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Application News

No.L503

Supercritical Fluid Extraction / Chromatography

Application of Nexera UC SFE Pretreatment System for Extracting Pesticide Residues from Soil

Evaluating the persistence of pesticides in environmental soil is an important criteria for evaluating the safety of pesticides and analyzing pesticides in soil is extremely important for initial evaluations or registration of pesticides. However, in most cases, analyzing pesticides in soil using liquid-liquid extraction to extract the pesticides is very time-consuming, requires special equipment and reagents, and can cause problems, such as metal ions or other introduced ionic substances contaminating analytical instruments or the target substances being decomposed by oxidation, exothermic reactions, or other consequences of the extraction process.

In contrast, supercritical fluid extraction (SFE) provides excellent extraction efficiency using supercritical carbon dioxide as the extraction solvent, which offers the low viscosity and high diffusivity of a gas and the high solubility of a fluid. Consequently, it extracts target substances quickly using smaller quantities of organic solvent than existing solvent extraction methods, making it a more environmentally-friendly method as well.

This article describes an example of using the Nexera UC SFE pretreatment system to extract residual pesticides from soil.

Off-Line SFE System

The operating principle of the Nexera UC SFE pretreatment system is shown in Fig. 1. An extraction vessel filled with a sample is placed in the SFE unit and heated to 40 °C (Fig. 1 A). The extraction vessel is then filled with supercritical carbon dioxide and the target components are extracted statically without pumping the liquid (Fig. 1 B). After static extraction, the target components are extracted dynamically by pumping supercritical carbon dioxide through the extraction vessel (Fig. 1 C). After trapping the extract material in the trap column, the eluate that contains the target components is then collected in the fraction collector (Fig. 1 D).

Sample Preparation

Liquid-liquid extraction is typically used to pretreat soil samples for residual pesticide analysis. However, due to the extraction time and equipment required, throughput is low, limiting the number of samples that can be processed in a day. It also requires using organic solvent during extraction. Therefore, an alternative extraction method to liquid-liquid extraction is desirable, in terms of both the environment and cost.

In contrast, the Nexera UC SFE pretreatment system requires only mixing 1 g of soil with 1 g of a dehydrating agent* and placing the mixture in the extraction vessel, as shown in Fig. 2. This not only improves productivity and minimizes environmental impact, but also avoids human errors involved in the sample pretreatment process. Furthermore, a specially designed rack changer can be used to perform extraction consecutively for up to 48 samples.

