Two Novel GC Column Stationary Phases Designed for the Analysis of Pesticide Residues

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Abstract

The current work demonstrates the use of two new and unique phases, which have been optimized for the analysis of all classes of pesticides. The phase chemistry improves separation and peak shape for the more polar pesticide compounds when compared to standard 5 % phenyl columns. Selectivity data is compared between a 5ms type phase and the two new columns.

Multi-pesticide residue screening was evaluated for over 250 different pesticides commonly analyzed from fruits and vegetables. The unique selectivity offered by the two phases improves resolution for multi-component analytes providing a more unique elution pattern, which can be used to identify closely eluting analytes.

Since the phases have orthogonal selectivity, they are also a good choice for dual column methods. Some data is presented for EPA specified testing procedures.

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Introduction

Pesticides are widely used by farmers to control pests, weeds, and molds that would otherwise decrease crop production. While this has significantly increased worldwide food productions, these same pesticides pose significant health and environmental risks. The restrictions for specific pesticides differ from one country to the next. As world trade increases, the potential threat to other countries' populations increases. For this reason, pesticides are the subjects of increasing regulation.

Since many different types of pesticides can be used on the same food product, Multi-Residue screening approaches are used to look for multiple classes of pesticide compounds at one time. Considering that there are more than 500 registered pesticides, no single analysis technique is capable of screening for all possible contaminates. However, gas chromatography (GC) is still the most commonly used method for the majority of the pesticide classes. While analytes specific detectors such as ECD or NPD may be used for screening, Mass Spectrometer (MS) detection must be em-

Introduction *(cont'd)*

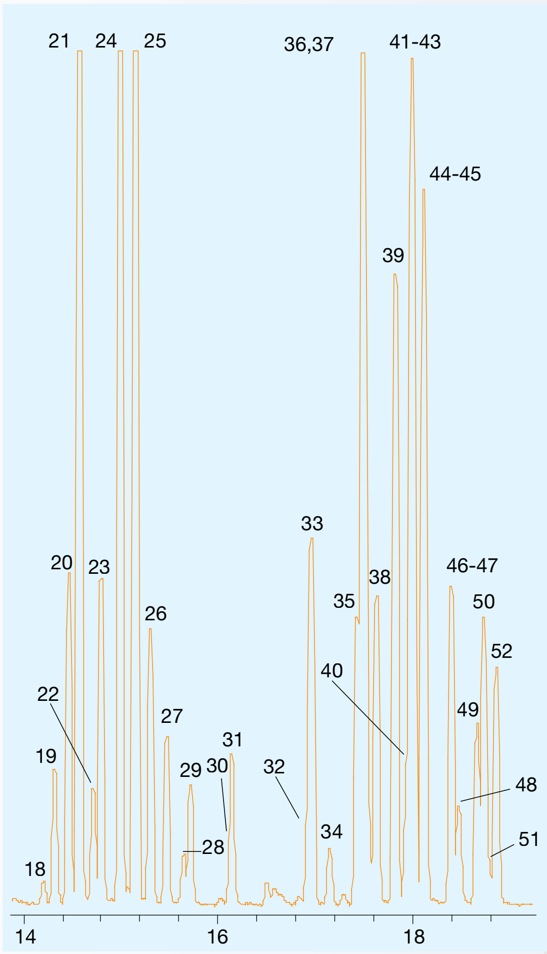
ployed to provide positive confirmation. Zebron MultiResidue™ columns were specially designed for pesticides analysis. The columns were developed using two new stationary phases that are unlike any other commercially available columns. The phases were designed to provide orthogonal selectivity to provide maximum resolving power in complex samples. Zebron MultiResidue™ columns provide low bleed on ECD and NPD detectors and both columns are MS certified, so they can also be used with GC/MS for multi-residue pesticide methods.

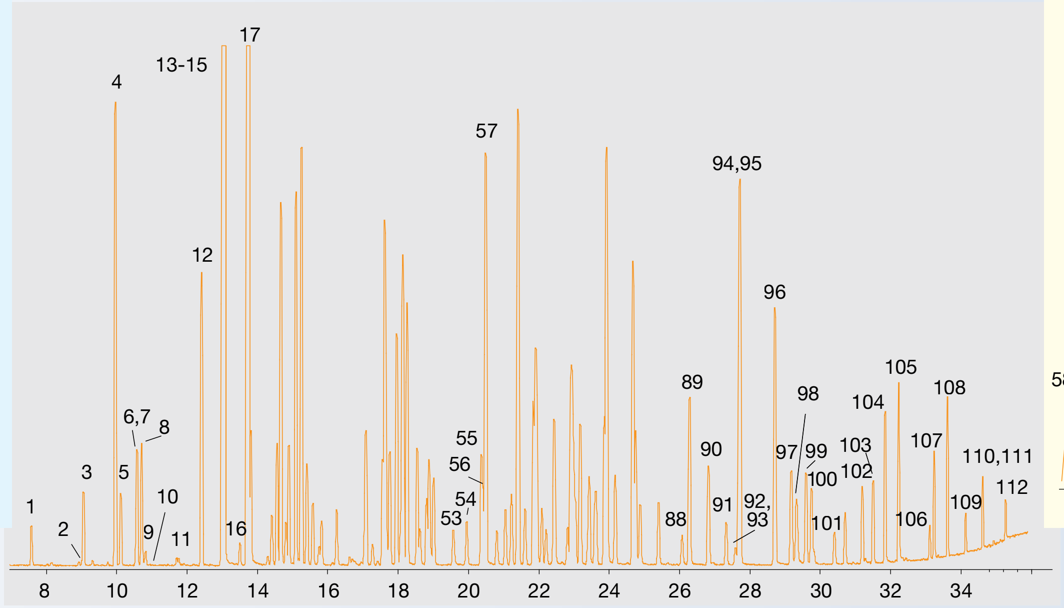
GC/MS screening of multi-residue pesticide standards was evaluated using the new Zebron MultiResidue™ columns and compared with the results obtained using a standard 5ms type column. Dual column approaches were also evaluated using a chlorinated pesticides sample following EPA Method 8081A.

