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Multiresidue Determination of Pesticides in Malt Beverages by Capillary Gas Chromatography with Mass Spectrometry and Selected Ion Monitoring

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A method was developed to determine pesticides in malt beverages using solid phase extraction on a polymeric cartridge and sample cleanup with a $MgSO_4$-topped aminopropyl cartridge, followed by capillary gas chromatography with electron impact mass spectrometry in the selected ion monitoring mode [GC-MS(SIM)]. Three GC injections were required to analyze and identify organophosphate, organohalogen, and organonitrogen pesticides. The pesticides were identified by the retention times of peaks of the target ion and qualifier-to-target ion ratios. GC detection limits for most of the pesticides were 5−10 ng/mL, and linearity was determined from 50 to 5000 ng/mL. Fortification studies were performed at 10 ng/mL for three malt beverages that differ in properties such as alcohol content, solids, and appearance. The recoveries from the three malt beverages were greater than 70% for 85 of the 142 pesticides (including isomers) studied. The data showed that the different malt beverage matrixes had no significant effect on the recoveries. This method was then applied to the screening and analysis of malt beverages for pesticides, resulting in the detection of the insectide carbaryl and the fungicide dimethomorph in real samples. The study indicates that pesticide levels in malt beverages are significantly lower than the tolerance levels set by the United States Environmental Protection Agency for malt beverage starting ingredients. The use of the extraction/cleanup procedure and analysis by GC-MS(SIM) proved effective in screening malt beverages for a wide variety of pesticides.

KEYWORDS: Beer; malt beverages; gas chromatography−mass spectrometry (GC-MS); selected ion monitoring (SIM); solid phase extraction; pesticides

INTRODUCTION

In the United States, malt beverages (e.g., beer, lager, ale, porter, and stout) are important food commodities subjected to Alcohol and Tobacco Tax and Trade Bureau (TTB, formerly the Bureau of Alcohol, Tobacco, and Firearms) regulations and revenue collection, as pertaining to its labeling and alcohol content. It is also TTB's mission to monitor alcohol-based products available to the marketplace for contaminants in order to ensure consumer safety. Public concern over pesticide residues in food has been increasing such that it has become a significant food safety issue. However, little data are available of human exposures to pesticides through the consumption of processed and finished food products.

Procedures are needed to reliably and rapidly detect and quantitate as many contaminants as possible, including pesticides, in the most cost effective manner. The presence of a variety of pesticides in wines (*1*) and other food products, as well as the potential presence of pesticide residues in malt beverages and beers (*2*−*8*), has stimulated interest in developing a screening procedure for malt-based alcohol beverages. Re-

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cently, TTB initiated a pesticide screening analysis of wines in their Alcohol Beverage Sampling Program to identify and quantitate pesticides in beverage alcohol products using gas chromatography−mass spectrometry in the selected ion monitoring mode [GC-MS(SIM)] (*9*). In this paper, we describe the development of a revised GC-MS quantitative screening procedure applicable to malt beverages.

This method of screening malt beverages for pesticides involves concentration and cleanup steps with polymeric and aminopropyl (topped with $MgSO_4$) solid phase extraction (SPE) cartridges, respectively, and quantitative analysis and identification of the pesticides by GC-MS(SIM). This procedure differs from that used previously for wines (*9*) in that larger sample volumes (50 mL) of malt beverage and a different polymer sorbent (NEXUS) were utilized. GC-MS is widely regarded as a standard procedure for screening pesticides that are less susceptible to thermal decomposition. In fact, Hengel and Shibamoto (*3*) and Miyake et al. (*6*, *7*) developed GC and GC-MS procedures, respectively, to screen for pesticide residues in both finished malt beverages and at various stages of the fermentation process. Both groups investigated the fate of pesticides during the brewing process by fortifying pesticides in the raw materials (e.g., hops and malt) or in various stages of the brewing process (e.g., mashing, wort boiling, and fermentation). Both groups found significant decreases and losses of the pesticides studied as a result of the brewing process.

