Analysis of Pesticide Residues in Rice by QuEChERS and LC MS/MS Detection

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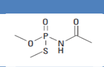
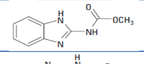
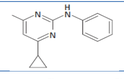
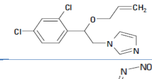
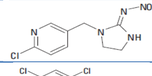
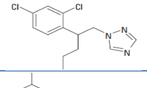
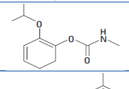
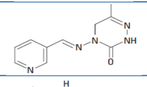
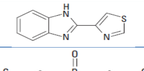
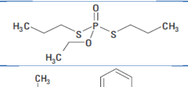
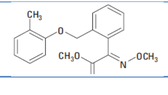
Introduction

The AOAC QuEChERS method has been widely employed in the analysis of pesticides in food. The method uses acetonitrile extraction, followed by salting out of the water from the sample using anhydrous magnesium sulfate (MgSO4), and buffering acetate salts to induce partitioning. For cleanup, a dispersive solid phase extraction (dispersive SPE) is employed using a combination of primary secondary amine (PSA) to remove organic acids from the sample matrix, and anhydrous MgSO4 to reduce the remaining water in the extract. According to different food matrices, other ingredients may be added in this step, such as graphitized carbon black (GCB) to remove pigments and sterol, or C18 to remove lipids and waxes.

The AOAC dispersive SPE kits for products with fats and waxes was selected for this application. The kit contains 50 mg of PSA, 50 mg of C18, and 150 mg MgSO4, per mL of ACN extracts. In this study, 12 pesticides were used for evaluating the performance of the Agilent Bond Elut QuEChERS AOAC buffered extraction kit and Bond Elut AOAC dispersive SPE kits for fruits and vegetables with fats and waxes. The method was validated in terms of recovery and reproducibility. Table 1 shows the chemical and regulatory information for these pesticides in rice.

Experimental

Table 1. Pesticides Chemical and Regulatory Information

Name	Class	Log P	pKa	Structure	MRLs (ng/g)
Acephate	Organophosphate	-0.89	8.35		20
Carbaryl	Carbamate	2.36	10.4		50
Carbendazim	Benzimidazole	1.48	4.2		100
Cyprodinil	Anilinopyrimidine	4	4.44		500
Imazalil	Imidazole	3.82	6.53		20
Imidacloprid	Neonicotinoid	0.57	NA		1000
Penconazole	Triazole	3.72	1.51		50
Propoxur	Carbamate	0.14	NA		2000
Pymetrozine	Pyridine	-0.19	4.06		600
Thiabendazole	Benzimidazole	2.39	4.73 12.00		50
Ethoprophos	Organophosphate	2.99	NA		5
Kresoxim-methyl	Strobilurin	3.4	NA		50

Experimental

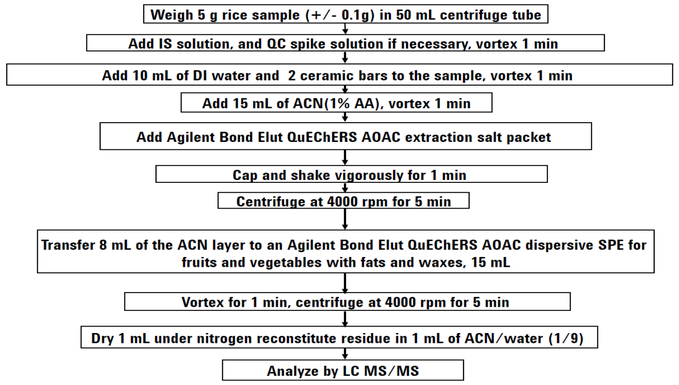


Figure 1. General Overview of QuEChERS Extraction Procedure

Experimental

LC MS/MS Conditions

Column: Agilent Poroshell 120 EC-C18, 2.7 um, 2.1 x 100 mm
Flow rate: 0.4 mL/min
Column Temperature: 30°C
Injection volume: 5 µL
Mobile Phase: A: 0.1% FA/Water; B: 0.1% FA/ACN

Gradient:

Time(min)	%B
0	5
1	5
3	50
7	90
8	90
8.2	5
9	5

MS Conditions:
Positive mode
GT: 350 °C
GF: 10 L/min
Nebulizer: 40 psi
SGT: 350 °C
SGF: 12 L/min
Capillary: 3500 V

