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Efficient extraction of residual pesticides in agricultural products and soils for GC/MS and LC/MS analysis using supercritical fluid extraction

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Introduction

A solvent extraction is commonly used for pretreatment of residual pesticides in foods and soils. In the method, a substantial amount of time and effort are required and large quantities of organic solvents are consumed. Supercritical fluid extraction (SFE) that employs supercritical carbon dioxide as an extraction solvent provides good extraction efficiency due to high diffusivity and solubility. It affords extremely short time as well as less damaging to the environment due to small consumption of organic solvent compared to that of solvent extraction methods. We have developed an efficient SFE system that can perform up to 48 automatic and serial extractions and applied it to extraction of residual pesticides in agricultural products and soils.

Methods and Materials

Sample Preparation

Sample-preparation procedures of agricultural products and soils for SFE were quite simple. Figure 1 shows the procedures. 1 g of sample (homogenized agricultural products or soils) and 1 g of dehydrating absorbent were mixed then the mixture was enclosed into an extraction vessel.

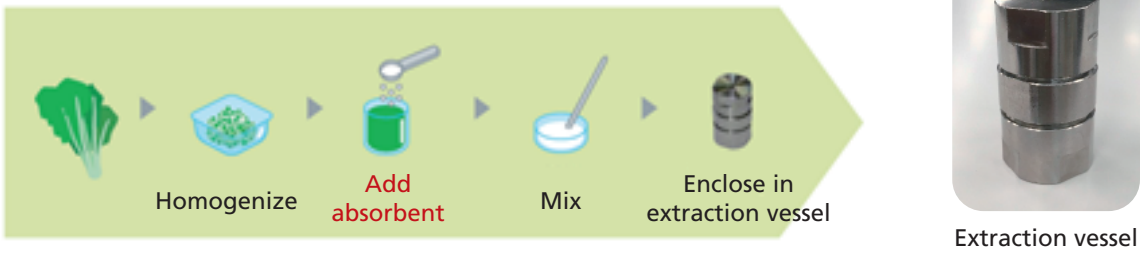

Figure 1 Sample-preparation procedures

Experimental

SFE was carried out using Nexera UC SFE pretreatment system (Shimadzu Corporation, Japan) both in static and dynamic extraction modes with carbon dioxide and methanol as extractant. After trapping extracted material in the trap column, eluent that contains target compounds was then collected in the fraction collector. The extraction liquid obtained was made up to 2 mL using eluent, and analyzed by GC-MS (GCMS-TQ8040) or LC-MS (LCMS-8060). Figure 3 shows the process flow from pretreatment to analysis.

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Automatic extraction of up to 48 samples serially

Figure 2 Nexera UC SFE Pretreatment system, GCMS-TQ8040 and LCMS-8060

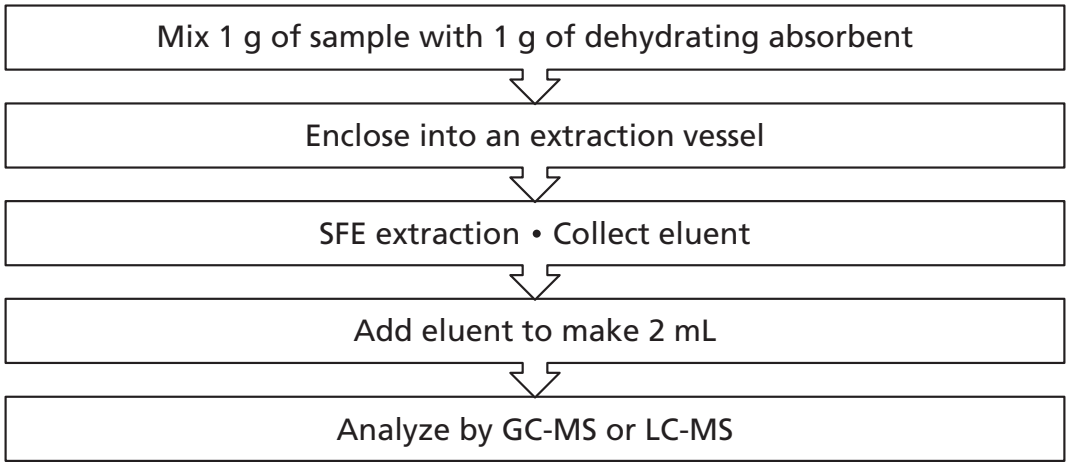

Figure 3 Process flow from pretreatment to analysis

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Table 1 Extraction and analytical conditions

