat.# 32277)
8141 OP Pesticides Calibration Mix B (cat.# 32278)
Triphenylphosphate Standard (cat.# 32281)
Tributylphosphate Standard (cat.# 32280)
1µL, 100ppm each (100ng on column)
Inj.: 1.0µL splitless (hold 0.4 min.), 4mm ID double gooseneck inlet liner (cat.# 20785)
Inj. temp.: 250°C
Carrier gas: helium, constant flow
Flow rate: 1.0mL/min.
Oven temp.: 80°C (hold 0.5 min.) to 140°C @ 20°C/min. to 210°C @ 4°C/min. (hold 1 min.) to 280°C @ 30°C (hold 5 min).
Det: MS
Transfer line temp.: 280°C
Scan range: 35-400amu
Ionization: EI

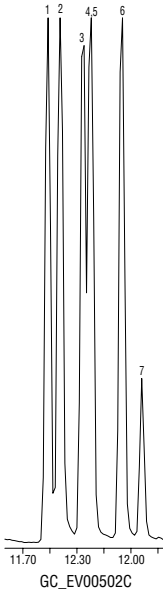
Figure 4—Adjusting the flow rate can affect elution time and resolution (and elution order) for OPPs on an Rtx®-OPPesticides2 column.



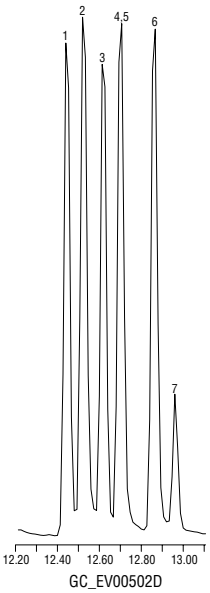
83cm/sec.
dead time 0.6 min.



71cm/sec.
dead time 0.7 min.



56cm/sec.
dead time 0.9 min.



46cm/sec.
dead time 1.1 min.

Column: Rtx®-OPPesticides2 30m, 0.32mm, 32µm (cat.#11241)
Injector: 200°C split/splitless, purge off, hold 1 min
Oven temp.: 80°C (hold 0.5 min.) to 280°C @ 12°C/min. (hold 10 min.)
Detector: FPD @ 250°C
Sample: 0.5µL 200ng/mL of custom OP pesticides mix described in Figure 3 (GC_EV00602) (partial chromatograms shown)
Other conditions as described for Figure 2 (GC_EV00394)

1. terbufos
2. dimethoate
3. diazinon
4. dioxathion
5. fonophos
6. disulfoton
7. phosphamidon isomer

Rtx®-OPPesticides (-20 to 310/330°C)

ID (mm)	df (µm)	20-meter	30-meter
0.18	0.25	56898	—
0.25	0.40	—	55239
0.32	0.50	—	11239
0.53	0.83	—	11240

Rtx®-OPPesticides2 (-20 to 310/330°C)

ID (mm)	df (µm)	20-meter	30-meter
0.18	0.20	11244	—
0.25	0.25	—	11243
0.32	0.32	—	11241
0.53	0.50	—	11242

Inlet Liners

For Agilent GCs

Uniliner® *(4.0mm ID, 6.3mm OD, 78.5mm length)*

20335 (ea.) 20336 (5-pk.)

Hole makes use with EPC possible!

Drilled Uniliner® *(4.0mm ID, 6.3mm OD, 78.5mm length)*

21054 (ea.) 21055 (5-pk.)

Open-top Uniliner® w/Wool *(4.0mm ID, 6.3mm OD, 78.5mm length)*

20843 (ea.) 20844 (5-pk.)

Gooseneck Splitless (4mm) *(4.0mm ID, 6.3mm OD, 78.5mm length)*

20798 (ea.) 20799 (5-pk.) 20800(25-pk.)

Double Gooseneck Splitless (4mm) *(4.0mm ID, 6.5mm OD, 78.5mm length)*

20784 (ea.) 20785 (5-pk.) 20786(25-pk.)

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Method 8140/8141 OP Pesticide Calibration Mix A

azinphos methyl
bolstar (sulprofos)
chlorpyrifos
coumaphos
demeton, O and S
diazinon
dichlorvos
disulfoton
ethoprop
fensulfothion
fenthion
merphos
methyl parathion
mevinphos
naled
phorate
ronnel
stirofos
tokuthion (prothiofos)
trichloronate

200µg/mL each in hexane/acetone (95/5), 1mL/ampul

	Each	5-pk.	10-pk.
	32277	32277-510	
w/data pack	32277-500	32277-520	32377

Method 8141 OP Pesticide Calibration Mix B

dimethoate
EPN
malathion
monocrotophos
parathion
sulfotepp
TEPP

200µg/mL each in hexane/acetone (95/5), 1mL/ampul

	Each	5-pk.	10-pk.
	32278	32278-510	
w/data pack	32278-500	32278-520	32378

Method 8140/8141 Internal Standards & Surrogates

These solutions are prepared at 1,000µg/mL in acetone, 1mL/ampul

NPD Detector:
Internal Standard: 1-bromo-2-nitrobenzene
Surrogate: 4-chloro-3-nitrobenzotrifluoride

1-bromo-2-nitrobenzene

	Each	5-pk.	10-pk.
	32279	32279-510	
w/data pack	32279-500	32279-520	32379

4-chloro-3-nitrobenzotrifluoride

	Each	5-pk.	10-pk.
	32282	32282-510	
w/data pack	32282-500	32282-520	32382

FPD Detector:
Internal Standard: none recommended
Surrogate: tributylphosphate and triphenylphosphate

tributylphosphate

	Each	5-pk.	10-pk.
	32280	32280-510	
w/data pack	32280-500	32280-520	32380

triphenylphosphate

	Each	5-pk.	10-pk.
	32281	32281-510	
w/data pack	32281-500	32281-520	32381