Figure 1: Multi-Pesticide Residue Analysis using Zebron MultiResidue™-1

Conditions

Column: Zebron MultiResidue-1
Dimensions: 30 meter x 0.25 mm x 0.25 µm
Part Number: 7HG-G016-11
Injection: Splitless at 260 °C, 1 µL
Carrier Gas: Helium @ 0.9 mL/min (Constant Flow)
Oven Program: 80 °C for 0.5 min to 150 °C at 10 °C/min to 240 °C at 4 °C/min to 320 °C at 15 °C/min for 3 min
Detection: MSD @ 320 °C; 45-400 amu





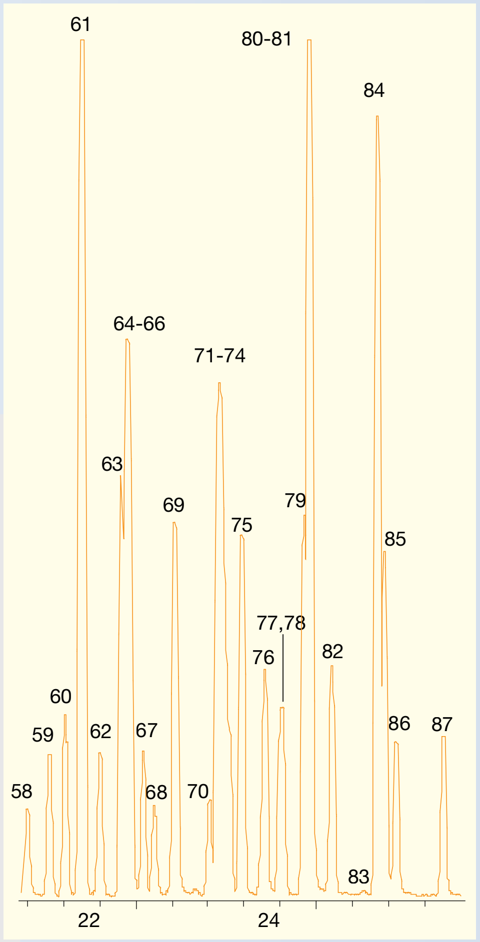


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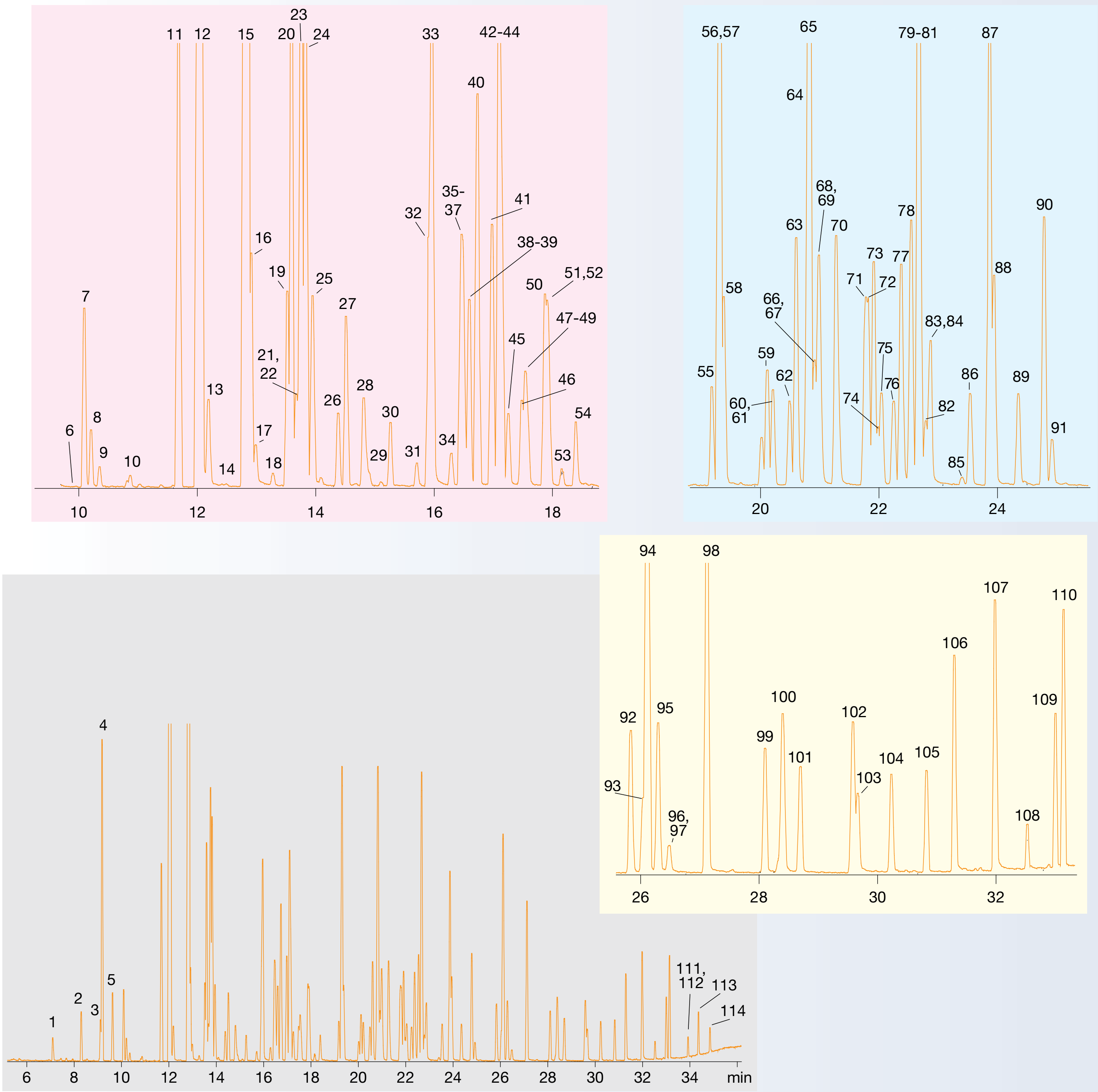
Figure 2: Multi-Pesticide Residue Analysis using Zebron MultiResidue™-2



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Conditions

Column: Zebron MultiResidue-2
Dimensions: 30 meter x 0.25 mm x 0.20 µm
Part Number: 7HG-G017-10
Injection: Splitless at 260 °C, 1 µL
Carrier Gas: Helium @ 0.9 mL/min (Constant Flow)
Oven Program: 80 °C for 0.5 min to 150 °C at 10 °C/min to 240 °C at 4 °C/min to 320 °C at 15 °C/min for 3 min
Detection: MSD @ 320 °C; 45-400 amu

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Peaks for Figure 1 and Figure 2:

Peak No.	Sample Analyte
1	Dichlorvos
2	EPTC
3	Butylate
4	3,5-Dichlorobenzoic acid (methyl ester)
5	Vernolate
6	Pebulate
7	Mevinphos
8	4-Nitrophenol (methyl ester)
9	Mevinphos Isomer
10	Trichlorfon
11	Dicamba (methyl ester)
12	MCPP (methyl ester)
13	Molinate
14	Tebuthiuron
15	MCPA (methyl ester)
16	DEET
17	Tetraethyl pyrophosphate (methyl ester)
18	Demeton
19	Dichloroprop (methyl ester)
20	Trifluralin
21	Thionazin
22	Cycloate
23	Benefin
24	Propachlor
25	Ethoprop
26	Chlorpropham
27	2,4-D (methyl ester)
28	Sulfotep
29	Naled
30	Phorate
31	Dicrotophos
32	Pentachlorophenol (methyl ester)

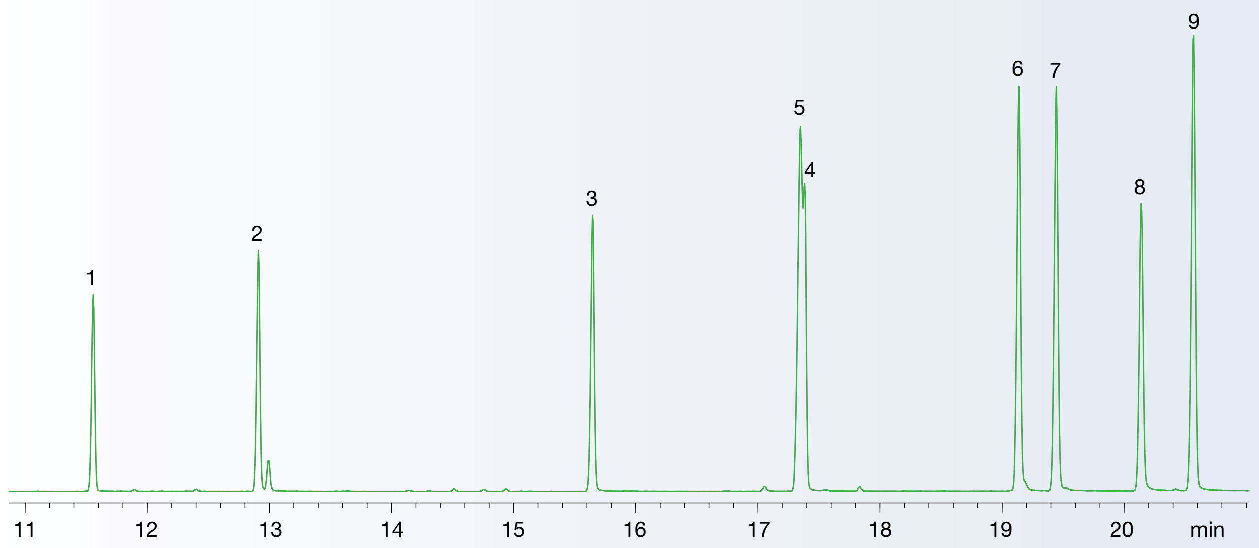
Peak No.	Sample Analyte
33	Profluralin
34	Demeton Isomer
35	Prometon
36	Atraton
37	Monocrotophos
38	Atraton Isomer
39	Silvex (methyl ester)
40	Terbufos
41	Propazine
42	Diazinon
43	Pronamide
44	Atrazine
45	Simazine
46	Terbuthylazine
47	Dioxathion
48	Fonofos
49	Dimethoate
50	2,4,5-T Methyl ester
51	Disulfoton
52	Chloramben (methyl ester)
53	Phosphamidon Isomer
54	Secbumeton
55	Dichlofenthion
56	2,4-DB (methyl ester)
57	Terbacil
58	Dinoseb (methyl ester)
59	Alachlor
60	Chlorpyrifos methyl
61	Phosphamidon
62	Ronnel
63	Prometryn
64	Ametryn

Peak No.	Sample Analyte
65	Bentazon (methyl ester)
66	Aspon
67	Simetryn
68	Metribuzin
69	Methyl parathion
70	Terbutryn
71	Metolachlor
72	Malathion
73	DCPA
74	Fenitrothion
75	Chlorpyrifos
76	Trichloronate
77	Triadimeton
78	Pichloram (methyl
79	Isopropalin
80	Fenthion
81	MGK-264 Isomer
82	Parathion
83	Merphos
84	Bromacil
85	Clofenvinfos Isomer
86	MGK-624
87	Pendimethalin
88	Diphenamid
89	Clofenvinfos
90	Butachlor
91	Crotoxyphos
92	Stirofos
93	Tokuthion
94	Oxadiazon
95	Merphos Oxide
96	Napropamide

Peak No.	Sample Analyte
97	Fenamiphos
98	Oxyflurofen
99	Acifluorfen
100	Carboxin
101	Ethion
102	Tricyclazole
103	Fensulfothion
104	Carbofenotion
105	Famfur
106	Norflurazon
107	Hexazinone
108	EPN
109	Phosmet
110	Leptophos
111	Azinphos-Methyl
112	Fenarimol
113	Azinphos-ethyl
114	Coumaphos

Figure 3: Nitrogen & Phosphorous Pesticides (NPM-102)

ZB-MR-1
30 meter x 0.25 mm x 0.25 µm



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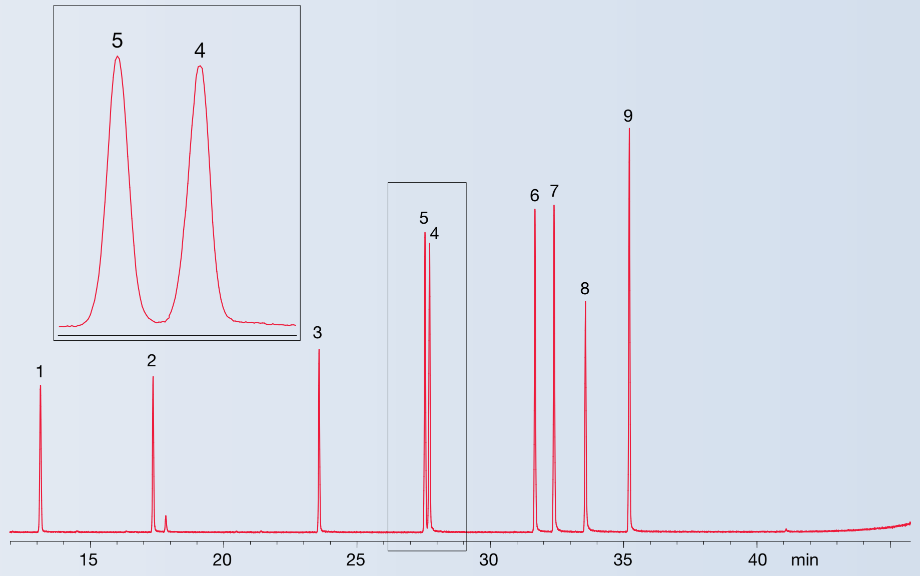
ZB-MR-2
30 meter x 0.20 mm x 0.20 µm



