Application Note

Analysis of Pesticides using Supercritical Fluid Chromatography with Mass Spectrometry (SFC-MS)

Introduction

Pesticide analysis is required for consumer safety for food consumption. In 1996 the US FDA implemented regular monitoring of domestic and imported foods. There are 1000 registered pesticides by the US and 1100 by the European Union. The upper allowable limit is 10ppb or less. Japan has 16 pesticides that have zero tolerance. With the above requirements, extremely sensitive pesticide analysis is required.

Jasco PU-2080 Plus pump

HPLC with fluorescence detection is a common system used to analyze certain pesticides. Fluorescence is a very sensitive detector, but of course it does not aid in the identification that MS can offer. The speed of SFC combined with the sensitivity and identification of Mass Spectrometry was explored for pesticides.

Keywords: SFC, Pesticides, achiral, C18 column, MS Detector

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Experimental

Equipment

CO_2 Delivery Pump:	PU-2080-CO2
Modifier Pump:	DG-2080
Mixer:	MX-2080-32
Autosampler:	AS-2057
Column Oven:	CO-2060
PDA Detector:	MD-2018
Mass Spec:	Agilent G6130
Back Pressure Regulator:	BP-2080

Conditions

Column:	Luna C18(4.6mmIDx150mmL,5 µm)
CO_2 Flowrate:	5.0mL/min
Modifier:	20mM Ammonium acetatein Methanol
Modifier Gradient:	0min95% CO_2 : 5% MeOH 4 min 65% CO_2 : 35% MeOH 4.1min 50% CO_2 : 50% MeOH 7 min 50% CO_2 : 50% MeOH 7.1 min 95% CO_2 : 5% MeOH
Column Temperature:	40 °C
Back Pressure:	100
Wavelength:	220 nm

APCI Source

Drying Gas Flow:	12 L/min
Nebulizer Press:	35psi
Drying Gas Temp:	250°C
Vaporizer Temp:	250°C
Capillary Voltage:	3000V
Corona Current:	4.0uA

Selected Ion Monitor (SIM)

Fragmentor:	70.0
Gain:	1.0
Threshold:	150
Step size:	0.1

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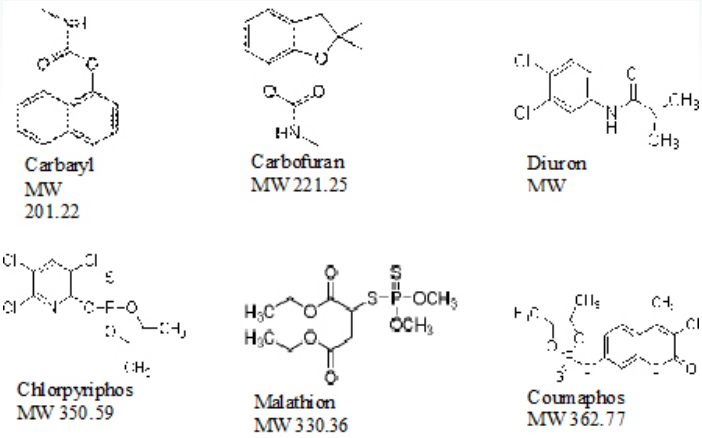

Figure 1. Structures of the 6 pesticides used for initial UV detector testing.

