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Multiresidue Pesticide Analysis of Wines by Dispersive Solid-Phase Extraction and Ultrahigh-Performance Liquid Chromatography−Tandem Mass Spectrometry

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A multiresidue pesticide method is described for the determination of 72 pesticides in wines. Pesticides were extracted using acetonitrile saturated with magnesium sulfate and sodium chloride, followed by solid-phase dispersive cleanup using primary−secondary amine and graphitized carbon black sorbents. Analysis is performed by ultraperformance liquid chromatography−electrospray ionization−tandem mass spectrometry (UPLC-MS/MS). The limits of quantitation (LOQs) for most of the pesticides ranged from 0.3 to 3.3 μg/L with the exception of cyromazine, fenhexamid, and acibenzolar *S*-methyl (LOQ > 10 μg/L), and quantitation was determined from calibration curves of standards containing 5.0−2500 μg/L with $r^2 > 0.99$. Recovery studies were performed by fortifying wine samples with the pesticides to concentrations of 10, 100, and 1000 μg/L, resulting in recoveries of >80% for most of the pesticides. Lower (<70%) and higher (>120%) recoveries were most likely from complications of pesticide lability or volatility, matrix interference, or inefficient desorption from the solid-phase sorbents. The method was used to analyze 10 wines collected from a market basket survey, and 19 different pesticides, primarily fungicides, were present at concentrations ranging from <1.0 to 1000 μg/L.

KEYWORDS: Multiresidue pesticide analysis; wines; UPLC-MS/MS

INTRODUCTION

Wine is an important agricultural and food commodity, resulting in sales in the United States of an estimated 745 million gallons for a total retail value of $30 billion dollars in 2007 (*1*). To prevent economic losses of this commodity, pesticides may be used against pests such as insects and molds that damage the wine grapes and vines. Despite the usefulness of pesticides in agricultural practices, there are concerns about their excessive use, presence, and levels in foods and beverages. Although conventionally grown grapes are treated with pesticides, most of the pesticides are degraded during the wine process, but residual levels remain (*2*, *3*). Therefore, it is important to identify the residues present and determine their concentrations in conventional and organic (pesticide-free) wines.

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There are analytical methods to screen for pesticides in wines, malt beverages, and fruit juices (*4*−*22*). These methods usually involve organic extraction of the pesticides from the liquid, and sometimes a cleanup procedure is used to remove coextractives and interfering components from the matrix, followed by subsequent instrumental analysis such as capillary gas chromatography (GC) (*4*−*14*) or high-performance liquid chromatography (HPLC) (*15*−*22*). At the U.S. Alcohol and Tobacco Tax and Trade Bureau, a multiresidue method using gas chromatography−mass spectrometry in selective ion monitoring mode (GC-MS/SIM) was developed to analyze 153 pesticides in domestic and foreign wines (*11*) and malt beverages (*12*). The procedure utilizes solid-phase extraction (SPE) involving a polymer sorbent to extract the pesticides from the wine, a cleanup step using aminopropyl SPE solid-phase extraction, and analysis using GC-MS/SIM. However, many pesticides that are thermally unstable or nonvolatile are difficult, if not impossible, to analyze using GC and GC-MS. HPLC coupled to tandem mass spectrometry

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(HPLC-MS/MS) is a technique that can analyze these types of pesticides in foods and beverages because it can provide sufficient sensitivity, identification, and quantitation at trace levels at ambient conditions.

A recent advance in chromatographic separations is ultraperformance (or ultrahigh-performance) liquid chromatography (UPLC, UHPLC), which uses columns containing particles of diamter of $< 2\ \mu$m and fluidic systems that operate at higher back pressures, resulting in faster analysis times and increases in peak resolution, capacity, and sensitivity (*23*). In addition, the equilibration times of the UPLC columns after chromatographic runs are significantly reduced compared to HPLC columns, which increase and improve sample throughput and optimization of the analysis.

This work is inspired by Fillion et al. (*24*), and the QuEChERS (*Qu*ick, *E*asy, *Ch*eap, *E*ffective, *R*ugged, and *S*afe) procedure developed by Anastassiades et al. (*25*) by using salt-out organic solvent extraction and sorbent cleanup of the resulting organic extracts. The Agriculture and Agri-Food Canada method developed by Fillion et al. has been commonly used and modified by others by using salt-out acetonitrile extraction, followed by SPE cleanup using a weak cation exchange/charcoal-based tandem cartridge and analysis by GC-MS/SIM and HPLC (*18*, *26*, *27*). A benefit of the QuEChERS method is that it can be used to generate extracts that are compatible with both GC-MS and HPLC-MS/MS analyses (*28*). In this work, we propose a multiresidue pesticide procedure for wines utilizing salt-out acetonitrile extraction using magnesium sulfate and sodium chloride and solid-phase dispersive cleanup using primary−secondary amine (PSA) and graphitized carbon black (GCB) sorbents and toluene, followed by analysis using ultraperformance liquid chromatography−tandem mass spectrometry (UPLC-MS/MS).

MATERIALS AND METHODS

Materials and Standards Preparation. The majority of pesticide standards were obtained from the U.S. Environmental Protection Agency (U.S. EPA) National Pesticide Standard Repository (Ft. Meade, MD). Other pesticides were purchased from Fluka Chemicals (Milwaukee, WI) or Chem Service Inc. (West Chester, PA). Pesticide-grade acetonitrile, toluene, HPLC-grade water, and certified-grade anhydrous magnesium sulfate and sodium chloride were purchased from Fisher Scientific (Pittsburgh, PA). Internal and quality control standards, fluconazole and benzanilide, were purchased from Aldrich Chemical Corp. (Milwaukee, WI) and ChemService. PSA and GCB sorbents were purchased from United Chemical Technologies (Bristol, PA) and Supelco Co. (Bellefonte, PA), respectively. Pesticide-free and conventional red and white wines were purchased from commercially available sources through the Alcohol and Tobacco Tax and Trade Bureau's market basket program.

Stock solutions of individual pesticide standards were prepared by dissolving 25−50 mg of pesticides in 25 mL of acetonitrile for calibration and fortification standards. The working standards used for quantitation were prepared by mixing 2−5 mL of each standard using a 250 mL volumetric flask to prepare a 20 μg/mL working standard. The lower fortification solutions were prepared in acetonitrile by dilution of the 20 μg/mL working standard into 2.0 and 0.2 μg/mL prepared in acetonitrile. Successive dilutions of the stock pesticide standards were used to prepare 10, 5.0, 2.5, 1.0, 0.5, 0.25, 0.10, 0.05, 0.025, 0.010, 0.005, 0.0025, and 0.001 μg/mL standards in acetonitrile (each 50 mL standards). The internal and quality control standards were prepared by dissolving fluconazole and benzanilide to make 10 and 50 μg/mL working solutions, respectively.

Sample Preparation. A schematic of the extraction and cleanup procedure is shown in **Figure 1**. Wine (20 mL) was quantitatively transferred into a polypropylene screw-capped centrifuge tube. Acetonitrile (20 mL) and the internal standard, fluconazole (250 μL, 10 μg/mL), were added to the centrifuge tube containing the wine and vigorously

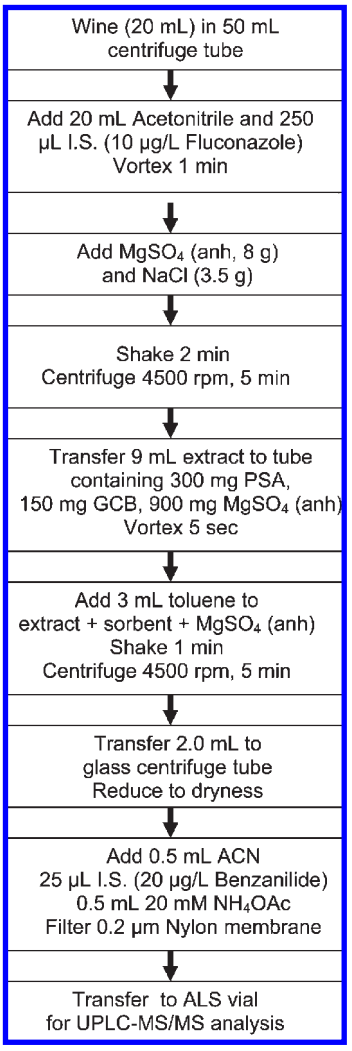

Figure 1. Schematic multiresidue procedure to analyze pesticides in wines.

vortexed for 10−15 s. Magnesium sulfate (8.0 g) and sodium chloride (3.5 g) were slowly added to the wine/acetonitrile mixture, which was shaken for 1 min. The sample was centrifuged at 4500 (4300 rcf) for 5 min using a centrifuge (ThermoElectron Corp., Milford, MA). Nine milliliters of the organic top layer was transferred to a centrifuge tube containing 300 mg of PSA sorbent, 150 mg of GCB, and 900 mg of anhydrous magnesium sulfate (United Chemical Technologies), followed by vortexing the test tube for 5−10 s. Toluene (3.0 mL) was added to the test tube, and the test tube was shaken for 1 min. The tube was centrifuged at 4500 rpm (4300 rcf) for 5 min. The extract (2.0 mL) was quantitatively transferred to a glass centrifuge tube and was reduced to complete dryness using a gentle nitrogen stream and a nitrogen evaporator (N-Evap, Organomation Associates, Berlin, MA). Five hundred microliters of acetonitrile, 25 μL of benzanilide solution as a quality control standard (20 μg/mL), and 500 μL of 20 mM ammonium acetate in 1% acetonitrile were added to the dried extract. The tube was vortexed and filtered into autosampler vials using a 17 mm, 0.2 μm nylon membrane (Sun SRI, Rockwood, TN) attached to a 3 mL luer-lock plastic disposable syringe (National Scientific, Rockwood, TN).

