

Multi-residue analysis of pesticides in agricultural products using QuEChERS and SFC/MS

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Introduction

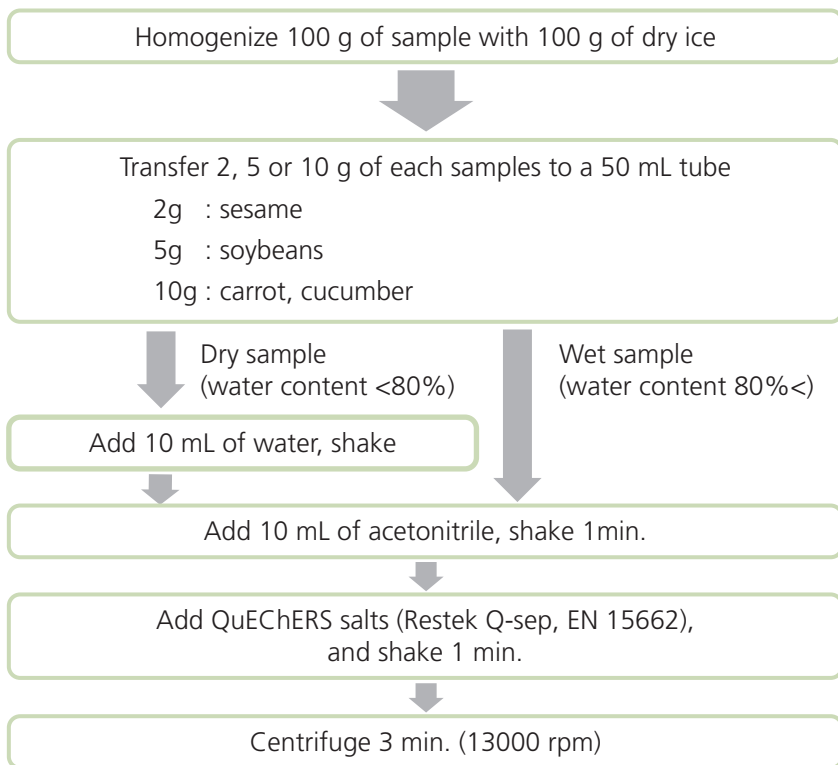
Analysis of pesticide residues in food is typically time-consuming due to the separation for multiple pesticides with a wide range of polarity and matrix co-eluting issues. To deal with the ever-growing number of pesticides, food safety laboratories need to ideally screen as many compounds as possible in a short time which may exceed maximum residual limits; typically 10

ppb in food matrices. Supercritical fluid chromatography (SFC) is one of the separation techniques, and it offers high resolution at high flow rates and various separation modes. Therefore, it has the potential to separate multiple pesticides in a single run. In this study, we developed an analytical method for 441 pesticides in food matrices by QuEChERS and SFC/MS.

Methods and Materials

Sample Preparation

Step 1. Acetonitrile extraction



Samples	Water content (%)
Cucumber	95
Carrot	90
Soybeans	13
Sesame	2



Carrot



Soybeans

Pesticides standard mixtures

- PL2005 Pesticide GC-MS Mix 1-7
- PL2005 Pesticide LC-MS Mix 1-10
- STQ-LC Pesticides Mixture (Hayashi pure chemical, Japan)

