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Application News

High Performance Liquid Chromatograph Mass Spectrometer LCMS-8050RX

Analysis of Pesticides Residue in Brown Rice by LCMS-8050RX —Comparison of On-Line Purification vs QuEChERS Methods—

Yayoi Ichiki and Manami Kobayashi

User Benefits

- Enables quick and simple sample preparation by combining the QuEChERS extraction process with an on-line purification column.
- LCMS-8050RX enables analysis with good recovery rates and reproducibility.

■ Introduction

With the increase in the number of regulated pesticides, more effective methods for simultaneous analysis of residual pesticides in food are required.

The QuEChERS method, which is widely used for pesticide residue analysis, is a pretreatment method that consists of an extraction step with acetonitrile and salts or a buffer and a purification step with dispersive solid-phase extraction (dSPE). The method can efficiently extract and purify pesticides without special equipment, but there are problems with operator-dependent data variability and the long time required for the process.

Revive in-line sample preparation (ILSP) columns[1)] (RESTEK Co.) are pretreatment columns that can be incorporated into the LC flow path for on-line cleanup of matrix-derived components. It makes the sample preparation process quicker and simpler, and it can be expected to reduce plastic consumable waste and costs associated with pretreatment.

This article describes the results of comparing the purification efficiency of a Revive ILSP column versus a dSPE using an LCMS-8050RX.

■ LCMS-8050RX

The LCMS-8050RX system (Fig. 1) used for this analysis was equipped with a newly developed nebulizer nozzle, CoreSpray. which improves nebulizer flow uniformity and enables more consistent ionization.

Fig. 1 LCMS-8050RX and CoreSpray

■ Sample Preparation

Commercially available brown rice and pesticide mixture standard solutions 54, 58, 74, 75, and 78 (Kanto Chemical Co., Inc.) were used for this analysis. The sample preparation process is shown in Fig. 2.

A Q-sep QuEChERS extraction salts kit (AOAC method, RESTEK Co.) was used for the brown rice extraction process. 1.0 g of ground brown rice and 1 mL of water was put into a 50 mL tube. After 15 min, 15 mL of acetonitrile containing 1 % acetic acid was added and then the tube was shaken. Subsequently, the QuEChERS extraction salt kit was added and mixed. The tube was centrifuged and the supernatant was collected.

In order to compare the purification efficiency of the dSPE and ILSP columns, the pesticide mixture was added to the collected supernatant to make a matrix solution with a final concentration of 2 ng/mL of pesticides. That matrix solution was used for all subsequent purification steps.

■ Analytical Conditions

The pesticides were analyzed using the methods included in the LC/MS/MS Method Package for Residual Pesticides Ver. 3. The analysis conditions are shown in Table 1.

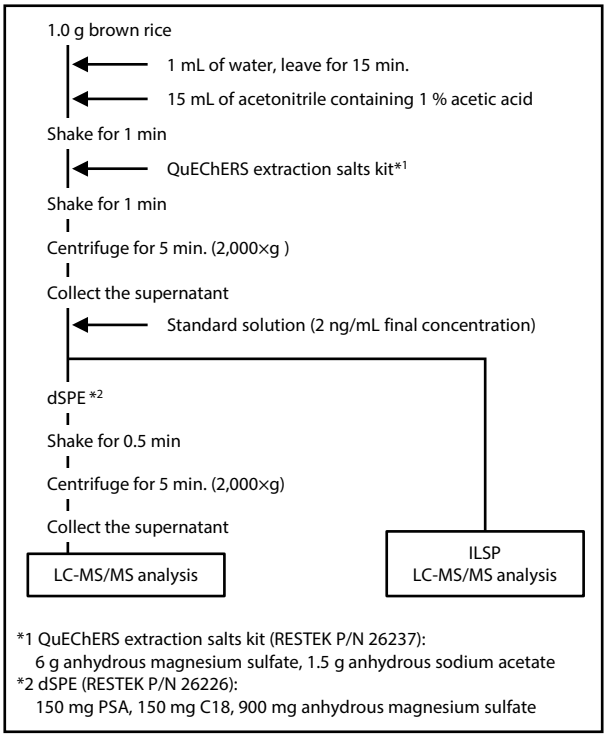

Fig. 2 Sample Preparation Process Flow

Table 1 Analytical Conditions

HPLC Conditions (Nexera™ X3)	
Column:	Shim-pack Velox™ Biphenyl (100 mm L × 2.1 mm I.D., 2.7 µm) P/N 227-32015-03 Revive ILSP Pesticides Single 5 × 2.1 mm Cartridge (RESTEK) P/N 27882
Mobile Phase A:	2 mM Ammonium formate-0.002 % formic acid-water
Mobile Phases B, C (wash):	2 mM Ammonium formate-0.002 % formic acid-methanol
Gradient Program:	B conc. 3 % (0 min) – 10 % (1 min) – 55 % (3 min) – 100 % (10.5 to 12 min) – 3 % (12.01 to 15 min)
Flowrate:	0.4 mL/min
Injection Volume:	2 µL (Co-injection 40 µL Water)

MS Conditions LCMS-8050RX	
Ionization:	ESI (positive, negative)
Mode:	MRM
Nebulizing Gas Flow:	3.0 L/min
Drying Gas Flow:	10.0 L/min
Heating Gas Flow:	10.0 L/min
DL Temp.:	150 °C
Block Heater Temp.:	300 °C
Interface Temp.:	350 °C
Probe Position:	+3 mm

The flow path diagram incorporating the ILSP column and the LC time program are shown in Fig. 3 and 4, respectively.