Miyake et al. (*6*) developed a multiresidue method for malt beverages capable of analyzing 129 pesticides, and recoveries of 46−196% could be achieved in 79 pesticides amenable to GC analysis. The method developed by Hengel and Shibamoto (*3*) utilized simple SPE and cleanup procedures for their analysis of seven pesticides. The work in this research combines the advantages of methods used by both groups to effectively and efficiently identify and quantitate a wide variety and large number of pesticides in different types of malt beverages.

MATERIALS AND METHODS

Materials and Standards Preparation. 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 high-performance liquid chromatography (HPLC) grade water were purchased from Pharmco (Bridgeport, CT). Anhydrous magnesium sulfate was purchased from Fluka Chemical Corp. (Milwaukee, WI). The internal standards (IS) acenaphthalene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12} were purchased from Aldrich Chemical (Milwaukee, WI). NEXUS (6 mL, 200 mg) and aminopropyl (LC-NH_2, 6 mL, 500 mg) cartridges were either generously donated or purchased from Varian Corp. (Harbor City, CA). Malt beverages were either purchased from local retail stores or obtained from the TTB's (or previously, ATF) Alcohol Beverage Sampling Program.

Stock solutions of individual pesticide standards (approximately 500 mg/L) were prepared by dissolving approximately 50 mg of each into 100 mL of ethyl acetate. Working standards used for quantitative and fortification studies were prepared by transferring 2 mL of each pesticide stock solution into a 200 mL volumetric flask, followed by dilution with 0.1% corn oil in ethyl acetate to give a 5 mg/L concentration. Further dilution with the 0.1% corn oil/ethyl acetate led to the preparation of 1, 2.5, 5, 10, 25, 50, 100, 250, 500, 1000, and 2500 ng/mL standards. IS stock solutions were prepared by dissolving acenaphthalene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12} in ethyl acetate (500 mg/L of each).

SPE of Pesticides in Malt Beverages. A schematic of the extraction procedure is shown in **Figure 1**, and this required a pair of SPE manifolds (Supelco Corp., Bellefonte, PA). The first was used for extracting the malt beverages with NEXUS cartridges, while the second was for the cleanup of the NEXUS cartridge eluates with $MgSO_4$-topped aminopropyl cartridges. The NEXUS cartridges were first rinsed with 2 column volumes each of 50:50 ethyl acetate:hexane, methanol, and HPLC grade water. The column conditioning was performed under gravity, which sometimes required an initial mild vacuum for priming. The aminopropyl cartridges were loaded with approximately one-third cartridge volume of magnesium sulfate, which was packed by slightly tapping the cartridge. The cleanup cartridges were conditioned with approximately 5 mL of 50:50 ethyl acetate:hexane. When all but 0.5−1.0 mL of ethyl acetate:hexane remained in the column, the manifold valves were closed to prevent drying of the stationary phase.

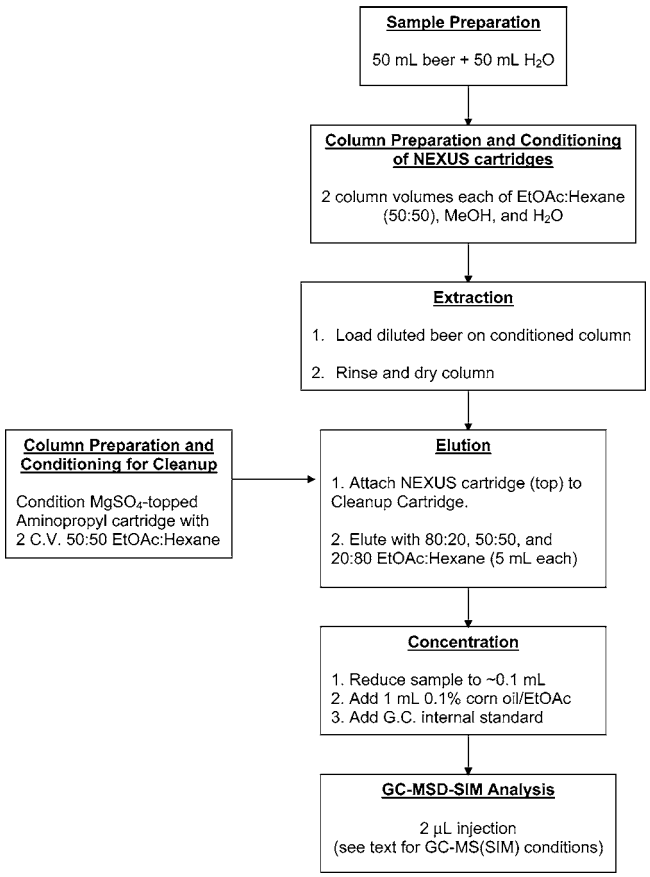

Figure 1. Flowchart of the SPE and cleanup procedures for the analysis of pesticides in malt beverages.

