1148 *J. Agric. Food Chem.* **2003,** *51,* 1148–1161

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Multiresidue Pesticide Analysis in Wines by Solid-Phase Extraction and Capillary Gas Chromatography–Mass Spectrometric Detection with Selective Ion Monitoring

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A method was developed to determine pesticides in wines. The pesticides were extracted from the wine using solid-phase extraction on a polymeric cartridge, and the coextractives were removed with an aminopropyl−$MgSO_4$ cartridge. Analysis was performed using capillary gas chromatography with electron impact mass spectrometric detection in selective ion monitoring mode (GC-MSD/SIM). Three injections are required to analyze all 153 organohalogen, organonitrogen, organophosphate, and organosulfur pesticides and residues. Pesticides were confirmed by retention times of the target ions and three qualifier-to-target ion ratios. Detection limits for most of the pesticides were less than 0.005 mg/L, and quantitation was determined from approximately 0.01 to 5 mg/L. Spike recoveries were performed by fortifying red and white wines at 0.01 and 0.10 mg/L. At the 0.01 ppm level, the spike recoveries were greater than 70% for 116 and 124 pesticides (out of 153) in red and white wines, respectively, whereas at the higher spike concentration of 0.10 mg/L, the recoveries were greater than 70% for 123 and 128 pesticides in red and white wines, respectively. The recoveries of less than 70% were most likely from pesticide polarity or lability, resulting in the inefficient adsorption of the pesticide to the polymeric sorbent, ineffective elution of the pesticide from the sorbent, or thermal degradation of the pesticide under GC-MSD conditions.

KEYWORDS: Wine; gas chromatography−mass spectrometric detection/selective ion monitoring (GC-MSD/SIM); solid-phase extraction; pesticides

INTRODUCTION

Pesticides are used on agricultural commodities such as grapes and wine grapes to protect against insects, fungi, molds, and other agents that may affect crop yield, cosmetic appearance, and flavor properties. Wine is an important agricultural commodity subjected to Bureau of Alcohol, Tobacco and Firearms (BATF) regulations and revenue collection, as pertaining to its labeling (e.g., grape variety and region of origin) and alcohol content. It is also BATF's mission to monitor alcohol-based products available to the marketplace for contaminants in order to ensure public (e.g., consumer) safety. Various pesticides are used for grape production, and the residues left on the grapes during harvest can be carried through into the wine (*1*).

Public concern over pesticide residues in food has been increasing such that it has become a significant food safety concern. Very little data are available regarding human exposure to pesticides through consumption of processed and finished food products. However, a study by Andrey and Amstutz (*2*) showed that 61% of 83 labeled "organic" wines and 87% of 15 conventional wines found in Swiss marketplaces contained pesticide residues. Currently, there are few studies in the United States on the presence of pesticides in wines or alcohol-based beverage products, although there are tolerances set for table and wine grapes (*3*, *4*). These concerns have caused many regulatory agencies to increase their scope of analysis as well as the number of samples analyzed in their monitoring programs for risk assessment. Recently, the Italian government has established a maximum residue limit (MRL) for wines (*5*).

Procedures are needed to reliably and rapidly detect and quantitate as many contaminants as possible, including pesticides, in the most cost-effective manner. For example, since

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10.1021/jf0209995 CCC: $25.00

1986, the Liquor Control Board of Ontario has maintained a program to monitor pesticide residues in wine and has developed a multiresidue method for analyzing 17 pesticides that might be found in wine (*6*). Recently, BATF has initiated a pesticide screening analysis of wines in their Alcohol Beverage Sampling Program to determine the identity and concentration of possible pesticides in beverage alcohol products.

Cabras et al. (*4* and references therein) and Navarro et al. (*7*−*9*) researched the fate of pesticides from the processed grapes through the vinification process to the final wine product. There have been many multiresidue pesticide procedures for beverage alcohol products such as beer (*10*) and wine (*6*, *11*−*14*). In a previous work, we developed a multiresidue method to analyze 48 pesticides in wines using C-18 solid-phase extraction cartridges and capillary gas chromatography with electron impact mass spectrometric detection in selective ion monitoring mode (GC-MSD/SIM) (*14*). The weakness of the method lies in the fact that it relied on the use of standards prepared in wine matrix to offset matrix enhancement effects. In this current work, we adopted a strategy inspired by the works of Fillion et al. (*15*, *16*), Holland et al. (*11*), and Jiménez et al. (*17*) to develop and validate a rapid and efficient multiresidue method for the analysis of pesticides in wines by capillary gas chromatography−mass spectrometry with selective ion monitoring. Holland et al. (*11*) provided the first major work that attempted to analyze pesticides in wines using capillary gas chromatography with nitrogen−phosphorus and electron capture detection; Fillion et al. (*15*, *16*) showed that it was possible to develop and manage a comprehensive method to analyze 199 pesticides using GC-MSD/SIM; Jiménez et al. (*17*) utilized a polymer-based extraction sorbent for extracting pesticides from wines and investigated matrix enhancement. This phenomenon misrepresents the actual concentration of the analyte due to the effects of the substituents present in the matrix adsorbed on the injection liner during GC analysis (*18*, *19*). The method proposed in this work utilizes polymeric (Oasis HLB cartridges) solid-phase extraction cartridges to concentrate the pesticide from the wine, a cleanup procedure using aminopropyl solid-phase extraction cartridges topped with $MgSO_4$, and quantitative analysis and confirmation of the pesticides by GC-MSD/SIM.

METHODS AND MATERIALS

Materials and Standards Preparation. The pesticide standards were obtained from the United States Environmental Protection Agency (U.S. EPA) Pesticide Repository (Ft. Meade, MD), with the exception of benalaxyl, furalaxyl, iprodione, cholozinate, and vinclozolin, which were purchased from Crescent Chemicals (Hauppage, NY). Residue-analysis-grade methanol, ethyl acetate, hexane, and acetone and HPLC-grade water were purchased from Pharmco (Bridgeport, CT). Magnesium sulfate was purchased from Fluka Chemical Corp. (Milwaukee, WI). The internal standards, acenaphthalene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12}, were purchased from Aldrich Chemical Co. (Milwaukee, WI). Oasis HLB cartridges (6 mL, 200 mg) and aminopropyl cartridges (LC-NH2, 3 mL, 500 mg) were purchased from Waters (Milford, MA) and Supelco Co. (Bellefonte, PA), respectively. Red (Cabernet Sauvignon) and white (Chardonnay) wines were purchased commercially from a local store for comparison, spike, and matrix studies.

Stock solutions (approximately 500 mg/L) of individual pesticide standards were prepared by dissolving approximately 0.050 g of the pesticide in 100 mL of ethyl acetate. The working standards used for quantitative and spike recovery studies were prepared by diluting 2 mL of the stock pesticide standards with 0.1% corn oil/ethyl acetate using a 200-mL volumetric flask to prepare a 5 mg/L mixed working standard. Successive dilutions, with 0.1% corn oil in ethyl acetate, of the 5 mg/L standard were used to prepare the 2.5, 1.0, 0.5, 0.250, 0.100, 0.050, 0.025, 0.010, 0.005, 0.0025, and 0.001 mg/L standards (each 100-mL standards). The 0.0025 and 0.001 mg/L standards were prepared by 1:10 dilution of the 0.025 and 0.010 mg/L standards, respectively. The internal standards were prepared by dissolving acenaphthalene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12} in ethyl acetate to make a 500 mg/L working solution.

Solid-Phase Extraction of Pesticides in Wine. A schematic of the extraction procedure is shown in **Figure 1**. Two Supelco VISIPREP-24 manifolds were used for solid-phase extraction and cleanup of the wines. The first is used for extraction of the wines with the Oasis cartridges, and the second is used for sample cleanup with the $MgSO_4$-topped aminopropyl cartridges. Wine (20 mL) was transferred to a 50-mL volumetric flask. For spike recovery studies, the wine was fortified with the appropriate spike concentration of pesticide standards (0.4 mL of either a 5 or 0.5 mg/L standard to make a 0.1 or 0.01 mg/L spiked sample, respectively). HPLC-grade water (20 mL) was added to the wine, for a total volume of 40 mL, and mixed vigorously to ensure homogeneous distribution. For solid-phase extraction, Oasis HLB cartridges were first rinsed with two column volumes each of 50:50 ethyl acetate/hexane, methanol, and HPLC-grade water. The column conditioning was performed under gravity, which may require an initial mild vacuum for priming. The 40-mL sample of diluted wine was loaded onto the cartridge via a Pasteur pipet, and extraction required little or no vacuum to be applied. Once the entire wine sample was loaded, the sample flask was rinsed with approximately 10−15 mL of HPLC-grade water and loaded onto the cartridge. Once all the liquid passed through the cartridge, the cartridge was dried for approximately 15 min under vacuum.

During the time the cartridges were being dried, aminopropyl cartridges (to be attached to the second vacuum manifold) were prepared by loading magnesium sulfate to fill approximately one-third of the cartridge volume. The magnesium sulfate was allowed to settle, and any observable gaps were removed by slight tapping of the cartridge. The cleanup cartridge (magnesium sulfate−aminopropyl cartridge) was conditioned with approximately 5 mL of 50:50 ethyl acetate/hexane. When all but 0.5−1 mL of ethyl acetate/hexane remained in the column volume, the cartridge valves to the manifold were closed to prevent drying of the cartridges.

The Oasis HLB cartridges were then detached from the first vacuum manifold, and tube adapters were attached on the eluting end of the cartridges and connected to the top of the cleanup cartridges. Graduated conical tubes (15 mL) were placed in a sample rack inside the manifold to collect the extract. The tandem cartridge setup was eluted under gravity with 5 mL each of 80:20, 50:50, and 20:80 ethyl acetate/hexane (initial priming with slight vacuum may be required). Once elution was completed, the sample collection tubes (containing approximately 15 mL of eluant) were removed from the manifold and placed in an N-evap, and the volume was reduced to approximately 0.1 mL under a gentle N_2 stream. To this sample was added 1 mL of 0.1% corn oil/ethyl acetate, the mixture was transferred to GC sample vials, and 50 μL of the internal standard (I.S.) solution was added. The vials were capped and readied for GC-MSD analysis.