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Step 2. Clean up

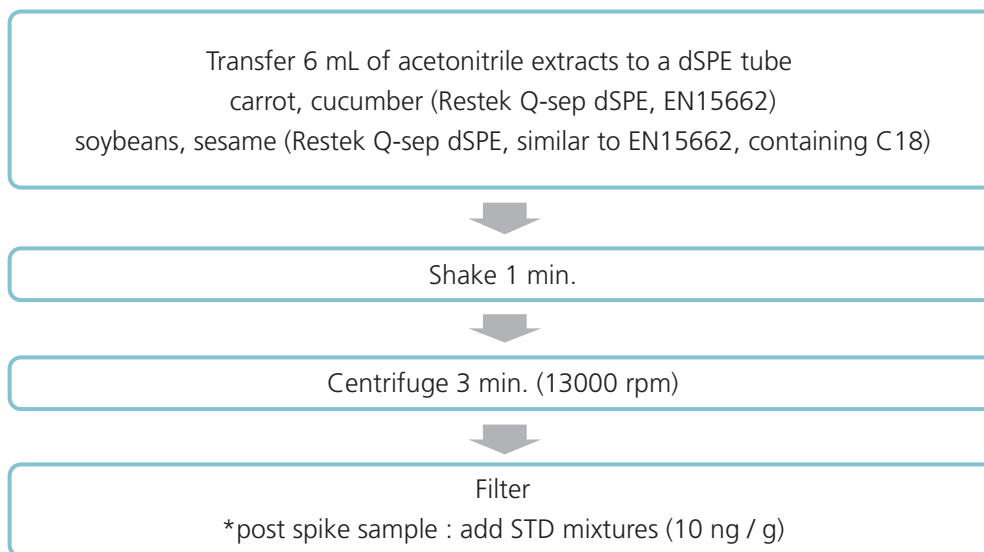


Figure 1 Protocol of sample preparation

Analytical conditions

SFC conditions	
Instrument	: Nexera UC (Shimadzu)
Column	: Shim-pack UC-RP (2.1 x 150 mm, 3 µm, Shimadzu)
Modifier	: 1 mM ammonium formate – Methanol
Flow rate	: 0.6 mL / min.
Gradient program	: 2% B (0 min.) ->10% B (12 min.) ->80% B (20-25 min.) ->2% B (25.01-30 min.)
Make-up solvent	: Methanol
Make-up flow rate	: 0.1mL / min.
Oven temperature	: 40 °C
Injection volume	: 2 µL
LC conditions	
Instrument	: Nexera X2 (Shimadzu)
Column	: Shim-pack FC-ODS (2.0 x 150 mm, 3 µm, Shimadzu)
Mobile phase A	: 1 mM ammonium formate – water
Mobile phase B	: 1 mM ammonium formate – Methanol
Flow rate	: 0.2 mL / min.
Gradient program	: 5% B (0 min.) ->95% B (15-25 min.) ->5% B (25.01-30 min.)
Oven temperature	: 40 °C
Injection volume	: 2 µL
MS conditions (common with SFC and LC)	
Instrument	: LCMS-8060 (Shimadzu)
Ionization	: ESI (+/-)
Mode	: MRM (441 events, 844 MRM transitions) Dwell time : 1 msec. / Pause time : 1 msec.
Polarity switching	: 5 msec. (Fixed)

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Results

Study for optimum conditions in SFC/MS

Concentration of ammonium salt in the modifier

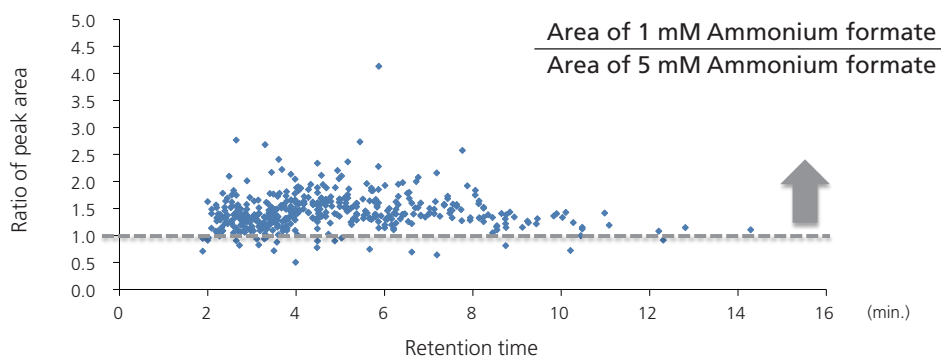


Figure 2 Comparison of area acquired with 1 mM / 5mM of ammonium formate in the modifier

Flow rate of make-up solvent

It is common practice to use make-up solvents to enhance ionization in MS interface. We tested three different flow rates of make-up solvents, 0.1, 0.2 and 0.4 mL/min, and evaluated the overall sensitivity by taking the ratios of

peak areas for each compound with respect to data acquired at 0.2 mL/min. As shown in Figure 3, flow rate of 0.1 mL/min showed better overall sensitivity.