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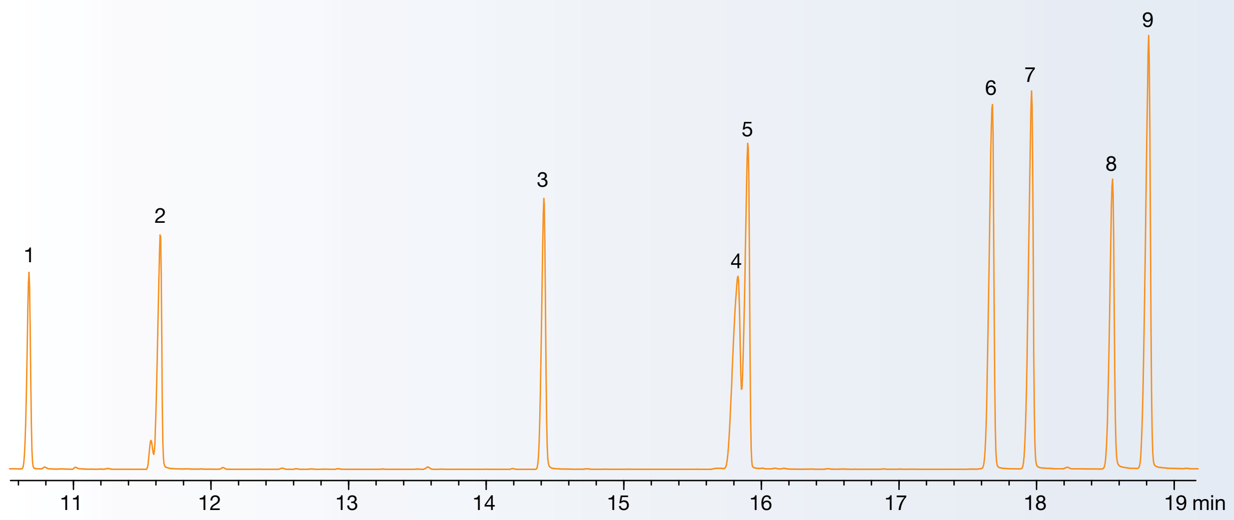
ZB-5ms
30 meter x 0.25 mm x 0.25 µm



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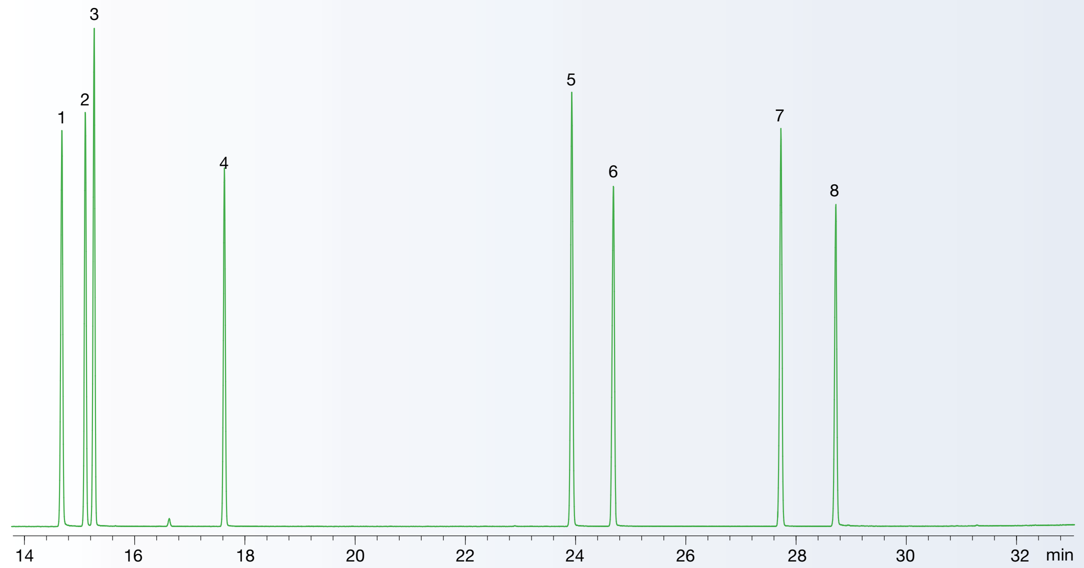
Samples:
1. EPTC
2. Mevinphos
3. Ethoprop
4. Atrazine
5. Propazine
6. Prometryn
7. Terbutryn
8. Triadimefon
9. Diphenamid

Figure 4: Nitrogen & Phosphorous Pesticides (NPM-106)