GC-MSD/SIM Analysis. A HP6890 gas chromatograph was equipped with a HP5973 mass selective detector (MSD, Agilent Technologies, Little Falls, DE) and fitted with an HP-5MS column (30 m × 0.25 mm × 0.25 μm film thickness, Agilent Technologies). The carrier gas was ultrapure helium (Air Products, Hyattsville, MD) set at constant pressure mode using the retention time locking (RTL) program on the HP6890 and methyl chlorpyrifos as the RTL standard. The temperature program consisted of 70 °C (2 min hold) to 150 °C at a rate of 25 °C/min, increased to 200 °C at a rate of 3 °C/min, followed by a final ramp to 280 °C (10 min hold) at a rate of 8 °C/min, for a total run time of 41.87 min (this is the temperature program used by Agilent Technologies' RTL databases). The MSD was operated in electron impact (EI) mode at 70 eV. The inlet, MSD transfer line, MSD source, and quadrupole temperatures were 250, 280, 230, and 150 °C, respectively. The wine extracts, standards, and blanks were injected (2 μL) into the GC in splitless mode using an HP6890 series autoinjector.

The MSD system was routinely programmed in selective ion monitoring (SIM) using one target and three qualifier ions, as indicated in **Table 1**. A sample is analyzed three times (3 × 41.87 min) by using

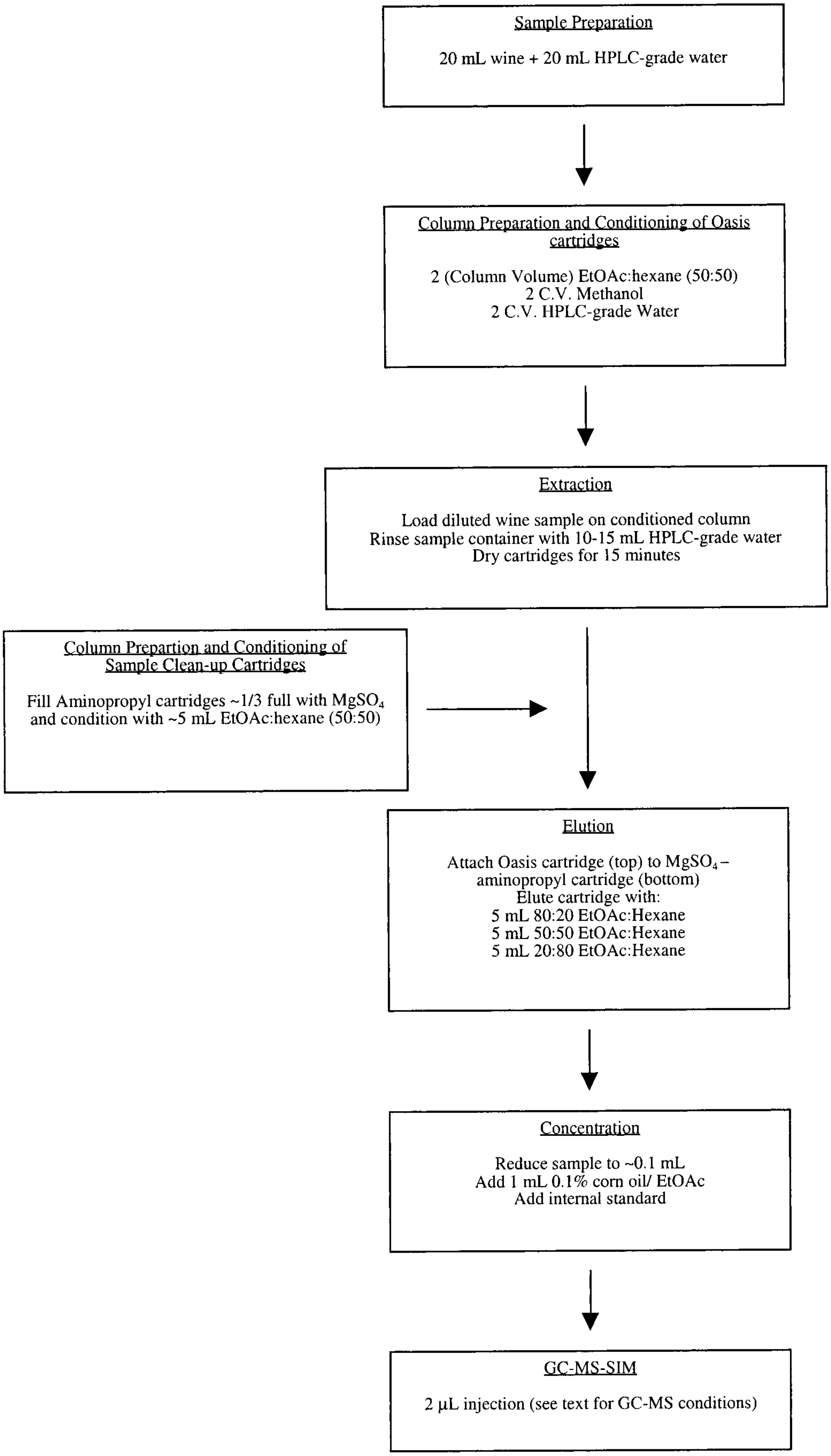

Figure 1. Flow chart of the SPE procedure for the extraction of pesticides in wines.

three different SIM programs, SIM-1, SIM-2, and SIM-3, as listed in **Table 2**. Confirmation of the pesticide was established by the retention time of the target ion and the presence of three qualifier-to-target ion ratios. The target and qualifier ion abundances (most of the target and qualifier ions are similar to the ones used in the Agilent RTL MSD database) were determined by injection of individual pesticide standards

Table 1. Pesticide Name, Molecular Weight, GC-MSD/SIM Retention Time, Target and Qualifier Ions, Percentage of Qualifier to Target Ratios,[a] Limit of Detection, Concentration Range, and Regression Coefficient of All Pesticides Used in This Study

pesticide	MW	t_R (min)	target (T)	qualifier ion 1 (Q_1)	Q_1/T^b (%)	qualifier ion 2 (Q_2)	Q_2/T^b (%)	qualifier ion 3 (Q_3)	Q_3/T^b (%)	LOD (mg/L)	range (mg/L)	r^2
Acephate	183.2	7.69	136	94	43.5	95	22.8	125	13.1	25	60–3100	0.9957
acenaphthalene-d_{10} (I.S.)	164.3	8.39	164	162	92.3	160	42.2	80	15.3			
Alachlor	269.8	17.10	160	188	91.1	146	48.2	237	29.9	1.0	7.0–3450	0.9999
Aldrin	364.9	18.56	263	265	66.6	261	64.1	66	61.0	1.5	12–5760	1.0000
Allethrin	302.4	21.81, 21.90	123	79	27.0	136	23.4	107	23.0	3.0	12–6100	0.9998
Atrazine	215.7	13.27	200	215	53.9	202	35.2	58	25.9	1.0	10–5120	0.9992
Azinphos-ethyl	345.4	30.68	132	160	87.4	77	51.4	105	26.1	1.0	10–5205	0.9992
Azinphos-methyl	317.3	29.68	160	132	73.9	77	57.0	105	22.0	3.0	10–5100	0.9985
Benalaxyl	325.4	26.75	148	91	40.1	206	28.6	204	20.8	1.0	11–5450	0.9998
Benfluralin	335.3	11.76	292	264	17.3	276	12.1	293	11.9	< 1.0	10–4950	0.9996
BHC-α	290.8	12.15	181	183	94.0	219	89.5	217	72.7	1.0	7.0–3280	0.9992
BHC-δ	290.8	14.74	181	219	103.0	183	99.2	217	80.8	2.0	8.0–3820	0.9999
BHC-γ (Lindane)	290.8	13.52	181	183	97.4	219	89.6	111	70.6	1.5	6.0–3060	1.0000
Bitertanol I	337.4	31.21	170	168	16.3	171	13.3	57	8.5	0.5	13–2500	0.9986
Bitertanol II	337.4	31.34	170	168	20.5	171	14.0	57	9.0	0.5	13–2500	0.9997
Bromophos-ethyl	394.1	22.54	359	303	81.0	357	75.0	301	59.8	< 1.0	11–5475	0.9997
Bromophos-methyl	366.0	20.08	331	329	75.5	333	29.4	125	27.3	< 1.0	12–5950	0.9999
Bromopropylate	428.1	28.71	341	183	52.1	339	52.0	343	49.7	0.5	6.0–2890	0.9995
Bromoxynil	276.9	11.68	277	275	54.0	279	49.3	88	28.5	10	51–5070	0.9425
Captafol	349.1	27.79	79	80	33.4	77	22.2	151	18.2	25	50–4630	0.9743
Captan	300.6	21.35	79	80	23.1	151	18.9	77	16.4	10	25–5140	0.9943
Carbaryl	201.2	16.89	144	115	63.1	116	30.3	145	9.6	10	30–5190	0.9911
Carbofuran	221.3	13.09	164	149	72.9	131	26.0	123	22.0	2.0	11–5100	0.9901
Carbophenothion	342.9	26.66	157	342	56.6	121	44.4	199	27.0	< 1.5	11–5630	0.9997
Chlorbenside	269.2	21.93	125	127	32.6	268	13.1	270	9.2	1.0	6.0–3140	0.9991
cis-Chlordane	409.8	22.91	373	375	94.5	377	49.4	371	43.6	< 1.0	9.0–4460	1.0000
trans-Chlordane	409.8	22.13	373	375	93.7	377	51.9	371	42.6	< 1.0	7.0–3650	0.9996
Chlorfenvinphos	359.6	21.61	267	323	67.4	269	65.9	325	42.9	1.0	12–5900	0.9996
Chlorothalonil	265.9	14.90	266	264	79.4	268	46.6	270	10.0	1.0	11–5450	0.9982
Chlorpyrifos	350.6	19.25	197	199	94.6	314	88.0	97	66.8	1.0	11–5420	0.9997
Chlorpyrifos-methyl	322.5	16.61	286	288	68.9	125	40.4	290	15.2	< 1.0	8.0–7800	0.9999
Chlozolinate	332.1	21.52	188	259	87.8	186	84.4	187	76.6	1.5	12–5750	0.9999
chrysene-d_{12} (I.S.)	240.4	28.46	240	236	24.2	241	19.9	238	5.1			
Coumaphos	362.8	31.71	362	226	46.3	109	34.1	210	32.1	1.0	12–6000	0.9986
Cyanazine	240.7	19.47	212	213	37.7	214	37.0	68	16.7	3.0	12–6160	0.9998
Cyfluthrin I	434.3	32.35	163	206	78.7	165	69.4	227	46.6	1.5	13–2540	0.9982
Cyfluthrin II	434.3	32.50	163	206	63.8	165	66.1	227	46.1	1.5	13–2540	0.9983
Cyfluthrin III	434.3	32.61	163	206	73.6	165	67.2	227	51.8	2.5	13–2540	0.9963
Cyfluthrin IV	434.3	32.67	163	206	65.1	199	47.6	227	47.2	2.5	13–2540	0.9993
Cyhalothrin	449.9	30.44	181	197	79.6	208	50.4	209	25.1	1.5	14–7210	0.9999
Cypermethrin I	416.3	32.79	181	163	108.5	165	71.0	209	51.5	2.0	8.0–1625	0.9987
Cypermethrin II	416.3	32.95	181	163	122.3	165	79.9	209	57.5	2.0	8.0–1625	0.9979
Cypermethrin III	416.3	33.07	163	181	89.5	165	67.1	209	44.0	2.0	8.0–1625	0.9981
Cypermethrin IV	416.3	33.16	163	181	81.5	165	68.2	209	40.9	2.0	8.0–1625	0.9977
Cyprodinil	225.3	20.66	224	225	65.3	210	10.2	77	8.7	< 1.5	15–7485	0.9996
o,p′-DDT	354.5	25.84	235	237	63.2	165	35.8	236	14.0	< 0.5	2.0–850	0.9932
p,p′-DDT	354.5	27.06	235	237	66.2	165	36.6	236	15.1	< 1.0	6.0–2770	0.9988
Deltamethrin	505.2	36.07	181	253	82.7	251	43.9	255	41.5	8.0	20–4180	0.9946
Demeton-O	230.3	10.37	88	60	28.7	89	28.5	171	12.7	2.5	10–4900	0.9999
Demeton-S	230.3	12.55	88	60	28.6	170	17.6	89	13.6	2.5	10–4900	0.9997
Desmetryn	213.3	16.09	213	198	57.8	171	28.0	58	17.9	< 1.5	12–6040	0.9992
Dialifos	393.9	30.86	208	173	71.6	210	34.0	76	30.1	1.0	10–5200	0.9995
Diallate I	270.2	11.99	86	234	78.3	236	30.9	128	30.1	< 0.5	5.0–2510	0.9999
Diallate II	270.2	12.32	86	234	85.7	236	35.5	128	25.9	< 0.5	5.0–2510	1.0000
Diazinon	304.3	14.47	179	137	86.0	199	61.6	152	60.6	< 1.0	13–6600	0.9998
Dichlobenil	172.0	6.77	171	173	65.4	136	17.0	100	16.7	< 1.5	13–6700	1.0000
Dichlofluanid	333.2	18.49	123	224	54.4	167	51.3	226	37.8	< 1.5	11–5425	0.9993
4,4′-Dichlorobenzophenone	251.1	19.30	139	111	35.4	141	32.9	250	30.7	0.5	5.0–2590	0.9998
Dichlorvos	221.0	5.83	109	185	43.2	79	17.4	187	14.9	< 1.0	7.0–3330	0.9998
Dicloran	207.0	12.64	206	176	127.6	178	81.0	208	63.8	4.0	8.0–3990	0.9985
Dicrotophos	237.2	11.49	127	67	19.7	193	11.9	72	8.8	3.0	12–6210	0.9998
Dieldrin	380.9	23.93	79	263	47.8	277	37.2	279	33.4	2.0	7.0–3260	0.9998
Dimethoate	229.3	12.72	87	93	61.3	125	58.6	143	12.0	2.5	10–5070	0.9998
Dinoseb	240.2	14.57	211	163	33.9	147	20.9	240	18.2	150	350–6620	0.9050
Dioxathion	456.0	31.87	97	125	80.2	271	66.3	153	29.1	5.0	10–5000	0.9987
Disulfoton	274.4	14.55	88	89	39.1	97	30.0	142	18.4	1.0	13–6570	0.9995
Endosulfan-α	406.9	22.70	241	195	90.1	239	90.0	237	89.9	1.5	5.0–2700	0.9999
Endosulfan-β	406.9	25.24	195	237	91.5	241	88.4	207	82.0	3.0	5.0–2700	0.9999
Endrin	380.9	24.83	317	263	78.9	315	68.0	319	62.2	3.5	6.0–3220	0.9977
Endrin aldehyde	380.9	25.99	67	345	71.8	250	62.2	347	47.5	2.0	7.0–3630	0.9999
Endrin ketone	380.9	28.31	317	67	85.0	315	65.0	319	62.8	< 1.0	9.0–4580	0.9999
EPN	323.3	28.68	157	169	53.1	141	44.9	185	29.7	< 1.0	10–5025	0.9949
Eptam	189.3	6.80	128	43	101.2	86	61.6	132	28.8	1.0	10–4795	1.0000