SFE conditions (Nexera UC SFE pretreatment system, Shimadzu)	
Solvent	: A CO_2
	: B Methanol
Flow rate	: 5 mL / min.
Extraction	: 8 min for agricultural products
(Static mode → Dynamic mode)	: 4 min for soils
Extraction vessel temp.	: 40°C
BPR	: 15 MPa
Trap column	: Shim-pack VP-ODS 5 µm (50 mm x 4.6 mm I.D.)
Eluent solvent	: Acetone / Hexane = 50 / 50 (2 mL / min, 2 min)
GC-MS conditions (GCMS-TQ8040, Shimadzu)	
Column	: Rxi®-5Sil MS 30 m x 0.25 mm I.D., df = 0.25 µm
Column temp.	: 50°C (1 min) → (25°C/min) → 125°C
	→ (10°C/min) → 300°C (15 min)
Carrier gas	: He (Constant linear velocity mode)
Linear velocity	: 47.2 cm/sec
Injection mode	: Splitless (Sampling time 1.00 min)
High press inj.	: 250 kPa (1.5 min)
Injection volume	: 1 µL
Interface temp.	: 250°C
Ion source temp.	: 200°C
MS mode	: MRM mode
Loop time	: 0.3 sec
LC-MS conditions (Nexera X2 system, LCMS-8060, Shimadzu)	
Column	: Shim-pack UC-RP 3 µm (150 mm x 2.1 mm I.D.)
Mobile phase	: A 10 mM Ammonium formate
	: B 10 mM Ammonium formate in methanol
Gradient program	: 0% B (0 min.) → 100% B (14-17 min.)
	→ 0% B (17.1-20 min.)
Flow rate	: 0.4 mL / min.
Column temp.	: 40°C
Injection volume	: 3 µL
Ionization	: ESI (positive or negative MRM mode)

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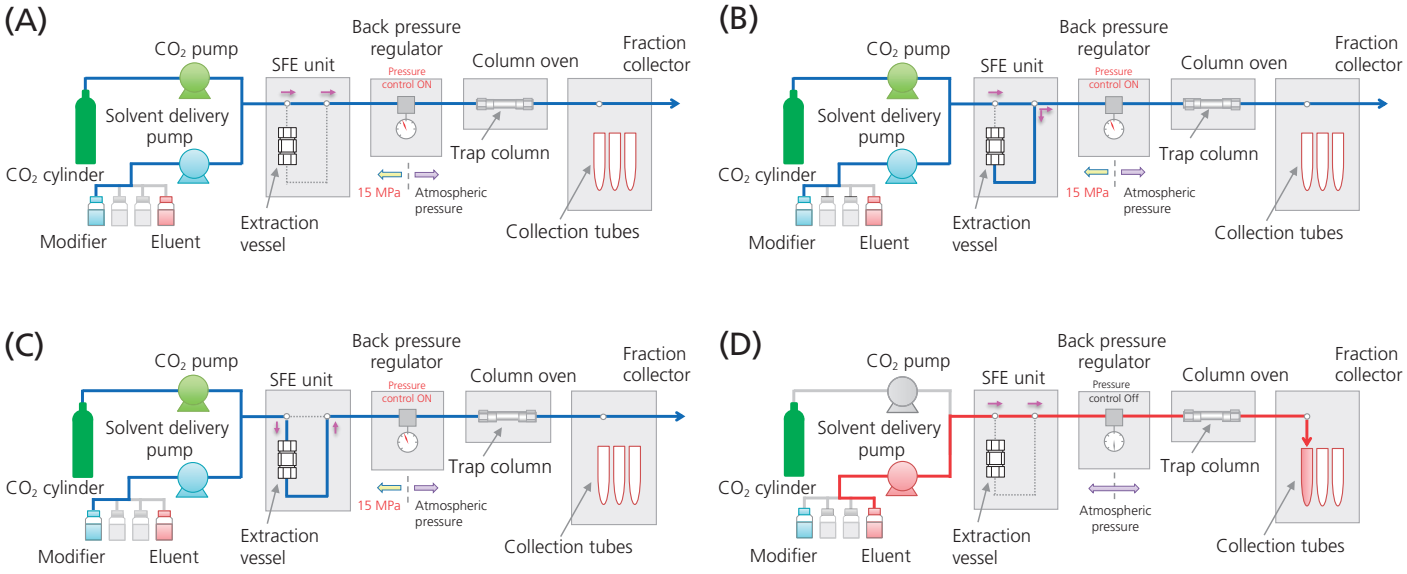

Figure 4 Process flow of SFE extraction

Result

Analysis of Pesticides in Agricultural Products using off-line SFE/GC-MS

354 pesticides for GC/MS were analyzed using off-line SFE/GC-MS system. Brown rice that was spiked with 100 ng/g of standard pesticides was used as a test sample. Figure 5 shows the MRM chromatogram of eluate of brown rice obtained using GC-MS. As a result, 301 pesticides were reliably analyzed (Peak area RSD <10%) and were recovered properly within a range of 70-120%.