UPLC-MS/MS Analysis. Analyses were performed with a Waters ACQUITY UPLC system (Waters, Milford, MA) consisting of an ACQUITY UPLC binary solvent manager and an ACQUITY UPLC sample manager. Chromatographic separation was performed using an ACQUITY UPLC BEH C_{18} column (100 × 2.1 mm i.d., 1.7 μm particle size) attached to an in-line mobile phase filter. The flow rate was set at 0.2 mL/min. The gradient program used consisted of 10% acetontrile in 10 mM ammonium acetate ramped linearly over the course of 10 min to 90% acetonitrile in 10 mM ammonium acetate. This composition was held

for a further 4.5 min before returning to the initial condition. The column was re-equilibrated for 3.5 min at the initial mobile phase composition. The total run time was 18 min. The injection volume was 3 μL.

The UPLC was connected to a Quattro Premier XE triple-quadrupole mass spectrometer (Waters), equipped with an electrospray ionization interface with polarity switching mode. The capillary voltage was set at 1.5 kV and the source temperature at 120 °C with nitrogen flow rates of 50 and 800 L/h for the cone and desolvation gases, respectively. The multiple reaction monitoring experiments were conducted with a dwell time of 10 ms. Argon was used as the collision gas, and the pressure in the collision cell was set at 5.0×10^{-3} mbar (0.35 mL/min). Optimization of the cone voltages and collision energy (CE) for the individual pesticides was achieved by infusing the pesticides with the LC mobile phase using a syringe pump at 10 μL/min. Using the infusing procedure resulted in a method that screens for 72 pesticides, the internal and quality control standards using two ion transitions for most compounds (**Table 1**; **Figure 2**). MassLynx software, version 4.1, was used for instrument control and data acquisition and processing.

Fortification Studies. For fortification studies, 20 mL of wine was fortified with 250 μL of the internal standard solution and 1.0 mL of the appropriate fortification solution (0.2, 2.0, or 20 μg/mL standards prepared in acetonitrile) to a final concentration of 10, 100, or 1000 μg/L, respectively, and the centrifuge tube was vigorously vortexed to distribute the pesticides. Quantitation was performed by using the peak area ratio responses of the analyte to that of the internal standard, fluconazole, and calculating the concentration by preparing a calibration

Table 1. Experimental Parameters (Pesticide Name, Molecular Formula, and Weight) and UPLC-MS/MS Conditions of the Analytes Studied[a]

no.	pesticide	mol formula	mol wt	RT (min)	CV (V)	quantification ion transition	CE 1 (eV)	confirmatory ion transition	CE 2 (eV)	MRM group
1	acephate	$C_4H_{10}NO_3PS$	183.17	2.14	20	184.0→143.0	15	184.0→ 95.0	25	1
2	acetamiprid	$C_{10}H_{11}N_3ClN_4$	222.67	5.79	30	223.4→126.1	20	223.4→ 56.1	20	3
3	acibenzolar *S*-methyl	$C_8H_6N_2OS_2$	210.27	9.44	35	211.1→136.0	25	211.1→140.0	25	8
4	aldicarb	$C_7H_{14}N_2O_2S$	190.27	6.57	12	208.1→116.0	10	208.1→ 89.0	15	4
5	aldicarb sulfone	$C_7H_{14}N_2O_4S$	222.27	4.17	15	240.0→222.9	8	240.0→147.8	15	2
6	aldicarb sulfoxide	$C_7H_{14}N_2O_3S$	206.26	3.06	15	224.2→206.9	7	224.2→131.7	10	2
7	atrazine	$C_8H_{14}ClN_5$	215.69	7.82	35	215.9→173.85	18	215.9→ 96.0	25	5
8	avermectin B_{1b}	$C_{48}H_{70}O_{14}$	873.09	12.42	20	876.6→553.4	15			12
9	avermectin B_{1a}	$C_{48}H_{72}O_{14}$	873.09	13.15	20	890.7→567.5	15	890.7→305.4	30	12
10	azoxystrobin	$C_{21}H_{17}N3O_5$	403.30	9.31	25	404.0→372.1	15	404.0→344.1	25	6
11	benalaxyl	$C_{20}H_{23}NO_3$	325.41	10.64	26	326.1→148.1	20	326.1→208.1	15	9
12	benfuracarb	$C_{20}H_{30}N_2O_5S$	410.53	11.98	20	411.2→190.0	15	411.2→252.0	15	10
QC	benzanilide	$C_{13}H_{11}NO$	197.24	8.16	30	198.1→105.1	20	198.1→77	30	5
13	bifenazate	$C_{17}H_{20}N_2O_3$	300.35	9.76	20	301.3→170.2	25	301.3→152.1	40	8
14	bitertanol	$C_{20}H_{23}N_3O_2$	337.42	9.82	20	338.2→ 99.1	15	338.2→269.2	10	8
15	buprofezin	$C_{16}H_{23}N_3OS$	305.44	12.73	25	306.3→201.2	15	306.3→116.1	15	12
16	carbaryl	$C_{12}H_{11}NO_2$	201.22	7.84	22	202.1→145.1	15	202.1→127.0	25	5
17	carbendazim	$C_9H_9N_3O_2$	191.19	5.43	30	192.0→160.0	15	192.0→132.0	30	3
18	carbofuran	$C_{12}H_{15}NO_3$	221.26	7.52	26	222.1→123.1	20	222.1→165.0	15	4
19	chloroxuron	$C_{15}H_{15}ClNO_2$	290.75	9.14	35	291.0→ 72.2	20	291.0→ 46.2	20	6
20	cyprodinil	$C_{14}H_{15}N_3$	225.29	10.43	45	226.1→ 93.0	35	226.1→108.1	30	9
21	cyromazine	$C_6H_{10}N_6$	166.19	2.21	25	167.2→ 85.1	20	167.2→125.1	20	1
22	diclobutrazol	$C_{15}H_{19}C_{l2}N_3O$	328.24	9.60	30	328.1→70.2	20	328.1→159	40	9
23	dimethoate	$C_5H_{12}NO_3PS_2$	229.26	5.72	20	230.1→199.0	10	230.1→170.9	15	3
24	dimethomorph	$C_{21}H_{22}ClNO_4$	387.86	8.65	35	388.0→301.1	20	388.0→165.0	35	6
25	dimoxystrobin	$C_{19}H_{22}N_2O_3$	326.39	10.08	20	327.1→206	10	327.1→116	20	9
26	dinotefuran	$C_7H_{14}N_4O_3$	202.20	3.47	20	203.5→14.0	15	203.5→129.0	15	2
27	diuron	$C_9H_{10}Cl_2N_2O$	233.10	8.01	30	233.0→72.1	20	233.0→46.3	20	5
28	ethofumesate	$C_{13}H_{18}O_5S$	286.35	9.80	30	286.9→258.9	10	286.9→120.9	20	8
29	famoxadone	$C_{22}H_{18}N_2O_4$	374.39	10.86	−32	373.2→ 282	−20	373.2→322.1	−20	11
30	fenamidone	$C_{17}H_{17}N_3OS$	311.40	9.39	25	312.2→236.2	15	312.2→264.2	10	6
31	fenbuconazole	$C_{19}H_{17}ClN_4$	336.82	9.80	35	337.1→125.0	35			8
32	fenhexamid	$C_{14}H_{17}Cl_2NO_2$	302.20	7.93	65	301.9→261.9	20	301.9→281.9	15	5
33	fenpropimorph	$C_{20}H_{33}NO$	304.49	14.11	40	304.4→147.1	30	304.4→130.1	25	12
IS	fluconazole	$C_{13}H_{12}F_2N_6O$	306.27	5.04	30	307.2→220	18	307.2→238	18	3
34	fludioxinil	$C_{12}H_6F_2N_2O_2$	248.19	9.18	−45	247.0→180.0	−30	247.0→126.0	−30	7
35	furathiocarb	$C_{18}H_{26}N_2O_5S$	382.48	12.07	30	383.2→195.1	20	383.2→252.2	15	10
36	hexaconazole	$C_{14}H_{17}Cl_2N_3O$	314.21	9.91	35	314.0→ 70.2	20			9
37	imazalil	$C_{14}H_{14}Cl_2N_2O$	297.18	9.63	35	297.1→159.0	25	297.1→ 69.2	25	8
38	imidacloprid	$C_9H_{10}ClN_5O_2$	255.65	5.54	25	256.1→175.0	20	256.1→209.0	20	3
39	ipconazole	$C_{18}H_{24}ClN_3O$	333.86	10.62	35	334.1→70.2	20	334.1→125	36	9
40	iprovalicarb	$C_{18}H_{28}N_2O_3$	320.43	9.07	24	321.2→119.0	15	321.2→203.1	10	6
41	kresoxim:methyl	$C_{18}H_{19}NO_4$	313.35	10.52	20	314.1→116.0	20	314.1→131.0	20	9
42	mepanipyrim	$C_{14}H_{13}N_3$	223.28	9.84	30	224.4→ 77.3	35	224.4→106.2	35	8
43	metalaxyl	$C_{15}H_{21}NO_4$	279.34	7.93	25	280.1→220.1	15	280.1→192.1	20	5
44	methamidophos	$C_2H_8NO_2PS$	141.13	1.90	22	142.0→ 94.0	15	142.0→124.9	15	1
45	methomyl	$C_5H_{10}N_2O_2S$	162.21	4.38	20	163.0→ 88.0	10	163.0→106.0	10	2
46	methoxyfenozide	$C_{22}H_{28}N_2O_3$	368.47	9.67	15	369.5→149.0	20	369.5→313.4	10	8
47	mevinphos	$C_7H_{13}O_6P$	224.15	5.93	22	225.1→192.8	10	225.1→126.8	15	3
48	myclobutanil	$C_{15}H_{17}ClN_4$	288.78	9.36	35	289.1→ 70.2	15	289.1→125.0	30	8
49	omethoate	$C_5H_{12}NO_4PS$	213.14	2.54	20	214.1→183.0	10	214.1→155.0	15	1
50	oxadixyl	$C_{14}H_{18}N_2O_4$	278.31	6.86	20	279.1→219.1	10	279.1→132.0	25	4
51	piperonyl butoxide	$C_{19}H_{30}O_5$	338.45	11.97	17	356.2→177.0	15	356.2→119.0	35	10