Malt beverage samples were degassed by rapidly transferring approximately 250 mL of malt beverage into two 600 mL beakers and repeating the procedure 25 times. An aliquot (50 mL) was then transferred to a 100 mL volumetric flask. For fortification studies, three representative malt beverage types ($n = 5$ for each type) were degassed, and the aliquot was then fortified with 0.5 mL of pesticide standard (500 ng/mL) to produce a 10 ng/mL spiked sample. The volumetric flasks were brought to volume with HPLC grade water (50 mL) and mixed vigorously to ensure homogeneous distribution of the 100 mL diluted and degassed malt beverage samples. Next, these solutions were loaded onto the NEXUS cartridge via Pasteur pipet and extracted with little or no vacuum; the volumetric flasks were also rinsed with approximately 15 mL of HPLC grade water, and this volume was loaded onto the cartridges. Following the completed passage of all liquid through the NEXUS cartridges, the cartridges were dried under vacuum for approximately 15 min.

The dried NEXUS cartridges were removed from the first vacuum manifold and stacked on top of the cleanup columns using adapters, and graduated conical tubes (15 mL) were placed 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). The sample eluate

was evaporated to ca. 0.1 mL volume with a nitrogen evaporator, and 1 mL of 0.1% corn oil/ethyl acetate was then added. Next, the solution was transferred to a sample vial, and 50 μL of the IS solution was added.

GC-MS(SIM) Analysis. A HP6890 GC was equipped with a HP5973 mass selective detector (Agilent Technologies, Little Falls, DE) and fitted with a HP-5MS column (30 m × 0.25 mm × 0.25 μm film thickness, Agilent Technologies). The MS was operated in electron impact mode at 70 eV. The inlet, MS transfer line, MS source, and quadrupole temperatures were 250, 280, 230, and 150 °C, respectively. The carrier gas was ultrapure helium (Air Products, Hyattsville, MD) set at constant pressure mode of 21.7 psi (the pressure varies depending on the individual GC-MSD instrument) using the Retention Time Locking (RTL) Program on the HP6890 GC and methyl chlorpyrifos as the RTL locking standard at a retention time (t_R) of 16.59 min. The GC temperature program used in this study was the same one used by Agilent Technologies for compiling its RTL database (*10*). The temperature program started at a temperature of 70 °C (2 min hold), increased to 150 °C at a rate of 25 °C/min, increased to 200 °C at a rate of 3 °C/min, and attained by a final temperature of 280 °C (10 min hold) at a rate of 8 °C/min for a total run time of 41.87 min. Malt beverage extracts, standards, and blanks were injected (2 μL) in the splitless mode using a HP 6890 series autoinjector.

The MS system was routinely programmed in SIM using one target and three qualifier ions, as indicated in **Table 1**. The samples were analyzed with each of three different SIM programs: SIM-1, SIM-2, and SIM-3, as listed in **Table 2**. Confirmation of the pesticide was based on the retention time of the target ion and on three qualifier-to-target ion ratios. The target and qualifier ion abundances, which were similar to those used in the RTL database, were determined by injecting individual pesticide standards under the same chromatographic conditions, except in full scan mode (40−500 *m*/*z*). The qualifier-to-target ion percentage was then determined by dividing the abundance of the selected qualifier ion by the target ion (nearly always the base peak) and multiplying by 100. The sample quantitation was based on the pesticide target ion:IS peak area ratio, using the IS with the retention time closest to that of the pesticide. Quantitation was achieved by linear regression against calibration standards and using the GC-MS ChemStation software. For fortification studies, quantitation was determined from linear regression curves using pesticide standards ranging from 50 to 5000 ng/mL.