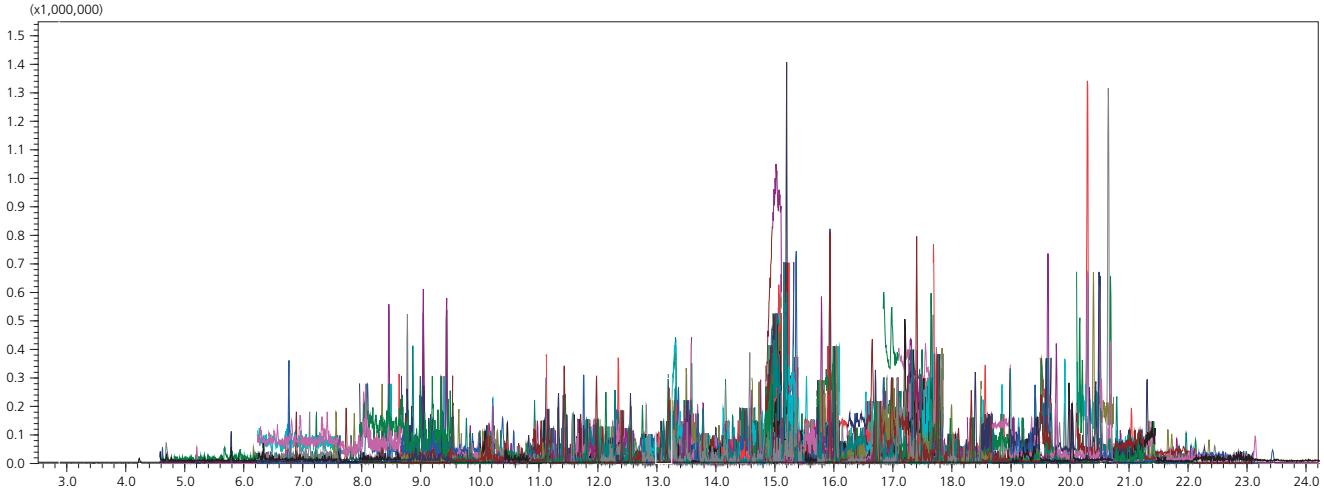

Figure 5 MRM chromatograms of eluate of brown rice spiked with 100 ng/g of standard pesticides

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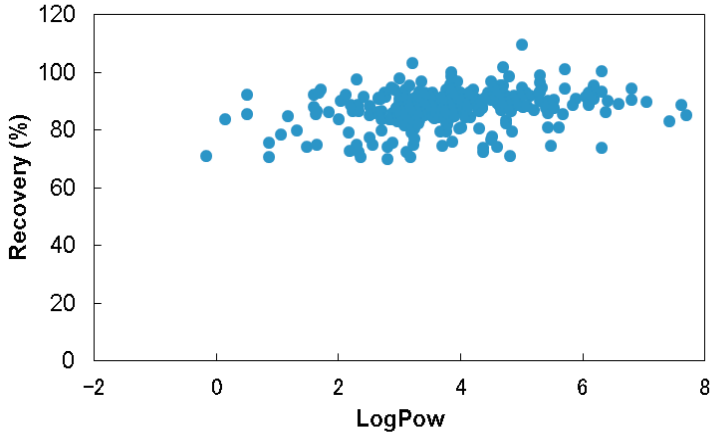

Figure 6 LogPow–recovery for brown rice analysis

Table 2 Repeatability and recovery for representative pesticides

compounds	repeatability (%RSD, n=6)	Recovery (%)
Cyhalofop-butyl	4.2	93
Etofenprox	3.8	90
Iprodione	2.5	93
Malathion	3.2	93
Piperonyl butoxide	3.8	89

Analysis of Pesticides in Soils using off-line SFE/LC-MS

In the extraction of residual pesticides in soils, we evaluated 8 of pesticides (alachlor, atrazine, diflufenican, fipronil, flumioxazin, fluxapyroxad, pyraclostrobin and trifloxystrobin). A mixed standard solution of the pesticides was added to dry soils to make a content of 200 ng/g. Figure 7 shows the MRM chromatograms of eluate of the soil obtained using LC-MS. As a result by LC-MS, good repeatability (relative standard deviation of peak area <5%) and recovery (70-120%) were obtained for all the compounds. Repeatability and recovery rate values for the 8 pesticide compounds are shown in Table 3.