Hydrophobic compounds from the matrix in injected samples are separated from pesticides by the Revive ILSP column, whereas the pesticides were eluted through the analytical column (upper Fig. 3). After the target pesticide components were eluted from the Revive ILSP column, the 6-port valve was switched to discharge the matrix components remaining in the Revive ILSP column into the drain by backflushing with the washing pump (lower Fig. 3 and Fig. 4). That enabled the Revive ILSP column to be reused. The samples purified by dSPE were analyzed only in the flow path shown in the lower diagram of Fig. 3.

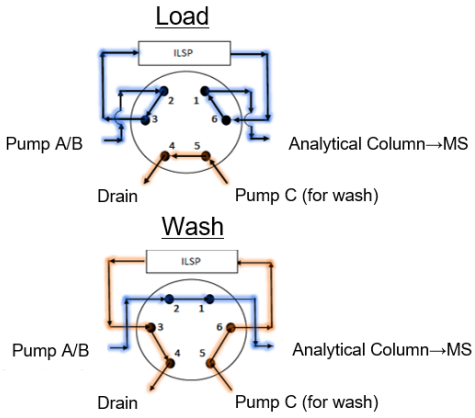

Fig. 3 Overview of ILSP System

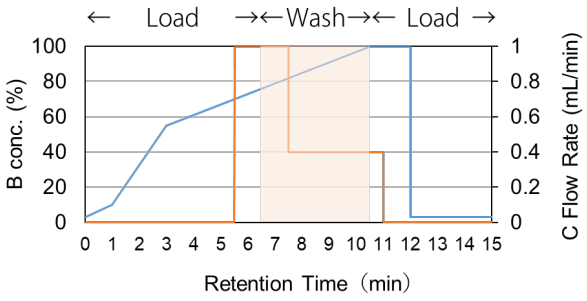

Fig. 4 LC Time Program

■ Linearity of Calibration Curves

Pesticide mixture standard solutions for the range from 0.5 to 50 ng/mL were measured to prepare calibration curves. Coefficient of determination R^2 values and calibration ranges for all compounds are shown in Table 2. Linearity was good for both flow paths. The calibration curve for acetamiprid and the chromatograms for 164 pesticides are shown (Fig. 5, 6).

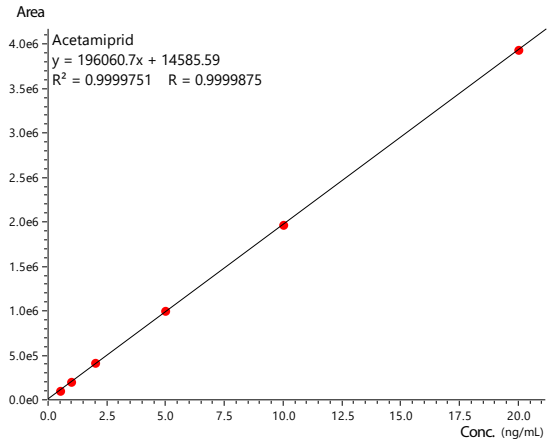

Fig. 5 Calibration Curve for Acetamiprid (for ILSP)