Quality Control. A typical analytical sequence for the analysis of pesticides in malt beverages consisted of 12−15 beverage samples, one spiked beverage sample, three water blanks, one water spike, eight calibration standards (ranging from 50 to 5000 ng/mL of SIM-1, SIM-2, or SIM-3 standards), one calibration check standard, and ethyl acetate rinses. Each of the three SIM programs (**Table 2**) consisted of its own calibration standards, malt beverage and water spikes, and calibration check standard. The malt beverage chosen for spiking was randomly chosen, usually from one of the last three samples of the batch. The malt beverage and water spikes were fortified at 20 ng/mL with either a SIM-1, SIM-2, or SIM-3 spike standard and analyzed as described previously. Acceptable spike recoveries ranged from 50 to 150% depending on pesticide fortification results.

Identifications of pesticides in malt beverages were made by comparing the retention time, identifying the target and qualifier ions, and determining the qualifier-to-target ratios of the peak in the malt beverages with that of a pesticide standard. Acceptance criteria for positive identification consisted of retention times within ±0.50 min of the expected value and % qualifier-to-target ratios within 20% of the standard (500 ng/mL) for qualifier-to-target abundance percentages (i.e., Q_1/T, Q_2/T, or Q_3/T) greater than 50%. For less than 50%, the criterion for the qualifier-to-target ratios was set at 30% of the calibration standard. Water blanks and spikes were analyzed to account for any residual carry over or possible contamination sources such as the glassware. The identification of pesticide residues in the water blanks resulted in repeating the extraction and analysis of the entire batch.

After completion of the standards, blanks, spikes, sample extracts, and rinses, a 250 ng/mL 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 malt beverage extract was determined as described previously.

Determination of the Chemical and Physical Properties of Malt Beverages. Procedures for the analysis of alcohol content, total acids, real extract, specific gravity, fusel oil content, and bitterness units are described elsewhere (*11*, *12*).

RESULTS AND DISCUSSION

GC-MS(SIM) of Pesticides. Our method to use GC-MS(SIM) to screen for pesticides in malt beverages was based on the methods established by Fillion et al. (*13*, *14*), who used this technique to screen, identify, and quantitate pesticide residues in fruits and vegetables.

Three separate injections are required for the analysis of all 129 pesticides (142 including isomers), and each injection is screened using a different selective ion monitoring (SIM-1, SIM-2, and SIM-3) program (**Table 2**). Chromatograms of injected extracts from a blank and spiked malt beverage (concentrated from a fortified 10 ng/mL level) obtained with data acquisition using the three SIM programs are shown in **Figure 2**. Compounds are identified by their t_R values and their qualifier-to-target abundance ratios, as listed in **Table 1**. Few interferences were observed. The limit of detection (LOD) of each pesticide also listed in **Table 1** was determined from the injection of standards and was defined as approximately three times the level of the noise. Of the 142 compounds studied, 126 had LODs less than or equal to 10 ng/mL. The highest LODs were for pesticides known to be problematic for GC analysis due to their thermal and/or chemical instabilities, such as captafol (100 ng/mL), captan (50 ng/mL), carbaryl (25 ng/mL), and iprodione (25 ng/mL) (*9*, *15*). Coincidentally, most of these same compounds also gave poor (<0.990) r^2 values for standard curves ranging from 50 (for most compounds) to 5000 ng/mL, while the vast majority of pesticides tested (107 pesticides) had $r^2 > 0.990$. Additional compounds that exhibited r^2 values < 0.990 were chlorothalonil (0.989), fenpropathrin (0.985), folpet (0.985), and nitralin (0.984).

Chemical and Physical Properties of Malt Beverages Used for Pesticide Fortification Studies. Three different malt beverages were selected for pesticide fortification studies based on their different properties. The purpose of choosing the three different malt beverages for the pesticide fortification studies was to determine whether the proposed multiresidue method is applicable to different malt beverage matrices regardless of their properties. The results of these properties, alcohol content, total acids, real extract, specific gravity, fusel oil content, and bitterness units, are listed in **Table 3**. Beer 1 differs from the other two beers due to its dark color and higher density and bitterness units, the latter indicative of malt beverages with a higher hops content. Beer 3 was chosen for this study because it is representative of a standard beer found commonly in U.S. markets. Its chemical and physical properties, particularly color, alcohol content, and real extract, are lower than the other two malt beverages. Beer 2 was chosen for the study based on its similarity to beer 1 in terms of alcohol content, total acids, and real extract, but it is different because of color and bitterness units. The sample matrix has been shown to have an influence on pesticide analysis because coextractives from the matrix can coelute and interfere with the chromatography of the analyte as well as promote matrix enhancement and suppression effects that can lead to erroneous quantitation vs standards in solvent only solutions (*15*−*21*).