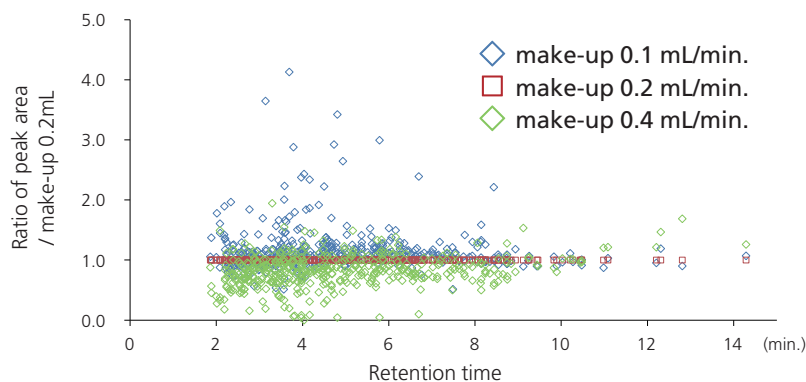


Figure 3 Comparison of area in different flow rate of make-up solvent

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We additionally checked the sensitivity and repeatability in 0.05 mL/min flow rate (Figure 4) because 0.1 mL/min flow rate showed the best result in the preliminary test (Figure 3). Most compounds showed the highest

sensitivity at 0.1 or 0.2 mL/min flow rate, and it tended to decrease at 0.05 mL/min. The repeatability (CV) was also worse at 0.05 mL/min.

Table 1 Flow rates

tR (min)	Modifier (mL/min)	Make-up flow (mL/min)		Total flow (mL/min)	
		0.1 mL/min	0.4 mL/min	0.1 mL/min	0.4 mL/min
2	0.02	0.1	0.4	0.12	0.52
4	0.03			0.13	0.53
6	0.04			0.14	0.54
8	0.05			0.15	0.55
10	0.05			0.15	0.55
12	0.06			0.16	0.56
14	0.27			0.37	0.77

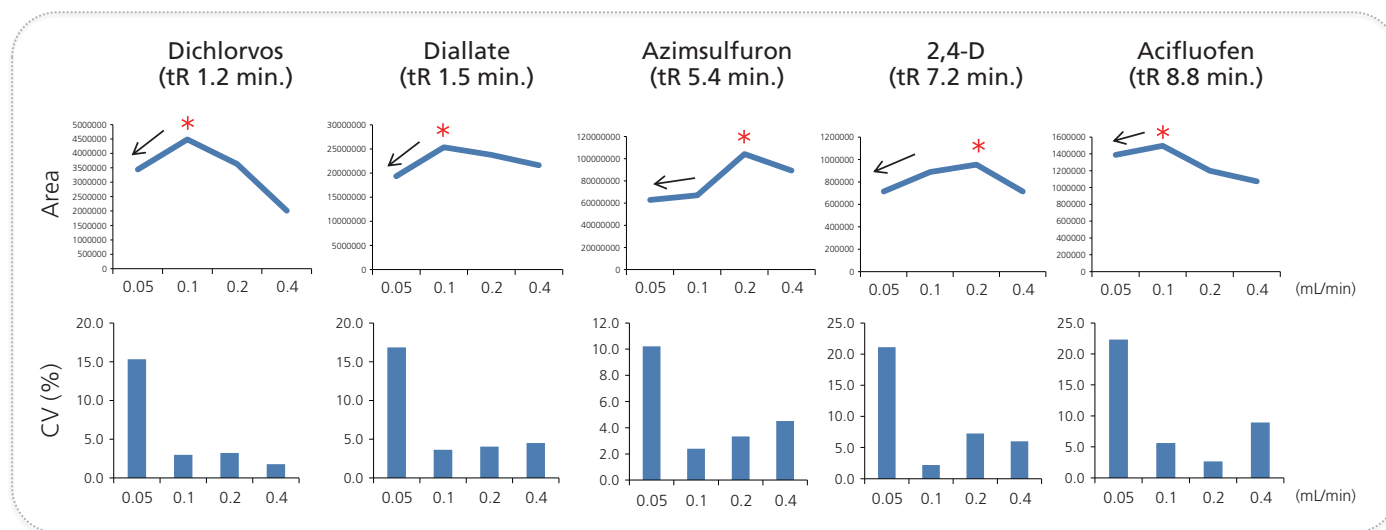


Figure 4 Comparison of area (upper) and %RSD (lower) at different flow rate of make-up solvent

MS parameters (comparison between SFC/MS and LC/MS)

Optimum value of major MS parameters (interface and DL temperature, interface voltage and flow rate of nebulizing gas, drying gas and heating gas) were checked in LC and SFC respectively. The parameters of temperature and flow

rate of gases showed the same tendency that the default value was the best in both instrument. However, optimum value of the interface voltage was totally different between LC and SFC.

