QuEChERS Multiresidue Pesticide Method for The Determination of Multiple Pesticides in Wines*

Part Number:
ECQUVIN50CT (50 mL centrifuge tube, 8 grams anhydrous $MgSO_4$ & 2 grams NaCl)
ECMPSCB15CT (900 mg anhydrous $MgSO_4$, 300 mg PSA &150 mg GCB)
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This summary describes a multiresidue pesticide method for the determination of 72 pesticides in wines. Pesticides are extracted using acetonitrile saturated with magnesium sulfate and sodium chloride followed by a dispersive solid-phase cleanup with primary-secondary amine (PSA) and graphitized carbon black (GCB) sorbents. Analysis is performed using ultraperformance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) in ESI mode.

1. Sample Preparation

a) Add 20 mL acetonitrile (ACN) and internal standard fluconazole (250µL) to **ECQUVIN50CT**
b) Quantitatively add 20.0 mL of wine
c) Shake for approximately 2 minutes
d) Centrifuge at 4500 rpm for 5 minutes (use refrigerated centrifuge if available)
e) Transfer 9.0 mL of top layer and add to **ECMPSCB15CT** (900 mg anhydrous $MgSO_4$, 300 mg PSA &150 mg GCB)
f) Vortex tube for approximately 10 seconds
g) Open tube and add 3.0 mL of toluene and shake for 1 minute
h) Centrifuge the tube for 5 minutes @ 4500 rpm
i) Quantitatively transfer 2.0 mL of supernatant to a glass centrifuge tube
j) Evaporate to dryness at < 40 ˚C using N_2
k) Add 500 µL of acetonitrile 25 µL of benzanilide (2.0 µg/L) surrogate standard for QC and 500 µL of 20 mM ammonium acetate in 1% acetonitrile to the dried extract
l) Vortex for approximately 5 seconds and filter into autosampler vial using 17mm, 0.2 µm nylon membrane cartridges attached to a disposable syringe

2. UPLC/MS/MS Analysis

UPLC Conditions:

Column: Water's Acquity UPLC BEH C_{18} column 100 x 2.1 mm, 1.7 µm particle or equivalent

Flowrate: 0.2 mL/minute

Injection volume: 3 µL

Analytical Standards: Matrix Matched

Gradient Program:

Time	% Acetonitrile	% 10mM Ammonium Acetate
0	10	90
10	90	10
14.5	90	10
14.6	10	90
20.1	10	90

Triple Quadrupole MS Conditions--electrospray ionization mode (ESI)

Capillary Voltage: 1.5 kV

Source Temperature: 120 °C

N_2 Flow: cone 50 L/h, desolvation 800 L/h

Collision Gas: Argon

Dwell Time: 10 µS for multiple reaction monitoring (MRM) experiments

Collision Cell Pressure: 5.9 x 10^{-3} mbar

Summary of MS/MS Conditions

Pesticide	Molecular Weight	CV (V)	Quantification Transition
Acephate	183.17	20	184.0→143.0
Acetamiprid	222.67	30	223.4→126.1
Acibenzolar S-methyl	210.27	35	211.1→136.0
Aldicarb	190.27	12	208.1→116.0
Aldicarb sulfone	222.27	15	240.0→222.9
Aldicarb sulfoxide	206.26	15	224.2→206.9
Atrazine	215.69	35	215.9→173.85
Avermectin B_{1b}	873.09	20	876.6→553.4
Avermectin B_{1a}	873.09	20	890.7→567.5
Azoxystrobin	403.30	25	404.0→372.1
Benalaxyl	325.41	26	326.1→148.1
Benfuracarb	410.53	20	411.2→190.0
Benzanilide	197.24	30	198.1→105.1
Bifenazate	300.35	20	301.3→170.2
Bitertanol	337.42	20	338.2→ 99.1
Buprofezin	305.44	25	306.3→201.2
Carbaryl	201.22	22	202.1→145.1
Carbendazim	191.19	30	192.0→160.0
Carbofuran	221.26	26	222.1→123.1
Chloroxuron	290.75	35	291.0→ 72.2
Cyprodinil	225.29	45	226.1→ 93.0
Cyromazine	166.19	25	167.2→ 85.1
Diclobutrazol	328.24	30	328.1→70.2
Dimethoate	229.26	20	230.1→199.0
Dimethomorph	387.86	35	388.0→301.1
Dimoxystrobin	326.39	20	327.1→206
Dinotefuran	202.20	20	203.5→14.0
Diuron	233.10	30	233.0→72.1
Ethofumesate	286.35	30	286.9→258.9
Famoxadone	374.39	-32	373.2→ 282
Fenamidone	311.40	25	312.2→236.2
Fenbuconazole	336.82	35	337.1→125.0
Fenhexamid	302.20	65	301.9→261.9
Fenpropimorph	304.49	40	304.4→147.1
Fluconazole	306.27	30	307.2→220
Fludioxinil	248.19	-45	247.0→180.0
Furathiocarb	382.48	30	383.2→195.1
Hexaconazole	314.21	35	314.0→ 70.2
Imazalil	297.18	35	297.1→159.0
Imidacloprid	255.65	25	256.1→175.0
Ipconazole	333.86	35	334.1→70.2
Iprovalicarb	320.43	24	321.2→119.0
Kresoxim-methyl	313.35	20	314.1→116.0
Mepanipyrim	223.28	30	224.4→ 77.3
Metalaxyl	279.34	25	280.1→220.1
Methamidophos	141.13	22	142.0→ 94.0
Methomyl	162.21	20	163.0→ 88.0