Table 1. Continued

no.	pesticide	mol formula	mol wt	RT (min)	CV (V)	quantification ion transition	CE 1 (eV)	confirmatory ion transition	CE 2 (eV)	MRM group
52	prochloraz	$C_{15}H_{16}Cl_3N_3O_2$	376.67	10.21	20	376.1→308.0	15	376.1→ 70.2	25	9
53	propamocarb	$C_9H_{20}N_2O_2$	188.27	3.90	30	189.1→102.1	20	189.1→144.1	15	2
54	propargite	$C_{19}H_{26}O_4S$	350.48	12.73	20	368.1→231.0	10	368.1→174.9	15	12
55	propiconazole	$C_{15}H_{17}Cl_2N_3O_2$	342.22	10.16	35	342.0→159.0	25	342.0→ 69.2	20	9
56	propoxur	$C_{11}H_{15}NO_3$	209.24	7.41	20	210.0→111.0	15	210.0→168.0	10	4
57	pyraclostrobin	$C_{19}H_{18}ClN_2O_4$	387.83	10.98	23	388.0→194.0	15	388.0→163.0	25	10
58	pyridaben	$C_{19}H_{25}ClN_2OS$	364.94	13.22	22	365.3→309.1	15	365.3→147.1	25	12
59	pyrimethanil	$C_{12}H_{13}N_3$	199.25	9.03	40	200.1→107.0	25	200.1→ 82.1	25	6
60	quinoxyfen	$C_{15}H_8Cl_2FNO$	308.14	12.00	50	307.8→196.8	35	307.8→161.9	45	10
61	rotenone	$C_{23}H_{22}O_6$	394.42	10.04	40	395.3→213.2	25	395.3→192.1	25	9
62	simazine	$C_7H_{12}ClN_5$	201.66	6.80	30	202.2→131.4	30	202.2→123.9	35	4
63	spinosyn A	$C_{41}H_{65}NO_{10}$	731.97	12.00	40	732.6→142.2	35			12
64	spinosyn D	$C_{42}H_{67}NO_{10}$	746.00	13.26	30	746.6→142.2	30			12
65	spiroxamine	$C_{18}H_{35}NO_2$	297.48	10.00	30	298.2→144.0	25	298.2→100.0	25	9
66	tebuconazole	$C_{16}H_{22}ClN_3O$	307.82	9.59	30	308.2→ 70.2	20	308.2→125.0	30	8
67	thiabendazole	$C_{10}H_7N_3S$	201.25	5.80	35	202.0→175.0	30	202.0→131.0	30	3
68	triadmimefon	$C_{14}H_{16}ClN_3O_2$	293.75	9.46	30	294.0→197.1	15	294.0→225.1	15	8
69	trifloxystrobin	$C_{20}H_{19}F_3N_2O_4$	408.38	11.45	25	409.0→186.0	20	409.0→206.1	15	10
70	triflumizole	$C_{15}H_{15}ClF_3N_3O$	345.75	10.94	20	346.0→278.1	10	346.0→ 73.2	15	10
71	vamidothion	$C_8H_{18}NO_4PS_2$	287.34	4.95	20	288.1→146.0	15	288.1→117.95	25	3
72	zoxamide	$C_{14}H_{16}Cl_3NO_2$	336.54	10.96	35	336.0→187.0	25	336.0→159.0	40	10

[a] NA, not analyzed; IS, internal standard; QC, quality control standard; CV, cone voltage; CE, collision energy.

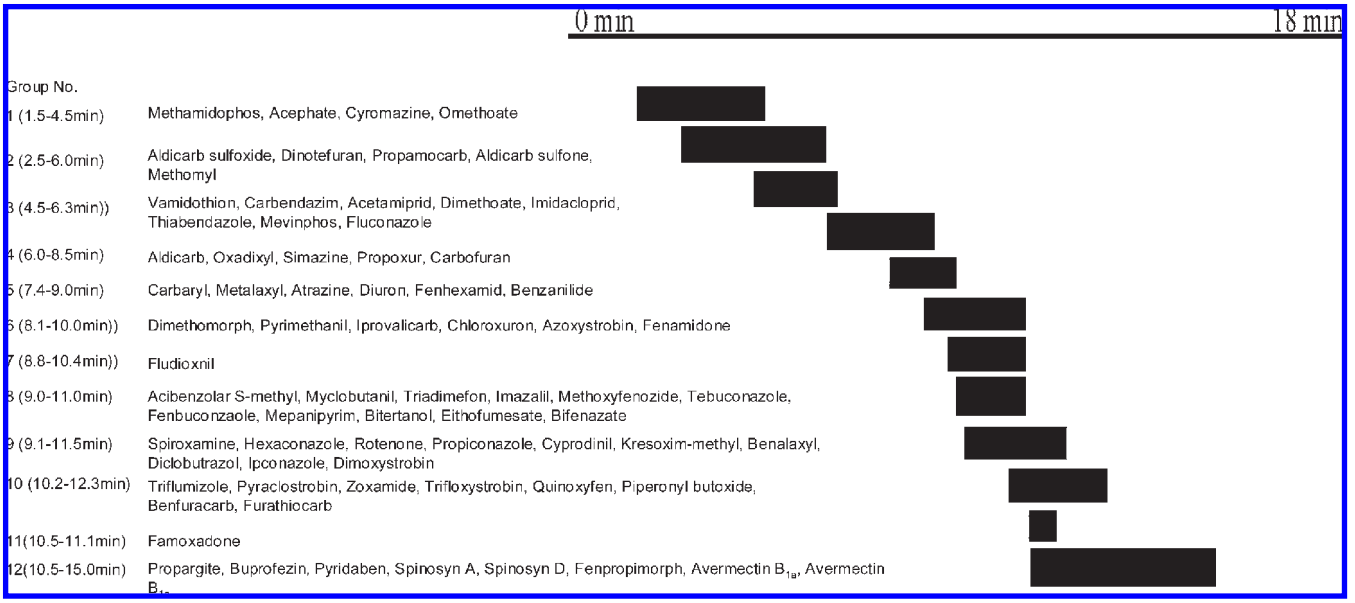

Figure 2. UPLC-MS/MS acquisition sequence of 12 groups used to analyze 72 pesticides, the internal standard (fluconazole), and quality control standard (benzanilide) in the wine.

curve using the peak area ratios of matrix-matched calibration standards to that of the same internal standard, fluconazole. Matrix-matched standards were prepared by extracting pesticide-free wine samples (as described above) and fortifying the wine extracts with standards dissolved in the LC-MS buffer. Standards were prepared at concentration levels of 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 1.0, and 2.5 μg/mL.

Statistics and Calculations. Averages and standard deviations from fortification and sample studies and linear regressions and correlation coefficients for calibration curves were determined using Microsoft Excel 2003. Pesticide concentrations from UPLC-MS/MS analysis were determined by using Micromass MassLynx software (version 4.1) and developing calibration curves using the peak area response ratios of the primary ion transitions of the pesticide analyte to the internal standard (fluconazole) versus pesticide calibration standards.

RESULTS AND DISCUSSION

Sample Preparation and Extraction. The purpose of this work was to develop a quick, easy, efficient, and robust procedure for the analysis of pesticides in wines. The procedure must be developed for routine analysis with high throughput and low cost. Adaptation of the Fillion et al. (*24*) and QuEChERS (*25*) procedures seems to be a reasonable and practical approach for sample preparation for LC-MS analysis. Jezussek et al. (*20*) compared QuEChERS and direct injection of the wine for