Table 1 (Continued)

pesticide	MW	t_R (min)	target (T)	qualifier ion 1 (Q_1)	Q_1/T (%)	qualifier ion 2 (Q_2)	Q_2/T (%)	qualifier ion 3 (Q_3)	Q_3/T (%)	LOD (mg/L)	range (mg/L)	r^2
Ethalfluralin	333.3	11.32	276	316	92.4	292	47.0	333	24.8	1.0	11–5300	0.9983
Ethion	384.5	26.02	231	153	49.4	97	42.6	125	32.6	1.0	13–6570	0.9993
Fenamiphos	303.4	23.65	303	154	46.0	288	28.0	217	25.2	< 1.0	11–5480	0.9991
Fenarimol	331.2	30.48	139	219	75.4	251	69.2	107	66.7	0.6	11–5560	0.9999
Fenitrothion	277.2	18.10	277	125	97.3	109	72.3	260	55.5	1.0	10–5175	0.9993
Fenpropathrin	349.4	29.05	97	181	70.0	125	40.3	265	28.0	0.6	12–5780	1.0000
Fenpropimorph	305.5	19.28	128	129	9.2	303	4.4	117	2.9	< 0.5	11–5580	0.9996
Fenson	268.7	19.76	77	141	92.8	268	48.0	51	13.8	10	30–3750	0.9998
Fenthion	278.3	19.14	278	125	33.3	109	26.4	169	24.7	< 1.5	11–5300	0.9998
Fenvalerate I	419.9	34.45	167	125	98.3	181	74.1	152	55.9	3.0	11–5550	0.9992
Fenvalerate II	419.9	34.87	167	125	96.8	181	66.0	169	62.3	3.0	11–5550	0.9995
Flucythrinate I	451.4	33.16	199	157	63.1	181	37.6	107	16.6	2.5	12–2430	0.9985
Flucythrinate II	451.4	33.49	199	157	61.7	181	38.3	107	14.7	2.5	12–2430	0.9980
Fludioxinil	248.2	24.25	248	127	30.0	154	24.2	182	15.7	1.0	11–5335	0.9993
Fluvalinate tau-I	502.9	34.88	250	252	33.8	181	19.4	208	9.1	0.5	5.0–2550	0.9968
Fluvalinate tau-II	502.9	35.02	250	252	33.1	181	20.1	208	9.3	0.5	5.0–2550	0.9974
Folpet	296.6	21.72	147	104	95.7	76	80.4	260	69.2	15	30–5460	0.9339
Fonofos	246.3	13.89	109	246	58.5	137	52.1	110	26.5	< 1.0	11–5490	0.9996
Furalaxyl	301.3	22.05	95	242	48.6	152	17.9	146	12.4	1.0	10–5050	0.9992
Heptachlor	373.3	16.83	272	274	82.1	100	72.7	270	54.5	0.5	6.0–2990	0.9998
Heptachlor epoxide	389.3	20.79	353	355	81.1	351	51.6	357	35.9	0.5	6.0–2880	0.9999
Hexachlorobenzene	284.8	12.42	284	286	82.2	282	51.8	288	36.1	< 0.5	6.0–2780	0.9999
Hexaconazole	352.9	23.52	83	214	60.6	216	38.7	82	34.2	1.0	11–5480	0.9997
Hexazinone	252.3	27.41	171	83	14.5	128	11.9	71	10.1	1.0	10–5050	0.9997
Imazalil	297.2	23.78	41	215	67.2	173	50.2	217	42.8	6.0	30–5550	0.9996
Iprodione	330.2	28.51	314	187	59.5	189	41.4	244	24.9	5.0	10–4980	0.9894
Isofenphos	345.4	21.64	213	58	81.1	121	54.5	255	44.0	1.0	13–6600	0.9997
Malaoxon	314.3	16.90	127	99	39.7	109	22.4	125	19.1	3.0	10–5180	0.9996
Malathion	330.4	18.83	173	127	84.6	125	77.3	93	56.8	< 1.5	11–5500	0.9997
Metalaxyl	279.3	17.35	206	45	62.3	160	52.0	249	49.5	1.0	10–4880	0.9993
Methidathion	302.3	22.33	145	85	61.2	93	16.8	125	16.3	1.0	11–5580	0.9995
Methoxychlor	345.7	28.94	227	228	17.3	152	9.0	113	3.7	< 1.0	11–5500	0.9998
Metolachlor	283.8	18.95	162	238	62.0	240	21.2	146	13.0	< 1.0	9.0–4350	0.9977
Mevinphos	224.2	7.59	127	192	59.0	109	41.0	67	18.4	< 1.5	7.0–3400	0.9998
Mirex	545.6	29.89	272	274	80.0	270	52.1	237	44.7	< 1.0	11–5500	0.9998
Monocrotophos	223.2	11.74	127	67	17.9	192	16.3	97	14.9	3.0	13–6555	0.9996
Myclobutanil	280.8	24.44	179	150	49.5	82	35.4	181	31.8	1.0	11–4455	0.9998
Naled	380.8	11.22	109	185	31.2	79	16.8	145	16.5	6.5	30–6480	0.9984
Napropamide	271.4	23.51	72	128	51.9	100	35.1	271	30.2	< 1.0	11–5525	0.9999
Nitralin	345.4	28.26	316	274	70.6	300	15.1	317	14.7	0.5	10–5110	0.9918
Nitrofen	284.1	24.95	283	253	85.5	283	66.1	202	46.0	3.0	10–5120	0.9946
Nitrothal-isopropyl	295.3	19.93	236	194	73.4	212	63.6	254	52.2	1.0	11–5520	0.9956
Norflurazon	303.7	27.05	303	145	90.7	102	41.3	305	34.1	1.0	10–5120	0.9990
Omethoate	213.2	10.01	156	110	85.7	79	25.0	109	20.4	6.0	25–5840	0.9985
Oryzalin	346.4	31.32	317	275	47.2	258	12.5	58	8.8	100	250–5030	0.8945
Oxadiazon	345.2	24.49	175	177	65.8	258	58.9	260	38.0	0.6	11–5375	1.0000
Oxadixyl	278.3	25.97	105	163	113.1	45	80.5	132	76.5	1.5	11–5310	0.9999
Oxyfluorfen	361.7	24.72	252	361	38.3	302	23.3	331	15.6	1.0	12–5790	0.9955
Paraoxon	275.2	17.38	109	149	39.7	275	33.0	139	30.8	6.0	22–11000	0.9996
Parathion	291.3	19.30	291	109	83.4	97	80.9	139	45.9	1.0	12–6000	0.9989
Parathion-methyl	263.2	16.62	263	109	91.9	125	78.6	79	23.5	1.0	12–6000	0.9972
Penconazole	284.2	21.08	248	159	93.7	161	60.0	250	33.5	1.0	10–5220	0.9998
cis-Permethrin	391.3	31.45	183	163	18.8	165	16.4	184	16.3	< 0.5	5.0–2530	0.9999
trans-Permethrin	391.3	31.64	183	163	28.0	165	23.1	184	18.1	< 0.5	6.0–2900	0.9999
phenanthrene-d_{10} (I.S.)	188.3	13.80	188	189	16.0	184	14.5	187	10.0			
Phorate	260.4	11.95	75	121	44.0	260	24.7	97	22.4	< 1.0	12–5760	0.9996
Phosalone	367.8	29.71	182	367	44.4	121	35.6	184	34.2	< 1.0	11–5580	0.9996
Phosmet	317.3	28.54	160	161	11.2	77	5.6	93	5.4	< 1.5	14–7245	0.9994
Prochloraz	376.7	31.81	180	70	69.9	308	45.2	310	45.1	6.0	12–5940	0.9970
Procymidone	284.1	22.89	96	283	64.1	285	41.5	67	41.4	1.0	9.0–4290	0.9999
Profenophos	373.6	23.93	208	339	91.7	139	84.9	206	78.4	3.0	10–5100	0.9997
Prometryn	241.4	17.44	241	184	64.5	226	50.8	105	24.8	< 1.5	12–5800	0.9992
Propargite	350.5	27.74	135	150	14.6	231	13.0	64	6.4	0.5	10–4780	0.9970
Propazine	229.7	13.47	214	229	59.6	172	44.5	58	37.0	< 1.0	10–5070	0.9993
Propetamphos	281.3	13.94	138	194	50.9	236	34.1	222	24.8	< 1.0	11–5580	0.9997
Propyzamide	256.1	14.05	173	175	58.0	145	29.1	255	26.6	1.5	12–5750	0.9998
Pyrimethanil	199.3	14.21	198	199	47.0	77	6.0	200	5.8	< 1.0	10–4970	0.9994
Quinalphos	298.3	21.65	146	157	61.0	118	15.4	156	11.2	50	100–9125	0.9997
Quintozene	295.3	13.74	237	249	75.5	295	65.1	214	63.2	< 2.0	18–8800	0.9997
Simazine	201.7	13.04	201	186	58.3	173	39.4	68	25.8	3.0	10–5190	0.9990
Tebuconazole	307.8	27.43	125	250	87.4	70	55.4	83	51.3	1.5	12–6050	0.9994
Tecnazene	260.9	11.45	203	261	83.1	215	81.9	201	80.3	1.0	8.0–4240	0.9967
Terbufos	288.4	13.79	231	57	77.5	103	26.9	153	25.4	< 1.0	14–6900	0.9999
Terbuthylazine	229.7	13.91	214	173	38.3	216	32.3	229	29.8	< 1.5	12–5860	0.9994