Efficient extraction of residual pesticides in agricultural products and soils for GC/MS and LC/MS analysis using supercritical fluid extraction

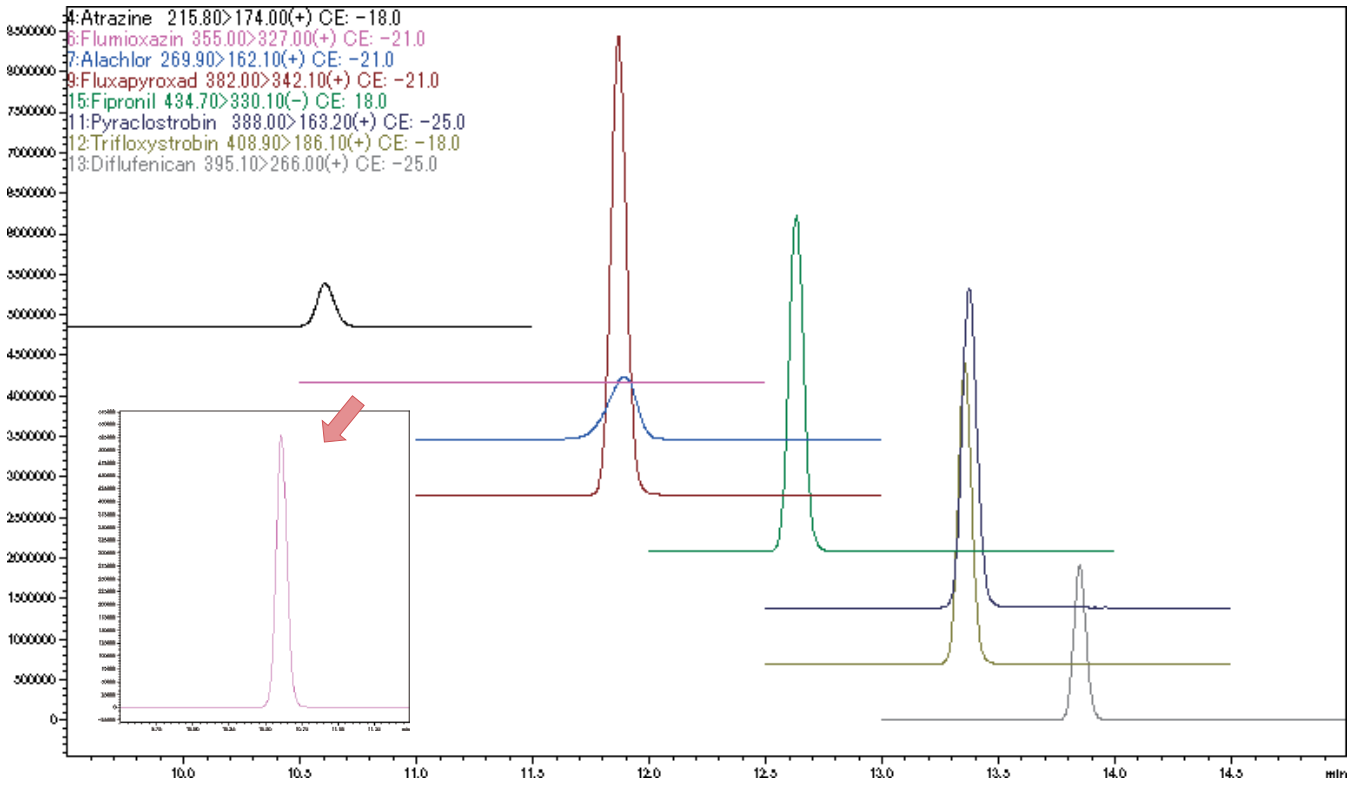

Figure 7 MRM chromatograms of eluate of soil spiked with 200 ng/g of standard pesticides

Table 3 Repeatability and recovery for representative pesticides

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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Conclusions

We have developed an efficient SFE system for pretreatment of residual pesticides in agricultural products and soils. This system uses a simpler and faster pretreatment process than liquid-liquid extraction, which enables us to finish extraction within about 30 minutes per a sample. 301 pesticides in brown rice and 8 in soil were successfully determined with preferable repeatability and recovery using this SFE system. Furthermore, extremely decreased consumption of organic solvent affords significant profits both for operational cost and environmental load.

Disclaimer: Nexera UC SFE Pretreatment Sysyem, GCMS-TQ8040, and LCMS-8060 are intended for Research Use Only (RUO). Not for use in diagnostic procedures.

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