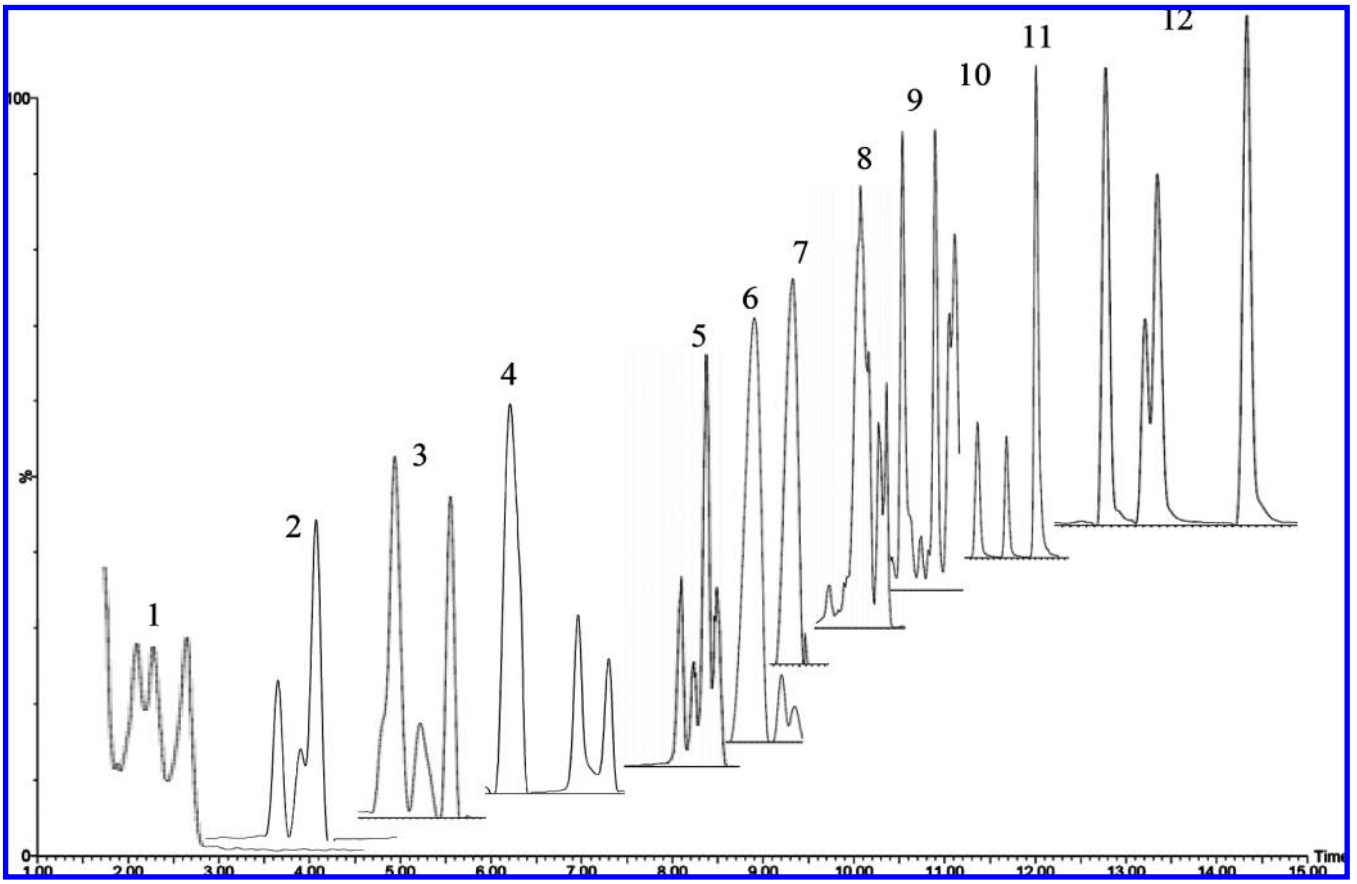

Figure 3. Reconstructed UPLC-MS/MS chromatogram of 72 pesticides in a red wine matrix at 100 μg/L. The units of each axis are percent intensity (unitless) versus time (minutes).

LC-MS measurements and showed that the QuEChERS procedure was effective for both quantitation and identification using matrix-matched standards. In this procedure, we investigated the use of GCB along with PSA to remove additional coextractives from the wine matrix and to determine if this can provide a better cleanup than the original QuEChERS procedure. A combination of GCB in tandem with aminopropyl or PSA sorbents and the addition of toluene to SPE of fresh produce was shown to be effective to remove pigments, sterols, polar components, and fatty acids from food matrices (*18*, *24*, *27*, *29*). In this modified version of the QuEChERS procedure, rather than the use of tandem GCB/PSA SPE cartridges, GCB and PSA sorbents and $MgSO_4$ were combined in a centrifuge tube for the solid-phase dispersive step followed by the addition of toluene to provide a 3:1 acetonitrile/toluene extract (**Figure 1**). This extract was then reduced to dryness with N_2 and resuspended in a buffer for LC-MS analysis. The use of toluene is necessary to desorb planar and aromatic compounds, such as carbendazim, cyprodinil, pyrimethanil, and thiabendazole, which are well-known to adsorb to GCB (*30*). A drawback of the procedure is the need to remove an organic solvent (toluene), which is immiscible in aqueous LC mobile phases. Removal of toluene may result in losses of volatile pesticides, such as acephate and methamidophos. The original QuEChERS procedure utilizes acetonitrile, which is miscible and can be diluted with the LC buffer, but the benefit of a drying step in the modified version is that extraneous coextractives can be left behind because they are insoluble in LC buffer, resulting in a cleaner extract. The recoveries of the polar and volatile organophosphates, acephate and methamidophos, in the fortification studies of the red and white wines showed acceptable recoveries $>73\%$ at the 10, 100, and 1000 μg/L levels (**Table 3**). Recoveries of the planar and aromatic pesticides (carbendazim, cyprodinil, pyrimethanil, and thiabendazole) were typically lower (lowest being 63% for thiabendazole) than the other pesticides studied, indicating that GCB showed retention of these compounds. Recoveries of the planar and aromatic pesticides were still satisfactory and acceptable at 60−120%.

UPLC-MS-MS Chromatographic and Identification Analysis. UPLC-MS-MS has been demonstrated to be an effective solution for multiresidue pesticide analysis in foods due to improved resolution, peak capacity, and sensitivity with a shorter separation time as compared to conventional HPLC-MS-MS (*31*, *32*). Recently, Romero-González et al. (*22*) developed an UPLC-MS-MS method for the simultaneous determination of 90 pesticides in fruit juices with a run time of 11 min. In the current study, gradient elution with aqueous acetonitrile−ammonium acetate generated good separation in all tested matrices with retention times ranging from 1.81 to 14.5 min. Using a column (100 × 2.1 mm i.d.) packed with 1.7 μm particles at a flow rate of 0.2 mL/min, the UPLC method achieved an average base peak width of 15−25 s, which results in a peak capacity of approximately 40−60 for a 15 min separation (**Figure 3**).

The chemical formulas, molecular weights, cone voltages, quantification and confirmatory ion transitions, and corresponding collision voltages are listed in **Table 1**. Multireaction monitoring (MRM) was used for the detection of all pesticides to provide additional separation of the pesticides based on distinct mass ion transitions from the precursor ion to two product ions. The data acquisition sequence included 12 overlapping MRM functions (**Figure 2**). For each pesticide identification, MS/MS acquisitions using two single reaction monitoring ion transitions with a dwell time of 10 ms per ion transition were used. Quantitation was determined by using the more abundant ion transition, whereas the less abundant ion transition was used for

Table 2. Matrix Effect Study Results Include Method Limits of Detection and Quantitation, Ion Ratio (Ratio of the Quantitation and Confirmation Ions), Slope, and r^2 of Red and White Wines (Matrix-Matched Standards Prepared in Acetonitrile) and Solvent (Acetonitrile)[a]