Table 1 (Continued)

pesticide	MW	t_R (min)	target (T)	qualifier ion 1 (Q_1)	Q_1/T (%)	qualifier ion 2 (Q_2)	Q_2/T (%)	qualifier ion 3 (Q_3)	Q_3/T (%)	LOD (mg/L)	range (mg/L)	r^2
Terbutryn	241.4	18.06	226	185	64.9	241	62.0	170	52.4	< 1.0	10–5000	0.9992
Tetrachlorovinphos	366.0	22.98	329	331	97.2	109	57.8	333	33.2	< 1.0	10–5025	0.9993
Tetradifon	356.1	29.47	159	111	67.1	229	65.0	227	63.0	1.0	10–5180	0.9998
Thiometon	246.3	12.35	88	125	66.5	89	38.6	93	34.1	1.5	13–6360	0.9998
Tolyfluanid	347.3	21.34	137	238	41.2	106	5.3	63	3.2	2.6	12–5220	0.9999
Triadimefon	293.8	19.39	57	208	84.0	85	31.1	210	27.6	1.0	10–5060	0.9996
Triadimenol	295.8	21.67	112	168	77.0	128	48.8	70	26.6	4.0	8.0–4050	0.9995
Tri-allate	304.7	14.98	86	268	58.8	270	39.2	128	26.1	< 1.0	10–5200	0.9997
Trifluralin	335.3	11.35	306	264	62.9	290	12.4	307	12.1	< 1.0	11–5580	0.9992
Vinclozolin	286.1	16.73	212	198	95.6	187	82.9	285	81.4	1.0	9.0–4560	0.9992

[a] The qualifier-to-target ratios (Q_1, Q_2, and Q_3) were determined by dividing the ion abundance (data not shown) of the qualifier by the abundance of the target ion (T). [b] Q/T (%) are the results of abundance values of the qualifier ion (Q_1, Q_2, or Q_3) divided by the abudnace of the target ion (T) × 100%.

under the same chromatographic conditions but utilizing full-scan conditions with the mass/charge scan ranging from 40 to 500 *m*/*z*. The qualifier-to-target percentage was then determined by dividing the abundance of the selected qualifier ion to that of the target ion multiplied by 100%. Quantitation was based on the peak area ratio of the target ion divided by the peak area of the internal standard (the internal standard with the retention time closest to that of the pesticide) versus concentration of the calibration standards and using the GC-MSD ChemStation software.

Quality Control. Quality control for the analysis of pesticides in wines consisted of 15 wine samples, 1 wine spike, 3 water blanks, 1 water spike, 8 calibration standards (ranging from 0.010 to 2.50 mg/L of SIM-1, SIM-2, or SIM-3 standards), a calibration check standard, and ethyl acetate rinses. Each of the three SIM programs consisted of its own calibration standards, wine and water spikes, and calibration check standard. The wine spikes were chosen randomly, usually from one of the last three samples of the batch, and consisted of fortifying the wine with either a SIM-1, SIM-2, or SIM-3 spike standard. Wine and water samples were fortified at 0.020 mg/L and analyzed as described previously. Acceptable spike recoveries ranged from 50 to 150%. Positive results in the wine samples were confirmed by comparing the retention time, identifying the target and qualifier ions, and determining the qualifier-to-target ratios of the peak in the wine sample with respect to that of a pesticide standard. Retention times had to be within ±0.50 min of the expected retention times, and qualifier-to-target ratios of the sample must be within 25% of the standard for positive confirmation. The water blanks and spikes were analyzed in order to account for any residual carryover or possible contamination sources, such as the glassware. The presence and confirmation of pesticides or pesticide residues in the water blanks resulted in the extraction and analysis of the entire batch being repeated. After completion of the standards, blanks, spikes, sample extracts, and rinses, a 0.250 mg/L calibration standard was analyzed to account for any differences or variations during the entire batch analysis. Any deviation beyond 20% required repeat injection or analysis of the entire batch. Quantitation of any pesticide(s) present in the wine extract was determined as described previously.

RESULTS AND DISCUSSION

GC-MSD/SIM, Sensitivity, and Linearity. Samples are analyzed by GC-MSD/SIM according to the conditions listed in the Methods and Materials (**Figure 1**; **Table 2**). Three injections in selective ion monitoring (SIM) mode under the same chromatographic temperature conditions (but different target and qualifier ions) were required to cover all 153 compounds. Chromatograms of an injected extract from a blank and spiked (1 mg/L) red wine, with data acquisition using the three SIM programs, are shown in **Figure 2**. Compounds are identified by their retention times and their qualifier-to-target abundance ratios, as listed in **Table 1**. Quantitation is based on the target ion and standards prepared in 0.1% corn oil/ethyl acetate to compensate for any possible matrix effects (*19*). The limit of detection (LOD) of each pesticide listed in **Table 1** was determined from injection of the standards and was defined as approximately 3 times the standard deviation. Of these pesticides, 138 had LODs less than 0.005 mg/L, with 82 pesticides having LODs equal to or less than 0.001 mg/L. The highest LOD was determined for Dinoseb, at 150 mg/L. Linearity was obtained for pesticides by using standards ranging from 0.010 to 5.0 mg/L, and 147 of the compounds have $r^2 > 0.99$. Pesticides with $r^2 < 0.99$ were Bromoxynil, Captafol, Dinoseb, Folpet, Imazalil, and Oryzalin, which coincidentally had LODs greater than 0.010 mg/L. Due to the low r^2 and high LOD values, capillary gas chromatography may not be the appropriate method to fully optimize the analysis of these compounds. Most of these compounds, such as the polar organochlorine (Captafol and Folpet), the dinitro (Dinoseb and Oryzalin), and the hydroxybenzonitrile compounds (Bromoxynil), have been effectively measured by high-performance chromatography (HPLC) methods (*21*).

Spike Recoveries. Spike recoveries were determined by adding the pesticides and pesticide residues (SIM-1, SIM-2, or SIM-3 standards) to a red or white wine at a final concentration of 0.01 or 0.10 mg/L and analyzing the spiked wines using the proposed method (**Tables 3–5**). For the high spike concentration (0.10 mg/L), spike recoveries greater than 70% were found for 123 and 128 pesticide residues (out of 153 total pesticides) from extracted red and white wines, respectively. Recoveries of 52 and 62 compounds higher than 90% were observed for extracted red and white wines, respectively. The data also showed that 30 pesticides in red wines and 25 pesticides in white wines had spike recoveries below 70%. These numbers are similarly reflected for the red and white wines spiked at the low-spiked concentration (0.01 mg/L). Spike recoveries above 70% for the low spiked samples were found in 116 and 124 pesticide residues from extracted red and white wines, respectively. The data at 0.01 mg/L were similar to the recoveries at 0.10 mg/L, which revealed 50 and 52 pesticides with spike recoveries higher than 90% for the red and white wines.