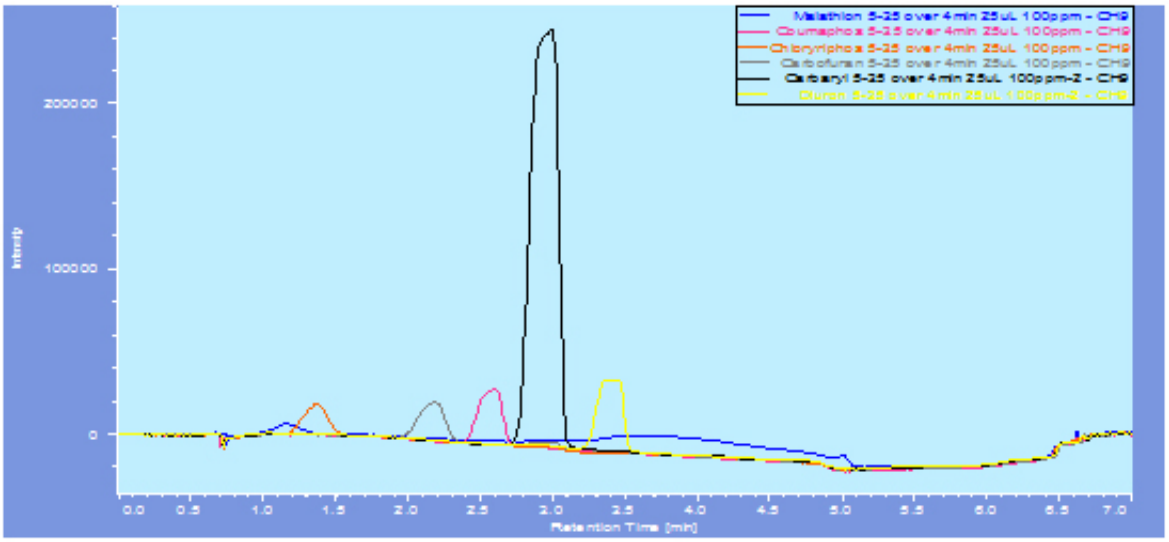

Figure 2. Overlay of SFC-UV chromatograms of 6 Pesticides.
1. Malathion, 2. Chloryriphos, 3. Carbofuran, Coumaphos, 5. Carbaryl, 6. Duron.

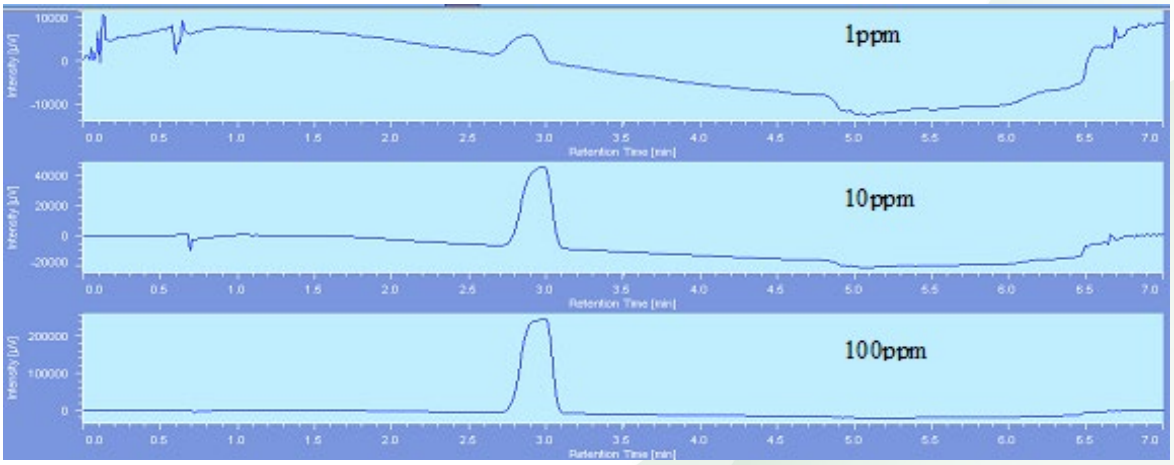

Figure 3. Stacked SFC-UV chromatograms of Carbaryl.

The structures of the 6 pesticides is shown in figure 1 and those 6 were each run and an overlay of their chromatograms is shown in figure 2. Carbaryl is shown at various concentrations in figure 3. Five out of the six pesticides were detected at 1ppm with UV alone. The MS was next used to increase the sensitivity.