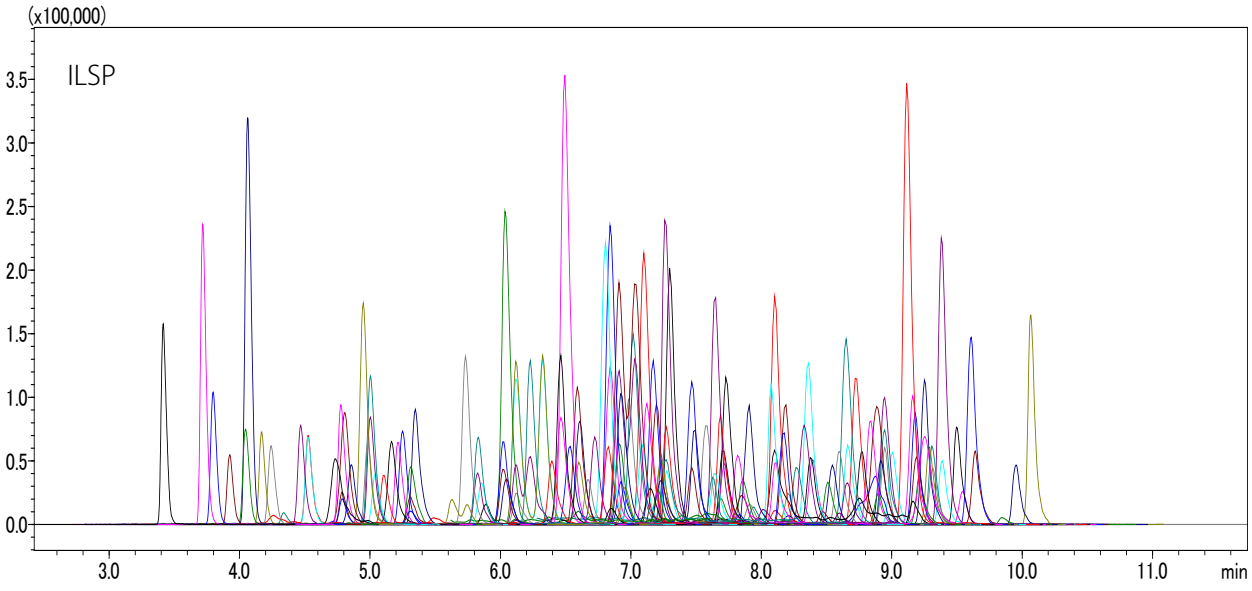

Fig. 6 Chromatogram for Pesticide Compounds

Table 2 Coefficients of Determination R^2 and Calibration Ranges

Compound	dSPE		ILSP	
	R^2	Range (ng/mL)	R^2	Range (ng/mL)
Acetamiprid	0.999	0.5 - 20	0.999	0.5 - 20
Acibenzolar-S-methyl	0.999	1.0 - 50	0.999	1.0 - 50
Aldicarb	0.998	0.5 - 20	0.999	0.5 - 20
Aldicarb-sulfone (Aldoxycarb)	0.999	0.5 - 20	0.999	0.5 - 20
Anilofos	0.999	0.5 - 20	0.999	0.5 - 20
Avermectin B1a	0.999	1.0 - 50	0.999	1.0 - 50
Azamethiphos	0.999	0.5 - 20	0.999	0.5 - 20
Azinphos-methyl	0.999	0.5 - 20	0.999	0.5 - 20
Azoxystrobin	0.999	0.5 - 10	0.999	0.5 - 20
Benalaxyl	0.998	0.5 - 20	0.999	0.5 - 20
Bendiocarb	0.998	0.5 - 20	0.999	0.5 - 50
Bensulide	0.999	0.5 - 20	0.999	0.5 - 20
Benthiavalicarb-isopropyl	0.998	0.5 - 20	0.999	0.5 - 20
Benzofenap	0.999	0.5 - 20	0.999	0.5 - 20
Bitertanol (diastereo isomers)	0.999	0.5 - 10	0.999	0.5 - 10
Boscalid	0.999	0.5 - 20	0.998	1.0 - 20
Bromacil	0.999	0.5 - 20	0.999	0.5 - 20
Bromobutide	0.999	0.5 - 10	0.999	0.5 - 50
Bromobutide-debromo	0.999	0.5 - 20	0.999	0.5 - 20
Buprofezin	0.999	0.5 - 10	0.999	0.5 - 20
Butachlor	0.999	0.5 - 20	0.999	0.5 - 20
Butafenacil	0.999	0.5 - 20	0.999	0.5 - 20
Carbaryl (NAC)	0.999	0.5 - 20	0.999	0.5 - 20
Carbofuran	0.999	0.5 - 10	0.999	0.5 - 20
3-Hydroxycarbofuran	0.999	0.5 - 10	0.999	0.5 - 20
Carpropamid	0.998	0.5 - 20	0.999	2.0 - 20
Chloridazon	0.999	0.5 - 20	0.999	0.5 - 20
Chloroxuron	0.998	0.5 - 20	0.999	0.5 - 20
Chlorpyrifos	0.996	0.5 - 10	0.999	0.5 - 20
Chromafenozide	0.999	0.5 - 20	0.999	0.5 - 20
Clofentezine	0.999	0.5 - 20	0.999	0.5 - 20
Clomeprop	0.999	0.5 - 20	0.999	0.5 - 20
Cloquintocet-mexyl	0.999	0.5 - 20	0.999	0.5 - 20
Clothianidin	0.999	0.5 - 20	0.999	0.5 - 20
Cumyluron	0.999	0.5 - 20	0.999	0.5 - 20
Cycloate	0.998	0.5 - 50	0.999	1.0 - 20
Cyenopyrafen	0.999	0.5 - 20	0.999	0.5 - 20
Cyflufenamid	0.999	0.5 - 20	0.999	0.5 - 20
