

Application News

No. C100

Liquid Chromatography Mass Spectrometry

Quantitative Analysis of Pyrethroids in Soil and Sediment Using the Shimadzu LCMS-8050 Triple Quadrupole Mass Spectrometer

Pyrethroid pesticides are used widely around the world as agricultural and household insecticides. Synthetic pyrethroids are slightly soluble in water and easily adsorbed in soil. In recent years, pyrethroid residues have been confirmed in soil and sediment in both agricultural and urban areas. Pyrethroids, while posing little danger to humans, exhibit a high toxicity to aquatic organisms and insects, making their impact on the ecosystem a matter of concern. Therefore, there is

a need for a sensitive technique which can rapidly measure pyrethroid pesticides in soil and sediment. Due to their low polarity, pyrethroid pesticides are typically measured by GC and GC-MS, however this Application News demonstrates simultaneous positive- and negative-ion mode analysis of 14 pyrethroid pesticides using LC-MS/MS with electrospray ionization (ESI).

MRM Analysis of Standards and Generation of Calibration Curves

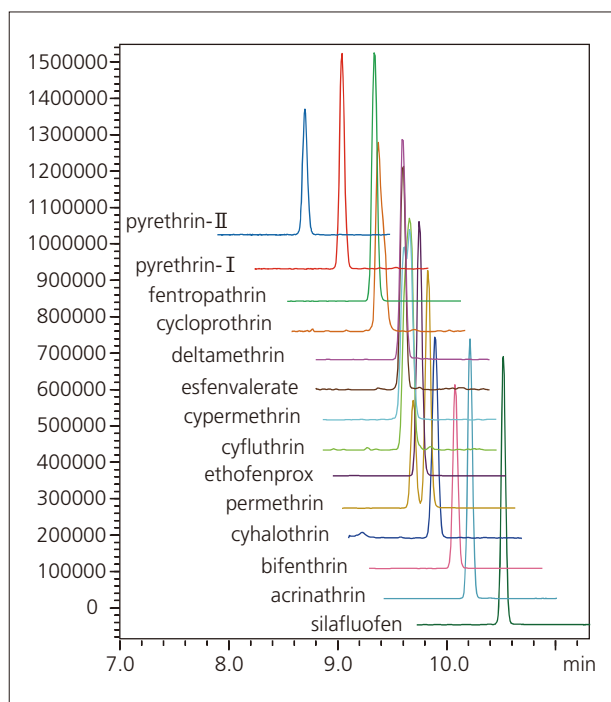


Fig. 1 MRM Chromatograms of Pyrethroids

Table 1 MRM Transitions and Calibration Curves of Pyrethroids

Compound Name	Polarity	Precursor (m/z)	Product (m/z)	Calibration Curve Range (µg/L)	r ²
Pyrethrin-I	+	329.20	161.10	0.5 - 500	0.9996
Pyrethrin-II	+	373.20	161.20	0.5 - 500	0.9997
Fenprothrin	+	367.20	125.20	0.02 - 100	0.9993
Cycloprothrin	+	498.90	181.10	0.5 - 100	0.9991
Deltamethrin	+	522.80	280.90	0.05 - 100	0.9992
Esfenvalerate	+	437.10	167.30	0.5 - 100	0.9990
Cypermethrin	+	433.10	191.10	0.05 - 100	0.9986
Cyfluthrin	+	450.90	191.00	0.5 - 100	0.9976
Ethofenprox	+	394.20	177.30	0.01 - 100	0.9993
trans-Permethrin	+	408.10	183.30	0.02 - 100	0.9996
cis-Permethrin	+	408.10	183.30	0.02 - 100	0.9994
Cyhalothrin	+	467.10	225.10	0.1 - 100	0.9993
Bifenthrin	+	440.00	181.20	0.02 - 100	0.9995
Acrinathrin	-	540.10	372.20	0.1 - 100	0.9994
Silafluofen	+	426.20	287.10	0.01 - 100	0.9999