	red wine						white wine						solvent					
no. pesticide	LOD (μg/L)	LOQ (μg/L)	ion ratio	slope	slope ratio red wine / solvent	r^2	LOD (μg/L)	LOQ (μg/L)	ion ratio	slope	slope ratio white wine / solvent	r^2	LOD (μg/L)	LOQ (μg/L)	ion ratio	slope	r^2	range, solvent and matrix (μg/L)
1 acephate	3.3	10	3.77	36.14	1.14	0.994	6.7	6.7	3.88	33.49	1.05	0.994	3.3	6.7	4.07	31.83	0.999	10−2500
2 acetamiprid	3.3	3.3	3.17	23.93	0.77	0.986	2	2	1.77	26.06	0.84	0.997	2	2	3.01	31.02	0.991	5.0−2500
3 acibenzolar *S*-methyl	3.3	10	1.63	0.99	1.39	0.99	3.3	10	2.07	0.94	1.32	0.98	3.3	10	2.72	0.71	0.993	10−2500
4 aldicarb	1.0	1.0	1.63	154.11	0.97	0.998	0.7	2.0	1.67	129.66	0.82	0.992	0.7	0.7	1.66	158.44	0.999	5.0−2500
5 aldicarb sulfone	2.0	3.3	2.62	72.00	0.88	0.995	3.3	6.7	2.43	82.38	1.01	0.991	1.7	3.3	2.41	81.36	0.998	10−2500
6 aldicarb sulfoxide	10	17	1.31	33.32	1.32	0.999	6.7	13	1.15	30.01	1.19	0.995	6.7	13	1.41	25.22	1.000	25−2500
7 atrazine	0.7	0.7	2.4	136.36	0.99	0.999	0.7	2.0	2.51	153.72	1.11	0.994	0.7	0.7	2.25	138.05	0.999	5.0−2500
8 avermectin B_{1b}	1.3	2.2	nd	0.31	1.19	0.991	1.7	2.6	nd	0.31	1.19	0.988	1.3	2.2	nd	0.26	0.988	5.0−2500
9 avermectin B_{1a}	1.2	1.7	1.34	9.60	0.96	0.998	1.5	1.5	1.01	9.51	0.95	0.994	0.9	1.7	1.32	10.02	0.998	5.0−2500
10 azoxystrobin	0.3	0.7	3.97	416.69	1.00	0.993	0.3	0.7	3.73	406.05	0.97	0.991	0.3	0.7	3.93	417.61	0.997	5.0−2500
11 benalaxyl	0.3	0.3	2	532.73	1.05	0.991	0.3	0.7	1.95	571.57	1.13	0.993	0.3	0.7	1.91	505.46	0.996	5.0−2500
12 benfuracarb	0.3	0.3	1.06	128.88	0.92	0.994	0.3	0.7	0.96	125.92	0.90	0.993	0.3	0.3	1.03	139.52	0.995	5.0−2500
13 bifenazate	0.7	1.3	3.69	59.96	0.92	0.992	1.3	1.7	3.51	64.48	0.99	0.99	0.7	1.3	3.66	65.2	0.997	5.0−2500
14 bitertanol	0.7	1.0	1.03	17.72	1.36	0.996	1.3	2.0	1.02	16.21	1.24	0.994	0.2	0.3	0.89	13.07	0.997	5.0−2500
15 buprofezin	0.1	0.7	1.98	281.13	0.88	0.994	0.1	0.7	1.53	322.18	1.00	0.99	0.1	0.7	1.91	320.75	0.997	5.0−2500
16 carbaryl	0.7	1.3	3.2	96.08	1.34	0.995	0.7	1.3	2.57	72.67	1.01	0.995	0.7	1.3	3	71.87	0.997	5.0−2500
17 carbendazim	2.0	3.3	5.19	55.81	0.91	0.998	1.3	3.3	4.83	63.3	1.03	0.994	1.0	2.0	5.34	61.5	0.998	5.0−2500
18 carbofuran	0.3	0.7	1.12	405.18	0.95	0.995	0.2	0.4	1.27	437.81	1.03	0.991	0.2	0.4	1.13	426.76	0.995	5.0−2500
19 chloroxuron	0.3	1.0	3.51	145.18	1.26	0.978	0.1	0.3	1.97	116.3	1.01	0.992	0.1	0.3	3.55	115.34	0.990	5.0−2500
20 cyprodinil	0.7	1.0	1.6	83.91	0.98	0.999	0.7	1.3	1.48	96.31	1.12	0.995	0.3	0.7	1.48	85.66	1.000	5.0−2500
21 cyromazine	10	10	3.71	6.53	1.08	0.992	10	10	3.37	6.71	1.11	0.993	6.7	10	3.11	6.05	0.996	50−2500
22 diclobutrazol	1.3	1.7	11.36	75.21	0.94	0.996	1.3	1.7	12.26	72.66	0.91	0.994	1.3	1.7	12.02	79.85	0.999	5.0−2500
23 dimethoate	0.7	1.0	2.13	110.99	0.95	0.992	1.3	1.7	1.76	108.16	0.92	0.989	0.5	0.8	2.2	117.15	0.996	5.0−2500
24 dimethomorph	1.3	2.0	1.75	75.77	0.97	0.998	1.0	1.7	1.54	64.37	0.82	0.994	1.0	1.7	1.78	78.33	0.998	5.0−2500
25 dimoxystrobin	0.3	0.7	1.45	483.07	1.12	0.972	0.2	0.3	1.34	467.62	1.09	0.992	0.2	0.3	1.52	429.8	0.987	5.0−2500
26 dinotefuran	6.7	10	3.34	2.23	5.19	0.994	6.7	10	1.56	0.83	1.93	0.987	3.3	10	1.95	0.43	0.995	10−2500
27 diuron	1.3	2.7	3.2	29.02	0.85	0.989	1.0	1.3	3.41	37.04	1.09	0.993	1.0	1.3	3.04	33.96	0.996	5.0−2500
28 ethofumesate	3.3	6.7	1.5	5.54	0.98	0.971	3.3	6.7	1.8	5.6	0.99	0.989	3.3	3.3	1.61	5.63	0.990	10−2500
29 famoxadone	3.3	6.7	5.04	2.67	1.70	0.995	3.3	6.7	3.86	1.84	1.17	0.99	3.3	6.7	4.47	1.57	0.998	10−2500
30 fenamidone	0.3	0.3	2.27	33.32	0.95	0.999	0.7	0.7	2.32	28.77	0.82	0.995	0.2	0.3	2.32	35.02	0.997	5.0−2500
31 fenbuconazole	0.7	2.0	nd	26.07	0.78	0.999	1.3	3.3	nd	27.3	0.82	0.991	0.1	0.4	nd	33.24	0.997	5.0−2500
32 fenhexamid	13	17	2.12	0.04	1.00	0.975	13	17	1.92	0.04	1.00	0.996	13	17	1.94	0.04	0.994	50−2500
33 fenpropimorph	0.3	0.3	2.83	615.62	0.93	0.997	0.3	0.3	2.9	591.67	0.89	0.994	0.3	0.3	2.87	664.46	0.999	5.0−2500
34 fludioxinil	0.3	0.7	1.25	41.56	0.90	0.984	0.3	0.3	1.26	47.64	1.03	0.993	0.2	0.4	1.23	46.24	0.995	5.0−2500
35 furathiocarb	3.3	10	2.7	103.16	0.94	0.98	3.3	10	2.3	107.72	0.98	0.99	3.3	10	1.89	109.76	0.992	5.0−2500
36 hexaconazole	1.7	3.3	nd	68.03	1.09	0.999	1.0	1.7	nd	65.41	1.05	0.99	1.0	2.0	nd	62.38	0.999	5.0−2500
37 imazalil	3.3	6.7	1.42	66.48	1.00	0.995	3.3	3.3	1.51	62.67	0.94	0.996	3.3	3.3	1.47	66.52	0.993	5.0−2500
38 imidacloprid	2.0	3.3	1.25	9.56	1.59	0.998	2.0	4.0	1.23	7.39	1.23	0.998	1.3	2.7	1.1	6.03	0.999	5.0−2500
39 ipconazole	0.3	1.3	11.47	117.93	0.91	0.999	0.3	0.7	10.62	137.47	1.07	0.995	0.3	0.3	11.98	128.92	0.999	5.0−2500
40 iprovalicarb	0.7	1.0	2.34	552.08	0.90	0.991	0.3	0.7	2.59	551.54	0.90	0.992	0.3	0.7	2.22	613.76	0.995	5.0−2500
41 kresoxim-methyl	0.7	1.3	1.39	41.63	0.89	0.997	0.7	1.3	1.51	48.26	1.03	0.99	0.7	1.3	1.29	46.93	0.999	5.0−2500
42 mepanipyrim	1.3	3.3	1.82	24.26	0.73	0.991	1.0	2.0	1.92	29.66	0.89	0.99	1.0	2.0	1.8	33.14	0.994	5.0−2500
43 metalaxyl	0.3	0.7	1.62	499.06	1.12	0.993	0.3	0.7	1.52	488.54	1.10	0.993	0.2	0.7	1.54	444.19	0.997	5.0−2500
44 methamidophos	2.0	4.0	3.09	27.55	0.90	0.998	3.3	6.7	2.99	31.8	1.04	0.995	1.3	3.3	3.15	30.53	0.998	10−2500
45 methomyl	0.1	0.4	1.66	133.38	0.87	0.994	0.1	0.3	1.55	156.33	1.03	0.991	0.1	0.3	1.6	152.48	0.997	5.0−2500
46 methoxyfenozide	0.7	1.3	4.53	46.06	1.01	0.97	0.7	1.3	2.79	48.92	1.07	0.99	0.3	0.3	4.81	45.83	0.984	5.0−2500
47 mevinphos	0.1	3.3	1.57	77.54	1.06	0.999	0.7	0.7	2.13	58.21	0.80	0.994	0.1	0.2	1.5	72.96	0.998	5.0−2500
48 myclobutanil	0.7	1.7	3.73	59.15	1.01	0.996	0.7	2.0	3.09	52.83	0.90	0.993	0.7	0.7	3.64	58.61	0.999	5.0−2500
49 omethoate	3.3	6.7	1.02	32.50	0.96	0.999	3.3	6.7	1.15	35.56	1.05	0.993	3.3	6.7	1.19	33.88	0.998	10−2500
50 oxadixyl	0.7	1.3	2.75	263.24	1.00	0.995	0.7	1.0	2.64	215.18	0.82	0.992	0.7	1.0	2.71	262.1	0.996	5.0−2500
51 piperonyl butoxide	0.1	0.1	3.6	1365.67	1.03	0.995	0.1	0.1	3.29	1316.42	1.00	0.984	0.1	0.1	3.62	1321.79	0.983	5.0−2500
52 prochloraz	0.7	1.3	1.76	50.84	1.12	0.999	0.3	0.7	1.42	51.84	1.14	0.995	0.3	0.3	1.7	45.38	0.997	5.0−2500
53 propamocarb	0.7	1.0	4.3	435.97	1.04	0.993	0.7	0.7	3.45	434.6	1.03	0.994	0.3	0.7	4.32	420.2	0.997	5.0−2500
54 propargite	0.7	1.3	1.26	85.28	1.18	0.994	1.0	2.0	1.25	78.44	1.08	0.996	0.5	1.3	1.26	72.4	0.996	5.0−2500
55 propiconazole	1.3	2.7	0.83	58.70	1.05	0.996	1.3	2.7	0.86	58.45	1.05	0.993	1.0	1.3	0.86	55.74	0.999	5.0−2500
56 propoxur	0.3	0.3	1.7	311.11	0.94	0.996	0.2	0.3	1.53	287.65	0.87	0.992	0.2	0.3	1.68	331.62	0.998	5.0−2500
57 pyraclostrobin	1.0	1.3	1.24	173.76	0.83	0.996	1.0	1.7	1.34	192.35	0.92	0.991	0.7	1.0	1.34	208.3	0.998	5.0−2500
58 pyridaben	0.3	0.7	1.65	168.21	0.94	0.998	0.3	0.7	1.79	168.02	0.93	0.992	0.3	0.7	1.67	179.85	0.998	5.0−2500
59 pyrimethanil	1.3	2.0	1.57	73.50	1.06	0.999	1.7	1.7	1.49	77.43	1.12	0.995	1.3	2.0	1.69	69.12	0.997	5.0−2500
60 quinoxyfen	0.7	1.7	1.5	47.21	1.32	0.998	0.7	1.7	1.46	39.83	1.11	0.994	0.7	1.3	1.46	35.89	0.999	5.0−2500
61 rotenone	0.7	0.7	1.42	11.43	1.16	0.993	1.3	1.7	1.02	6.05	0.62	0.992	0.7	0.7	1.34	9.83	0.995	5.0−2500