Cymoxanil	0.999	0.5 - 20	0.999	1.0 - 20
Cyprodinil	0.997	0.5 - 20	0.999	0.5 - 50
Daimuron (Dymron)	0.999	0.5 - 20	0.999	0.5 - 20
Di-allate	0.998	0.5 - 20	0.997	1.0 - 20
Diethofencarb	0.999	0.5 - 20	0.999	0.5 - 20
Difenoconazole (isomer)	0.998	0.5 - 20	0.999	0.5 - 20
Diflubenzuron	0.999	0.5 - 10	0.999	0.5 - 10
Diflufenican	0.999	0.5 - 20	0.999	0.5 - 20
Dimethametryn	0.999	0.5 - 20	0.999	0.5 - 20
Dimethirimol	0.999	0.5 - 20	0.999	0.5 - 50
Dimethoate	0.998	0.5 - 20	0.999	0.5 - 20
Dimethomorph (E, Z)	0.999	0.5 - 20	0.999	0.5 - 20
Diuron (DCMU)	0.999	0.5 - 20	0.999	0.5 - 20
Epoxiconazole	0.996	0.5 - 20	0.999	0.5 - 20
Ethiprole	0.999	0.5 - 20	0.998	0.5 - 20
Etoxazole	0.999	0.5 - 20	0.999	0.5 - 20
Famoxadone	0.999	0.5 - 20	0.998	0.5 - 20
Fenamidone	0.999	0.5 - 20	0.999	0.5 - 20
Fenobucarb	0.998	0.5 - 20	0.999	0.5 - 20
Fenoxaprop-ethyl	0.999	0.5 - 20	0.999	0.5 - 20
Fenoxycarb	0.999	0.5 - 20	0.999	0.5 - 20
Fenpropimorph	0.998	0.5 - 20	0.999	0.5 - 20
Fenpyroximate (E)	0.999	0.5 - 20	0.999	0.5 - 20
Fensulfothion	0.999	0.5 - 20	0.999	0.5 - 20
Ferimzone (E)	0.999	0.5 - 20	0.999	0.5 - 20
Ferimzone (Z)	0.999	0.5 - 20	0.999	0.5 - 50
Flamprop-methyl	0.999	0.5 - 20	0.999	0.5 - 20
Flubendiamide	0.999	0.5 - 20	0.999	0.5 - 20
Fludioxonil	0.997	0.5 - 20	0.999	1.0 - 50
Flufenacet	0.999	0.5 - 20	0.999	0.5 - 20
Flufenoxuron	0.997	0.5 - 20	0.999	0.5 - 20
Fluometuron	0.999	0.5 - 20	0.999	0.5 - 20
Fluopicolide	0.999	0.5 - 20	0.999	0.5 - 20
Fluridone	0.998	0.5 - 20	0.999	0.5 - 20
Flusilazole	0.999	0.5 - 20	0.999	0.5 - 20
Flutriafol (isomer)	0.999	0.5 - 20	0.999	0.5 - 20
Furametpyr	0.999	0.5 - 20	0.999	0.5 - 20
Furathiocarb	0.998	0.5 - 20	0.999	0.5 - 20
Hexaflumuron	0.999	0.5 - 20	0.999	1.0 - 20
Hexythiazox	0.998	0.5 - 20	0.999	0.5 - 20
Imazalil	0.998	0.5 - 20	0.999	0.5 - 20
Imidacloprid	0.999	0.5 - 20	0.999	0.5 - 20
Indanofan	0.997	0.5 - 20	0.998	0.5 - 20
Indoxacarb	0.999	0.5 - 20	0.999	0.5 - 20