* "Miyazaki Hydro-Protect" Patent No. 3645552

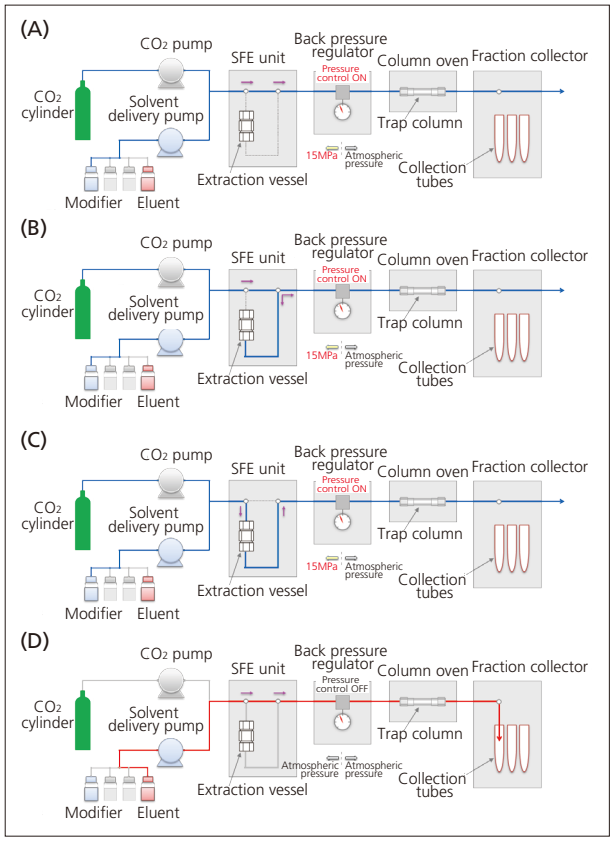

Fig. 1 Process Flow of SFE Extraction

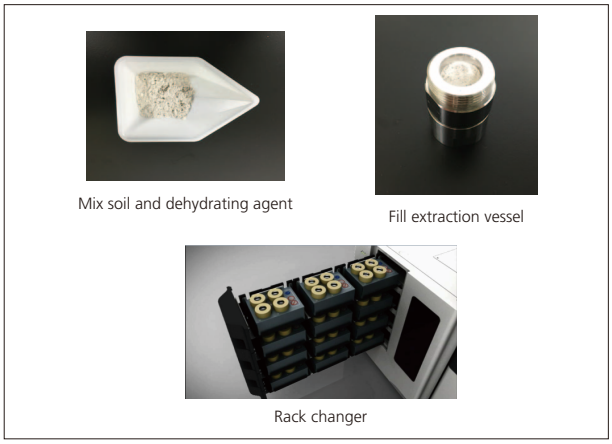

Fig. 2 Sample Preparation

Extraction and Analysis of Residual Pesticides in Soil

Soil was spiked with 200 ng/g each of eight pesticide components, which were then extracted by SFE using the conditions indicated in Table 1. Eluent was added to the extract obtained to make 2 mL, which was then analyzed by LC-MS/MS using the conditions indicated in Table 1. Repeatability and recovery rate values for the eight pesticide components are shown in Table 2. Recovery rates were determined by comparing the area of pesticide peaks measured from the extract obtained from the soil spiked with pesticide and measured from the extract obtained from unspiked soil to which the pesticides were added after extraction. This system uses a simpler and faster pretreatment process than liquid-liquid extraction, which enables it to finish extraction in about 30 minutes per sample. It also uses less organic solvent, so it is superior in terms of the environment and cost as well.

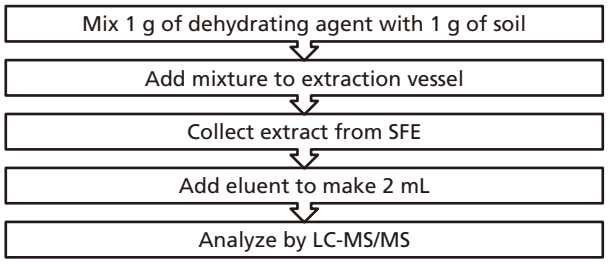

Fig. 3 Process Flow from Pretreatment to Analysis

Table 1 Extraction and Analytical Conditions

[SFE] Nexera UC SFE System
Solvent : A) Supercritical fluid of CO_2
B) Methanol
Flowrate : 5 mL/min
Extraction : 4 min (Static mode → Dynamic mode)
Extraction Vessel Temp. : 40 °C
BPR Pressure : 15 MPa
Trap Column : Shim-pack VP-ODS (50 mm L. × 4.6 mm I.D., 5 µm)
Column Oven Temp. : 40 °C
Elution Solvent : Acetone/Hexane = 50/50 (2 mL/min, 2 min)

[LC] Nexera X2 System
Column : Shim-pack UC-RP (150 mm L. × 2.1 mm I.D., 3 µm)
Mobile Phase : A) 10 mM Ammonium formate
B) 10 mM Ammonium formate in methanol
Time Program : B.Conc. 0 % (0 min) → 100 % (14-17 min) → 0 % (17.1-20 min)
Flowrate : 0.4 mL/min
Column Temp. : 40 °C
Injection Volume : 3 µL

[MS] LCMS-8060 (MRM mode)
Ionization : ESI (positive or negative)
DL Temp. : 200 °C
Block Heater Temp. : 400 °C
Interface Temp. : 300 °C
Nebulizing Gas Flow : 2 L/min
Drying Gas Flow : 10 L/min
Heating Gas Flow : 10 L/min

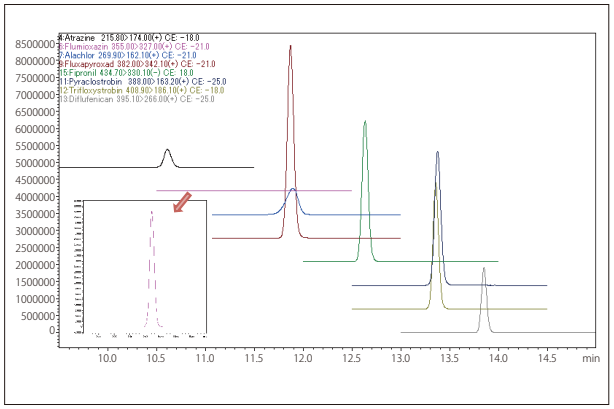

Fig. 4 MRM Chromatogram of Extract from Soil Spiked with Pesticides

Table 2 Repeatability and Recovery

Compounds	Repeatability (%RSD, n=6)	Recovery (%)
Alachlor	1.9	87.0
Atrazine	1.3	75.8
Diflufenican	1.2	86.2
Fipronil	1.5	80.6
Flumioxazin	3.8	70.1
Fluxapyroxad	2.2	72.9
Pyraclostrobin	1.8	73.3
Trifloxystrobin	1.5	87.7

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