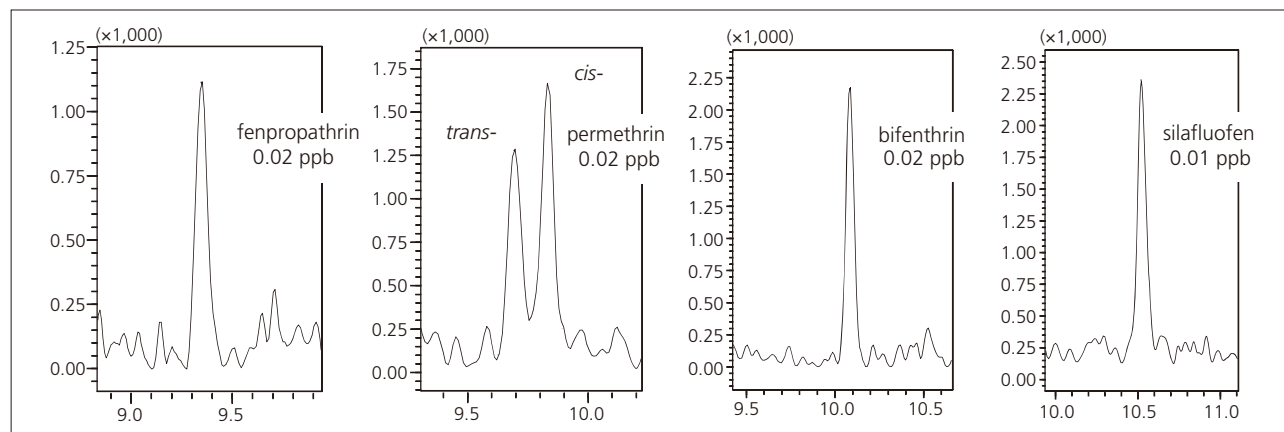


Fig. 2 MRM Chromatograms at Pyrethroid LOQs

Sample Preparation for Soil and Sediment Using QuEChERS Method

Soil samples are generally prepared using solid-phase extraction, however, this process can be both time-consuming and labor-intensive. In this application, the easy pretreatment method referred to as QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe), typically used for analysis of residual pesticides in food, was used for the pretreatment of soil and sediment samples. Fig. 3 shows the protocol employed to pretreat these soil and sediment samples. The combined acetonitrile extraction and cleanup process requires only 15 minutes per sample to complete.

Recoveries Using Actual Samples

A mixed pesticide standard solution was added to soil and sediment solutions respectively to obtain a concentration of 10 ppb before or after pretreatment was conducted by the QuEChERS method, and recovery tests were then conducted. Good recoveries of 70 to 120 % were obtained for both soil and sediment samples, as shown in Fig. 4.

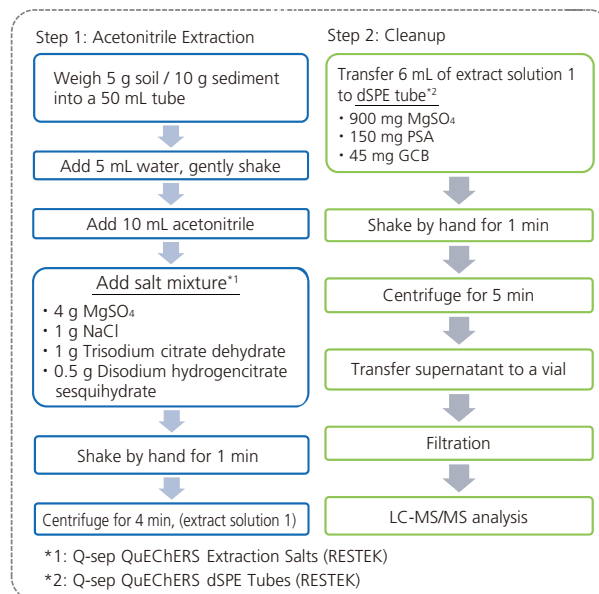


Fig. 3 Sample Preparation Using QuEChERS Method

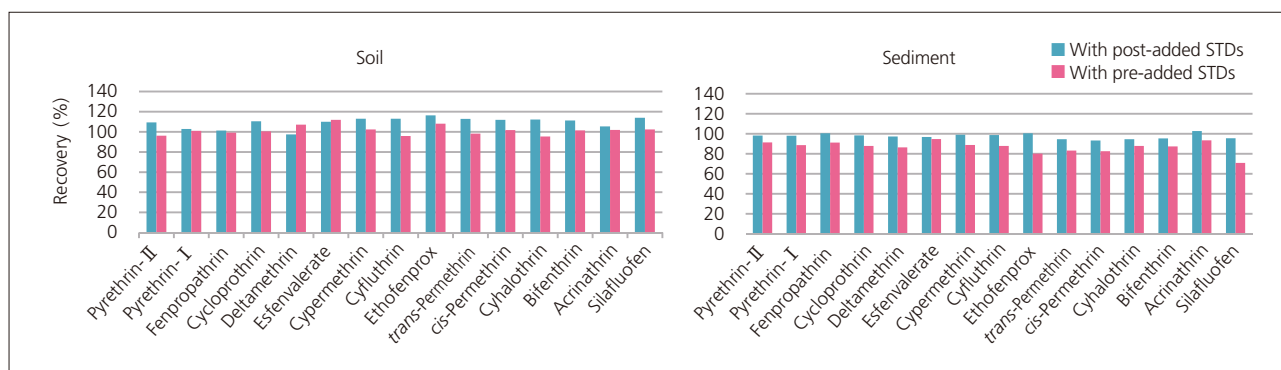


Fig. 4 Recoveries from Soil and Sediment

Table 2 Analytical Conditions

Column	: Phenomenex Kinetex 2.6 μm PFP 100Å (100 mm × 2.1 mm I.D.)
Mobile Phase A	: 5 mM Ammonium Acetate - Water
Mobile Phase B	: Methanol
Time Program	: 40 %B (0 min) → 100 %B (10 - 12 min) → 40 %B (12.01 - 15 min)
Flowrate	: 0.2 mL/min.
Injection Volume	: 1 μL
Oven Temperature	: 40 °C
Ionization Mode	: ESI (Positive / Negative)
Probe Voltage	: +4.0 kV / -3.0 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
Block Heater Temperature	: 400 °C