Table 2. Continued

		red wine						white wine						solvent					
no.	pesticide	LOD (μg/L)	LOQ (μg/L)	ion ratio	slope	slope ratio red wine / solvent	r^2	LOD (μg/L)	LOQ (μg/L)	ion ratio	slope	slope ratio white wine / solvent	r^2	LOD (μg/L)	LOQ (μg/L)	ion ratio	slope	r^2	range, solvent and matrix (μg/L)
62	simazine	3.3	5.3	1.99	0.35	0.97	0.99	3.3	6.7	2.05	0.37	1.03	0.99	2.0	3.3	2.57	0.36	0.990	10−2500
63	spinosyn A	0.1	0.4	nd	371.38	1.15	0.993	0.1	0.4	nd	374.01	1.15	0.99	0.1	0.4	nd	323.89	0.998	5.0−2500
64	spinosyn D	0.1	0.3	nd	104.16	0.91	0.999	0.2	0.7	nd	93.82	0.82	0.994	0.1	0.3	nd	113.85	0.999	5.0−2500
65	spiroxamine	0.3	0.5	1.94	1176.20	1.01	0.998	0.3	0.7	2.05	1138.68	0.97	0.993	0.1	0.3	1.92	1169.06	1.000	5.0−2500
66	tebuconazole	1.3	2.0	15.29	94.82	0.82	0.995	1.3	2.0	13.55	99.74	0.86	0.994	1.0	1.3	14.37	115.86	0.997	5.0−2500
67	thiabendazole	0.7	1.7	1.13	72.14	0.73	0.984	0.7	1.3	1.25	84.54	0.86	0.994	0.5	1.3	1.17	98.26	0.978	5.0−2500
68	triadmimefon	0.7	1.3	2.18	59.84	0.98	0.998	0.7	2.0	2.12	57.32	0.94	0.996	0.7	1.3	2.37	60.84	1.000	5.0−2500
69	trifloxystrobin	0.3	0.7	2.45	309.91	1.13	0.996	0.3	0.7	2.55	313.13	1.14	0.992	0.2	0.7	2.47	273.92	0.998	5.0−2500
70	triflumizole	0.7	0.7	3.92	140.39	0.88	0.997	0.7	1.3	4.58	167.31	1.05	0.996	0.7	0.7	4.39	159.34	0.999	5.0−2500
71	vamidothion	0.3	0.7	2.32	211.10	1.05	0.995	0.3	1.3	2.38	188.41	0.94	0.994	0.1	0.5	2.33	200.38	0.997	5.0−2500
72	zoxamide	2.0	3.3	2.88	33.32	0.90	0.987	1.3	2.0	2.64	34.56	0.94	0.994	1.0	1.7	2.95	36.92	0.991	5.0−2500

Table 3. Recoveries ($n = 4$) of Pesticides in Red and Wine Wines Fortified at Concentrations of 10, 100, and 1000 μg/L

		red wine			white wine		
		recovery (av % ± SD, $n = 4$)			recovery (av % ± SD, $n = 4$)		
no.	pesticide	10 μg/L	100 μg/L	1000 μg/L	10 μg/L	100 μg/L	1000 μg/L
1	acephate	91 ± 14	84 ± 4	79 ± 3	73 ± 5	79 ± 3	85 ± 4
2	acetamiprid	77 ± 7	83 ± 8	94 ± 7	111 ± 8	97 ± 7	93 ± 3
3	acibenzolar *S*-methyl	nd	80 ± 15	74 ± 7	nd	45 ± 5	65 ± 4
4	aldicarb	90 ± 6	92 ± 5	87 ± 3	86 ± 3	82 ± 5	91 ± 1
5	aldicarb sulfone	84 ± 4	91 ± 7	88 ± 4	95 ± 5	83 ± 4	89 ± 4
6	aldicarb sulfoxide	78 ± 6	83 ± 8	82 ± 7	78 ± 13	80 ± 1	80 ± 4
7	atrazine	91 ± 10	92 ± 5	86 ± 4	89 ± 6	83 ± 5	87 ± 3
8	avermectin B_{1b}	91 ± 4	94 ± 12	79 ± 4	122 ± 23	107 ± 13	81 ± 7
9	avermectin B_{1a}	81 ± 7	82 ± 8	77 ± 4	87 ± 9	80 ± 6	84 ± 2
10	azoxystrobin	84 ± 5	93 ± 5	89 ± 3	92 ± 7	86 ± 4	90 ± 3
11	benalaxyl	87 ± 4	92 ± 5	91 ± 3	90 ± 5	84 ± 4	91 ± 3
12	benfuracarb	nd			nd		
13	bifenazate	57 ± 9	69 ± 7	76 ± 3	64 ± 5	70 ± 8	77 ± 3
14	bitertanol	86 ± 6	86 ± 4	88 ± 1	67 ± 10	86 ± 11	86 ± 2
15	buprofezin	85 ± 3	92 ± 5	89 ± 3	88 ± 5	86 ± 4	90 ± 2
16	carbaryl	89 ± 7	91 ± 4	86 ± 3	89 ± 9	88 ± 6	96 ± 2
17	carbendazim	75 ± 7	77 ± 4	75 ± 3	91 ± 7	76 ± 4	79 ± 3
18	carbofuran	110 ± 8	126 ± 7	115 ± 4	101 ± 5	106 ± 7	115 ± 3
19	chloroxuron	79 ± 4	90 ± 4	90 ± 3	92 ± 2	86 ± 4	93 ± 2
20	cyprodinil	68 ± 5	75 ± 5	71 ± 3	75 ± 4	72 ± 2	75 ± 4
21	cyromazine	38 ± 12	38 ± 2	48 ± 3	57 ± 16	56 ± 5	50 ± 5
22	diclobutrazol	81 ± 5	89 ± 6	89 ± 4	101 ± 14	83 ± 5	90 ± 1
23	dimethoate	75 ± 5	89 ± 6	92 ± 5	93 ± 7	82 ± 4	90 ± 4
24	dimethomorph	79 ± 7	88 ± 7	86 ± 3	82 ± 9	84 ± 4	88 ± 1
25	dimoxystrobin	85 ± 6	95 ± 5	98 ± 4	88 ± 6	85 ± 4	91 ± 5
26	dinotefuran	89 ± 7	85 ± 5	86 ± 6	63 ± 7	74 ± 6	80 ± 2
27	diuron	84 ± 11	88 ± 4	87 ± 4	91 ± 5	78 ± 5	87 ± 1
28	ethofumesate	64 ± 13	74 ± 12	91 ± 5	72 ± 7	90 ± 1	94 ± 5
29	famoxadone	93 ± 10	92 ± 10	88 ± 6	77 ± 3	95 ± 14	85 ± 1
30	fenamidone	69 ± 5	87 ± 3	89 ± 2	85 ± 11	86 ± 5	90 ± 3
31	fenbuconazole	73 ± 5	88 ± 5	84 ± 3	88 ± 7	80 ± 5	86 ± 4
32	fenhexamid	nd	133 ± 21	86 ± 2	nd	90 ± 11	89 ± 4
33	fenpropimorph	93 ± 3	91 ± 5	89 ± 3	87 ± 2	83 ± 4	88 ± 2
34	fludioxinil	79 ± 7	86 ± 6	91 ± 3	77 ± 13	84 ± 4	94 ± 5
35	furathiocarb	nd	112 ± 4	89 ± 3	nd	101 ± 2	92 ± 2
36	hexaconazole	76 ± 5	91 ± 2	87 ± 3	101 ± 13	87 ± 8	96 ± 3
37	imazalil	76 ± 7	81 ± 4	85 ± 2	109 ± 4	77 ± 4	87 ± 2
38	imidacloprid	97 ± 16	90 ± 2	91 ± 3	85 ± 6	77 ± 7	79 ± 3
39	ipconazole	81 ± 5	89 ± 5	86 ± 4	78 ± 4	83 ± 5	90 ± 0
40	iprovalicarb	87 ± 5	94 ± 6	90 ± 3	92 ± 5	87 ± 4	91 ± 3

Table 3. Continued

		red wine			white wine		
		recovery (av % ± SD, $n = 4$)			recovery (av % ± SD, $n = 4$)		
no.	pesticide	10 μg/L	100 μg/L	1000 μg/L	10 μg/L	100 μg/L	1000 μg/L
41	kresoxim-methyl	91 ± 15	85 ± 5	86 ± 3	100 ± 7	86 ± 5	90 ± 3
42	mepanipyrim	67 ± 9	76 ± 6	75 ± 4	73 ± 16	94 ± 12	105 ± 9
43	metalaxyl	86 ± 5	94 ± 5	89 ± 3	91 ± 4	85 ± 5	91 ± 2
44	methamidophos	80 ± 11	82 ± 6	73 ± 4	76 ± 9	74 ± 5	74 ± 3
45	methomyl	82 ± 6	90 ± 4	87 ± 4	91 ± 5	81 ± 4	85 ± 3
46	methoxyfenozide	97 ± 12	102 ± 5	90 ± 4	92 ± 10	89 ± 5	91 ± 2
47	mevinphos	83 ± 5	84 ± 5	82 ± 4	78 ± 6	71 ± 4	79 ± 2
48	myclobutanil	95 ± 14	96 ± 8	88 ± 5	77 ± 9	90 ± 4	85 ± 7
49	omethoate	87 ± 7	82 ± 4	84 ± 4	92 ± 12	75 ± 4	79 ± 3
50	oxadixyl	84 ± 5	94 ± 3	92 ± 3	90 ± 6	88 ± 4	93 ± 1
51	piperonyl butoxide	82 ± 5	94 ± 5	83 ± 3	85 ± 4	87 ± 4	110 ± 4
52	prochloraz	73 ± 9	84 ± 3	81 ± 3	86 ± 12	84 ± 5	84 ± 4
53	propamocarb	71 ± 4	80 ± 3	77 ± 4	93 ± 5	80 ± 5	82 ± 2
54	propargite	88 ± 5	93 ± 6	89 ± 3	94 ± 12	86 ± 2	88 ± 3
55	propiconazole	89 ± 13	94 ± 4	91 ± 4	91 ± 8	86 ± 5	94 ± 4
56	propoxur	81 ± 6	89 ± 5	88 ± 4	88 ± 5	82 ± 4	86 ± 3
57	pyraclostrobin	71 ± 3	77 ± 6	79 ± 2	78 ± 2	76 ± 4	80 ± 4
58	pyridaben	76 ± 5	85 ± 4	89 ± 2	90 ± 7	83 ± 4	82 ± 2
59	pyrimethanil	71 ± 9	79 ± 6	75 ± 3	91 ± 12	75 ± 4	78 ± 2
60	quinoxyfen	71 ± 7	70 ± 5	69 ± 2	81 ± 9	68 ± 3	75 ± 1
61	rotenone	68 ± 13	81 ± 3	85 ± 4	60 ± 14	85 ± 9	91 ± 2
62	simazine	109 ± 6	85 ± 9	91 ± 7	84 ± 7	88 ± 7	96 ± 2
63	spinosyn A	75 ± 3	88 ± 7	84 ± 2	91 ± 6	83 ± 4	86 ± 1
64	spinosyn D	79 ± 4	87 ± 4	82 ± 2	88 ± 4	80 ± 3	84 ± 1
65	spiroxamine	86 ± 5	92 ± 5	87 ± 3	92 ± 3	84 ± 4	91 ± 2
66	tebuconazole	77 ± 7	90 ± 4	89 ± 4	85 ± 11	83 ± 5	91 ± 3
67	thiabendazole	63 ± 9	71 ± 3	78 ± 3	73 ± 4	75 ± 5	84 ± 3
68	triadmimefon	92 ± 8	89 ± 8	89 ± 6	101 ± 14	84 ± 7	86 ± 4
69	trifloxystrobin	85 ± 7	90 ± 8	89 ± 3	90 ± 6	84 ± 4	90 ± 2
70	triflumizole	92 ± 11	88 ± 6	84 ± 3	101 ± 10	86 ± 3	87 ± 2
71	vamidothion	79 ± 6	86 ± 4	89 ± 4	91 ± 5	83 ± 6	88 ± 2
72	zoxamide	80 ± 8	86 ± 4	92 ± 6	102 ± 4	80 ± 4	99 ± 9