Compound	dSPE		ILSP	
	R^2	Range (ng/mL)	R^2	Range (ng/mL)
Iprovalicarb	0.998	0.5 - 20	0.999	0.5 - 20
Isouron	0.998	0.5 - 20	0.999	0.5 - 50
Isoxaflutole	0.999	0.5 - 20	0.999	1.0 - 50
Isoxathion	0.999	0.5 - 20	0.999	1.0 - 50
Kresoxim-methyl	0.999	0.5 - 20	0.999	0.5 - 20
Lactofen	0.999	0.5 - 20	0.999	0.5 - 20
Linuron	0.998	0.5 - 20	0.999	0.5 - 20
Lufenuron	0.997	2.0 - 50	0.999	2.0 - 50
Malathion	0.999	0.5 - 20	0.999	0.5 - 20
Mandipropamid	0.999	0.5 - 10	0.999	0.5 - 20
Mepanipyrim	0.999	0.5 - 20	0.999	0.5 - 20
Metalaxyl/Metalaxyl-M	0.999	0.5 - 20	0.999	0.5 - 20
Metalaxyl-M (Mefenoxam)	0.999	0.5 - 20	0.999	0.5 - 20
Metconazole	0.999	0.5 - 20	0.999	0.5 - 20
Methabenzthiazuron	0.999	0.5 - 20	0.999	0.5 - 20
Methidathion	0.999	0.5 - 20	0.999	0.5 - 20
Methiocarb	0.998	0.5 - 20	0.999	0.5 - 20
Methomyl	0.999	0.5 - 20	0.999	0.5 - 20
Methoxyfenozide	0.999	0.5 - 20	0.999	0.5 - 20
Monolinuron	0.999	0.5 - 20	0.999	0.5 - 50
Naproanilide	0.999	0.5 - 20	0.999	0.5 - 20
Novaluron	0.997	0.5 - 20	0.999	2.0 - 20
Oryzalin	0.999	2.0 - 50	0.999	1.0 - 50
Oxadiargyl	0.998	0.5 - 20	0.999	0.5 - 20
Oxamyl	0.999	0.5 - 20	0.999	0.5 - 50
Oxaziclomefone	0.999	0.5 - 20	0.999	0.5 - 50
Oxycarboxin	0.999	0.5 - 20	0.999	0.5 - 20
Paclobutrazol	0.999	0.5 - 20	0.999	0.5 - 20
Pencycuron	0.999	0.5 - 20	0.999	0.5 - 20
Penthiopyrad	0.999	0.5 - 20	0.999	0.5 - 20
Phenmedipham	0.998	0.5 - 50	0.998	0.5 - 50
Phosphamidon	0.998	0.5 - 50	0.999	0.5 - 50
Phoxim	0.999	0.5 - 10	0.999	0.5 - 20
Piperonyl-butoxide	0.999	0.5 - 20	0.999	0.5 - 20
Pirimicarb	0.998	0.5 - 20	0.999	0.5 - 50
Pirimiphos-methyl	0.999	0.5 - 20	0.999	0.5 - 20
Prochloraz	0.998	0.5 - 20	0.999	0.5 - 20
Profenofos	0.999	0.5 - 10	0.999	0.5 - 20
Prometryn	0.999	0.5 - 20	0.999	0.5 - 50
Propaquizafop	0.999	0.5 - 20	0.999	0.5 - 20
Propoxur	0.999	0.5 - 20	0.999	0.5 - 20
Pyraclofos	0.999	0.5 - 20	0.999	0.5 - 20
Pyraclonil	0.999	0.5 - 20	0.999	0.5 - 20
Pyraclostrobin	0.999	0.5 - 20	0.999	0.5 - 20
Pyrazolynate	0.999	0.5 - 20	0.999	0.5 - 20
Pyrazophos	0.999	0.5 - 20	0.999	0.5 - 20
Pyrazoxyfen	0.999	0.5 - 10	0.999	0.5 - 20
Pyributicarb	0.999	0.5 - 20	0.999	0.5 - 20
Pyridaben	0.999	0.5 - 20	0.999	0.5 - 20
Pyriftalid	0.999	0.5 - 20	0.999	0.5 - 20
Pyriminobac-methyl (E)	0.998	0.5 - 20	0.999	0.5 - 50
Quinoxyfen	0.999	0.5 - 20	0.999	0.5 - 20
Quizalofop-ethyl	0.998	0.5 - 20	0.999	0.5 - 20
Simeconazole	0.999	0.5 - 20	0.999	0.5 - 20
Spinosyn A	0.997	0.5 - 20	0.999	0.5 - 20
Spinosyn D	0.997	0.5 - 20	0.994	2.0 - 20
Spirodiclofen	0.998	0.5 - 20	0.999	0.5 - 20
Tebuconazole	0.999	0.5 - 20	0.999	0.5 - 20
Tebufenozide	0.999	0.5 - 20	0.999	0.5 - 20
Tebuthiuron	0.998	0.5 - 20	0.999	0.5 - 20
Teflubenzuron	0.998	0.5 - 20	0.998	2.0 - 20
Terbacil	0.999	2.0 - 50	0.999	1.0 - 50
Tetrachlorvinphos (CVMP)	0.998	0.5 - 20	0.997	0.5 - 20
Tetraconazole	0.999	0.5 - 20	0.999	0.5 - 20
Thiabendazole	0.999	0.5 - 10	0.999	0.5 - 50
Thiacloprid	0.999	0.5 - 20	0.999	0.5 - 20
Thiamethoxam	0.999	0.5 - 20	0.999	0.5 - 20
Thiodicarb	0.998	0.5 - 20	0.999	0.5 - 20
Tiadinil	0.999	2.0 - 50	0.999	1.0 - 50
Tolfenpyrad	0.999	0.5 - 20	0.999	0.5 - 20
Tralkoxydim	0.997	1.0 - 10	0.999	0.5 - 10
Triadimefon	0.999	0.5 - 20	0.999	0.5 - 20
Triadimenol (isomer)	0.998	0.5 - 20	0.999	0.5 - 20
Trichlamide	0.999	2.0 - 50	0.998	2.0 - 50
Tridemorph (isomer)	0.999	0.5 - 20	0.999	0.5 - 20
Trifloxystrobin	0.999	0.5 - 20	0.999	0.5 - 20
Triflumizole	0.999	0.5 - 50	0.999	0.5 - 20
Triflumizole Metabolite	0.999	0.5 - 20	0.999	0.5 - 50
Triflumuron	0.999	0.5 - 20	0.999	0.5 - 20
Triforine (isomer)	0.999	0.5 - 20	0.999	0.5 - 20
Triticonazole	0.998	0.5 - 20	0.999	0.5 - 20
XMC	0.999	0.5 - 20	0.999	0.5 - 20