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Interface voltage

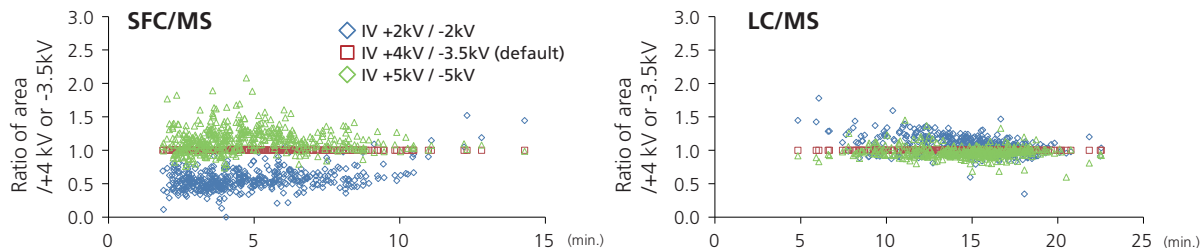
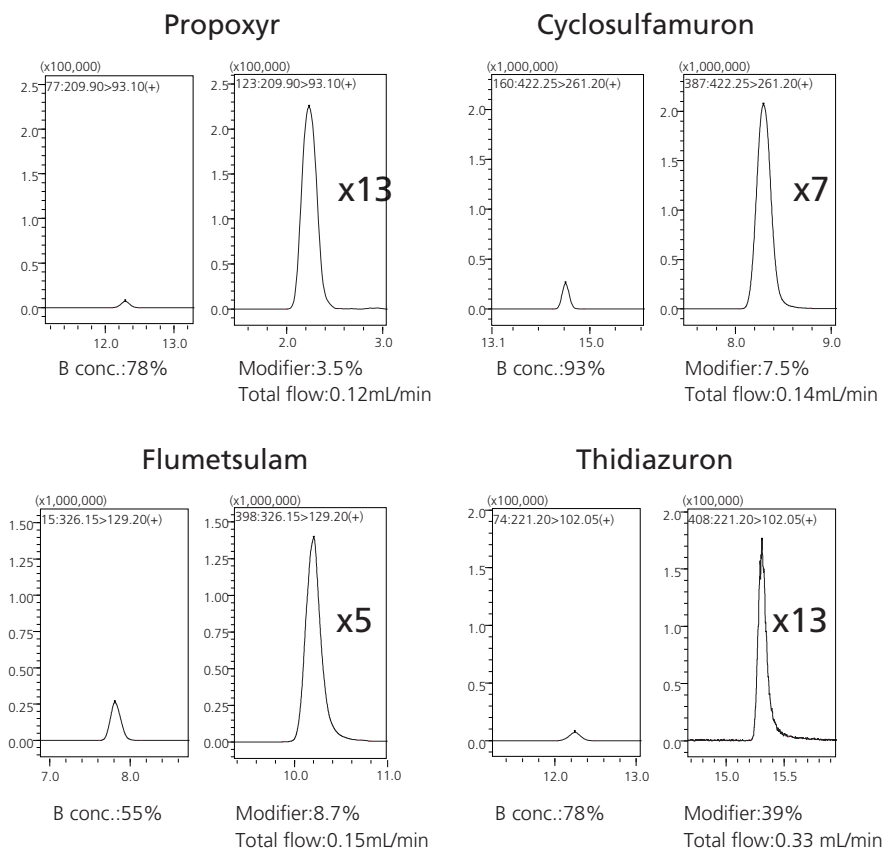


Figure 5 Comparison of peak area at different interface voltage in SFC/MS and LC/MS

Sensitivity comparison between SFC/MS & LC/MS

In SFC/MS, total flow rate of mobile phase is usually less than LC because supercritical CO₂ is vaporized before MS, and water is not contained in the modifier. Therefore, ionization efficiency in ESI is generally increased. In this study, we observed that 90% of compounds showed better sensitivity in SFC than LC regardless of the modifier ratio.