Tables 3, **4**, and **5** list spike recoveries for primarily halogen-, nitrogen-, and phosphorus-containing pesticides using the SIM-1, SIM-2, and SIM-3 programs, respectively. Since most of the pyrethroid pesticides eluted later using the GC temperature program, these compounds were split among the SIM-1 and SIM-2 programs as shown in **Table 2**, and the spike recovery data are listed in **Table 3**. From **Table 5**, organophosphate pesticides and the organosulfur pesticide, Propargite, generally had spike recoveries greater than 80% for high- and low-spiked

Table 2. SIM Programs (SIM-1, SIM-2, and SIM-3) Used To Analyze and Confirm Pesticides in Wines

group	time (min)	pesticides and internal standards (I.S.)	ions (amu)	dwell time (ms)	scan rate (cycles/s)
		SIM-1			
1	5.00	acenaphthalene-d_{10} (I.S.)	80, 160, 162, 164	30	5.41
2	10.00	Tecnazene	201, 203, 215, 261	30	5.41
3	11.75	Diallate I, BHC-α, Diallate II, Hexachlorobenzene, Dicloran	86, 128, 176, 178, 181, 183, 206, 208, 217, 219, 234, 236, 282, 284, 286, 288	25	1.55
4	13.00	Lindane, Pentachloronitrobenzene, Phenanthrene-d_{10} (I.S.), Propyzamide, BHC-δ	111, 145, 173, 175, 181, 183, 184, 187, 188, 189, 214, 217, 219, 237, 249, 295	25	1.46
5	15.50	Vinclozolin, Heptachlor, Alachlor	45, 100, 146, 160, 187, 188, 198, 212, 270, 272, 274, 285	30	1.83
6	17.75	Aldrin, 4,4′-Dichlorobenzophenone	66, 111, 139, 141, 250, 261, 263, 265	30	2.74
7	20.00	Heptachlor epoxide	351, 353, 355, 357	30	5.41
8	20.90	Penconazole, Captan, Chlozolinate	77, 79, 80, 151, 159, 161, 186, 187, 188, 248, 250, 259	30	1.83
9	21.55	Folpet, Triadimenol, Chlorbenside, Allethrin, Furalaxyl, Procymidone, trans-Chlordane	67, 70, 76, 79, 95, 96, 104, 107, 112, 123, 125, 127, 128, 136, 146, 147, 152, 168, 242, 260, 268, 270, 283, 285, 371, 373, 375, 377	20	1.02
10	22.45	Endosulfan-α, cis-Chlordane	195, 237, 239, 241, 371, 373, 375, 377	30	2.74
11	23.25	Hexaconazole, Dieldrin	79, 82, 83, 214, 216, 263, 277, 279	30	2.74
12	24.35	Endrin, Nitrofen, Endosulfan-β, o,p′-DDT, Endrin aldehyde	67, 165, 195, 202, 207, 235, 236, 237, 241, 250, 253, 263, 283, 285, 315, 317, 319, 345, 347	25	1.24
13	26.35	Benalaxyl, p,p′-DDT	91, 148, 165, 204, 206, 235, 236, 237	30	2.74
14	27.25	Tebuconazole, Captafol	70, 77, 79, 80, 83, 125, 151, 250	30	2.74
15	27.95	Endrin ketone, chrysene-d_{12}, Iprodione, Bromopropylate, Methoxychlor	67, 113, 152, 183, 187, 189, 227, 228, 236, 238, 240, 241, 244, 314, 315, 317, 319, 339, 341, 343	20	1.42
16	29.15	Tetradifon, Mirex	111, 159, 227, 229, 237, 270, 272, 274	30	2.74
17	31.10	Permethrin I, Permethrin II, Prochloraz	70, 163, 165, 180, 183, 184, 308, 310	30	2.74
18	32.05	Cyfluthrin I–IV	163, 165, 199, 206, 227	30	4.35
19	33.50	Fenvalerate I–II, Fluvalinate tau I–II	125, 152, 167, 169, 181, 209, 250, 252	30	2.74
20	35.50	Deltamethrin	181, 251, 253, 255	30	5.41
		SIM-2			
1	6.00	acenaphthalene-d_{10} (I.S.), Dichlobenil, Eptam	43, 80, 86, 100, 128, 132, 136, 160, 162, 164, 171, 173	30	1.83
2	9.00	Benfluralin, Bromoxynil, Ethalfuralin, Trifluralin	88, 264, 275, 276, 277, 279, 290, 292, 293, 306, 307, 316, 333	30	1.69
3	12.50	Atrazine, Carbofuran, Phenanthrene-d_{10} (I.S.), Propazine, Simazine, Terbuthylazine	44, 58, 123, 131, 149, 164, 172, 173, 184, 186, 187,188, 189, 200, 201, 202, 214, 215, 216, 229	30	1.10
4	14.05	Chlorothalonil, Dinoseb, Pyrimethanil, Tri-allate	77, 86, 117, 128, 147, 163, 198, 199, 200, 211, 240, 264, 266, 268, 270	30	1.47
5	15.80	Carbaryl, Desmetryn, Vinclozolin	58, 115, 116, 144, 145, 171, 187, 196, 198, 212, 213, 285	30	1.83
6	17.05	Metalaxyl, Prometryn, Terbutryn	45, 105, 160, 170, 184, 185, 187, 198, 206, 212, 226, 241, 249, 285	30	1.57
7	18.85	Cyanazine, Cyprodinil, Fenpropimorph, Metolachlor, Nitrothal-isopropyl, Triadimefon	57, 68, 77, 85, 117, 128, 129, 146, 159, 162, 194, 208, 210, 212, 213, 214, 224, 225, 236, 238, 240, 254, 303	20	1.14
8	21.05	Fludioxonil, Imazalil, Myclobutanil, Napropamide, Oxadiazon, Oxyfluorfen, Procymidone	41, 67, 72, 82, 96, 100, 127, 128, 150, 154, 173, 175, 177, 179, 181, 182, 215, 217, 248, 252, 258, 260, 271, 283, 285, 302, 331, 361	20	1.02
9	25.45	Hexazinone, Norflurazon, Oxadixyl, Propargite	45, 71, 83, 102, 105, 128, 132, 135, 145, 150, 163, 171, 231, 303, 305, 350	30	1.38
10	28.00	chrysene-d_{12} (I.S.), Fenpropathrin, Iprodione, Nitalin	97, 125, 181, 187, 189, 236, 238, 240, 241, 244, 265, 274, 300, 314, 316, 317	30	1.38
11	29.95	Cyhalothrin, Fenarimol	77, 107, 139, 181, 197, 208, 209, 219, 251	30	2.44
12	30.95	Bitertanol I– II, Oryzalin	57, 58, 168, 170, 171, 258, 275, 317	30	2.74
13	31.85	Cypermethrin I–IV, Flucythrinate I–II	44, 77, 157, 163, 165, 181, 199, 207, 209	30	2.44
		SIM-3			
1	4.50	Dichlorvos	79, 109, 185, 187	30	5.41
2	6.75	Acephate, Mevinphos, acenaphthalene-d_{10}	42, 67, 80, 94, 95, 109, 127, 136, 160, 162, 164, 192	30	1.83
3	9.00	Omethoate, Demeton-O	60, 79, 88, 89 109, 110, 156, 170	30	2.74
4	10.90	Naled (Dibrom), Dicrotophos, Monocrotophos, Phorate	67, 72, 75, 79, 97, 109, 121, 127, 145, 185, 192, 193, 260	30	1.69
5	12.18	Thiometon, Demeton-S, Dimethoate	60, 87, 88, 89, 93, 125, 143, 170	30	2.74
6	13.20	phenanthrene-d_{10}, Terbufos, Fonophos, Propetamphos	57, 103, 109, 110, 137, 138, 153, 184, 187, 188, 189, 194, 222, 231, 236, 246	30	1.77

Table 2 (Continued)

group	time (min)	pesticides and internal standards (I.S.)	ions (amu)	dwell time (ms)	scan rate (cycles/s)
7	14.20	Diazinon, Disulfoton	88, 89, 97, 137, 142, 152, 179, 199	30	2.74
8	15.50	Chlorpyrifos-methyl, Parathion-methyl, Malaoxon	79, 99, 109, 125, 127, 263, 286, 288, 290	30	2.44
9	17.15	Paraoxon	109, 139, 149, 275	30	5.41
10	17.85	Fenitrothion, Dichlofluanid, Malathion	93, 109, 123, 125, 127, 167, 173, 224, 226, 260, 277	30	2.00
11	19.00	Fenthion, Chlorpyrifos, Parathion	97, 109, 125, 139, 169, 197, 199, 278, 291, 314	30	2.20
12	19.85	Bromophos-methyl	125, 329, 331, 333	30	5.41
13	20.90	Chlorvinfenphos, Isofenphos, Quinalphos, Tolyfluanid	58, 63, 106, 118, 121, 137, 146, 156, 157, 213, 238, 255, 267, 269, 323, 325	30	1.55
14	21.95	Methidathion, Bromophos-ethyl, Tetrachlorvinphos	85, 93, 109, 125, 145, 301, 303, 329, 331, 333, 357, 359	30	1.83
15	23.20	Fenamiphos, Profenophos	139, 154, 206, 208, 217, 288, 303, 339	30	2.74
16	25.05	Ethion	97, 125, 153, 231	30	3.64
17	27.50	Carbophenothion, Phosmet, EPN, Azinphos-methyl, chrysene-d_{12} (I.S.)	77, 93, 141, 157, 160, 161, 169, 185, 236, 238, 240, 241	30	1.83
18	29.15	Phosalone	121, 182, 184, 367	30	5.41
19	30.15	Azinphos-ethyl, Dialifos	76, 77, 105, 132, 160, 173, 208, 210	30	2.74
20	31.20	Coumaphos, Dioxathion	97, 109, 125, 153, 210, 226, 271, 362	30	2.74

concentrations in both red and white wines, with the exception of Acephate, Demeton-O and -S, Dichlorvos, Dicrotophos, Dimethoate, Mevinphos, Monocrotophos, Naled, and Omethoate. Most of the aforementioned pesticides have early GC retention times (<12 min) and are water-soluble and polar compounds. Although the Oasis HLB cartridges are known to retain both polar and nonpolar compounds, the nonpolar elution conditions used (ethyl acetate/hexane) may not have been optimized to elute these particular organophosphates.