Pesticide Recoveries from Malt Beverages. Recoveries of organophosphate, organohalogen, and organitrogen pesticides

Table 1. Pesticide Name, Molecular Weight (MW), GC-MS(SIM) Retention Time (t_R), Target and Qualifier Ions (T, Q_1, Q_2, and Q_3), Percentage of Qualifier-to-Target Ratios (Q_1/T, Q_2/T, and Q_3/T), LOD, Limit of Quantitation (LOQ), and Regression Coefficient (r^2) of All Pesticides Used in Study

pesticide	MW	t_R (min)	T	Q_1 (Q_1/T %)	Q_2 (Q_2/T %)	Q_3 (Q_3/T %)	LOD (ng/mL)	range (ng/mL)	r^2
acenaphthlene-d_{10} (IS)	164.3	8.35	164	162 (92.7)	160 (41.5)	80 (14.0)	NA	NA	NA
alachlor	269.8	17.00	160	188 (92.2)	146 (35.2)	237 (25.2)	5	50–5000	1.000
aldrin	364.9	18.44	263	265 (66.8)	261 (63.8)	66 (80.5)	5	50–5000	1.000
allethrin	302.4	21.51, 21.75	123	79 (24.5)	136 (20.1)	107 (19.8)	25	50–5000	0.999
atrazine	215.7	13.21	200	215 (59.2)	202 (34.0)	58 (25.5)	5	50–5000	0.999
azinphos-ethyl	345.4	30.64	132	160 (92.1)	77 (50.7)	105 (24.0)	5	50–5000	0.998
azinphos-methyl	317.3	29.69	160	132 (83.9)	77 (73.6)	105 (28.5)	10	50–5000	0.994
azoxystrobin	403.4	36.54	344	345 (30.5)	388 (29.4)	75 (14.0)	5	50–5000	0.998
benalaxyl	325.4	26.72	148	91 (35.7)	206 (29.0)	204 (20.9)	5	50–5000	0.999
benfluralin	335.3	11.70	292	264 (17.7)	276 (13.1)	293 (12.3)	5	50–5000	0.999
BHC-α	290.8	12.06	181	183 (98.1)	219 (88.6)	217 (71.0)	5	50–5000	1.000
BHC-δ	290.8	14.67	181	219 (95.2)	183 (95.9)	217 (74.0)	5	50–5000	0.998
bitertanol I	337.4	31.22	170	168 (14.0)	171 (13.6)	57 (11.7)	5	50–5000	0.999
bitertanol II	337.4	31.36	170	168 (21.3)	171 (13.5)	57 (13.0)	10	50–5000	0.998
bromophos-ethyl	394.1	22.48	359	303 (91.6)	357 (76.0)	301 (69.0)	5	50–5000	1.000
bromophos-methyl	366.0	20.04	331	329 (75.5)	333 (30.7)	125 (35.0)	5	50–5000	1.000
captafol	349.1	27.63	79	80 (26.9)	77 (24.2)	151 (3.0)	100	250–5000	0.958
captan	300.6	21.27	79	80 (21.6)	151 (5.0)	77 (24.6)	50	100–5000	0.967
carbaryl	201.2	17.94	144	115 (51.6)	116 (35.5)	145 (11.1)	25	50–5000	0.989
carbofuran	221.3	13.07	164	149 (58.6)	131 (15.6)	123 (14.9)	25	50–5000	0.991
