MP 211

Analysis of Residual Pesticides in Strawberries using the Quadrupole Time-of-Flight Mass Spectrometer

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1. Introduction

Currently, triple-quadrupole mass spectrometers are widely used for the analysis of residual pesticides in food, because they provide highly selective and sensitive quantitative results. However, this method can only detect the envisaged target compounds, and there is a limit to the number of compounds that can be measured at one time. Therefore, comprehensiveness is limited for use in screening applications. Against this background, comprehensive analysis for residual pesticides in full scan mode using a high-resolution mass spectrometer is attracting attention. In this poster, we report a case of using a quadrupole time-of-flight mass spectrometer to analyze residual pesticides in strawberries.

2. Methods

2-1. Sample Preparation

Commercially available strawberries and a pesticides mixture standard solution (Hayashi Pure Chemical Ind., Ltd.) were used. The strawberries were pretreated according to the QuEChERS (EN 15662) method. A purification process was performed by the membrane filtration method using the SPEEDIA residual pesticides purification kit (Miura Co., Ltd.). The detailed preparation processes are shown in Fig. 1. In addition, by adding a fixed concentration of pesticide standard solution to the strawberries, the recovery rate for losses in the preparation process and matrix effects were also evaluated.

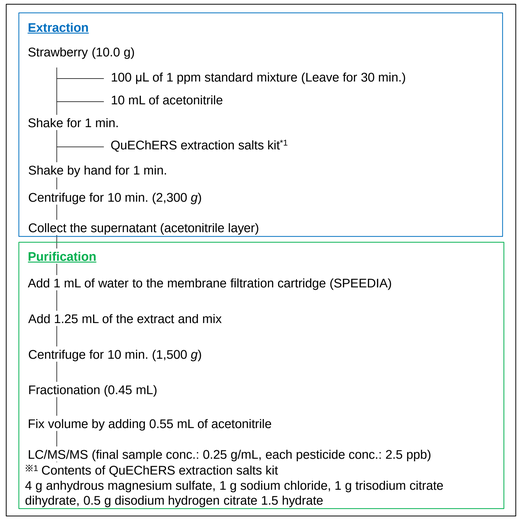

Fig. 1 Workflow for Sample Preparation

2-2. Analysis Conditions

For the analysis of pesticides, the method included in the LC/MS/MS Method Package Residual Pesticides Ver. 3 was applied to the LCMS-9030 (Fig. 2). The HPLC and MS conditions are shown in Table 1.

Fig. 2 Nexera™ X3 and LCMS-9030

Table 1 Analysis Conditions

LC-MS method	
UHPLC (Nexera X3 system)	**MS (LCMS-9030)**
Column: Shim-pack™ Velox Biphenyl (150 mmL.×2.1 mmI.D., 2.7 µm, Shimadzu)	Ionization: ESI (Positive)
Mobile phase A: 2 mM Ammonium formate-0.002% Formic acid-Water	TOF-MS: *m/z* 50-950
B: 2 mM Ammonium formate-0.002% Formic acid-Methanol	DL temp.: 250 °C
Gradient program: B conc. 3% (0 min)-10% (1 min)-55% (3 min)-100% (10.5-12 min)-3% (12.01-15 min)	HB temp: 400 °C
	Interface temp.: 300 °C
Flow rate: 0.4 mL/min	Drying gas: 10 L/min
Column temp.: 35 °C	Nebulizing gas: 2.0 L/min
Injection vol.: 2 µL (Co-injection 40 µL Water)	Heating gas: 10 L/min

3. Results

3-1. Analysis by LCMS-9030

54 pesticides standard mixture diluted to 2.5 ppb, the strawberry extract pretreated with the pesticide mixture standard solution (pesticide concentration in the sample after pretreatment was 2.5 ppb), and the strawberry extract with no pesticide added as a blank were analyzed, respectively. Extracted ion chromatograms (XIC) of the 54 pesticides in each are shown in Fig 3. The XIC drawing range was ±20 ppm or ±5 ppm. All 54 pesticides were detected at a concentration of 2.5 ppb in the pesticide mixture standard solution and the pesticide-added strawberry extract. By narrowing the XIC drawing range from ±20 ppm to ±5 ppm for strawberry extract with no pesticide additives, chromatograms with less noise and fewer foreign peaks were obtained. The LCMS-9030 is a Q-TOF analyzer with high sensitivity that covers the lower limit of quantitation required for routine analysis, and its high mass accuracy enables chromatograms with few foreign peaks to be obtained.