The organohalogenated pesticides (**Table 3**) such as the N-trihalomethylhalo compounds, Captafol and Folpet, the dicarboximide pesticides, Iprodione and Chlozolinate, and the organochlorine compound, Endrin aldehyde, showed recoveries less than 70% for both wine types and at both concentrations. Iprodione has been shown to thermally degrade to its (3,5-dichlorophenyl)hydantoin product under GC conditions (*21*), whereas the structural differences between Endrin aldehyde and its isomers Endrin and Endrin ketone may affect its retention and elution from the Oasis HLB sorbent. The method was shown to be effective in analyzing nitrogen-containing pesticides, as shown in **Table 4**. Recoveries in excess of 70% have been observed for most of these organonitrogen pesticides, such as the 1,3,5-triazines and amides (phenylamides, Napropamide, and Propyzamide), and most of the azole pesticides, such as Myclobutanil, Triadimefon, and its degradation product, Triadimenol. However, in addition to some of the polar organonitrogen pesticides previously mentioned, others, such as Chlorothalonil, Desmetryn, Fenpropimorph, Hexazinone, and Prochloraz, showed poor spike recoveries (<60%) in both red and white wines.

One aim of the study was to develop an analytical method that can qualitate, quantitate, and confirm as many pesticides as possible. The method was not set up to specify any one pesticide or particular group of pesticides, with the exceptions that the pesticide must be susceptible for GC analysis and that the procedures are focused and geared toward wines or similar beverage alcohol products. Unfortunately, in the case of multiresidue methods and procedures, the conditions for extraction, cleanup, and gas chromatography cannot be optimally set for all of the compounds to be screened and analyzed. Regarding the spike recovery data from **Tables 3−5**, most of the recoveries of pesticides from both red and white wines were greater than 70%, with the exception of a few, primarily polar compounds. The method could then probably be modified to accommodate the more polar of these pesticides by utilizing less hexane in the existing extraction solvent or a more polar solvent such as acetone or methylene chloride.

A cleanup step is required because pesticide recoveries greater than 125% have been observed in wines using C-18 extraction cartridges without any additional sample preparation (*11*, *14*). Schenck and Lehotay (*19*) proposed the use of $MgSO_4$ as a better anhydrous reagent than $NaSO_4$ to remove any water residues, in combination with a tandem graphitized carbon−aminopropyl cartridge to reduce any matrix interferences and effects. However, Hengel and Shibamoto (*20*) simplified the cleanup by eliminating the use of the graphitized carbon cartridge, utilizing the aminopropyl cartridge to remove any coextractives from malt beverages, and preparing standards and extracts in 0.1% corn oil/ethyl acetate. Other groups have utilized various cleanup procedures, such as the use of charcoal−Celite for fruit and vegetable matrices (*16*) and of florisil for malt beverages and wines (*10*, *17*).

The spike recovery data shown in **Tables 3−5** suggest that the combination of the eluting solvents (hexane/ethyl acetate) and the cleanup cartridge may have been effective in minimizing any matrix enhancement effects. Jiménez et al. (*17*) showed that eluting the pesticides in wine from an Oasis HLB cartridge using ethyl acetate resulted in spike recoveries ranging from 100% to as high as 530% for 37 pesticides analyzed. They avoided the matrix enhancement effect by utilizing a propanol aqueous rinse, florisil cleanup, and calibration standards prepared in fortified extracts. In the present work, we utilized an $MgSO_4$-topped aminopropyl cartridge for cleanup, a stronger nonpolar solvent mixture consisting of ethyl acetate and hexane, and preparation of standards and the wine extracts in 0.1% corn oil/ethyl acetate. The data at the low-spike concentrations (0.01 mg/L) revealed that only 7 of the 153 pesticides tested have recoveries greater than 110%, suggesting that the combination of these methods can be used to minimize possible matrix enhancement.

Analysis of a Wine Sample. An example of the pesticide screening in wines by GC-MSD/SIM is shown in **Figure 3**. A white wine sample was extracted using the procedures outlined in **Figure 1** and described under the Methods and Materials. Three injections of the wine extract were analyzed by GC-MS/SIM using slight modifications of the three SIM programs

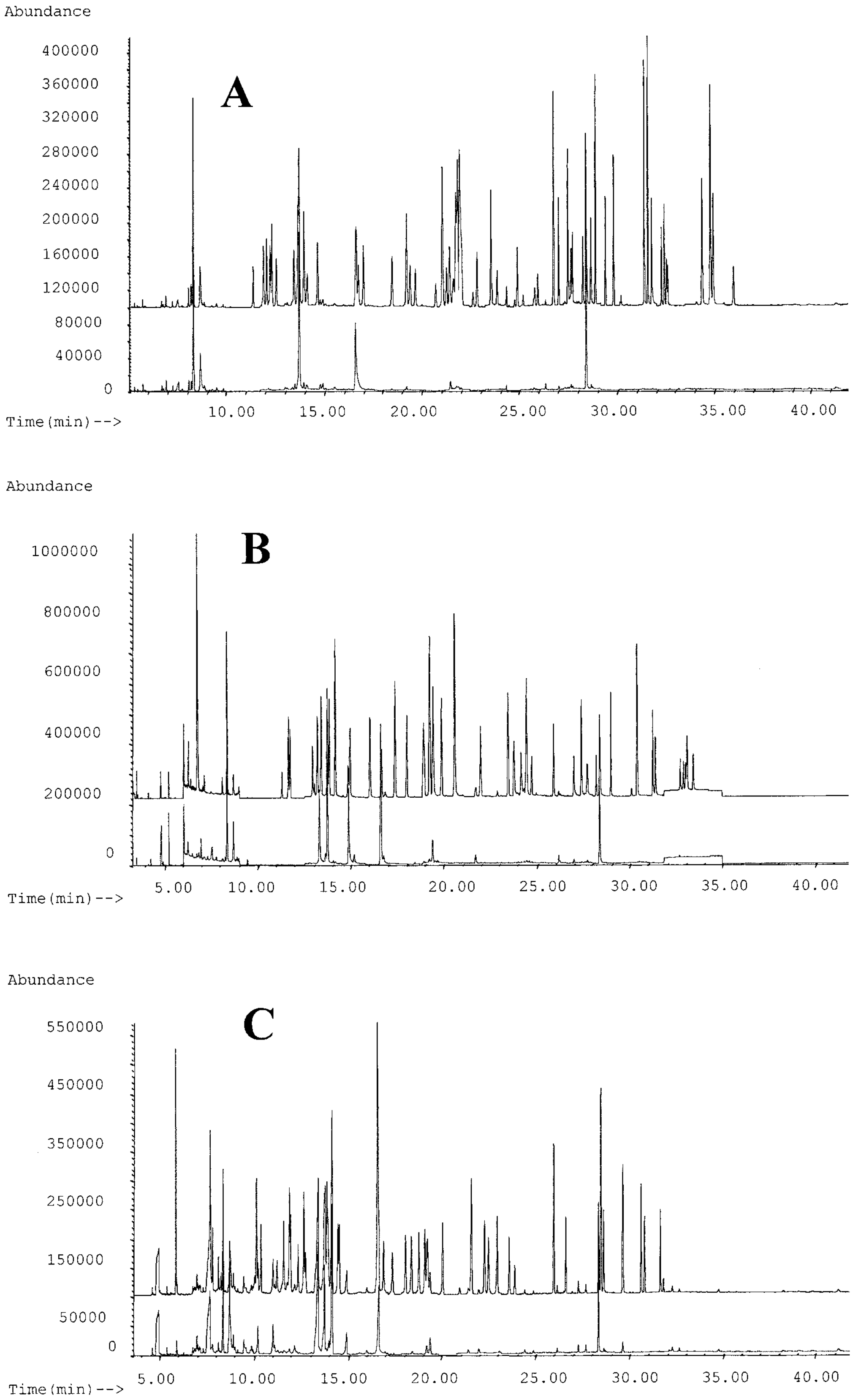

Figure 2. Reconstructed GC-MSD/SIM chromatograms from the three SIM programs used to screen pesticides in a red wine extract. Results from the three SIM programs, (A) SIM-1, (B) SIM-2, and (C) SIM-3, as described in **Table 2**. Each chromatogram shows a red wine blank extract (bottom) and a fortified extract of 1 mg/L (top). See Methods and Materials for extraction details and GC-MS conditions.

(pesticides with spike recoveries lower than 50% were eliminated). Both SIM-1 and SIM-3 results did not reveal any presence of the pesticides. However, Carbaryl and Metalaxyl were detected from the modified SIM-2 program (**Figure 3A**). The pesticide Carbaryl and the fungicide Metalaxyl are registered with the U.S. EPA and commonly used on grapes in the

Table 3. Spike Recoveries of Primarily Halogen-Containing and Pyrethroid Pesticides Extracted from Red and White Wines Spiked at "High Spike" (0.10 mg/L) and "Low Spike" (0.01 mg/L) Concentrations[a]