carbophenothion	342.9	26.62	157	342 (38.4)	121 (44.2)	199 (25.9)	5	50–5000	0.999
chlorbenside	269.2	22.03	125	127 (31.3)	268 (13.9)	270 (7.8)	5	50–5000	1.000
cis-chlordane	409.8	22.78	373	375 (95.5)	377 (51.3)	371 (44.3)	5	50–5000	0.999
trans-chlordane	409.8	22.00	373	375 (96.1)	377 (51.8)	371 (45.4)	5	50–5000	1.000
chlorfenvinphos	359.6	21.55	267	323 (58.7)	269 (64.0)	325 (39.4)	5	50–5000	0.999
chlorothalonil	265.9	14.90	266	264 (78.3)	268 (47.9)	270 (10.2)	10	50–5000	0.989
chlorpyrifos	350.6	19.19	197	199 (94.9)	314 (68.8)	97 (62.9)	5	50–5000	0.997
chlorpyrifos-methyl	322.5	16.57	286	288 (69.8)	125 (53.8)	290 (15.9)	5	50–5000	1.000
chlozolinate	332.1	21.39	188	259 (86.6)	186 (84.6)	187 (76.9)	5	50–5000	1.000
chrysene-d_{12} (IS)	240.4	28.40	240	236 (23.6)	241 (19.6)	238 (4.3)	NA	NA	NA
coumaphos	362.8	31.65	362	226 (74.2)	109 (70.9)	210 (56.1)	5	50–5000	0.999
cyfluthrin I	434.3	32.19	163	206 (79.9)	165 (67.4)	227 (26.2)	5	50–5000	0.999
cyfluthrin II	434.3	32.34	163	206 (65.0)	165 (63.2)	227 (18.6)	5	50–5000	0.999
cyfluthrin III	434.3	32.45	163	206 (71.5)	165 (62.7)	227 (21.7)	10	50–5000	0.999
cyfluthrin IV	434.3	32.52	163	206 (72.7)	199 (41.9)	227 (22.0)	10	50–5000	0.999
cyhalothrin	449.9	30.35	181	197 (77.9)	208 (48.8)	209 (26.4)	5	50–5000	0.999
cypermethrin I	416.3	32.66	181	163 (114.4)	165 (70.2)	209 (45.2)	10	50–5000	0.999
cypermethrin II	416.3	32.81	181	163 (135.3)	165 (83.8)	209 (37.4)	10	50–5000	0.999
cypermethrin III	416.3	32.93	163	181 (87.9)	165 (65.7)	209 (30.8)	25	50–5000	0.999
cypermethrin IV	416.3	33.01	163	181 (68.3)	165 (60.3)	209 (29.5)	25	50–5000	0.999
cyproconazole	291.8	24.94	222	139 (50.2)	224 (31.6)	125 (23.2)	5	50–5000	1.000
cyprodinil	225.3	20.56	224	225 (63.4)	210 (10.1)	77 (7.9)	5	50–5000	0.998
o,p′-DDT	354.5	25.73	235	237 (66.7)	165 (44.4)	236 (15.4)	5	50–5000	0.998
p,p′-DDT	354.5	26.96	235	237 (64.7)	165 (39.4)	236 (14.5)	5	50–5000	0.995
demeton-O	230.3	10.36	88	60 (28.4)	89 (69.9)	171 (27.1)	25	50–5000	1.000
demeton-S	230.3	12.64	88	60 (31.3)	170 (18.1)	89 (15.0)	25	50–5000	1.000