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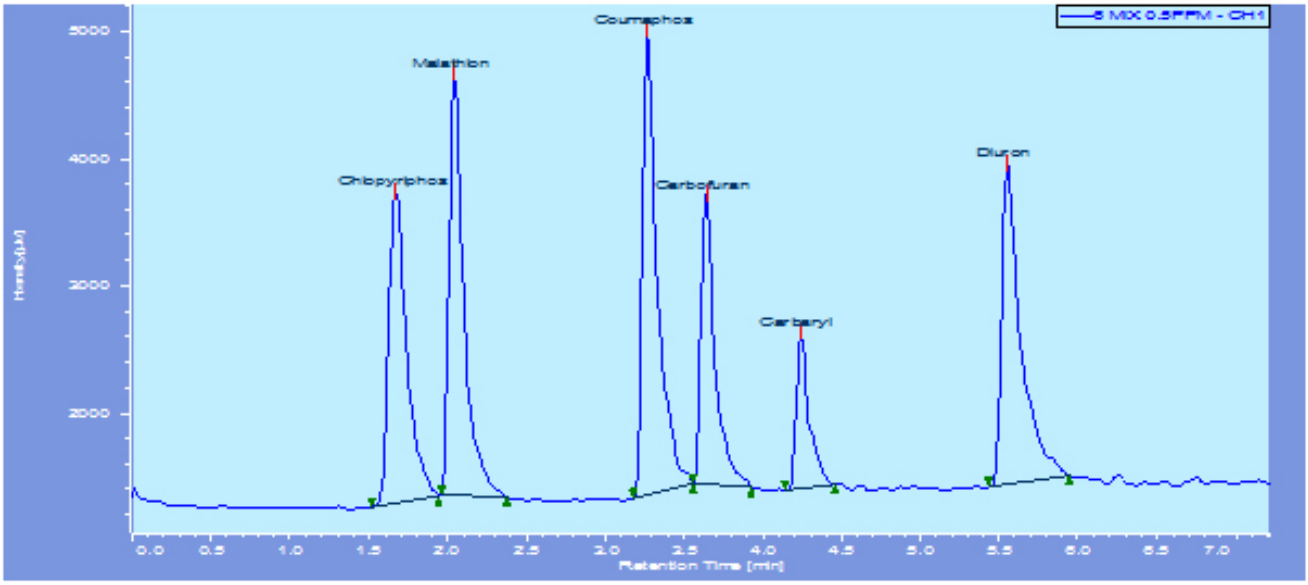

Figure 4. SFC-MS SIM chromatogram of 6 pesticide mix (0.5ppm each). Column SFC pak Sil-5 (4.6 x 250mm, 5um)

The SFC-MS chromatogram of the 6 pesticides at 0.5ppm and the corresponding spectra are shown in figure 4 and 5, respectively. The sensitivity was test at various concentrations 0.5pmm to 2ppb (Figure 6). A mixture of 32 pesticides (each 0.5ppm) was injected and 26 of them were detected and identified using the same conditions on the silica column. The identities and the retention times of each are shown in table 1.