Table 3 Recovery Rates and Reproducibility

Compound	dSPE		ILSP	
	Recovery rate (%)	%RSD	Recovery rate (%)	%RSD
Acetamiprid	90.6	2.0	96.2	2.4
Acibenzolar-S-methyl	93.2	9.6	104.2	13.8
Aldicarb	84.1	4.7	94.2	3.5
Aldicarb-sulfone (Aldoxycarb)	93.9	1.4	102.3	0.8
Anilofos	46.5	5.9	74.0	3.5
Avermectin B1a	116.4	6.6	118.5	9.2
Azamethiphos	45.0	11.3	95.3	7.3
Azinphos-methyl	50.8	8.1	71.3	2.1
Azoxystrobin	88.5	8.8	100.9	6.0
Benalaxyl	63.3	3.7	83.7	3.2
Bendiocarb	95.7	3.9	101.5	3.1
Bensulide	95.5	5.2	116.4	4.5
Benthiavalicarb-isopropyl	93.4	4.1	101.2	6.1
Benzofenap	79.2	2.3	99.4	1.7
Bitertanol (diastereo isomers)	61.2	6.8	142.2	5.5
Boscalid	49.1	12.7	36.2	32.4
Bromacil	62.6	2.9	69.2	1.6
Bromobutide	91.8	5.3	97.1	3.6
Bromobutide-debromo	93.4	2.2	100.0	1.2
Buprofezin	67.3	5.9	75.4	3.2
Butachlor	43.4	7.7	69.4	5.7
Butafenacil	94.9	4.7	96.8	6.4
Carbaryl (NAC)	86.2	4.8	96.4	3.6
Carbofuran	91.5	4.7	97.4	4.2
3-Hydroxycarbofuran	95.1	2.9	99.0	2.0
Carpropamid	74.4	10.4	62.4	16.4
Chloridazon	69.9	4.3	70.4	3.1
Chloroxuron	89.0	11.7	90.2	10.9
Chlorpyrifos	67.2	7.9	79.8	6.6
Chromafenozide	76.4	1.7	97.1	2.3
Clofentezine	33.2	9.2	42.9	9.9
Clomeprop	38.6	8.4	57.6	6.5
Cloquintocet-mexyl	81.7	4.0	99.4	5.2
Clothianidin	70.0	3.3	77.2	2.9
Cumyluron	87.8	2.8	97.5	3.1
Cycloate	86.6	12.1	103.1	15.0
Cyenopyrafen	76.2	3.6	96.1	2.8
Cyflufenamid	65.3	7.4	76.0	6.5
Cymoxanil	65.6	10.6	69.7	25.2
Cyprodinil	93.4	10.9	99.0	9.5
Daimuron (Dymron)	94.0	1.2	99.9	1.3
Di-allate	95.3	12.3	79.5	36.2
Diethofencarb	59.3	3.0	94.1	3.4
Difenoconazole (isomer)	53.6	5.9	88.1	1.8
Diflubenzuron	43.3	9.0	61.2	8.9
Diflufenican	47.0	8.2	69.3	6.1
Dimethametryn	90.0	4.2	98.9	3.0
Dimethirimol	90.3	4.4	93.0	4.5
Dimethoate	86.4	3.6	94.7	3.1
Dimethomorph (E, Z)	76.8	6.3	90.8	5.3
Diuron (DCMU)	85.6	4.2	97.9	3.9
Epoxiconazole	56.1	15.3	81.6	4.6
Ethiprole	68.5	7.4	83.4	9.7
Etoxazole	66.3	4.6	97.4	2.7
Famoxadone	35.6	5.7	56.7	2.6
Fenamidone	65.0	4.3	72.2	4.5
Fenobucarb	88.1	2.7	94.0	4.1
Fenoxaprop-ethyl	49.9	4.5	60.5	5.7
Fenoxycarb	63.4	4.2	88.1	5.2
Fenpropimorph	88.1	4.8	95.3	3.1
Fenpyroximate (E)	65.4	3.2	92.3	3.4
Fensulfothion	90.9	0.8	96.3	3.5
Ferimzone (E)	96.2	6.3	104.2	5.3
Ferimzone (Z)	94.8	0.7	99.8	3.4
Flamprop-methyl	87.6	5.4	87.0	4.1
Flubendiamide	73.7	9.8	88.9	7.8
Fludioxonil	129.8	10.5	122.5	10.4
Flufenacet	82.7	4.3	84.1	4.3
Flufenoxuron	52.7	12.0	61.2	4.8
Fluometuron	90.5	5.6	90.4	4.0
Fluopicolide	65.2	4.7	77.1	5.5
Fluridone	94.1	3.6	99.2	3.1
Flusilazole	57.8	5.1	68.4	4.1
Flutriafol (isomer)	49.8	3.4	62.2	3.5
Furametpyr	87.5	2.8	93.9	2.3
Furathiocarb	64.8	2.3	84.5	3.2
Hexaflumuron	238.0	12.7	232.3	7.5
Hexythiazox	71.8	2.5	87.9	2.6
Imazalil	107.8	8.5	101.1	4.1
Imidacloprid	86.7	2.2	105.6	6.0
Indanofan	39.8	25.0	68.6	14.6
Indoxacarb	81.3	9.7	107.0	7.3