Methoxyfenozide	368.47	15	369.5→149.0
Mevinphos	224.15	22	225.1→192.8
Myclobutanil	288.78	35	289.1→ 70.2
Omethoate	213.14	20	214.1→183.0
Oxadixyl	278.31	20	279.1→219.1
Piperonyl butoxide	338.45	17	356.2→177.0
Prochloraz	376.67	20	376.1→308.0
Propamocarb	188.27	30	189.1→102.1
Propargite	350.48	20	368.1→231.0
Propiconazole	342.22	35	342.0→159.0
Propoxur	209.24	20	210.0→111.0
Pyraclostrobin	387.83	23	388.0→194.0
Pyridaben	364.94	22	365.3→309.1
Pyrimethanil	199.25	40	200.1→107.0
Quinoxyfen	308.14	50	307.8→196.8
Rotenone	394.42	40	395.3→213.2
Simazine	201.66	30	202.2→131.4
Spinosyn A	731.97	40	732.6→142.2
Spinosyn D	746.00	30	746.6→142.2
Spiroxamine	297.48	30	298.2→144.0
Tebuconazole	307.82	30	308.2→ 70.2
Thiabendazole	201.25	35	202.0→175.0
Triadmimefon	293.75	30	294.0→197.1
Trifloxystrobin	408.38	25	409.0→186.0
Triflumizole	345.75	20	346.0→278.1
Vamidothion	287.34	20	288.1→146.0
Zoxamide	336.54	35	336.0→187.0