3-2. Linearity of Calibration Curve

Linearity of the calibration curve for each pesticide was evaluated by generating a 6-point calibration curve with the range 0.25-50 ppb (in solvent) or a 5-point calibration curve with the range 0.25-25 ppb (in strawberry extract). Both in solvent and in strawberry extract, linearity showed very good results (coefficient of determination R^2: 0.99 or more) for all compounds. Calibration curves for Boscalid in solvent and in extract are shown in Fig. 4 as an example, and calibration ranges for all 54 compounds are shown in Table 2.

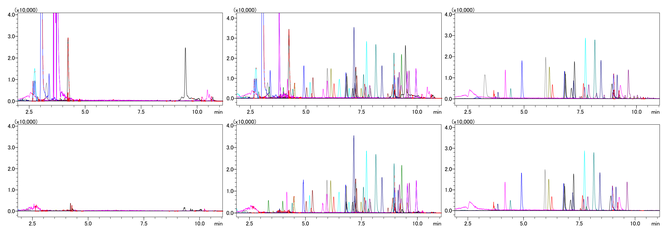

Fig. 3 Extracted ion chromatograms of 54 pesticide compounds (XIC drawing range: top row: ±20 ppm, bottom row: ±5 ppm) (A) strawberry extract with no pesticide added, (B) strawberry extract with pesticide added, (C) mixed standard solution of pesticides

Table 2 Linear Range, Recovery Rate, Reproducibility (%RSD) and Mass Error of 54 Pesticides

Compound	Calibration Range (ppb) in solvent	Calibration Range (ppb) in strawberry extract	Recovery Rate (%)	%RSD	Mass Error (mDa)	Compound	Calibration Range (ppb) in solvent	Calibration Range (ppb) in strawberry extract	Recovery Rate (%)	%RSD	Mass Error (mDa)
(E)-Fenpyroximate	0.25-50	0.25-25	93.2	8.5	-0.6	Flufenoxuron	0.25-50	0.25-25	108.1	4.7	-0.6
(Z)-Fenpyroximate	0.25-50	0.25-25	91.5	5.4	-0.6	Fluridone	0.25-50	0.25-25	96.4	6.5	-0.6
Acibenzolar-S-methyl	2.5-50	2.5-25	91.4	1.6	-0.6	Hexythiazox	0.25-50	0.25-25	90.9	5.8	-0.7
Aldicarb-sulfone (Aldoxycarb)	0.25-50	0.25-25	54.3	4.7	-0.5	Imazalil	0.50-50	2.5-25	81.9	9.4	-0.7
Anilofos	0.25-50	0.25-25	89.6	2.6	-0.6	Imidacloprid	0.25-50	0.25-25	97.1	2.5	-0.4
Azamethiphos	0.25-50	0.25-25	94.4	1.5	-0.5	Indanofan	2.5-50	5.0-25	92.5	20.3	-0.7
Azinphos-methyl	2.5-50	2.5-25	96.5	8.0	-0.9	Iprovalicarb	0.25-50	0.25-25	94.9	5.2	-0.9
Azoxystrobin	0.25-50	0.25-25	95.1	1.4	-0.6	Lactofen	0.50-50	0.25-25	100.2	3.5	-0.3
Benzofenap	5.0-50	2.5-25	85.3	2.8	-0.5	Mepanipyrim	2.5-50	2.5-25	85.0	4.5	-0.1
Boscalid	0.25-50	0.25-25	92.5	5.3	-0.6	Methabenzthiazuron	0.50-50	0.25-25	87.6	5.8	-0.6
Carbaryl (NAC)	0.50-50	2.5-25	92.5	7.2	-0.8	Methomyl	2.5-50	2.5-25	89.8	6.1	0.1
Carpropamid	0.25-50	0.25-25	96.7	2.2	-0.8	Monolinuron	0.25-50	0.25-25	89.2	6.5	-0.7
Chloridazon	0.25-50	0.25-25	64.4	1.4	-0.6	Novaluron	2.5-50	2.5-25	102.6	3.5	-0.7
Chloroxuron	0.25-50	0.25-25	100.8	1.4	-0.7	Oxaziclomefone	0.25-50	0.25-25	92.7	2.3	-0.6
Clofentezine	0.50-50	0.50-25	83.8	6.9	-0.4	Oxycarboxin	0.25-50	0.25-25	78.2	5.2	-0.6
Cloquintocet-mexyl	0.25-50	0.25-25	86.7	6.7	-0.5	Pirimicarb	0.25-50	0.25-25	73.7	3.3	-0.6
Clothianidin	0.50-50	2.5-25	53.6	2.2	-0.5	Pyraclostrobin	5.0-50	2.5-25	84.0	5.4	-0.7
Cumyluron	0.25-50	0.25-25	96.0	1.2	-0.5	Pyrazolynate	0.25-50	0.25-25	112.7	5.2	-0.7
Cyazofamid	0.25-50	0.50-25	96.4	5.9	-0.7	Pyriftalid	0.25-50	0.25-25	94.2	1.8	-0.5
Cyprodinil	0.25-50	0.25-25	82.7	6.5	-0.7	Simeconazole	0.25-50	0.25-25	104.6	1.3	-0.6
Dimethomorph (E, Z)	0.25-50	0.25-25	96.9	2.5	-0.5	Spinosyn A	0.25-50	2.5-25	88.7	4.8	-1.2
Diuron (DCMU)	0.25-50	0.25-25	89.9	4.3	-0.6	Spinosyn D	0.25-50	2.5-25	97.7	3.1	-1.2
Epoxiconazole	0.25-50	0.25-25	100.5	2.4	-0.5	Tebuthiuron	0.25-50	0.25-25	88.4	1.4	-0.7
Fenamidone	0.25-50	0.25-25	93.0	0.6	-0.7	Thiacloprid	0.25-50	0.25-25	92.1	4.7	-0.7
Fenobucarb	0.25-50	0.25-25	109.8	9.0	-0.5	Thiamethoxam	0.25-50	0.50-25	63.1	4.2	-0.5
Fenoxaprop-ethyl	0.25-50	0.25-25	90.6	2.3	-0.7	Thiodicarb	0.25-50	0.25-25	83.4	1.4	-0.4
Flufenacet	0.25-50	0.25-25	91.1	5.6	-0.5	Triflumuron	0.25-50	0.50-25	94.5	6.0	-0.5