Compound	dSPE		ILSP	
	Recovery rate (%)	%RSD	Recovery rate (%)	%RSD
Iprovalicarb	94.4	3.1	103.2	3.0
Isouron	91.8	1.6	96.5	1.7
Isoxaflutole	106.8	15.4	105.8	30.6
Isoxathion	67.6	6.4	117.5	9.7
Kresoxim-methyl	67.8	5.9	79.1	7.6
Lactofen	99.2	4.5	119.6	3.1
Linuron	88.8	6.9	91.4	6.3
Lufenuron	221.6	14.4	184.6	27.7
Malathion	88.9	2.7	92.2	1.5
Mandipropamid	97.3	4.8	100.1	8.1
Mepanipyrim	88.4	3.4	84.5	5.9
Metalaxyl/Metalaxyl-M	92.7	2.1	100.3	3.6
Metalaxyl-M (Mefenoxam)	94.2	2.6	100.6	3.4
Metconazole	47.4	3.5	68.3	4.3
Methabenzthiazuron	86.0	2.8	93.1	3.1
Methidathion	78.6	2.7	90.6	1.9
Methiocarb	86.6	6.9	97.0	3.3
Methomyl	88.1	1.8	96.8	1.8
Methoxyfenozide	84.2	0.8	87.2	5.0
Monolinuron	87.9	3.6	93.6	3.5
Naproanilide	62.5	1.9	80.5	3.4
Novaluron	35.7	12.4	55.9	22.9
Oryzalin	81.4	28.9	80.7	39.4
Oxadiargyl	66.9	2.7	77.3	6.9
Oxamyl	93.9	2.1	101.3	1.2
Oxaziclomefone	72.1	1.2	79.0	3.6
Oxycarboxin	85.4	3.1	91.4	5.8
Paclobutrazol	50.9	2.5	75.2	3.7
Pencycuron	64.8	7.5	89.7	5.6
Penthiopyrad	84.7	2.6	93.7	2.7
Phenmedipham	122.2	5.6	131.4	1.8
Phosphamidon	97.1	4.0	93.9	2.3
Phoxim	39.2	4.8	59.6	12.5
Piperonyl-butoxide	37.7	5.5	72.1	3.2
Pirimicarb	95.1	2.5	91.9	5.9
Pirimiphos-methyl	81.0	3.9	98.4	3.1
Prochloraz	66.6	1.7	74.4	1.0
Profenofos	44.1	9.8	61.3	6.1
Prometryn	95.6	6.6	100.2	3.7
Propaquizafop	78.2	7.1	101.2	3.2
Propoxur	91.6	2.3	96.6	4.4
Pyraclofos	56.5	8.0	81.4	1.3
Pyraclonil	85.4	2.8	89.1	1.3
Pyraclostrobin	66.4	4.8	70.7	4.1
Pyrazolynate	76.9	2.0	79.7	5.2
Pyrazophos	104.2	6.9	121.0	7.1
Pyrazoxyfen	59.7	3.9	73.5	2.5
Pyributicarb	81.7	4.2	94.8	3.2
Pyridaben	79.0	2.8	98.4	2.2
Pyriftalid	78.7	5.5	97.7	4.6
Pyriminobac-methyl (E)	86.0	7.6	89.0	5.3
Quinoxyfen	56.9	3.0	58.5	7.0
Quizalofop-ethyl	76.5	5.1	80.9	5.7
Simeconazole	50.5	4.1	71.6	4.1
Spinosyn A	73.6	4.0	90.9	3.4
Spinosyn D	70.0	11.6	151.4	15.2
Spirodiclofen	59.7	7.4	101.3	3.0
Tebuconazole	50.0	4.7	73.7	4.0
Tebufenozide	86.0	2.7	92.6	3.4
Tebuthiuron	89.5	1.6	92.9	2.7
Teflubenzuron	209.3	6.1	294.5	11.2
Terbacil	116.4	9.4	147.8	11.7
Tetrachlorvinphos (CVMP)	85.7	5.1	89.0	14.3
Tetraconazole	52.3	4.2	74.8	5.7
Thiabendazole	105.1	4.5	100.4	4.8
Thiacloprid	68.0	2.2	93.1	2.7
Thiamethoxam	83.5	4.8	88.6	4.1
Thiodicarb	91.5	6.2	99.5	3.4
Tiadinil	140.9	10.8	130.8	6.9
Tolfenpyrad	85.6	3.2	76.6	4.9
Tralkoxydim	112.8	2.4	126.2	2.0
Triadimefon	75.1	5.9	98.2	8.0
Triadimenol (isomer)	24.2	8.8	87.0	5.2
Trichlamide	146.9	17.8	121.5	14.0
Tridemorph (isomer)	76.6	7.9	96.7	4.3
Trifloxystrobin	67.3	7.8	75.4	7.1
Triflumizole	91.4	3.8	95.0	3.5
Triflumizole Metabolite	93.9	4.0	96.7	3.4
Triflumuron	54.2	6.7	66.9	5.2
Triforine (isomer)	51.1	4.9	70.3	5.1
Triticonazole	42.5	6.1	64.2	3.1
XMC	91.7	3.6	97.3	1.7

■ Spike Recovery Rate and Reproducibility

A brown rice matrix solution was spiked with 164 pesticides at 2 ng/mL and purified by ILSP column or dSPE. Then recovery rates were confirmed by an external standard method. The recovery rate and reproducibility (%RSD, n=6) results are shown in Table 3. A breakdown of the number of compounds with respective recovery rate levels is shown in Fig. 7.

dSPE purification resulted in recovery rates from 70 to 120 % for 98 of the 164 compounds measured. In contrast, ILSP purification resulted in recovery rates from 70 to 120 % for 130 of the 164 compounds measured, with equivalent or better results than dSPE. %RSD values were 20 % or lower for most compounds in both cases.