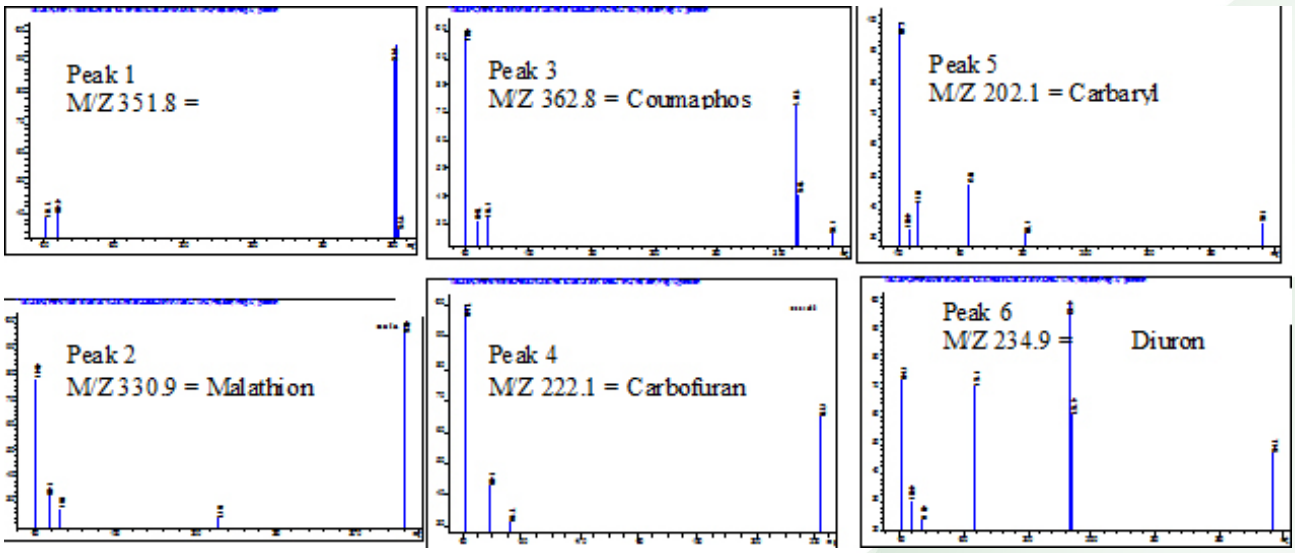

Figure 5. MS Peak Spectra Confirming Pesticide Identity.

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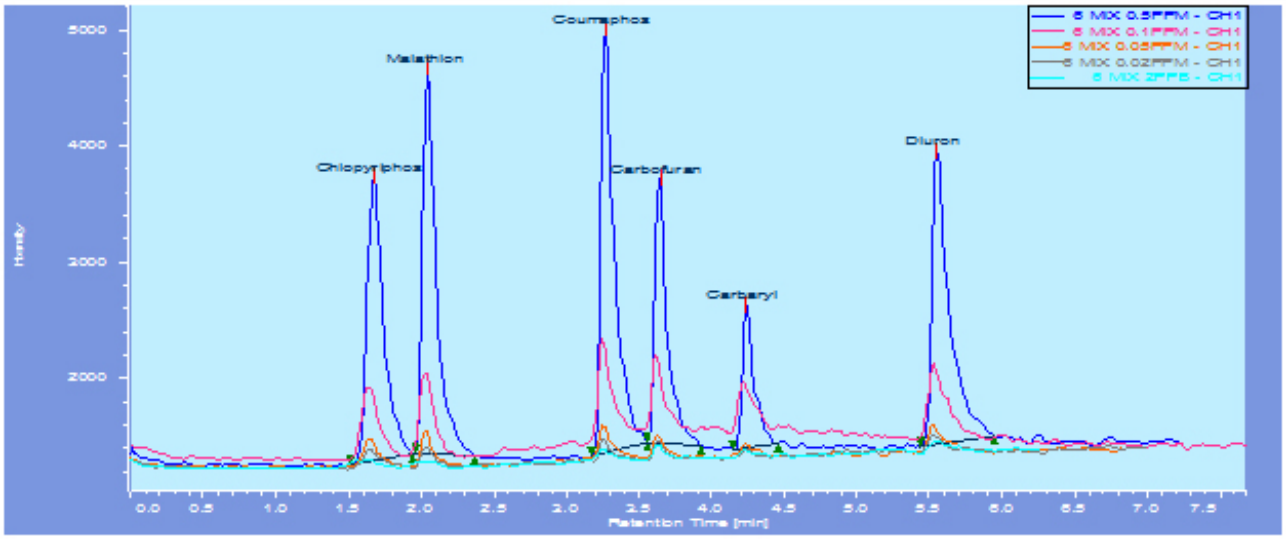

Figure 6. Stacked SFC-MS SIM chromatograms of 6 pesticide mix. Conditions were the same as shown in previous slides.