ZB-MR-1
30 meter x 0.25 mm x 0.25 µm



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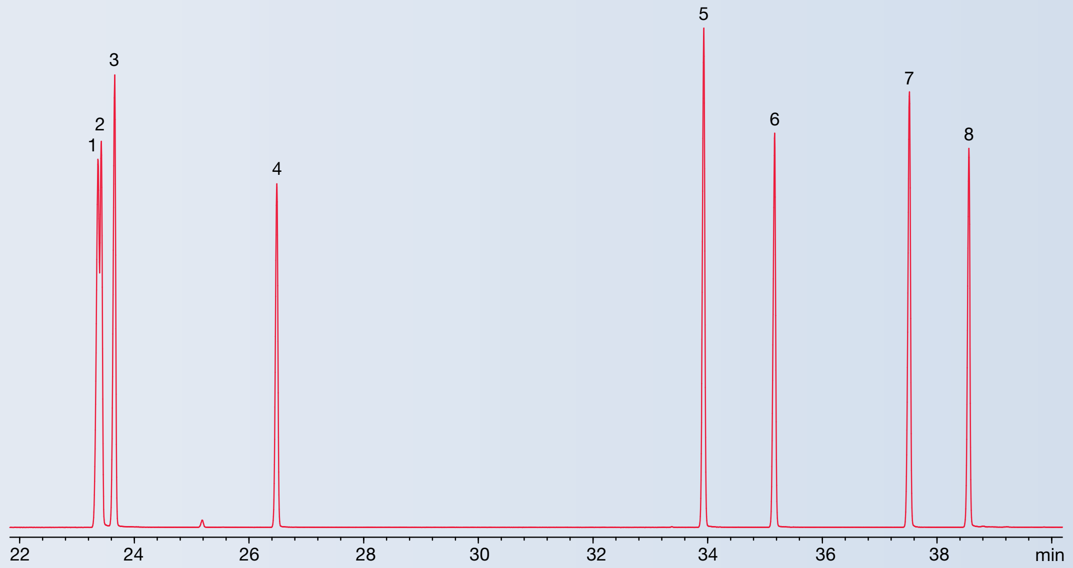
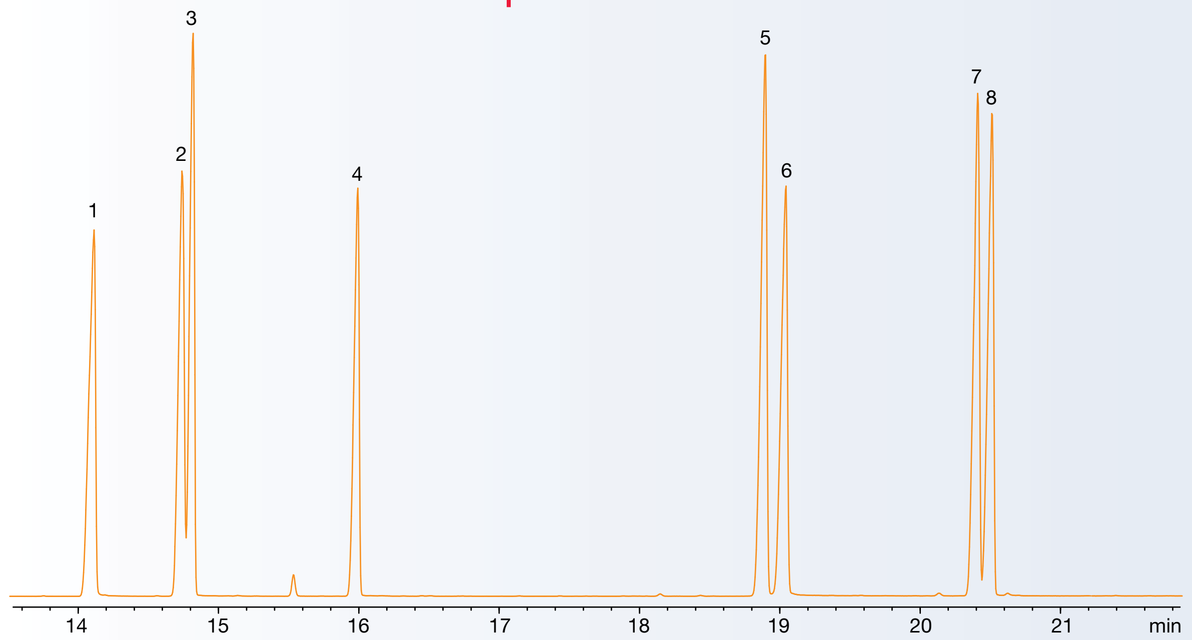
ZB-MR-2
30 meter x 0.25 mm x 0.20 µm



App ID 16383

ZB-5ms
30 meter x 0.25 mm x 0.25 µm



App ID 16369

Samples:
1. Propachlor
2. Trifluralin
3. Benefin (Benfluralin)
4. Profluralin
5. Isopropalin
6. Pendimethalin
7. Oxadiazon
8. Oxyfluorfen

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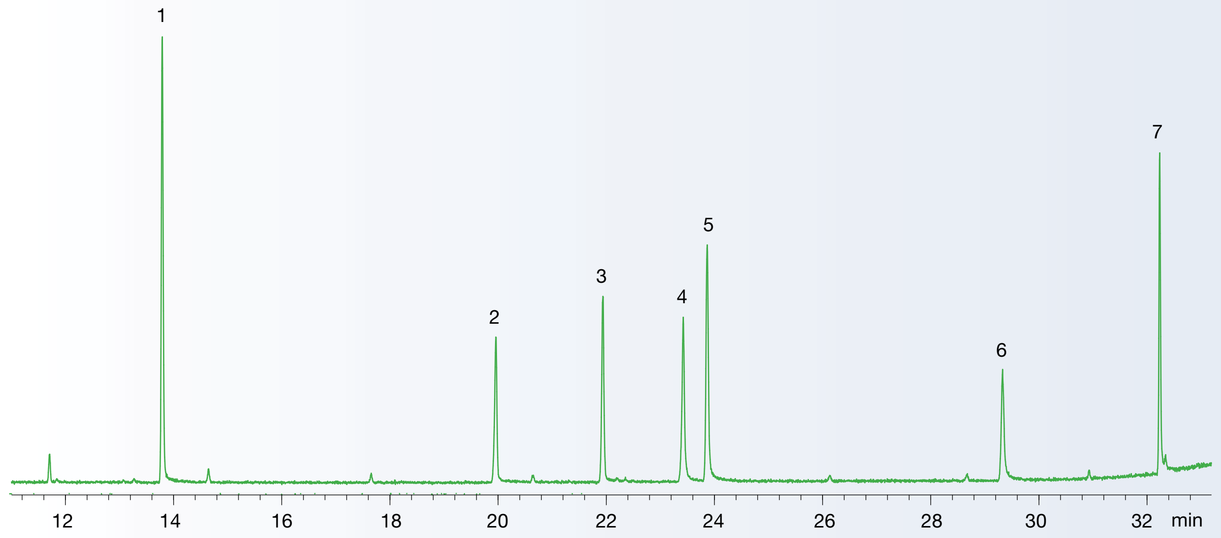
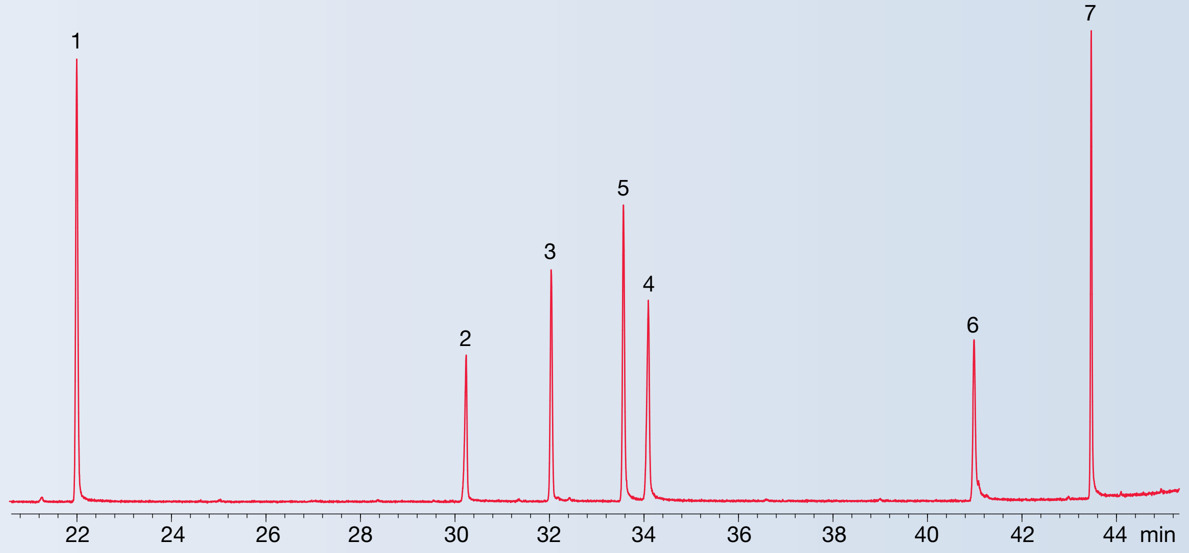
Figure 5: Nitrogen Pesticides (NPM-633)

