



Determination of Pesticides in Red Wine by QuEChERS Extraction, Quick QuEChERS Clean-up, and LC/MS/MS Detection

UCT Part Numbers:

RFV0050CT (50 mL polypropylene centrifuge tube)

ECQUUS2-MP (Mylar Pouch contains: 4000 mg MgSO₄, 2000 mg NaCl)

ECPURMPSMC (Quick QuEChERS cartridge, 110 mg MgSO₄, 180 mg PSA)

The analysis of pesticide residues in red wines is challenging due to the complexity of the matrix, which contains organic acids, sugars, phenols, and pigments, such as anthocyanins. A simple, faster, and easy to use method is developed for the determination of pesticide residues in red wines.

Eight pesticides with a wide range of polarities (LogP from -0.779 to 5.004) were selected as target analytes. Excellent accuracy and precision data were achieved using this method. Recoveries of planar pesticides, such as Carbendazim and Thiabendazole were not affected since PSA was used for clean-up instead of GCB. PSA removed organic acids, sugars and pigments from the red wine extract. Six red wine samples were extracted using this method. Cyprodinil and Carbendazim were detected in the red wine samples tested, with minimum reporting limits of 1.5 ng/mL.

Procedure

1. Extraction

- a) Add 10 mL of red wine sample to a 50 mL polypropylene centrifuge tube (**RFV0050CT**)
- b) Spike with the appropriate amount of target analytes for fortified samples
- c) Vortex 30 sec, then equilibrate for 15 min
- d) Add 10 mL of acetonitrile, vortex 30 sec
- e) Add salts in Mylar pouch (**ECQUUS2-MP**)
- f) Shake vigorously for 1 min
- g) Centrifuge at 5000 rpm for 5 min at 20° C
- h) Supernatant is ready for clean-up

2. Quick QuEChERS Clean-up

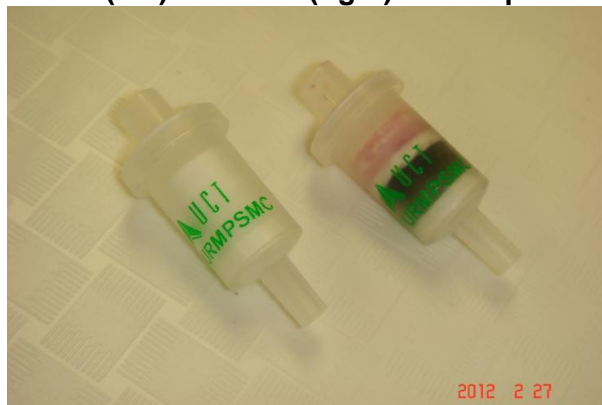
- a) Draw 1 mL of supernatant into a disposable polypropylene syringe
- b) Pass the supernatant slowly through the Quick QuEChERS cartridge (**ECPURMPSMC**)

- c) Collect 0.5 mL of the cleaned extract into a 2 mL auto-sampler vial
- d) Add 10 μL 5 ppm TPP as internal standard (IS)
- e) Samples are ready for LC/MS/MS analysis

Clean-up red wine extract with Quick QuEChERS



Quick QuEChERS before (left) and after (right) clean-up of 1 mL red wine extract



3. LC/MS/MS Detection

LC: Thermo Accela 1250 pump with PAL auto-sampler

LC Conditions

Column	Guard column: Restek C18, 2.1 x 20 mm Column: Sepax HP-C18, 2.1 x 100 mm, 3 μm , 120 \AA
Column Temperature	Ambient
Injection Volume	10 μL at 15° C
Mobile Phase	A: 0.1% formic acid in Milli-Q-water B: 0.1% formic acid in methanol
Flow Rate	200 $\mu\text{L}/\text{min}$

LC Gradient Program

Time	%A	%B
0	95	5
1	95	5
3	50	50
8	5	95
14.2	95	5
16	95	5

MS/MS: Thermo TSQ Vantage tandem MS

MS Conditions

Ion source:	Heated ESI
Ion polarity:	ESI +
Spray voltage:	3000 V
Sheath gas pressure:	N ₂ @ 40 psi
Auxiliary gas pressure:	N ₂ @ 10 psi
Ion transfer capillary temperature:	350 °C
Scan type:	SRM (0-16 min)
CID conditions:	Ar @ 1.5 mTorr

SRM transitions

Compound	Parent	Product ion 1	CE	Product ion 2	CE	S-Lens	Dwell time (s)
Methamidophos	142.044	94.090	14	125.050	16	59	0.15
Carbendazim	192.093	132.080	29	160.080	17	81	0.10
Thiabendazole	202.059	131.060	31	175.070	31	103	0.10
Pyrimethanil	200.116	107.060	23	183.140	22	66	0.10
Cyprodinil	226.122	77.030	40	93.050	33	88	0.10

TPP (IS)	327.093	77.020	37	152.070	33	98	0.10
Diazinon	305.135	153.090	15	169.08	14	89	0.10
Pyrazophos	374.103	194.060	20	222.130	20	104	0.10
Chlorpyrifos	349.989	96.890	32	197.940	17	69	0.10

Matrix matched calibration, LOD and LOQ

Compound	Linearity range (ng/mL)	R ²	LOD (ng/mL)	LOQ (ng/mL)
Methamidophos	2-400	0.9991	0.15	0.49
Carbendazim	2-400	0.9981	0.40	1.33
Thiabendazole	2-400	0.9940	0.09	0.31
Pyrimethanil	2-400	0.9990	0.01	0.05
Cyprodinil	2-400	0.9995	0.17	0.57
Diazinon	2-400	0.9982	0.06	0.21
Pyrazophos	2-400	0.9976	0.08	0.27
Chlorpyrifos	2-400	0.9981	0.10	0.32

Accuracy and Precision Data

Compound	Fortified at 10 ng/mL		Fortified at 50 ng/mL		Fortified at 100 ng/mL	
	Recovery%	RSD% (n=4)	Recovery%	RSD% (n=4)	Recovery%	RSD% (n=4)
Methamidophos	93.7	3.4	81.6	5.8	84.2	3.5
Carbendazim	105.7	10.8	100.1	10.6	90.5	7.6
Thiabendazole	91.2	4.9	87.9	6.8	85.0	4.0
Pyrimethanil	112.2	2.7	107.0	3.2	102.8	4.9
Cyprodinil	104.3	3.2	99.9	6.1	100.2	4.9
Diazinon	104.9	5.6	102.0	6.6	99.2	6.8
Pyrazophos	99.9	4.0	96.6	5.6	91.3	4.1
Chlorpyrifos	91.7	4.6	99.5	5.2	97.2	3.8

Pesticides detected in red wine samples (ng/mL)

Pesticide	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Methamidophos	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Carbendazim	< 1.5	< 1.5	< 1.5	10.2	8.7	2.3
Thiabendazole	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Pyrimethanil	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Cyprodinil	1.7	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Diazinon	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Pyrazophos	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Chlorpyrifos	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5