RESTEK Pure Chromatography

Highly Efficient LC-MS/MS Analysis of Organophosphorous Pesticides Utilizing ARC-18 Column Selectivity with Inert Column Technology

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Introduction

Pesticides are the natural or synthetic substances created to eliminate all types of pests. They are used ubiquitously to help increase crop yields; however, they can pose risks for public health and pollinators (honeybees) and are therefore strictly monitored.

However, monitoring this diverse, ever-growing group of chemicals is not always easy. Pesticides can often be modified by just a few atoms, leading to significant changes in their properties. To accurately quantify the resulting isomers and isobars, chromatographic separation is essential, which requires the careful selection of stationary phases, such as the Raptor ARC-18 demonstrated here.

Moreover, subgroups like e.g. organophosphorous pesticides are particularly difficult, as they tend to form nonspecific adsorption (NSA) or nonspecific binding (NSB) to metal surfaces inside analytical columns resulting in poor peak shape, low response and sensitivity.

In this work, Restek looks to establish the benefits of coated column technologies by comparing methods developed on Inert and standard hardware to increase sensitivity and peak shape on the one hand and decrease time and effort for matrix or chemical based passivation techniques on the other for a wide panel of organophosphorus pesticides.

Materials and Method

Table I: Method developed by Restek to analyze Pesticides with inert hardware for better peak shape and response.

Columns	Raptor (Inert) ARC-18		
Dimensions:	100 mm x 2.1 mm ID		
Particle Size:	2.7 µm		
Temp.:	50 °C		
Standard/Sample:	LC multiresidue pesticide standard #1 (cat. # 31972)		
Diluent:	Water, 0.1% Formic Acid		
Conc.:	1 ng/ mL		
Inj. Vol.:	5 µL		
Detector:	MS/MS		
Ion Mode:	ESI$^+$		
	MRM		
Mobile Phase A:	Water, 2 mM NH_4CH_3COO 0.1% formic acid		
Mobile Phase B:	MeOH, 2 mM NH_4CH_3COO, 0.1% formic acid		
Time (min)	Flow (mL/min)	%A	%B
0.00	0.4	95	5
2.00	0.4	40	60
4.00	0.4	25	75
6.00	0.4	0	100
7.50	0.4	0	100
7.51	0.4	95	5
9.00	0.4	95	5

See the complete method including chromatogram here

Results and Discussion

In the data table below, we analyse the area and height ratio between the analytes on each of the two hardware types. Values greater than 1 describing a positive improvement in response, and less than 1 describing a loss of sensitivity.

Across the full panel of 15 organophsphorous pesticides analyzed, **almost all analytes** showed an **improvement** in sensitivity for both peak area and peak height. Of the panel, **Carbaryl** was the **sole** compound which showed a **slight reduction** in both metrics, while Mevinphos Isomer 2 showed comparable results. All other components showed ratios up to **2.0**, meaning that **signal intensity** is **doubled** using inert columns.

The compounds Methamidophos, Acephate, Omethoate, Monocrotophos, Vamidothion and Temephos are typically more problematic to analyse in matrix samples, with a **tendency for NSA/NSB** interactions leading to poor sample recoveries and sensitivity issues.

The use of inert hardware here resulted in an **average of 1.6-fold improvement** in peak **area**, and **1.7-fold** improvement for peak **height** across the six compounds, along with significant improvement on signal/noise ratio and a reduction of tailing. This demonstrates the improvement in NSA/NSB interactions when switching to Inert columns.

Table II: Analysis of 15 organophosphorous pesticides with stainless steel (SS) and Inert Raptor ARC-18 column. Comparison of area and height ratios. Values > 1 = better sensitivity, Values < 1 = worse selectivity *(only Carbaryl, marked in orange)*.

Compound	Peak Area			Peak Height		
	Stainless Steel	Inert	Areas Ratio (Inert/SS)	Stainless Steel	Inert	Height Ratio (Inert/SS)
Methamidophos	254969	428941	**1.68**	52553	105189	**2.00**
Acephate	168776	300642	**1.78**	58418	104729	**1.79**
Omethoate	579502	892008	**1.54**	216157	337690	**1.56**
Monocrotophos	140095	215810	**1.54**	51402	78425	**1.53**
Dicrotophos	340978	404916	**1.19**	135380	159292	**1.18**
Dimethoate	461156	807805	**1.75**	188746	342939	**1.82**
Trichlorfon	84233	173942	**2.07**	34793	63266	**1.82**
Vamidothion	913264	1333829	**1.46**	354311	547308	**1.54**
Mevinphos Isomer 1	213632	311274	**1.46**	82105	129961	**1.58**
Mevinphos Isomer 2	56093	74030	**1.32**	29070	29802	**1.03**
Carbaryl	43590	39671	**0.91**	14563	11924	**0.82**
Isocarbophos	21587	33294	**1.54**	9062	11941	**1.32**
Dimethomorph Isomer 1	462425	511766	**1.11**	166990	172977	**1.04**
Dimethodmorph Isomer 2	896109	877031	**0.98**	311657	328826	**1.06**
Temephos	98793	164310	**1.66**	35383	64751	**1.83**

