The Evaluation of Multi-Pesticide Screening Methods by GC/MS

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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 has been evaluated for over 250 different pesticides commonly analyzed from fruits and vegetables (not all data presented here). 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.

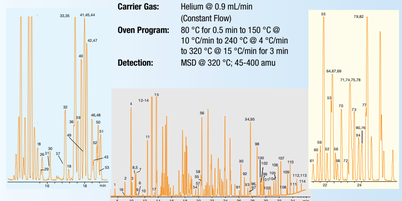
Introduction

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 analyte specific detectors such as ECD or NPD may be used for screening, Mass Spectrometer (MS) detection must be employed to provide positive confirmation. Zebron MultiResidue™ (MR) 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

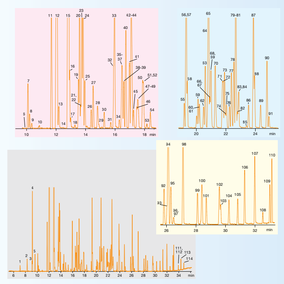


Conditions

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 @ 10 °C/min to 240 °C @ 4 °C/min to 320 °C @ 15 °C/min for 3 min
Detection:	MSD @ 320 °C; 45-400 amu

App ID 16184

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

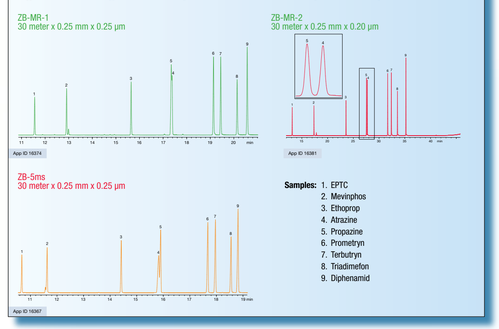


Conditions

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 @ 10 °C/min to 240 °C @ 4 °C/min to 320 °C @ 15 °C/min for 3 min
Detection:	MSD @ 320 °C; 45-400 amu

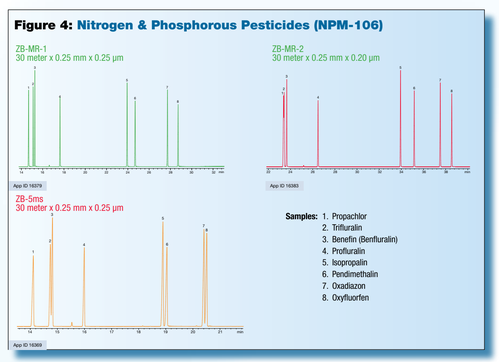
App ID 16183

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



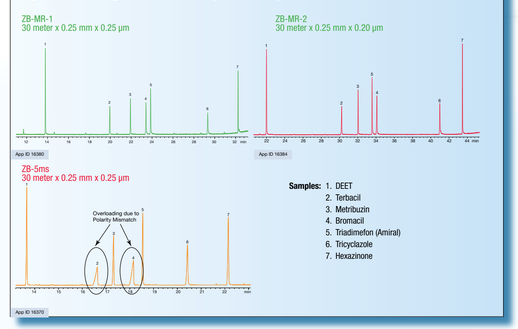
App ID 16374 App ID 16381 App ID 16367

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



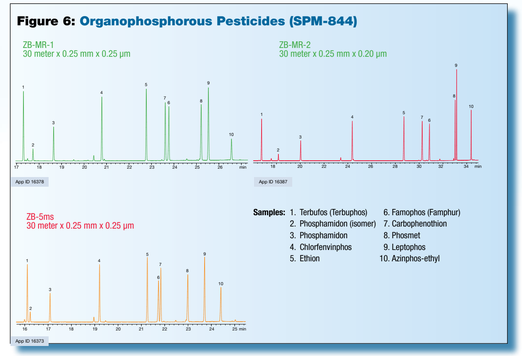
App ID 16378 App ID 16383 App ID 16369

Figure 5: Nitrogen Pesticides (NPM-633)



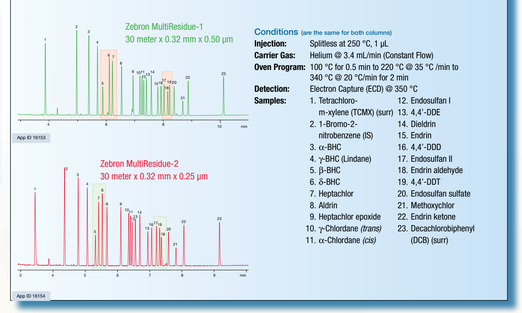
App ID 16380 App ID 16384 App ID 16376

Figure 6: Organophosphorous Pesticides (SPM-844)



App ID 16378 App ID 16387 App ID 16373

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



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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 pyrisphosphate (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)
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		Prosamide
44		Atrazine
45		Simazine
46		Terbuthylazine
47		Dioxathion
48		Fonofos
49		Dimethoate
50		2,4,5-T Methyl ester
51		Disulfoton
52		Chlorambem (methyl ester)
53		Phosphamidon Isomer
54		Secbumeton
55		Dichlofenthion
56		2,4-DB (methyl ester)
57		Terbacil
58		Dinoseb (methyl ester)
59		Atachlor
60		Chlorpyrifos methyl
61		Phosphamidon
62		Ronnel
63		Prometryn
64		Ametryn
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 ester)
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
97		Fenamiphos
98		Oxyfluorfen
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

Results & Discussion

Analysis of 114 different pesticides was done using both Zebron MultiResidue-1 and MultiResidue-2 column (Figures 1 & 2). The Zebron MultiResidue-2 columns showed additional peaks for certain pesticides compared to the Zebron MultiResidue-1 column, 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 relative 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.

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.

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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