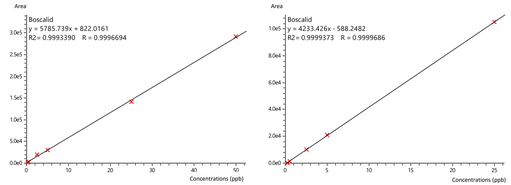

Fig. 4 Calibration Curve of Boscalid (Left: in Solvent, Right: in Strawberry Extract)

3-3. Spike and Recovery Test

A spike and recovery test was performed using strawberry extract to which 54 pesticides mixture standard solution was spiked at 10 ppb per sample (concentration in pretreated sample solution was 2.5 ppb), and the recovery rate and mass error (n=4) were evaluated. The results of recovery rate, reproducibility (%RSD), and mass error are shown in Table 2, and the breakdown of recovery rate is shown in Fig. 5. Recovery rates were 70-120% for 50 of the 54 compounds. Good recovery rate and reproducibility were obtained without significant matrix inhibition, even in solutions containing high sample concentration.

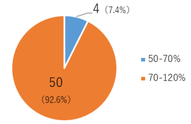

Fig. 5 Breakdown of Recovery Rate

4. Conclusion

- ✓ The sample preparation method combining the QuEChERS (EN 15662) and SPEEDIA made it possible to speed up and simplify the preparation process.
- ✓ It enables comprehensive measurement of residual pesticides by analysis using the LCMS-9030, which can obtain accurate mass.
- ✓ XIC with narrow *m/z* range can provide peaks with less noise and fewer contaminants.
- ✓ Analysis of pretreated strawberry samples using LCMS-9030 provided good results for spike recovery rate, reproducibility, and linearity.
- ➢ **It was demonstrated that the analytical method introduced in this poster enables "rapid, simple, and highly precise" analysis, and is useful for the analysis of residual pesticides in food.**