identification as listed in **Table 1**. Internal standards play a role in quantification and quality control, and preliminary experiments were performed to evaluate fluconazole, 4-bromo-3,5-dimethylphenyl-*N*-methylcarbamate and 1,3-[bis(nitrophenyl)]urea (nicarbazin) as potential quantitative internal standards. Fluconazole was chosen as the quantitative internal standard due to its stability and consistency throughout the extraction and instrumental analysis. Within every sample batch, the variation of fluconazole's response was $< 10\%$. Benzanilide was added to

each sample prior to instrumental analysis as the quality control standard. The day-to-day repeatability for benzanilide as indicator for instrument performance was < 5%.

Matrix Effects. Matrix effects were evaluated by comparing solvent-only and matrix-matched calibration standards in terms of retention time, relative ion intensity, coefficient of determination (r^2), response factor (slope), and slope ratios. Calibration curves were constructed on the basis of calibration standards fortified in red and white wine matrices prepared in acetonitrile and prepared in acetonitrile only at concentrations ranging from 1.0 to 2500 μg/L for most pesticides. Good linearity ($r^2 > 0.99$) was achieved for 68 of 72 pesticides in acetonitrile, for 63 of 72 in red wine, and for 66 of 72 in white wine. There were a few exceptions to $r^2 > 0.99$: in the red wine matrix fenhexamid ($r^2 = 0.975$), ethofumesate ($r^2 = 0.971$), and methoxyfenozide ($r^2 = 0.970$) and in the white wine matrix matrix acibenzolar *S*-methyl ($r^2 = 0.980$). The coefficients of determination (r^2) of the 72 pesticides in red and white wine matrices and solvent and calibration curve response factors (slopes) obtained in the matrices and solvent are listed in **Table 2**. For a majority of pesticides, slopes of their matrix-matched calibration were similar to those of calibration curves in solvents. The slope ratios (red or white wine slope/solvent slope) for red and white wines are also given in **Table 2**. Gilbert-López et al. (*33*) used this parameter to evaluate matrix effects in fruit and vegetable extracts and indicated that a slope ratio $\neq 1.0$ shows effects of matrix suppression (< 1.0) or enhancement (> 1.0). We applied the slope ratio to our studies to determine if there were effects from the wine matrix. The data in **Table 2** indicate no significant suppression or enhancement differences were observed for a majority of the pesticides in either red or white wines, as the slope ratios were within a 10% range of the slope ratio = 1.0 (0.9−1.1) and given the fact the majority of $r^2 > 0.99$. **Figure 4** presents the comparison of the calibration curves of nine pesticides (detected in wine samples in this or previous studies) in wine matrices and solvent, showing there were no significant differences between the matrix-matched and solvent standards up to the 1.0 ppm concentration level. The multiresidue pesticide studies in wines performed by Jezussek et al. (*20*) compared direct injection and traditional QuEChERS procedures with matrix-matched standards for quantitation of the pesticides in wines. The modified procedure presented in this work extended this work as the matrix effects could be minimized using the GCB/PSA sorbent cleanup procedure.

The intensities of the monitored ions in MRM mode are dependent on the composition of the mobile phase and the matrix components entering the interface and the MS detector. The presence of coeluted substances potentially could skew ion signal intensity via matrix suppression or enhancement. Therefore, to ensure the quantification and confirmation, EU legislation issued the guidelines for maximum permitted tolerance for relative ion intensities for tandem mass spectrometric detection (EC/2002/657) (*34*). For the pesticides monitored using two ion transitions, the corresponding relative ion intensities in wine matrices and solvent were calculated (**Table 2**). The reported relative ion intensities were calculated as the average of 10 levels of calibration standards in each matrix and solvent. Matrix effects were further evaluated by comparing the relative ion intensities in wine matrices and solvent. For most pesticides, the relative ion intensities in wine matrices are similar to those in solvent, and the corresponding variations do not exceed the maximum permitted tolerance according to European Commission Decision EC/2002/657 (*34*). These results suggest the matrix effects were minimized by the extraction and cleanup procedures discussed under Materials and Methods.

The analytical limits of detection (LOD) and quantitation (LOQ) were determined by analyzing the blank and calibration pesticide standards prepared in solvent (10 mM ammonium acetate/50:50 acetonitrile/water). The method LOD and LOQ, which are matrix dependent, were determined using the blank and calibration standards prepared in the red and white wine matrices (prepared in 10 mM ammonium acetate/50:50 acetonitrile/water). LOD calculations were based on 3 times the signal-to-noise (peak-to-peak) ratio of the confirmatory (the less abundant) ion transition. As shown in **Table 2**, the LODs for most pesticides were in the low (~1.0) micrograms per liter range. Only the LODs of

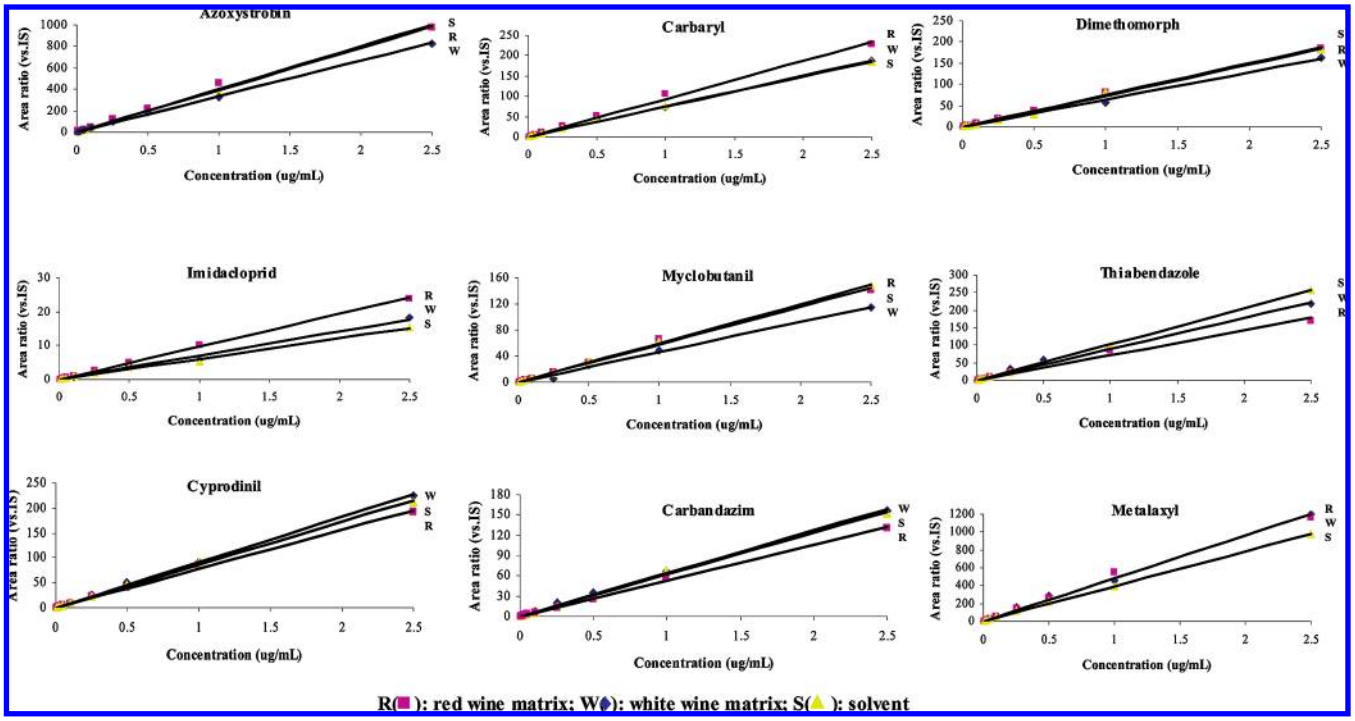

Figure 4. Comparison of the calibration curves of nine pesticides in wine matrices and solvent. R, red wine matrix; W, white wine matrix; S, solvent.

