

# Application Data Sheet

## No. 39

### LC-MS

Liquid Chromatograph Mass Spectrometer

## Quantitative Analysis of Pyrethroids in Soil Using Triple Quadrupole LC-MS/MS

Pyrethroids are insecticides used worldwide for both household and farming applications. Pyrethroids have limited water solubility and are easily adsorbed in soil. Recently, it has been reported that pyrethroids remain in the soil and sediment in farming and urban regions for long periods. Although pyrethroids are not particularly harmful for humans, they are very toxic for insects and water creatures and their influence on the ecosystem is a big concern. There is a demand for new methodology that enables measurement of pyrethroids in soil and sediment with high sensitivity and throughput.

Traditionally, pyrethroids are measured by Gas Chromatography with or without mass spectrometry. Here, we report a method using LC-MS/MS to show that LC-MS/MS can measure these compounds traditionally analyzed by GC. This report illustrates a simultaneous analysis of 15 pyrethroids using the Shimadzu UFMS Triple Quadrupole LCMS-8050 with ultrafast polarity switching. The polarity switching speed of the LCMS-8050 is just 5 milliseconds under any conditions.

Combined with the Nexera X2, the LCMS-8050 provides much faster run times without sacrificing the quality of results.

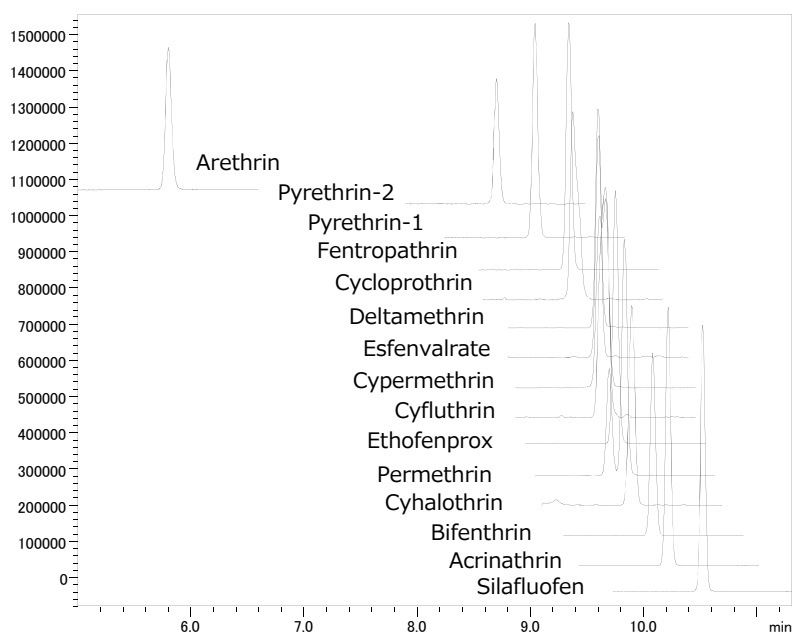


Figure 1: Representative MRM chromatograms of 15 pyrethroids

#### ■ Compounds List

Compounds	Polarity	Precursor (m/z)	Product (m/z)
Amethrin	+	228.00	186.10
Pyrethrin-1	+	329.20	161.10
Pyrethrin-2	+	373.20	161.20
Fenprothrin	+	367.20	125.20
Cycloprothrin	+	498.90	181.10
Deltamethrin	+	522.80	280.90
Esfenvalrate	+	437.10	167.30
Cypermethrin	+	433.10	191.10
Cyfluthrin	+	450.90	191.00
Ethofenprox	+	394.20	177.30
<i>trans</i> -Permethrin	+	408.10	183.30
<i>cis</i> -Permethrin	+	408.10	183.30
Cyhalothrin	+	467.10	225.10
Bifenthrin	+	440.00	181.20
Acrinathrin	-	540.10	372.20
Silafluofen	+	426.20	287.10