desmetryn	213.3	16.03	213	198 (60.5)	171 (29.1)	58 (17.8)	5	50–5000	0.998
dialifos	393.9	30.80	208	173 (12.5)	210 (32.0)	76 (12.6)	5	50–5000	0.999
diallate I	270.2	11.90	86	234 (66.1)	236 (25.7)	128 (28.5)	2.5	50–5000	1.000
diallate II	270.2	12.32	86	234 (76.5)	236 (28.5)	128 (25.2)	2.5	50–5000	1.000
diazinon	304.3	14.42	179	137 (99.6)	199 (61.0)	152 (67.8)	5	50–5000	1.000
dichlofluanid	333.2	18.38	123	224 (44.1)	167 (44.1)	226 (30.5)	5	50–5000	0.999
4,4′-dichlorobenzophenone	251.1	19.41	139	111 (33.3)	141 (31.4)	250 (31.3)	5	50–5000	1.000
dicloran	207.0	13.00	206	176 (107.9)	178 (94.9)	208 (87.8)	5	50–5000	0.998
dieldrin	380.9	23.82	79	263 (39.2)	277 (27.6)	279 (24.3)	10	50–5000	1.000
dimethoate	229.3	12.72	87	93 (61.3)	125 (58.6)	143 (12.0)	10	50–5000	0.999
dimethomorph-1	387.9	36.58	301	303 (33.5)	165 (30.6)	387 (27.5)	5	50–5000	0.998
dimethomorph-2	387.9	37.33	301	303 (35.1)	165 (32.1)	387 (27.8)	5	50–5000	0.999
dioxathion	456.0	13.56	97	125 (75.8)	271 (5.0)	153 (27.9)	25	50–5000	1.000
disulfoton	274.4	14.51	88	89 (40.4)	97 (28.7)	142 (19.5)	50	100–5000	1.000
endosulfan-α	406.9	22.57	241	195 (100.2)	239 (96.4)	237 (91.9)	10	50–5000	1.000
endosulfan-β	406.9	25.16	195	237 (88.6)	241 (82.6)	207 (93.6)	10	50–5000	1.000
endrin	380.9	24.71	317	263 (116.8)	315 (67.0)	319 (65.8)	10	50–5000	0.999
endrin aldehyde	380.9	25.90	67	345 (68.1)	250 (62.7)	347 (41.5)	5	50–5000	1.000
endrin ketone	380.9	28.22	317	67 (77.8)	315 (65.1)	319 (64.0)	25	50–5000	0.999
EPN	323.3	28.64	157	169 (57.5)	141 (29.4)	185 (30.1)	5	50–5000	0.995
ethalfluralin	333.3	11.26	276	316 (77.0)	292 (43.6)	333 (21.1)	5	50–5000	0.997
ethion	384.5	25.96	231	153 (55.0)	97 (52.2)	125 (39.0)	5	50–5000	0.999
febuconazole	336.8	32.20	129	198 (60.2)	125 (32.8)	103 (8.6)	25	100–5000	1.000
fenamiphos	303.4	23.62	303	154 (109.0)	288 (30.3)	217 (32.3)	5	50–5000	0.999
fenarimol	331.2	30.41	139	219 (68.1)	251 (59.3)	107 (69.8)	5	50–5000	1.000
fenitrothion	277.2	18.08	277	125 (109.5)	109 (88.2)	260 (52.2)	5	50–5000	0.998
fenpropathrin	349.4	28.96	97	181 (84.9)	125 (43.5)	265 (35.1)	5	50–5000	0.985