Table 4. Detected Pesticides in Wines[a]

	red wine samples (μg/L)					white wine samples (μg/L)				
pesticide	ID no. 0076	ID no. 1052	ID no. 0824	ID no. 0086	ID no. 2007-1	ID no. 1053	ID no. 1013	ID no. 0805	ID no. 0082	ID no. 2007-2
azoxystrobin				32.7 ± 7.1	24.8 ± 5.8	tr	1.9 ± 0.1	18.0 ± 0.2	2.8 ± 0.2	4.1 ± 0.28
benalaxyl			tr			tr				
carbaryl	369 ± 68	tr	tr	2.3 ± 0.7	1.8 ± 0.6	2.8 ± 0.6		35.2 ± 0.9		
carbendazim	tr		tr	1015 ± 235	825 ± 43	74.3 ± 14.1	4.1 ± 0.3	tr		
cyprodinil				3.0 ± 1.1			2.6 ± 0.4	2.1 ± 0.5		
dimethoate						tr			1.7 ± 0.2	
dimethomorph						tr				
fludioxinil				1.3 ± 0.4						
imidacloprid	7.2 ± 1.3	4.7 ± 1.4							4.3 ± 1.2	
iprovalicarb						2.5 ± 0.5				
kresoxim-methyl				239 ± 62	188 ± 8.0					79.4 ± 3.6
metalaxyl		tr		39.0 ± 8.8	24.7 ± 7.5	6.5 ± 1.3		15.3 ± 0.4		
myclobutanil	14.4 ± 3.2		3.8 ± 0.1				6.4 ± 0.8	4.8 ± 0.6	9.7 ± 0.8	
oxadixyl				8.8 ± 2.2	6.6 ± 1.6					42.9 ± 1.2
piperonyl butoxide				2.9 ± 0.5				tr	1.8 ± 1.9	
pyrimethanil						4.4 ± 0.9				
tebuconazole	tr	8.7 ± 0.7	22.2 ± 0.7			tr	15.7 ± 0.2		5.9 ± 1.2	
triadmimefon								2.4 ± 0.5		
triflumizole									1.0 ± 0.1	

[a] Wines are listed as an identification number and wine type (red or white). Pesticide concentrations (μg/L) are listed as average ± standard deviation (n = 3; tr = trace, <LOQ.

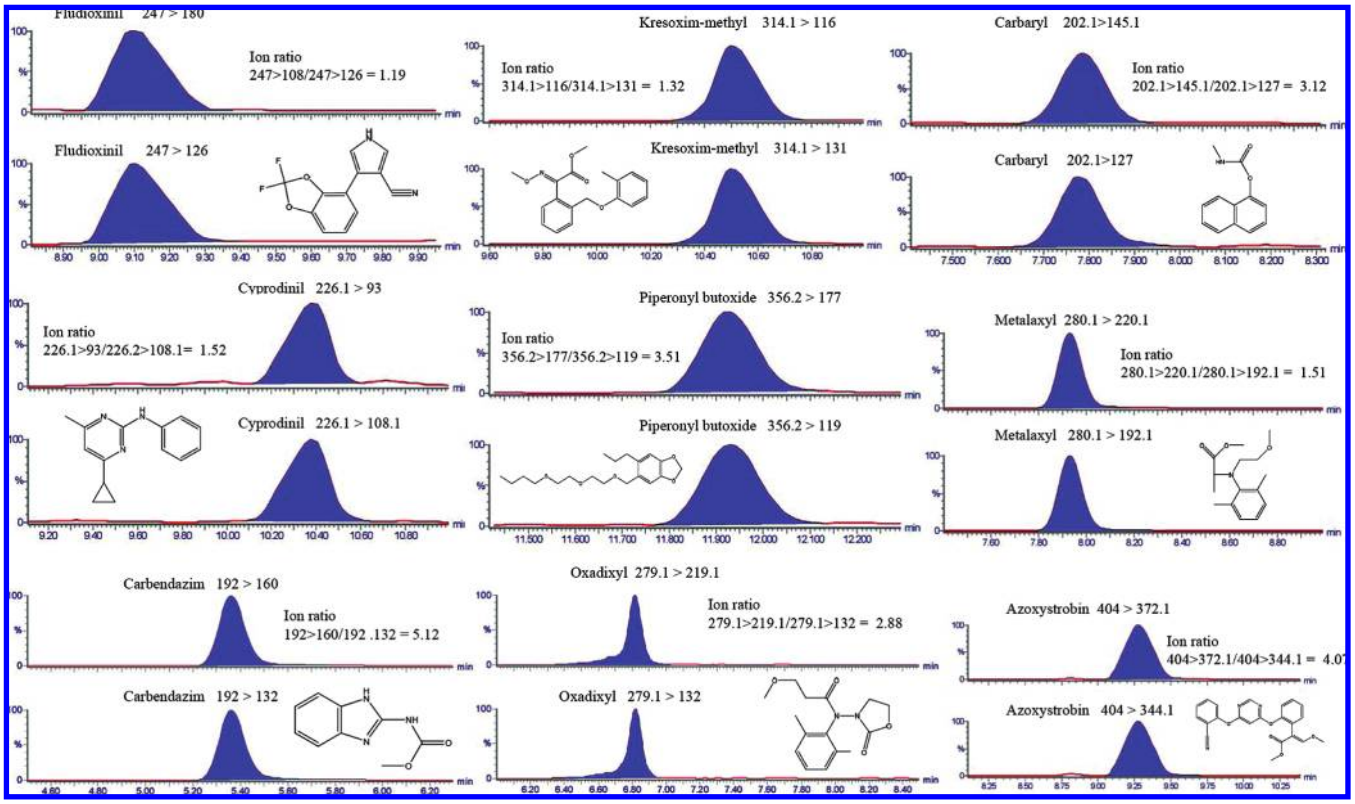

Figure 5. UPLC-MS/MS chromatograms of a red wine sample containing nine pesticides: (**a**) fludioxinil (1.3 ± 0.4 μg/L); (**b**) kresoxim-methyl (239.2 ± 61.8 μg/L); (**c**) carbaryl (2.3 ± 0.7 μg/L); (**d**) cyprodinil (3.0 ± 1.1 μg/L); (**e**) piperonyl butoxide (2.9 ± 0.5 μg/L); (**f**) metalaxyl (39.0 ± 8.8 μg/L); (**g**) carbendazim (1015 ± 234.8 μg/L); (**h**) oxadixyl (8.8 ± 2.2 μg/L); (**i**) azoxystrobin (32.7 ± 7.1 μg/L). Samples were quantitated and confirmed for n = 3.

cyromazine and fenhexamid were 10 μg/L or higher. Overall, the analytical LODs in solvent for most of the pesticides were similar with the method LODs for pesticides fortified in the red and white wine matrix, indicating that matrix effects have been minimized. The analytical and method LOQs were determined as 10 times the signal-to-noise of the quantitative (the more abundant) ion transition in the solvent and matrix, respectively, where the confirmatory ion transition must demonstrate at least a 3 times the signal-to-noise ratio. These results also demonstrated the sensitivity of the procedure and that matrix effects also have minimal effects on the LOQs, consistent with the LOD results (**Table 2**).

Recovery Studies. Recovery studies were performed to validate the UPLC-MS-MS method using wine samples fortified at three concentration levels (10, 100, and 1000 μg/L). The recoveries were calculated using five point matrix-matched calibration curves. **Table 3** lists recoveries in red and white wine matrices. For a

majority of the pesticides, recoveries ranged from 70 to 120% at the three fortified concentration levels, with standard deviations (SDs) of < 10%. Acibenzolar *S*-methyl, bifenazate, cyromazine, fenhexamid, furathiocarb, and rotenone were not detected or had low recoveries (< 70%) at the low fortification concentration (10 μg/L) in both red and white wines. Although calibration curves could be generated using standards prepared in solvent and wine matrices, benfuracarb was not detected in any fortified samples, indicating it was lost during sample preparation. Lower (< 70%) and higher (> 120%) recoveries of a few pesticides were most likely from complications of pesticide lability, matrix interference, or inefficient desorption from the solid-phase sorbents. The results of recovery studies demonstrate that the method and UPLC-MS-MS analysis achieved satisfactory recovery, reproducibility, and sensitivity for pesticide analysis in wine matrices.

Incurred Pesticides in Wines. The validated method was applied to analyze 10 wine samples collected from a market basket survey. **Table 4** summarizes the results of the wines analyzed by the procedure, which reveals that the wines contained at least 19 pesticides at concentrations ranging from trace (< 1.0 μg/L) to 1015 μg/L. Of these 19 pesticides, 3 were insecticides (carbaryl, dimethoate, and imidacloprid), 1 was a synergist (piperonyl butoxide), and the remaining were fungicides. The most prevalent pesticides were azoxystrobin and carbendazim, present in six wine samples, ranging from 1.9 to 32.7 and from trace to 1015 μg/L, respectively. As an example of a typical sample, the results of a red wine analysis are shown in **Figure 5**, which revealed the presence of nine pesticides. The pesticides listed in **Table 4** are registered for use on grapes and wine grapes in the United States and member countries of the European Union. Currently, there are very few maximum residue limits for wines. Our results indicating all 10 wine samples contained pesticides are consistent with the study conducted by Ortelli and Edder (*35*), where > 95% of the 176 organic and conventional wines they analyzed contained pesticides. Although concentrations for each pesticide varied in the wines studied, these measured concentrations are below the maximum residue limits for grapes and wine grapes set by either European Union directives (*36*) or the U.S. EPA (*37*).

In summary, a multiresidue procedure was developed and validated for the analysis of pesticides in wines using procedures based on QuEChERS and that of Fillion et al. using UPLC-MS/MS. Although the inclusion of GCB and toluene leads to an additional step (i.e., the extract is taken to full dryness before it is resuspended in the solvent), the extract seems to be much cleaner than the extract obtained from the original QuEChERS protocol. These extracts subjected to UPLC-MS/MS analysis did not exhibit any significant matrix effects for most of the pesticides. Another advantage is that this extract can be solvent exchanged to an organic solvent that is amenable for GC and GC-MS analysis. Future studies of this procedure include expanding the method to include more pesticides and to adapt the procedure to be amenable to GC, GC-MS, and LC-MS/MS analyses.

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