#### HPLC conditions (Nexera X2)

Column	: Phenomenex Kinetex 2.6u PFP 100A
Mobile phase A	: 5 mM Ammonium acetate water
Mobile phase B	: Methanol
Time program	: 40%B (0min) – 100%B(10-12min) – 70%B (12.01-15min)
Flow rate	: 0.2 mL / min.
Injection volume	: 1 µL
Oven temperature	: 40 °C

#### MS conditions (LCMS-8050)

Ionization	: ESI (Positive / Negative)
Probe voltage	: +4.5 kV / -3.5 kV
Nebulizing gas flow	: 3.0 L / min.
Drying gas flow	: 15.0 L / min.
Heating gas flow	: 15.0 L / min.
Interface temperature	: 100 °C
DL temperature	: 100 °C
Heat block temperature	: 400 °C

Table 1: Calibration range and linearity for 15 pyrethroids

Compounds	Range (µg/L)	r <sup>2</sup>
Amethrin	0.01 - 100	0.9992
Pyrethrin-1	0.5 - 500	0.9996
Pyrethrin-2	0.5 - 500	0.9997
Fenpropathrin	0.02 - 100	0.9993
Cycloprothrin	0.5 - 100	0.9991
Deltamethrin	0.05 - 100	0.9992
Esfenvalrate	0.5 - 100	0.9990
Cypermethrin	0.05 - 100	0.9986
Cyfluthrin	0.5 - 100	0.9976
Ethofenprox	0.01 - 100	0.9993
trans-Permethrin	0.02 - 100	0.9996
cis-Permethrin	0.02 - 100	0.9994
Cyhalothrin	0.1 - 100	0.9993
Bifenthrin	0.02 - 100	0.9995
Acrinathrin	0.1 - 100	0.9994
Silafluofen	0.01 - 100	0.9999