Schematic Diagram of Sample Preparation Steps

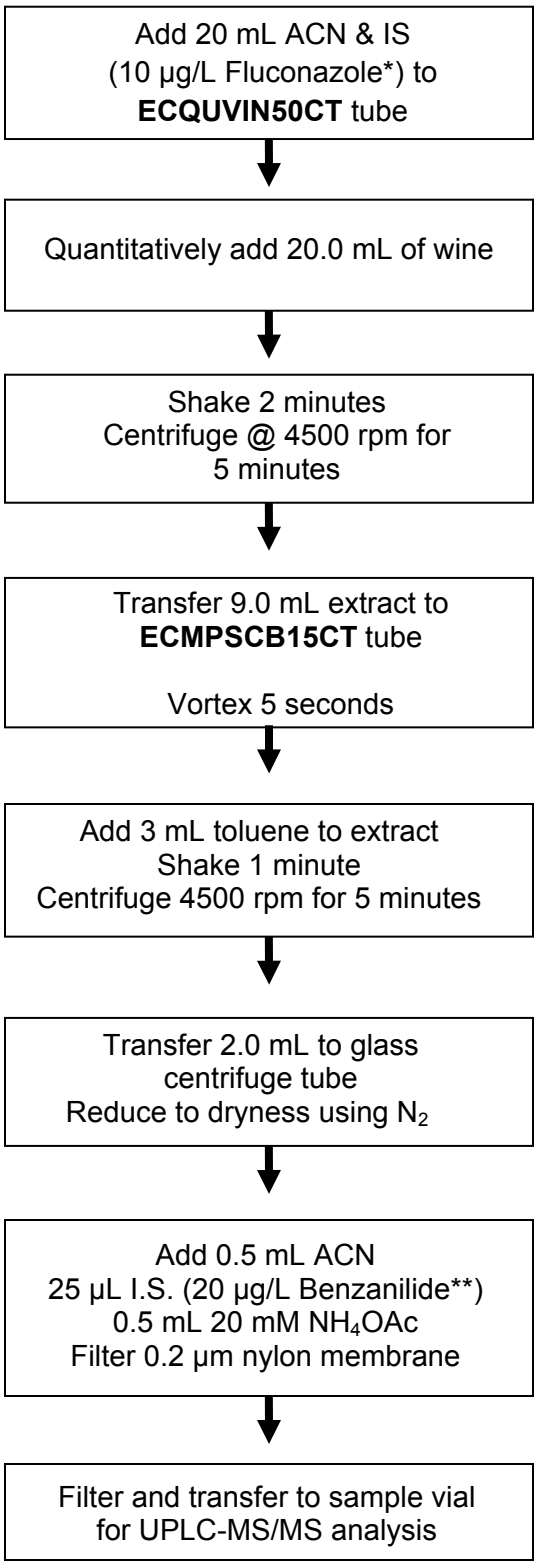

Table of Average Pesticide Recoveries at 100 g/L Spike

(average values with SD, n=4)

	Pesticide Recovery	
	Red Wine @ 100 µg/L	**White Wine @ 100 µg/L**
Acephate	84±4	79±3
Acetamiprid	83±8	97±7
Acibenzolar S-methyl	80±15	45±5
Aldicarb	92±5	82±5
Aldicarb sulfone	91±7	83±4
Aldicarb sulfoxide	83±8	80±1
Atrazine	92±5	83±5
Avermectin B_{1b}	94±12	107±13
Avermectin B_{1a}	82±8	80±6
Azoxystrobin	93±5	86±4
Benalaxyl	92±5	84±4
Benfuracarb	ND	ND
Benzanilide	69±7	70±8
Bifenazate	86±4	86±11
Bitertanol	92±5	86±4
Buprofezin	91±4	88±6
Carbaryl	77±4	76±4
Carbendazim	126±7	106±7
Carbofuran	90±4	86±4
Chloroxuron	75±5	72±2
Cyprodinil	38±2	56±5
Cyromazine	89±6	83±5
Diclobutrazol	89±6	82±4
Dimethoate	88±7	84±4
Dimethomorph	95±5	85±4
Dimoxystrobin	85±5	74±6
Dinotefuran	88±4	78±5
Diuron	74±12	90±1
Ethofumesate	92±10	95±14
Famoxadone	87±3	86±5
Fenamidone	88±5	80±5
Fenbuconazole	133±21	90±11
Fenhexamid	91±5	83±4
Fenpropimorph	86±6	84±4
Fluconazole	112±4	101±2
Fludioxinil	91±2	87±8
Furathiocarb	81±4	77±4
Hexaconazole	90±2	77±7
Imazalil	89±5	83±5
Imidacloprid	94±6	87±4
Ipconazole	89±5	83±5
Iprovalicarb	94±6	87±4
Kresoxim-methyl	85±5	86±5
Mepanipyrim	76±6	94±12
Metalaxyl	94±5	85±5
Methamidophos	82±6	74±5
Methomyl	90±4	81±4

Methoxyfenozide	102±5	89±5
Mevinphos	84±5	71±4
Myclobutanil	96±8	90±4
Omethoate	82±4	75±4
Oxadixyl	94±3	88±4
Piperonyl butoxide	94±5	87±4
Prochloraz	84±3	84±5
Propamocarb	80±3	80±5
Propargite	93±6	86±2
Propiconazole	94±4	86±5
Propoxur	89±5	82±4
Pyraclostrobin	77±6	76±4
Pyridaben	85±4	83±4
Pyrimethanil	79±6	75±4
Quinoxyfen	70±5	68±3
Rotenone	81±3	85±9
Simazine	85±9	88±7
Spinosyn A	88±7	83±4
Spinosyn D	87±4	80±3
Spiroxamine	92±5	84±4
Tebuconazole	90±4	83±5
Thiabendazole	71±3	75±5
Triadmimefon	89±8	84±7
Trifloxystrobin	90±8	84±4
Triflumizole	88±6	86±3
Vamidothion	86±4	83±6
Zoxamide	86±4	80±4

*Adapted from Kai Zhang, Jon W. Wong et al, Multiresidue Pesticide Analysis of Wines by Dispersive Solid-phase Extraction and Ultra-High Performance Liquid Chromatography-Tandem Mass Spectrometry *Journal of Agricultural and Food Chemistry*

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