	SIM program	high spike		low spike	
		red	white	red	white
Organohalogen					
benzilate					
Bromopropylate	1	89 ± 1	90 ± 1	90 ± 3	90 ± 2
chloroacetanilide					
Alachlor	1	97 ± 2	94 ± 1	88 ± 1	88 ± 2
Metolachlor	1	92 ± 2	88 ± 4	87 ± 12	106 ± 6
dicarboximide					
Chlozolinate	1	51 ± 4	71 ± 11	48 ± 5	77 ± 4
Iprodione	1	47 ± 3	37 ± 2	73 ± 6	77 ± 5
Procymidone	1	88 ± 2	91 ± 2	79 ± 5	82 ± 6
Vinclozolin	1	83 ± 2	80 ± 3	83 ± 2	91 ± 4
N-trihalomethylhalo					
Captafol	1	12 ± 2	33 ± 13	69 ± 3	100 ± 5
Captan	1	64 ± 3	80 ± 8	89 ± 4	109 ± 3
Dichlofluanid	1	90 ± 3	104 ± 2	80 ± 9	92 ± 7
Folpet	1	n.d.	9 ± 4	n.d.	57 ± 2
Tolyfluanid	1	112 ± 5	91 ± 6	107 ± 4	92 ± 16
organochlorine					
Aldrin	1	80 ± 2	80 ± 1	69 ± 2	74 ± 1
BHC-α	1	88 ± 1	85 ± 1	72 ± 2	73 ± 1
BHC-δ	1	90 ± 1	88 ± 1	85 ± 2	86 ± 2
cis-Chlordane	1	83 ± 2	84 ± 1	75 ± 3	81 ± 2
trans-Chlordane	1	81 ± 2	84 ± 1	74 ± 2	85 ± 3
o,p′-DDT	1	82 ± 4	85 ± 3	81 ± 5	93 ± 3
p,p′-DDT	1	82 ± 3	86 ± 1	78 ± 4	89 ± 2
4,4′-Dichlorobenzophenone	1	97 ± 1	96 ± 1	104 ± 4	107 ± 4
Dieldrin	1	94 ± 1	93 ± 1	87 ± 3	87 ± 3
Endosulfan-α	1	90 ± 1	91 ± 1	83 ± 2	86 ± 5
Endosulfan-β	1	95 ± 1	91 ± 1	86 ± 4	89 ± 5
Endrin	1	78 ± 1	81 ± 2	72 ± 4	75 ± 2
Endrin aldehyde	1	2 ± 0.3	3 ± 0.4	nd	nd
Endrin ketone	1	86 ± 2	85 ± 1	81 ± 3	83 ± 3
Heptachlor	1	80 ± 1	80 ± 1	74 ± 3	76 ± 2
Heptachlor epoxide	1	85 ± 1	85 ± 1	79 ± 2	80 ± 2
Hexachlorobenzene	1	77 ± 1	74 ± 1	68 ± 2	66 ± 1
Lindane	1	91 ± 1	89 ± 1	86 ± 2	85 ± 3
Methoxychlor	1	88 ± 2	90 ± 1	83 ± 3	91 ± 2
Mirex	1	78 ± 3	84 ± 2	70 ± 4	85 ± 2
Tetradifon	1	94 ± 2	94 ± 1	90 ± 3	91 ± 2
phenol sulfide					
Chlorbenside	1	93 ± 1	90 ± 1	101 ± 4	97 ± 6
Pyrethroid					
Allethrin	2	95 ± 2	93 ± 1	93 ± 5	91 ± 2
Cyfluthrin I	2	82 ± 3	88 ± 2	79 ± 5	94 ± 2
Cyfluthrin II	2	81 ± 3	87 ± 2	77 ± 5	92 ± 2
Cyfluthrin III	2	84 ± 3	88 ± 2	83 ± 5	93 ± 3
Cyfluthrin IV	2	86 ± 4	90 ± 2	82 ± 7	94 ± 4
Cyhalothrin	2	71 ± 2	78 ± 2	60 ± 4	69 ± 4
Cypermethrin I	2	73 ± 2	82 ± 2	66 ± 4	80 ± 4
Cypermethrin II	2	74 ± 1	81 ± 2	71 ± 4	85 ± 4
Cypermethrin III	2	72 ± 2	82 ± 2	69 ± 4	83 ± 4
Cypermethrin IV	2	71 ± 1	81 ± 2	65 ± 4	78 ± 4
Deltamethrin	2	78 ± 4	84 ± 2	75 ± 4	89 ± 2
Fenpropathrin	2	79 ± 2	86 ± 3	69 ± 6	79 ± 6
Fenvalerate I	2	82 ± 3	87 ± 2	76 ± 5	89 ± 2
Fenvalerate II	2	85 ± 4	92 ± 3	89 ± 11	110 ± 8
Flucythrinate I	2	71 ± 2	79 ± 2	64 ± 5	79 ± 4
Flucythrinate II	2	71 ± 1	79 ± 2	62 ± 4	77 ± 4
Fluvalinate tau-I	2	85 ± 4	82 ± 2	89 ± 11	86 ± 2
Fluvalinate tau-II	2	77 ± 3	83 ± 2	71 ± 4	84 ± 2
Permethrin I	2	83 ± 3	89 ± 2	79 ± 5	90 ± 2
Permethrin II	2	83 ± 3	88 ± 2	79 ± 5	89 ± 2

[a] Each spike recovery is an average ± standard deviation obtained from using $n = 6$ samples. nd, not detected. The "SIM program" column refers to the program (see **Table 2** for details) used to analyze the pesticide.

United States and most wine-producing countries (*2*, *3*). **Figure 3B**,**C** shows the extracted ions characteristic of the two pesticides from **Figure 3A**. The target ion (m/z 144) and three qualifier ions (m/z 115, 116, and 145) at a retention time of 16.87 min, as well as the qualifier-to-target ratios, were used to identify, quantitate (based on m/z 144 only), and confirm the presence of Carbaryl in the wine at a concentration of 0.024 mg/L. However, the split peak in **Figure 3B** suggests that the carbamate pesticide may be thermally degrading. Although Carbaryl can be analyzed by GC methods, it is also commonly

Table 4. Spike Recoveries of Primarily Nitrogen-Containing Pesticides Extracted from Red and White Wines Spiked at “High Spike” (0.10 mg/L) and “Low Spike” (0.01 mg/L) Concentrations[a]

	SIM program	high spike		low spike	
		red	white	red	white
		Organonitrogen			
1,2,4-triazinone					
Hexazinone	2	16 ± 6	53 ± 8	8 ± 5	28 ± 6
1,3,5-triazine					
Atrazine	2	91 ± 2	91 ± 3	104 ± 5	107 ± 3
Cyanazine	2	90 ± 3	98 ± 5	157 ± 8	150 ± 8
Desmetryn	2	59 ± 5	82 ± 5	52 ± 4	90 ± 5
Prometryn	2	78 ± 3	78 ± 10	87 ± 6	93 ± 3
Propazine	2	90 ± 2	89 ± 3	101± 5	98 ± 4
Simazine	2	97 ± 2	95 ± 3	127 ± 5	125 ± 3
Terbuthylazine	2	88 ± 2	88 ± 3	96 ± 4	94 ± 4
Terbutryn	2	76 ± 7	75 ± 12	82 ± 6	89 ± 3
2,6-dinitroaniline					
Benfluralin	2	70 ± 6	72 ± 3	67 ± 4	67 ± 3
Ethalfluralin	2	67 ± 7	69 ± 3	73 ± 4	75 ± 3
Nitralin	2	67 ± 1	64 ± 3	72 ± 2	78 ± 2
Oryzalin	2	50 ± 3	41 ± 1	nd	nd
Trifluralin	2	69 ± 6	70 ± 3	68 ± 4	68 ± 3
alkanamide					
Napropamide	2	94 ± 5	100 ± 3	88 ± 5	88 ± 7
amide					
Propyzamide	2	93 ± 2	95 ± 1	93 ± 2	96 ± 2
anilinopyrimidine					
Cyprodinil	2	72 ± 3	62 ± 12	64 ± 7	62 ± 12
Pyrimethanil	2	87 ± 3	94 ± 4	79 ± 6	109 ± 2
azole					
Bitertanol I	2	79 ± 4	84 ± 3	64 ± 6	61 ± 3
Bitertanol II	2	79 ± 4	84 ± 3	70 ± 5	67 ± 2
Hexaconazole	2	66 ± 5	25 ± 20	54 ± 6	40 ± 11
Imazalil	2	nd	nd	nd	nd
Myclobutanil	2	86 ± 4	96 ± 4	108 ± 8	110 ± 9
Penconazole	2	91 ± 2	88 ± 5	91 ± 4	87 ± 3
Prochloraz	2	14 ± 8	21 ±18	35 ± 1	49 ± 8
Tebuconazole	2	83 ± 2	70 ± 14	80 ± 4	83 ± 7
Triadimefon		92 ± 5	97 ± 3	105 ± 5	101 ± 6
Triadimenol	2	98 ± 1	89 ± 6	108 ± 10	98 ± 5
benzonitrile					
Bromoxynil	2	nd	nd	nd	nd
Chlorothalonil	2	53 ± 5	30 ± 4	81 ± 5	69 ± 3
Dichlobenil	2	67 ± 10	77 ± 6	62 ± 3	69 ± 4
carbamate/thiocarbamate					
Carbaryl	2	86 ± 5	71 ± 9	124 ± 12	100 ± 11
Carbofuran	2	78 ± 3	73 ± 4	144 ± 7	134 ± 6
Diallate-I	2	89 ± 1	86 ± 1	89 ± 2	87 ± 1
Diallate-II	2	89 ± 1	86 ± 1	88 ± 2	89 ± 2
Eptam	2	66 ± 10	74 ± 6	58 ± 3	69 ± 6
Tri-allate	2	71 ± 6	74 ± 3	78 ± 5	77 ± 3
dinitrophenol					
Dinoseb	2	nd	nd	nd	nd
diphenyl ether					
Oxyfluoren	2	73 ± 3	74 ± 3	72 ± 6	79 ± 2
morpholine					
Fenpropimorph	2	6 ± 0.1	8 ± 6	21 ± 0.6	27 ± 5
nitroaniline					
Dicloran	2	91 ± 2	87 ± 2	94 ± 2	102 ± 1
nitrobenzene					
Quintozene	2	80 ± 1	77 ± 1	72 ± 2	71 ± 1
Tecnazene	2	82 ± 1	77 ± 1	85 ± 2	79 ± 1
nitroisophthalate					
Nitrothal-isopropyl	2	78 ± 2	75 ± 3	86 ± 3	85 ± 2
nitrophenol ether					
Nitrofen	2	78 ± 2	76 ± 2	80 ± 2	83 ± 1
oxadiazole					
Oxadiazon	2	88 ± 3	94 ± 4	80 ± 6	82 ± 4
phenylamide					
Benalaxyl	2	98 ± 2	96 ± 1	95 ± 3	95 ± 3
Furalaxyl	2	97 ± 3	94 ± 2	95 ± 6	91 ± 2
Metalaxyl	2	89 ± 2	91 ± 3	100 ± 5	104 ± 2
Oxadixyl	2	86 ± 2	97 ± 3	82 ± 6	84 ± 5
phenylpyrrole					
Fludioxinil	2	92 ± 3	92 ± 5	77 ± 6	102 ± 5
pyridazinone					
Norflurazon	2	90 ± 3	98 ± 2	69 ± 5	123 ± 2
pyrimidinyl carbinol					
Fenarimol	2	84 ± 2	92 ± 2	80 ± 5	80 ± 5