ZB-MR-1
30 meter x 0.25 mm x 0.25 µm



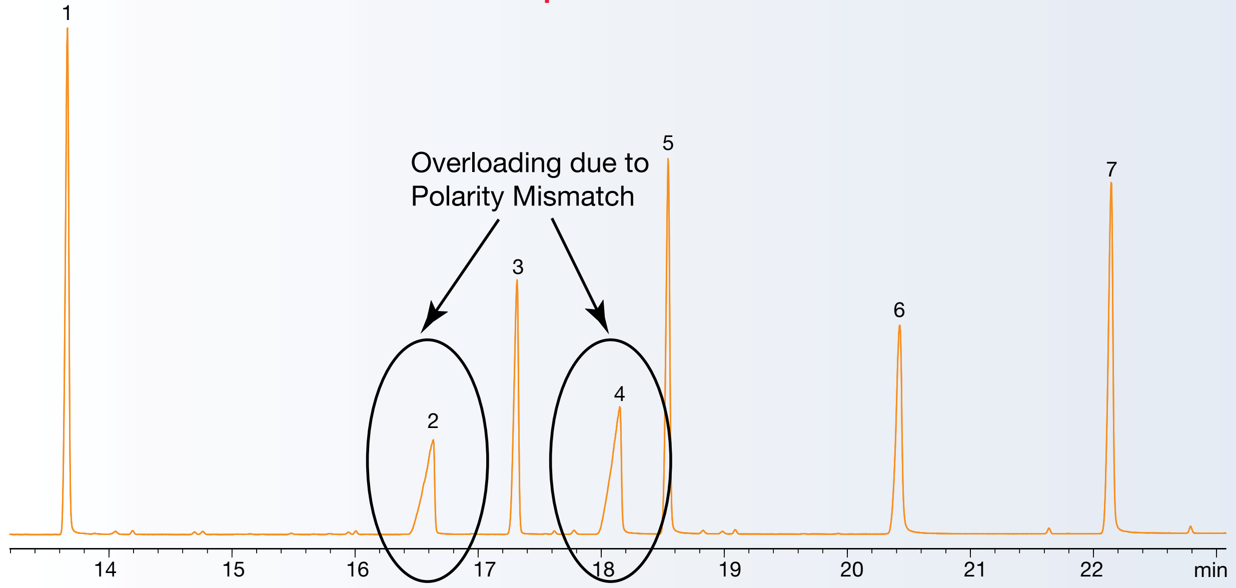
App ID 16380

ZB-MR-2
30 meter x 0.25 mm x 0.20 µm



App ID 16384

ZB-5ms
30 meter x 0.25 mm x 0.25 µm



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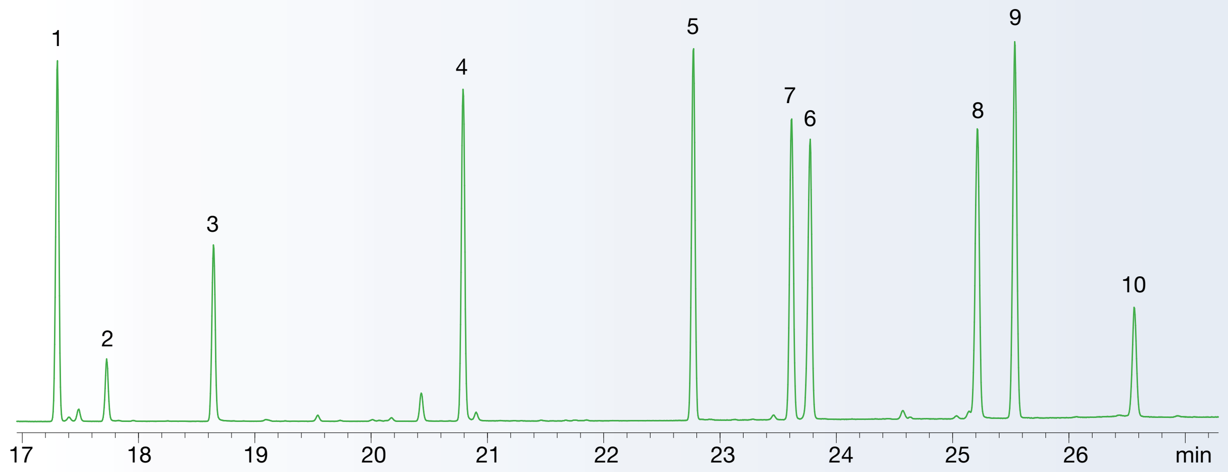
Samples:
1. Deet
2. Terbacil
3. Metribuzin
4. Bromacil
5. Triadimefon (amiral)
6. Tricyclazole
7. Hexazinone