Results

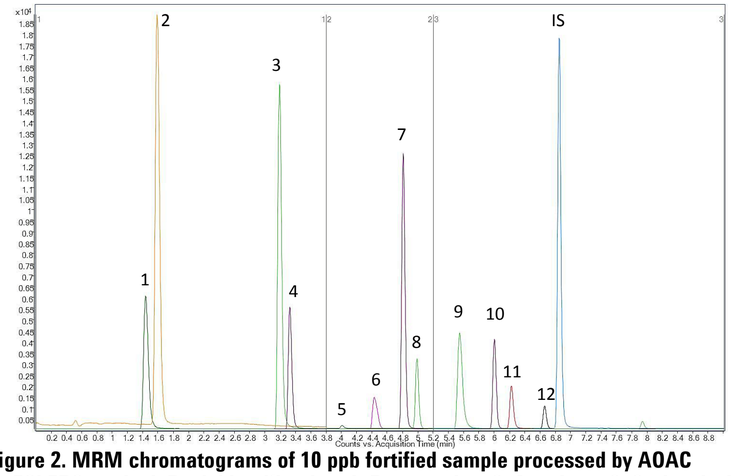


Figure 2. MRM chromatograms of 10 ppb fortified sample processed by AOAC QuEChERS method. Peak identification: 1. Pymetrozine, 2. Acephate, 3. Carbendazim, 4. Thiabendazole, 5. Imidacloprid, 6. Imazalil, 7. Propoxur, 8. Carbaryl, 9. Cyprodinil, 10. Ethoprophos, 11. Penconazole, 12. Kresoxim-methyl, IS: TPP.

Results and Discussion

Table 2. Recovery and Reproducibility of Pesticides in Fortified Rice with QuEChERS

Analytes	10 ng/g fortified QC Recovery	RSD (n=6)	50 ng/g fortified QC Recovery	RSD (n=6)	250 ng/g fortified QC Recovery	RSD (n=6)
Pymetrozine	80.3%	4.5%	76.3%	3.8%	90.1%	4.2%
Acephate	85.0%	2.3%	92.8%	3.2%	96.3%	1.9%
Carbendazim	102.3%	8.3%	99.0%	2.0%	108.2%	5.8%
Thiabendazole	94.6%	5.4%	89.4%	4.7%	83.9%	6.1%
Imidacloprid	100.5%	10.2%	105.4%	2.8%	91.7%	8.2%
Imazalil	99.2%	4.4%	92.6%	5.5%	93.8%	5.3%
Propoxur	96.7%	3.7%	103.6%	1.1%	108.2%	2.7%
Carbaryl	88.0%	5.6%	100.7%	3.0%	108.1%	3.9%
Cyprodinil	90.3%	1.9%	92.5%	8.9%	92.4%	5.1%
Ethoprophos	104.1%	3.4%	105.8%	4.8%	110.5%	6.1%
Penconazole	103.9%	2.2%	93.9%	6.9%	90.5%	3.0%
Kresoxim-methyl	107.5%	10.3%	94.7%	2.5%	100.6%	2.7%

Discussion

Due to the selectivity of the LC MS/MS, the MRM chromatogram of matrix blank did not show any interference peaks to the target analytes (not shown). Figure 2 shows the LC MS/MS chromatogram of the 10 ng/g fortified rice extract processed by the AOAC QuEChERS method.

The determined quantification limits LOQ (5 ng/g) established for all pesticides is lower than the MRLs of these pesticides in fruit and vegetables. The correlation coefficient (R^2) for the twelve pesticides ranged from 0.991-0.999.

The recovery and reproducibility were evaluated by spiking pesticides standards in comminuted samples at levels of 10, 50, and 250 ng/g. The recovery and reproducibility (shown as RSD) data are in Table 2. It can be seen from the results that 12 pesticides give excellent recoveries and precisions.

Conclusions

Agilent Bond Elut QuEChERS AOAC buffered extraction kits and dispersive SPE kits for fruits and vegetables with fats and waxes provide a simple, fast and effective method for the purification of representative pesticides in rice. The recovery and reproducibility, based on matrix spiked standards, were acceptable for multiclass, multi-residue pesticide determination in rice. The impurities and matrix effects from rice did not interfere with the quantitation for target compounds. The LOQs of the pesticides were lower than regulated MRLs in rice. As the selected pesticides represented a broad variety of different classes and properties, the Bond Elut QuEChERS AOAC extraction and dispersive SPE kits is an excellent choice for other pesticides in similar food matrices.