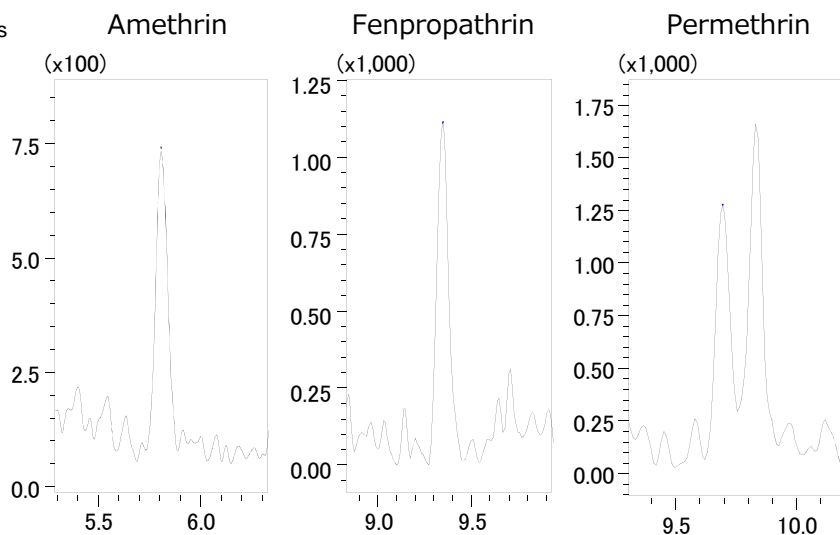


Figure 2: Chromatograms at the lowest calibration level

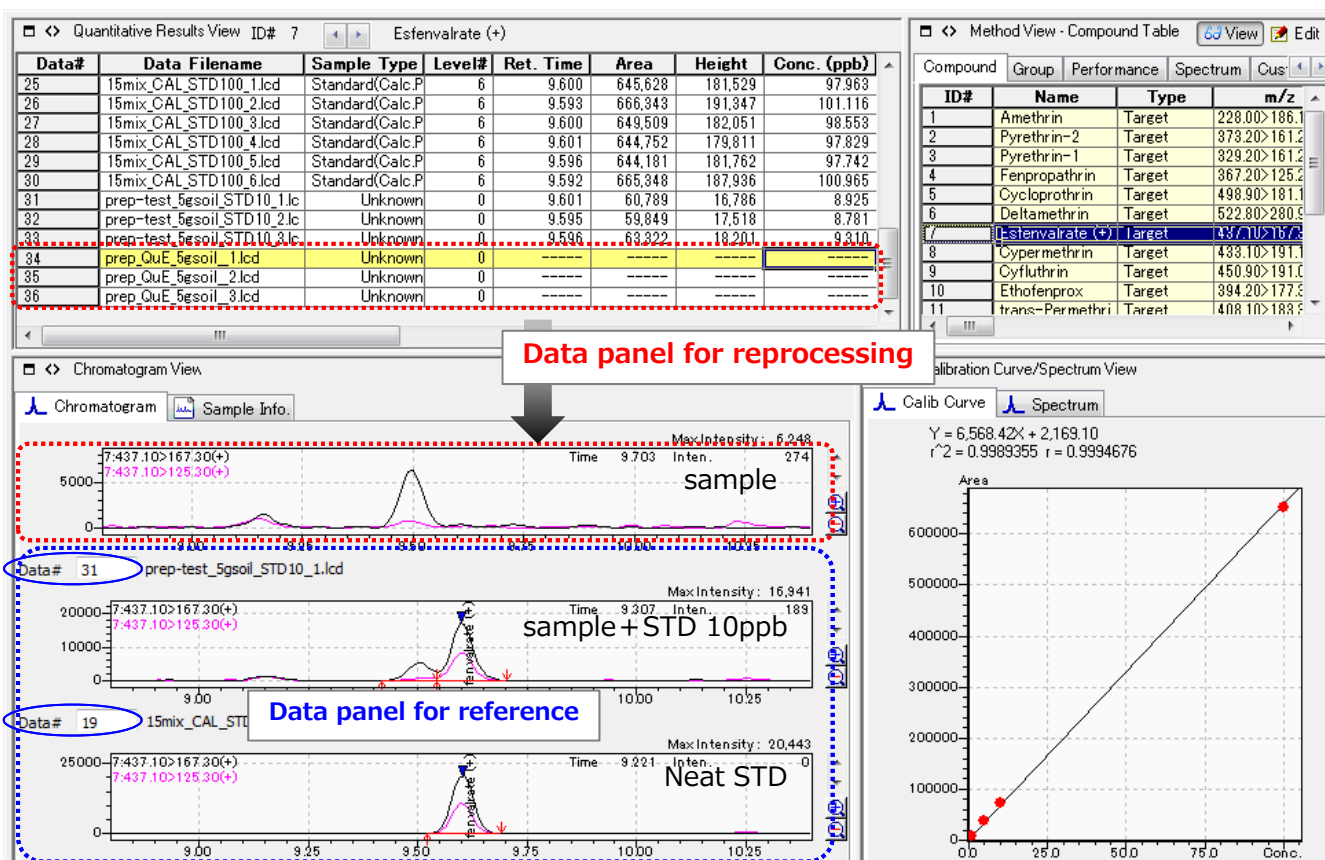


Figure 3: Quant Browser

The figure above is a screen shot of LabSolutions Quant Browser loaded with the data from a set of soil extracts, matrix matched calibration curve and neat standards. QuEChERS was used for sample clean-up for soil samples. Recoveries were excellent, ranging from 70 to 100%. In residual pesticide analysis, sample matrix is very complex. So, it is important to identify the analyte accurately and to carry out peak integration appropriately.

LabSolutions Quant Browser makes intuitive and “at-a-glance” data reprocessing possible with multiple data files. Figure 3 illustrates the quantitative results of Esfenvalerate. Esfenvalerate was not detected in real-world samples, but its possible isomer was detected at RT 9.5 minutes. Reviewing multiple results, such as sample, matrix matched standard and neat standard results, in a single panel saves data reprocessing time.

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