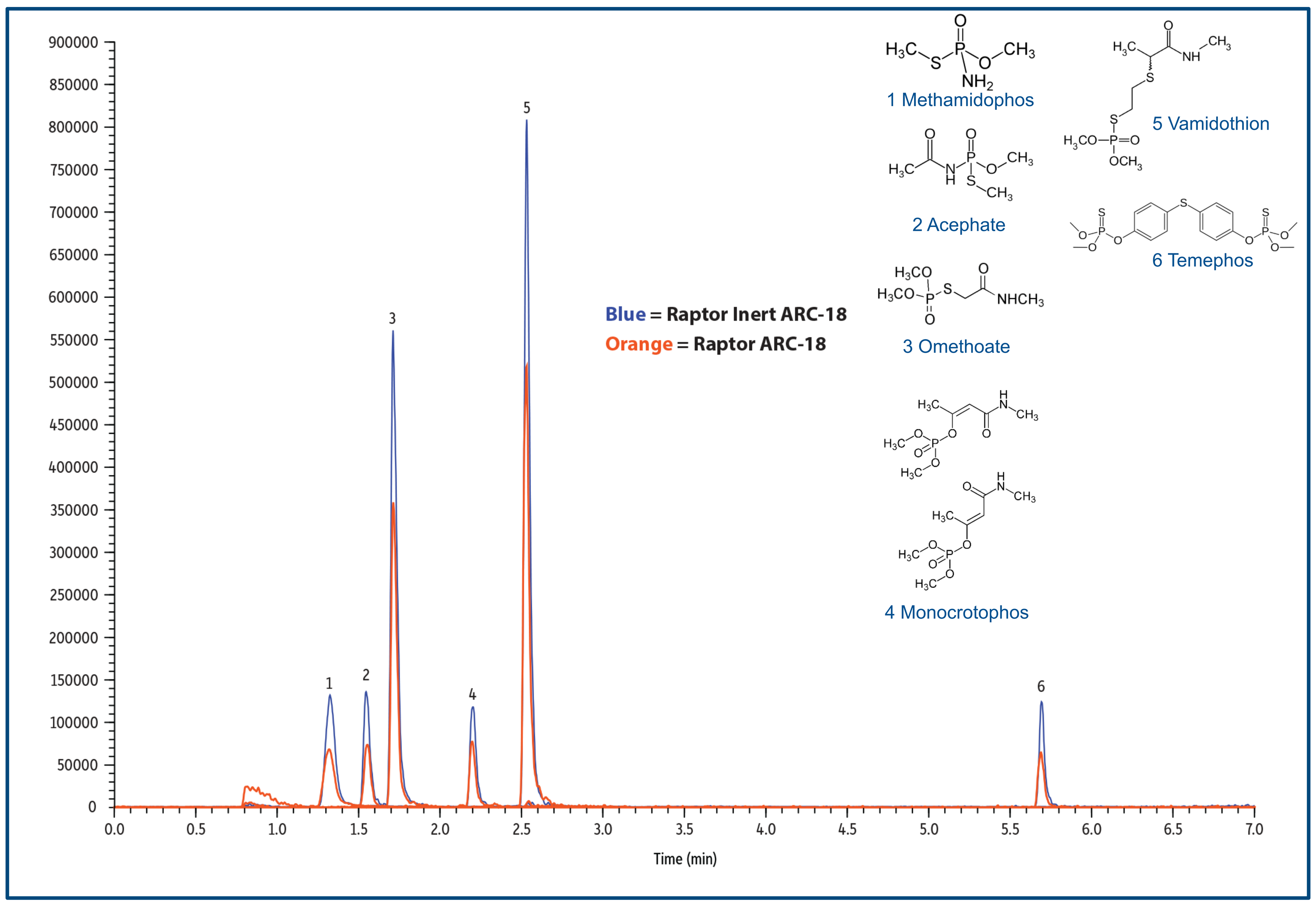

Figure 1: Comparison of different organophosphorous pesticides analyzed on Raptor Inert ARC-18 and traditional stainless steel Raptor ARC-18. Right: Chemical Structures of pesticides

Conclusion

Choosing the Raptor ARC-18 stationary phase resulted in a balanced retention profile over the whole gradient. Isobars like the Mevinphos or Dimetomorph isomers could be separated with high target resolution.

In combination with the inert column hardware technology enabled low detection limits, improved peak shapes and high response rates. Laborious conditioning and complicated passivation are not necessary with these coated inert columns, saving time and enables to measure more samples/time.

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