(a) MRM chromatograms (left : LC, right : SFC)



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(b) Ratio of area

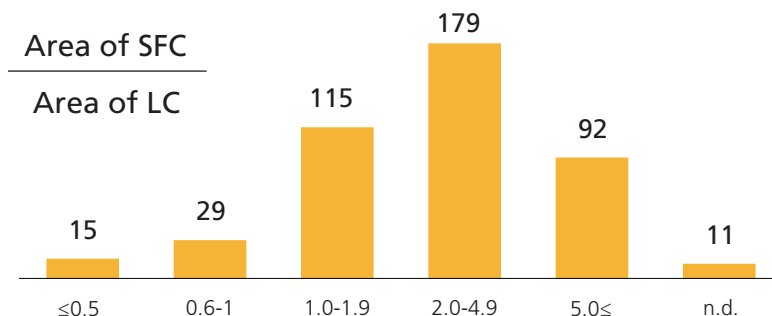


Figure 6 Results of sensitivity comparison between SFC/MS and LC/MS (at 10 µg/L)

Matrix effect at 10 ppb (10 ng/g)

In SFC/MS, 61-77% of compounds showed good recoveries ranging from 70 to 120% and repeatability (<30%) in cucumber, carrot and soybeans; this coverage was higher than in LC/MS in all tested matrices due to better sensitivity.

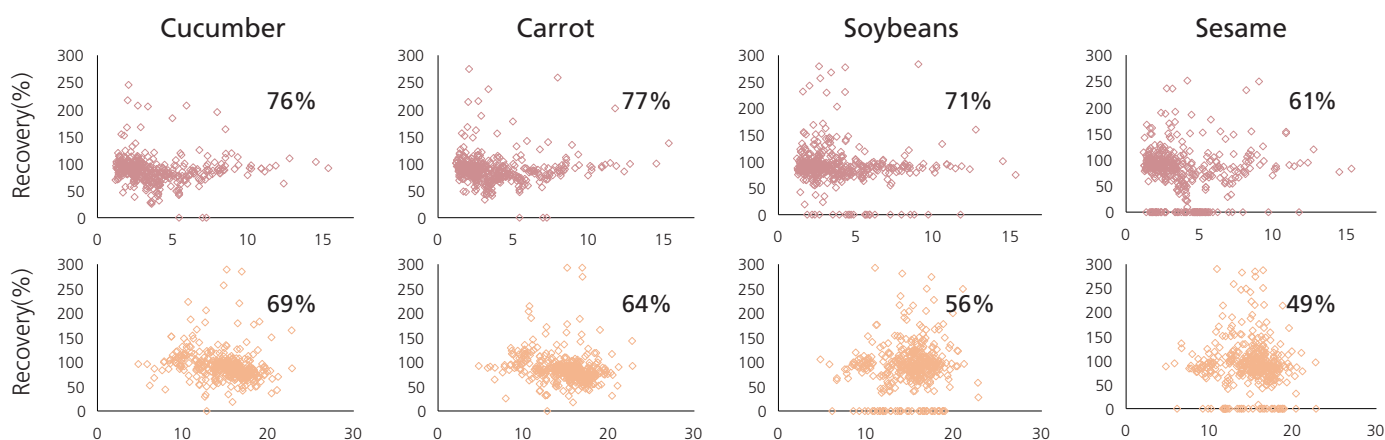


Figure 7 Recoveries of 441 pesticides in each samples (upper : SFC, lower : LC)

Table 2 Summary of matrix effect at 10 ppb (10 ng/g)

		Cucumber		Carrot		Soybeans		Sesame	
		SFC	LC	SFC	LC	SFC	LC	SFC	LC
Recovery	120% <	39	49	43	37	42	55	74	82
	< 70%	56	57	51	90	70	71	62	52
Detection	n.d.	7	20	7	20	9	35	35	60
	CV>30% (n=5)	3	11	1	11	7	32	3	33
Coverage	Total number of compounds	336	304	339	283	313	248	267	214
	%	76	69	77	64	71	56	61	49

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Conclusions

- In this study, we successfully developed the analytical method for numerous pesticides in food matrices by QuEChERS and SFC/MS.
- We confirmed that SFC/MS showed better sensitivity and recoveries than LC/MS.

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