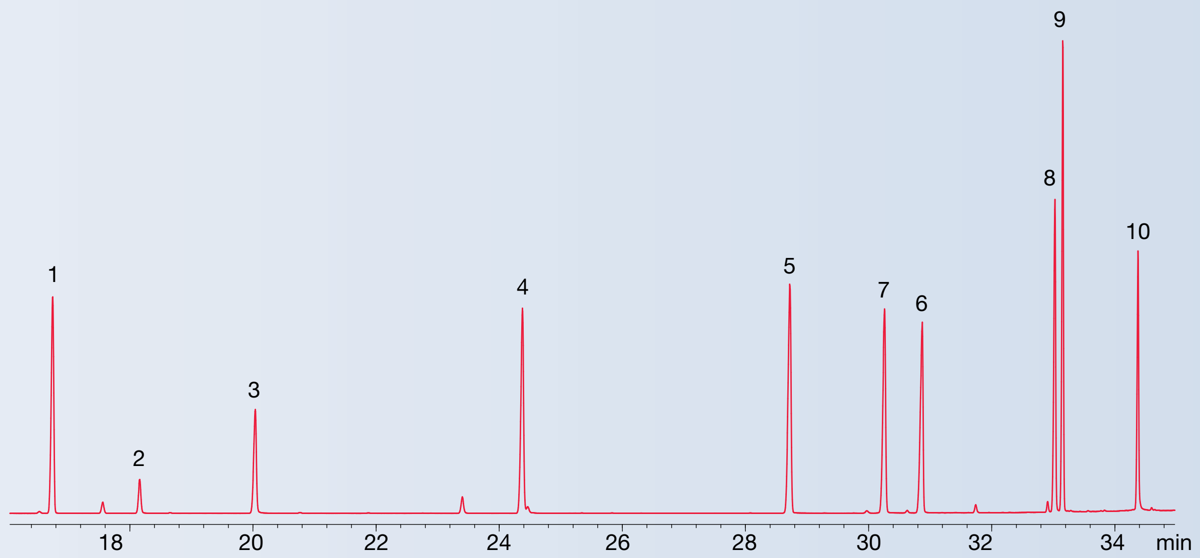
Figure 6: Organophosphorous Pesticides (SPM-844)