Table 5. Spike Recoveries of Phosphorus- and Sulfur-Containing Pesticides Extracted from Red and White Wines Spiked at "High Spike" (0.10 mg/L) and "Low Spike" (0.01 mg/L) Concentrations[a]

		high spike		low spike	
	SIM program	red	white	red	white
		Organophosphorus			
Acephate	3	11 ± 0.4	9 ± 2	109 ± 13	81 ± 1
Azinphos-ethyl	3	100 ± 2	98 ± 2	101 ± 2	96 ± 4
Azinphos-methyl	3	101 ± 2	98 ± 2	106 ± 2	100 ± 4
Bromophos	3	78 ± 6	94 ± 8	81 ± 1	94 ± 4
Bromophos-methyl	3	85 ± 6	87 ± 2	85 ± 1	72 ± 5
Carbophenothion	3	85 ± 6	89 ± 2	90 ± 1	79 ± 5
Chlorfenvinphos	3	96 ± 1	96 ± 1	101 ± 1	95 ± 4
Chlorpyrifos	3	89 ± 7	93 ± 3	98 ± 5	81 ± 5
Chlorpyrifos-methyl	3	89 ± 5	91 ± 3	91 ± 2	79 ± 6
Coumaphos	3	88 ± 4	90 ± 2	97 ± 2	88 ± 5
Demeton-O	3	65 ± 7	61 ± 4	64 ± 7	57 ± 6
Demeton-S	3	100 ± 2	105 ± 2	93 ± 1	79 ± 4
Dialifos	3	87 ± 8	91 ± 3	93 ± 2	85 ± 6
Diazinon	3	96 ± 2	95 ± 2	98 ± 1	89 ± 5
Dichlorvos	3	31 ± 4	55 ± 7	21 ± 7	50 ± 6
Dicrotophos	3	5 ± 0.4	5 ± 0.2	27 ± 1	nd
Dimethoate	3	48 ± 2	59 ± 2	52 ± 3	48 ± 4
Dioxathion	3	91 ± 7	95 ± 4	126 ± 8	93 ± 6
Disulfoton	3	92 ± 4	91 ± 3	84 ± 2	71 ± 5
EPN	3	80 ± 6	85 ± 3	85 ± 1	77 ± 4
Ethion	3	83 ± 6	89 ± 3	90 ± 1	81 ± 5
Fenamiphos	3	98 ± 2	95 ± 1	103 ± 2	94 ± 5
Fenitrothion	3	97 ± 2	96 ± 2	92 ± 2	82 ± 3
Fenthion	3	95 ± 5	96 ± 2	99 ± 1	84 ± 6
Fonophos	3	93 ± 4	95 ± 2	92 ± 1	89 ± 6
Isofenphos	3	92 ± 3	94 ± 2	98 ± 1	89 ± 6
Malaoxon	3	92 ± 2	96 ± 2	96 ± 5	98 ± 8
Malathion	3	103 ± 2	103 ± 2	98 ± 1	92 ± 4
Methidathion	3	100 ± 1	97 ± 1	102 ± 2	94 ± 4
Mevinphos	3	26 ± 2	31 ± 1	28 ± 2	31 ± 2
Monocrotophos	3	4 ± 1	3 ± 1	23 ± 0.2	nd
Naled (Dibrom)	3	11 ± 9	20 ± 8	nd	nd
Omethoate	3	5 ± 0.1	4 ± 0.01	45 ± 0.03	nd
Paraoxon	3	104 ± 2	104 ± 2	112 ± 7	108 ± 6
Parathion	3	92 ± 4	93 ± 2	86 ± 1	76 ± 4
Parathion-methyl	3	96 ± 2	99 ± 2	97 ± 2	102 ± 11
Phorate	3	91 ± 4	90 ± 2	82 ± 2	72 ± 6
Phosalone	3	94 ± 4	96 ± 3	118 ± 11	118 ± 9
Phosmet	3	89 ± 2	93 ± 1	88 ± 5	92 ± 4
Profenophos	3	81 ± 3	88 ± 3	86 ± 5	84 ± 5
Propetamphos	3	103 ± 2	102 ± 2	102 ± 1	94 ± 4
Quinalphos	3	98 ± 1	101 ± 3	119 ± 3	110 ± 6
Terbufos	3	82 ± 5	84 ± 3	79 ± 2	68 ± 6
Tetrachlorvinphos	3	91 ± 2	91 ± 1	96 ± 2	93 ± 4
Thiometon	3	96 ± 3	92 ± 2	92 ± 2	81 ± 3
		Organosulfur			
Propargite	2	96 ± 3	98 ± 4	91 ± 12	93 ± 8

[a] Each spike recovery is an average ± standard deviation obtained from using $n = 6$ samples. nd, not detected. The "SIM program" column refers to the program (see **Table 2** for details) used to analyze the pesticide.

analyzed by high-performance liquid chromatography with postcolumn derivatization/fluorescence detection (HPLC-PCD/FLD) or HPLC−mass spectrometry (HPLC-MSD) (*23*, *24*). Future work will be focused on solid-phase extraction and cleanup procedures for HPLC analysis.

Metalaxyl was determined and identified by the presence of its target ion (m/z 206) and three qualifier ions (m/z 45, 160, and 249) at a retention time of 17.38 min and confirmed by its three qualifier-to-target ratios. **Figure 3C** shows the extracted ions for Metalaxyl from **Figure 3A**. The peaks are symmetric, and the three qualifier-to-target ion ratios are within specifications of the standards. Quantitation of the target ion (m/z 206) reveals that Metalaxyl is present in the wine sample at a concentration of 0.006 mg/L. The identification, confirmation, and quantitation of these pesticides in a wine sample indicate that the proposed method is effective in screening pesticides whose ions have been incorporated into the SIM programs.

With the development of this multiresidue method, 153 pesticides were analyzed in wine. This methodology was shown to be rugged and sensitive for both red and white wine matrices and can be easily modified to accommodate more compounds. The utilization of mass spectrometric detection provides both quantitative information and confirmation of pesticide residues in wines. This proposed method is currently being incorporated for the routine analysis of domestic and foreign wines sold in the United States. It has already been used to screen 167 wine samples. Future consideration of the sample preparation method includes the analysis of thermally labile pesticides using HPLC-PCD/FLD and HPLC-MSD methods, as well as automating the extraction and cleanup procedures.

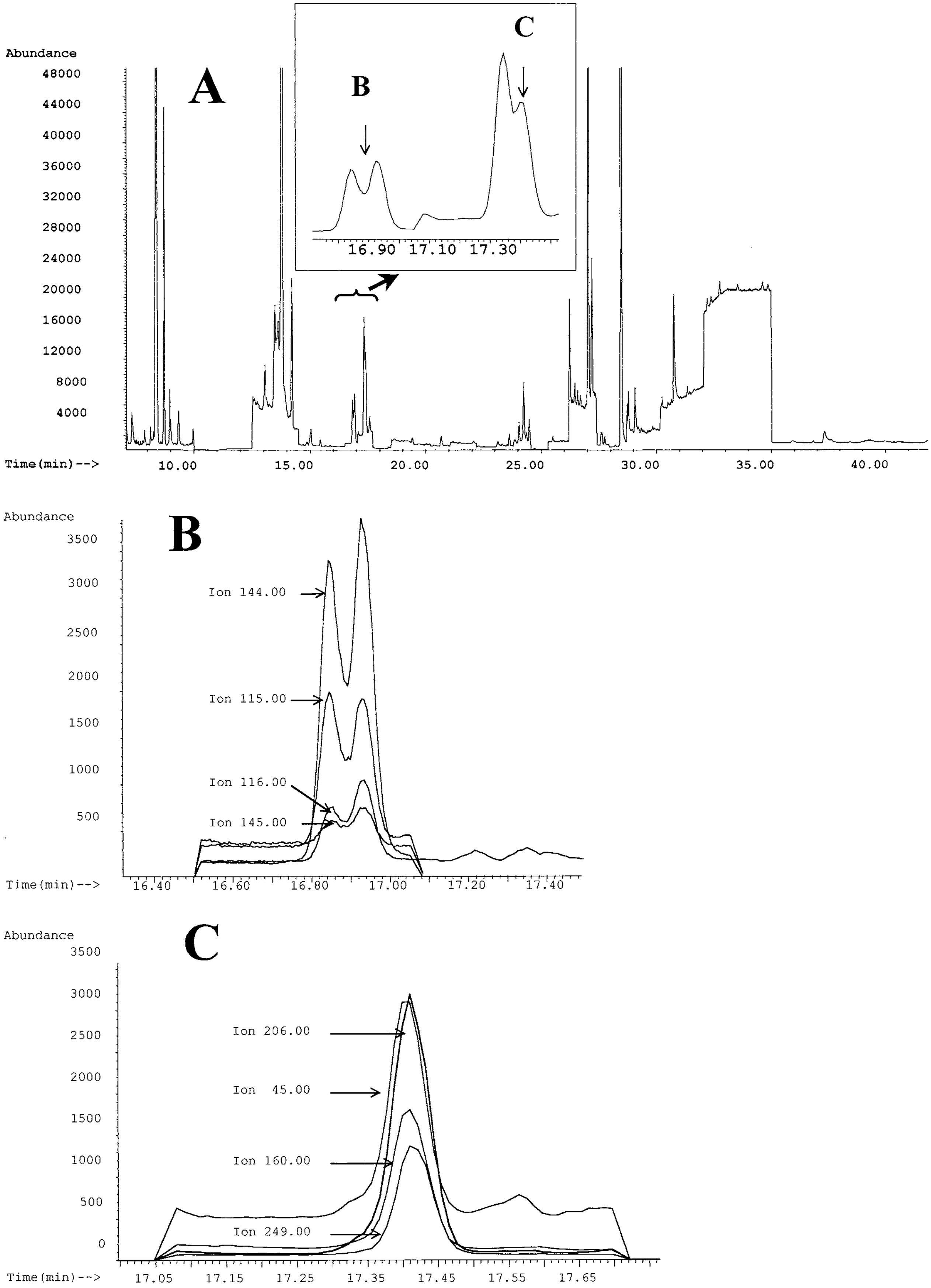

Figure 3. (A) Reconstructed GC-MSD/SIM chromatogram of a white wine extract using a modified version of the SIM-2 program. (Inset) SIM chromatogram of the white wine extract from 16.80 to 17.50 min, showing the possible presence of Carbaryl (16.87 min) and Metalaxyl (17.38 min), as indicated by the arrows. Extracted ions for (B) Carbaryl, *m*/*z* 144, 115, 116, and 145, extracted from (A) at a retention time of 16.87 min, and (C**)** Metalaxyl, *m*/*z* 206, 45, 160, and 249, extracted from (A) at 17.38 min. The two pesticides were confirmed by the retention time of the target ion and qualifier-to-target ratios.

ACKNOWLEDGMENT

We thank Mr. Michael McChesney (IR-4 Western Region Laboratory, University of California, Davis), Mr. Frank Schenck (United States Food and Drug Administration, Atlanta, GA), Mr. Alexander Krynitsky (United States Environmental Protection Agency, Ft. Meade, MD), and members of the Alcohol and Tobacco Laboratory, NLC, particularly Dr. Dawit Bezabeh and Ms. Julie Arthur, for their technical support, expertise, interest, and inspiration for this work. We appreciate and thank the U.S. EPA Pesticide Repository for providing the majority of the pesticide standards used in this study.

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Received for review September 27, 2002. Revised manuscript received December 3, 2002. Accepted December 3, 2002.

JF0209995