S/N of 2 or greater for all 6 pesticides at 2ppb.

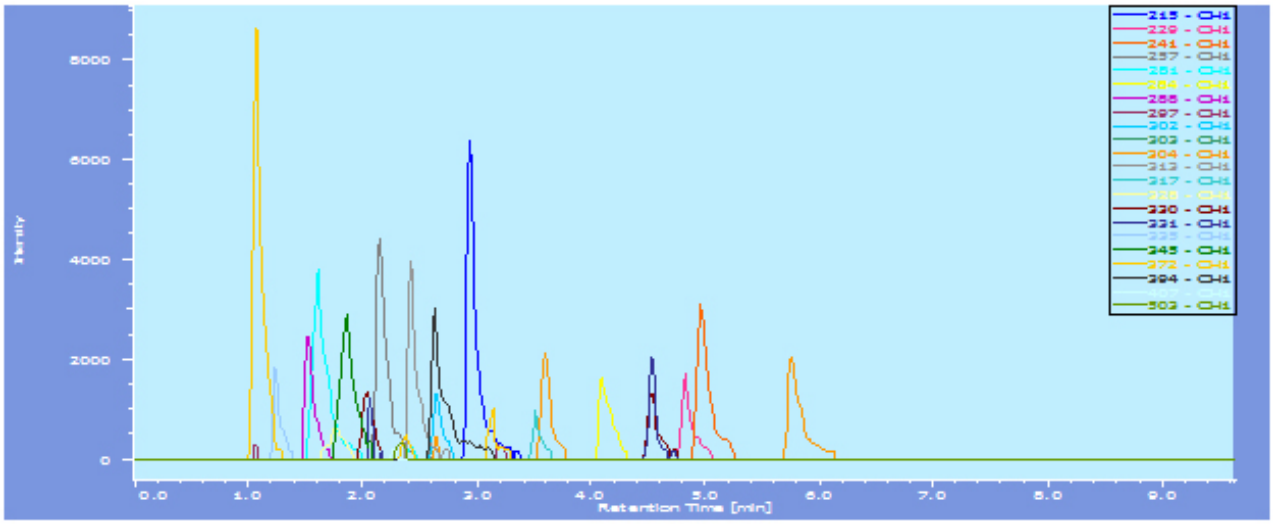

Figure 7. Overlay of XIC of 26 pesticides using SFC-MS.26 of 32 pesticides were detected using SFC-MS.

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Table 1. List of pesticides from figure 7 and their retention times.

Pesticide	Molecular Weight	Retention Time
Azinphosmethyl	317.3	3.6
Atrazine	215.7	3.03
Oxadiazon	345.2	1.9
Omethoate	213.2	5.8
Kresoxim-methyl	313.4	2.5
Chlorfenapyr	407.6	2.35
Diflufencian	394.3	2.7
Dimethoate	229.3	4.9
Spiroxamine	297.5	3.3
Thiobencarb	257.8	2.2
Tefluthrin	418.7	1.9
Terbutryn	241.4	5.04
Terbufos	288.4	1.6

Pesticide	Molecular Weight	Retention Time
Trifluralin	335.3	3.6
Norfluazon	303.7	3.03
Pyrethrins	328.4, 372.5	1.9, 1.1
Fenamiphos	303.4	5.9
Fenarimol	331.2	4.6
Fenpropimorph	303.5	5.8
Fluvalinate	502.9	2.4
Procymidone	284.1	4.2
Trans-permethrin	391.3	2.6
Pendimethalin	281.3	1.67
Malathion	330.4	2.1
Methidathion	302.3	2.7

Conclusion

The SFC-UV detected 5 out of 6 pesticides at 1ppm. All 6 pesticides produced a S/N of greater than 2 at 2ppb on a single quad MS in just over 5 minutes using SFC-MS. The SFC-MS identified26 out of 32 pesticides in 6 minutes.

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