ZB-MR-1
30 meter x 0.25 mm x 0.25 µm



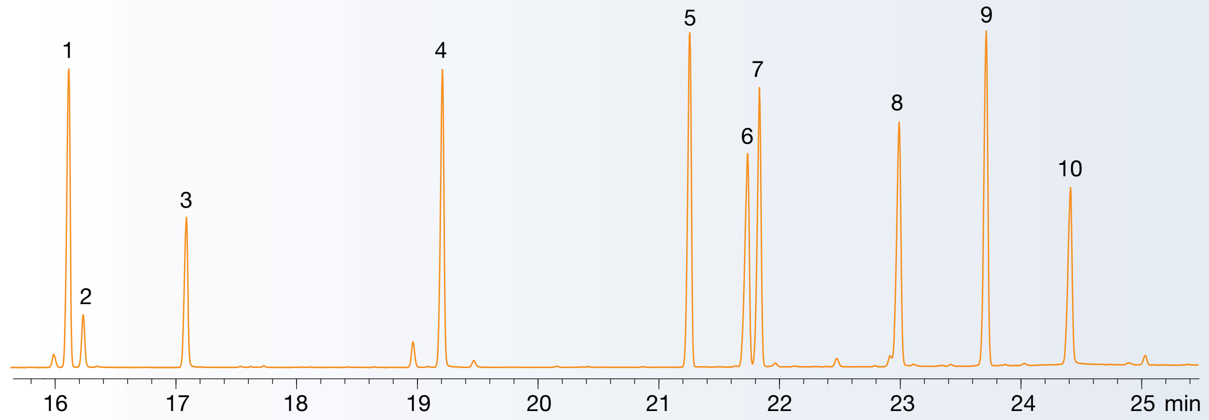
App ID 16378

ZB-MR-2
30 meter x 0.25 mm x 0.20 µm



App ID 16387

ZB-5ms
30 meter x 0.25 mm x 0.25 µm

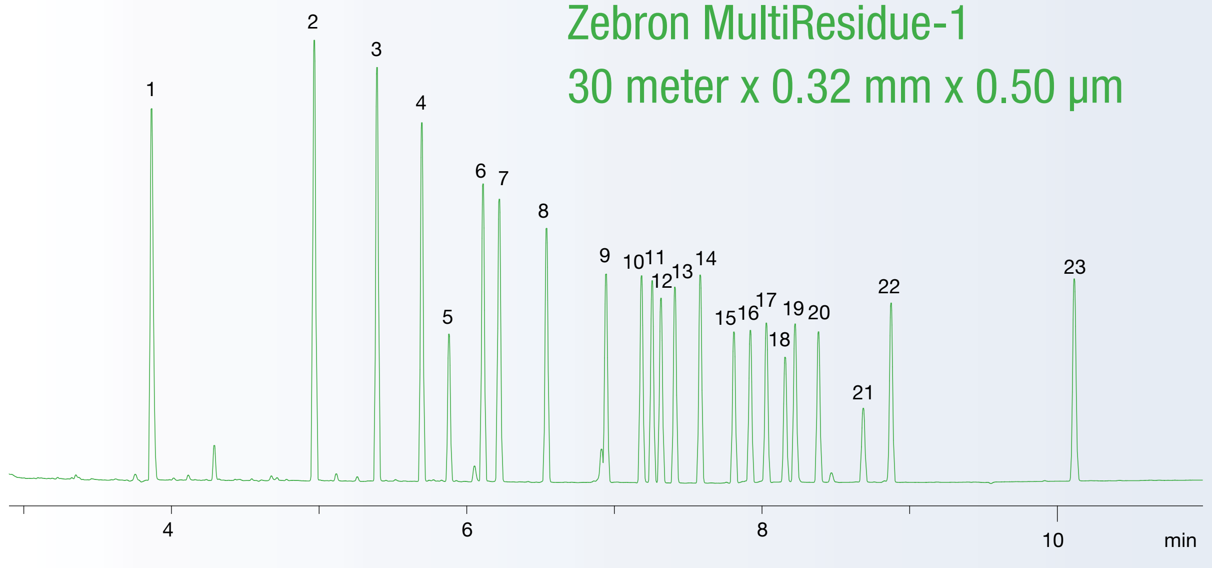


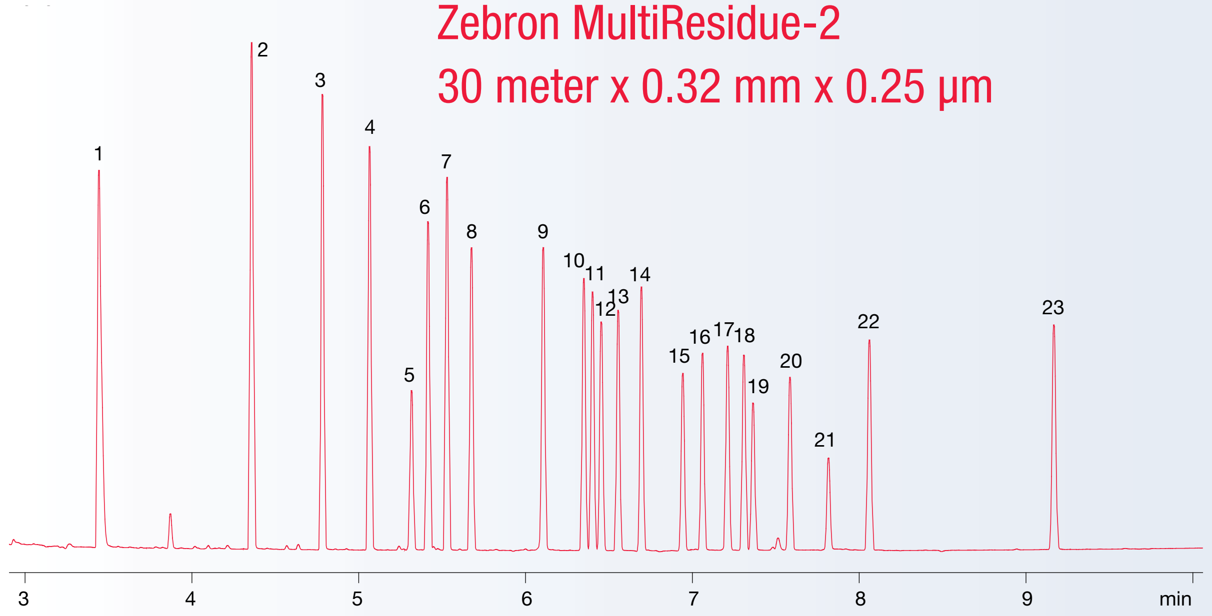
App ID 16373

Samples:

1. Terbufos (Terbuphos)
2. Phosphamidon (isomer)
3. Phosphamidon
4. Chlorfenvinphos
5. Ethion
6. Famophos (famphur)
7. Carbophenothion
8. Phosmet
9. Leptophos
10. Azinphos-ethyl

Figure 7: Dual Column Organochlorine Pesticide Testing Under EPA Method 8081A





Conditions (are the same for both columns)

Injection: Splitless at 250 °C, 1 µL

Carrier Gas: Helium @ 3.4 mL/min (Constant Flow)

Oven Program: 100 °C for 0.5 min to 220 °C at 35 °C /min to 340 °C at 20 °C/min for 2 min

Detection: Electron Capture (ECD) @ 350 °C

Samples:

1. 2,4,5,6 Tetrachloro-m-xylene (TCMX)
2. 1-Bromo-2-nitrobenzene
3. α-BHC
4. γ-BHC (Lindane)
5. β-BHC
6. δ-BHC
7. Heptachlor
8. Aldrin
9. Heptachlor epoxide
10. γ-Chlordane
11. α-Chlordane
12. Endosulfan I
13. 4,4'-DDE
14. Dieldrin
15. Endrin
16. 4,4'-DDD
17. Endosulfan II
18. Endrin aldehydes
19. 4,4'-DDT
20. Endosulfan sulfate
21. Methoxychlor
22. Endrin ketone
23. Decachlorobiphenyl (DCB, surr)

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Results & Discussion

Analysis of 114 different pesticides was done using both Zebron MultiResidue-1 and MultiResidue-2 columns (**Figures 1 & 2**). The Zebron MultiResidue-2 columns showed additional peaks for certain pesticides compared to the Zebron MultiResidue-1 columns, however both columns provide increased resolution compared to a standard 5ms type phase.

Resolution of specific compounds was compared with the Zebron ZB-5ms phase to demonstrate the increased separation power offered by these new columns. In **Figure 3**, the elution order for atrazine and propazine is reversed on both the MultiResidue-1 and the MultiResidue-2 columns compared to the ZB-5ms. The MultiResidue-2 demonstrates much longer retention for these two compounds and is able to provide baseline resolution. In **Figure 4**, the MultiResidue-1 provides increased resolution of trifluralin and benefin as well as several of the later eluting compounds. The polarity of the MultiResidue-2 caused the trifluralin to partially co-elute with propachlor, however resolution is substantially increased for the last four compounds.

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Results & Discussion *(cont'd)*

Asymmetrical peak shape such as fronting is commonly observed for polar pesticides on non-polar phases because the pesticides are not soluble in the phase. This can lead to poor sensitivity and/or co-elutions with other closely eluting pesticides. **Figure 5** shows overloading of terbacil and bromacil on the ZB-5ms phase due to the non-polar character of the phase. The phase chemistry of the MultiResidue-1 and MultiResidue-2 was specially designed to match the polarity of pesticide compounds and provide better overall peak shape.

Many pesticides contain a mixture of isomers. Resolving the isomers can provide additional confirmation for samples with interferences in the chromatographic region of the target analyte. In **Figure 6**, phosphamidon shows an isomer eluting just after terbufos on the ZB-5ms. If high levels of terbufos were present, it is unlikely resolution between the two compounds would be maintained. The MultiResidue-1 and the MultiResidue-2 columns significantly increase resolution of the phosphamidon isomer ensuring accurate identification.

Results & Discussion *(cont'd)*

The US EPA regulates the testing of 20 specific chlorinated pesticides under the official Method 8081A. The method specifies an Electron Capture Detector (ECD), which is extremely sensitive for chlorinated compounds, however, it does not provide any confirmatory information about the peak. To reduce the occurrence of misidentifications, the method requires the use of two GC columns of dissimilar selectivity in a parallel configuration. The EPA considers an analyte's presence confirmed if it has a peak at the pre-determined retention time on both columns.

The orthogonal selectivity provided by the Zebron MultiResidue-1 and the MultiResidue-2 allows for baseline resolution of all 20 chlorinated pesticides, surrogates, and internal standard in 10 minutes (**Figure 7**). Two elution order changes are observed between the phases, demonstrating that the phases are different enough to provide accurate confirmation.

Conclusion

As world trade increases, the potential threat to other countries' populations due to contaminated food products increases. Recent deaths caused by food exported from countries like China, emphasize the need for comprehensive testing procedures. The Zebron MultiResidue-1 and the MultiResidue-2 present a comprehensive solution for Multi-Pesticide residue testing by GC/MS and other hyphenated techniques. The columns provide additional confirmation, potential separation from matrix interferences, greater resolution of isomer peaks, and improved chromatography of more polar analytes.

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