Fig. 8 shows the chromatograms for prochloraz and pyridaben in the standard solution and each purification method. For dSPE purification, contaminant peaks were observed at around 8.9 to 9.2 min for procloraz and at around 10.7 min for pyridaben. On the other hand, these contaminant peaks were not observed in ILSP purification, indicating that the contaminants were removed.

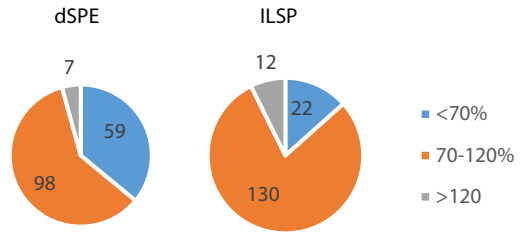

Fig. 7 Breakdown of Recovery Rate (Number of Compounds)

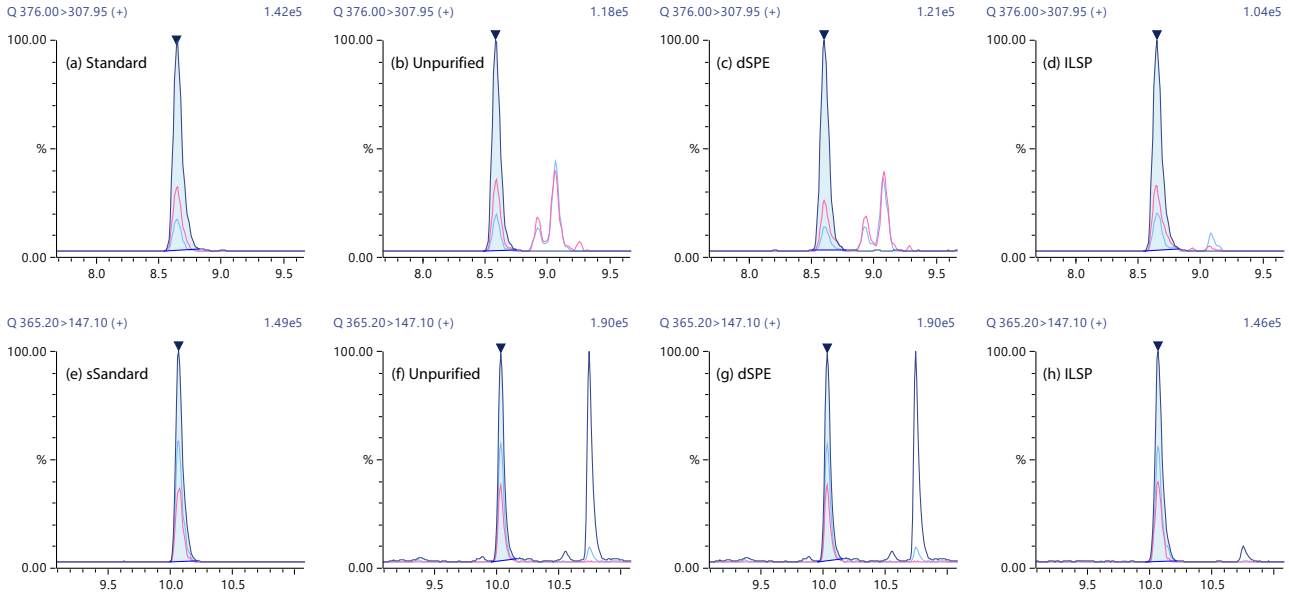

Fig. 8 Chromatograms of Prochloza (a to d) and Pyridaben (e to h)
From Acetonitrile (a, e) and Brown Rice Matrix Solutions

■ Conclusion

Simultaneous analysis of pesticides was performed using an LCMS-8050RX system. The combination of the QuEChERS method and Revive ILSP columns enabled the pretreatment process to be accelerated and simplified. On-line purification with a Revive ILSP column showed comparable recovery and reproducibility results to dSPE purification and demonstrated the ability to remove contaminants that remain with dSPE purification. Therefore, on-line purification with a Revise ILSP column could be used as a quick and simple alternative to dSPE for the QuEChERS method.

References

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Related Applications

1. Rapid Screening Analysis of On-Line Purified Residual Pesticides in Crop Extract Using Accurate Mass Information Application News 01-00547-EN

01-00744-EN First Edition: Sep. 2024

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