Table 1. (Continued)

pesticide	MW	t_R (min)	T	Q_1 (Q_1/T %)	Q_2 (Q_2/T %)	Q_3 (Q_3/T %)	LOD (ng/mL)	range (ng/mL)	r^2
fenpropimorph	305.5	19.16	128	129 (8.2)	303 (4.7)	117 (3.3)	10	50–5000	0.999
fenson	268.7	19.73	77	141 (88.9)	268 (35.8)	51 (15.8)	5	50–5000	1.000
fenthion	278.3	19.10	278	125 (31.5)	109 (25.0)	169 (21.1)	5	50–5000	1.000
fenvalerate I	419.9	34.45	167	125 (98.3)	181 (74.1)	152 (55.9)	5	50–2500	1.000
fenvalerate II	419.9	34.87	167	125 (96.8)	181 (66.0)	169 (62.3)	5	50–5000	0.999
flucythrinate I	451.4	33.03	199	157 (58.6)	181 (34.7)	107 (14.8)	5	50–5000	0.999
flucythrinate II	451.4	33.35	199	157 (60.8)	181 (35.8)	107 (15.0)	5	50–5000	0.999
fludioxinil	248.2	24.52	248	127 (30.5)	154 (20.0)	182 (14.3)	10	50–5000	0.999
fluvalinate τ-I	502.9	34.65	250	252 (33.0)	181 (20.2)	208 (9.1)	5	50–5000	0.996
fluvalinate τ-II	502.9	34.78	250	252 (32.6)	181 (20.4)	208 (8.9)	5	50–5000	0.997
folpet	296.6	21.65	147	104 (253.7)	76 (207.5)	260 (220.7)	10	50–5000	0.985
fonophos	246.3	13.85	109	246 (48.9)	137 (50.0)	110 (20.9)	5	50–5000	1.000
furalaxyl	301.3	21.91	95	242 (52.5)	152 (19.2)	146 (13.3)	2.5	50–5000	1.000
heptachlor	373.3	16.72	272	274 (80.3)	100 (88.3)	270 (54.7)	1	50–5000	0.999
heptachlor epoxide	389.3	20.66	353	355 (81.8)	351 (51.3)	357 (35.0)	1	50–5000	1.000
hexachlorobenzene	284.8	12.34	284	286 (80.5)	282 (53.4)	288 (33.4)	1	50–5000	1.000
hexaconazole	352.9	23.53	83	214 (79.5)	216 (51.3)	82 (36.2)	10	50–5000	0.999
iprodione	330.2	28.42	314	187 (57.7)	189 (38.9)	244 (21.5)	25	50–5000	0.792
lindane	290.8	13.44	181	183 (96.2)	219 (83.2)	111 (50.5)	5	50–5000	0.998
malaoxon	314.3	16.90	127	99 (39.7)	109 (22.4)	125 (19.1)	10	50–5000	0.990
malathion	330.4	18.78	173	127 (77.7)	125 (86.5)	93 (64.6)	5	50–5000	1.000
metalaxyl	279.3	17.34	206	45 (52.6)	160 (51.1)	249 (45.7)	5	50–5000	0.998
methidathion	302.3	22.31	145	85 (62.7)	93 (18.0)	125 (17.2)	5	50–5000	0.999
methoxychlor	345.7	28.84	227	228 (16.5)	152 (5.9)	113 (4.9)	25	50–5000	0.998
metolachlor	283.8	18.88	162	238 (59.9)	240 (20.5)	146 (13.6)	2.5	50–5000	0.998
mirex	545.6	29.77	272	274 (80.7)	270 (52.3)	237 (50.7)	2.5	50–5000	0.999
myclobutanil	280.8	24.48	179	150 (47.6)	82 (27.7)	181 (32.5)	5	50–5000	1.000
napropamide	271.4	23.45	72	128 (60.4)	100 (44.3)	271 (40.6)	5	50–5000	1.000
nitralin	345.4	28.19	316	274 (71.3)	300 (15.0)	317 (14.3)	10	50–5000	0.984
nitrofen	284.1	24.92	283	285 (69.1)	202 (48.1)	253 (22.5)	10	50–5000	0.990
nitrothal-isopropyl	295.3	19.84	236	194 (66.4)	212 (57.8)	254 (49.8)	5	50–5000	0.990
norflurazon	303.7	27.89	303	145 (95.6)	102 (63.3)	305 (27.1)	5	50–5000	1.000
oxadiazon	345.2	24.39	175	177 (64.5)	258 (56.1)	260 (36.5)	5	50–5000	0.999
oxadixyl	278.3	25.95	105	163 (112.0)	45 (68.3)	132 (81.9)	5	50–5000	1.000
oxyfluorfen	361.7	24.71	252	361 (29.5)	302 (11.5)	331 (2.5)	5	50–5000	0.990
paclobutrazol	293.8	22.59	236	125 (48.0)	238 (34.5)	167 (26.0)	5	50–5000	0.999
paraoxon	275.2	17.38	109	149 (39.7)	275 (33.0)	139 (30.8)	10	50–5000	0.998
parathion	291.3	19.30	291	109 (82.3)	97 (75.8)	139 (50.5)	10	50–5000	0.997
parathion-methyl	263.2	16.63	263	109 (119.5)	125 (100.3)	79 (31.9)	5	50–5000	0.996
penconazole	284.2	21.08	248	159 (93.7)	161 (60.0)	250 (33.5)	5	50–5000	1.000
cis-permethrin	391.3	31.33	183	163 (19.1)	165 (15.9)	184 (15.7)	5	50–5000	0.998
trans-permethrin	391.3	31.52	183	163 (25.5)	165 (21.0)	184 (15.3)	5	50–5000	0.998
phenanthrene-d_{10} (IS)	188.3	13.74	188	189 (14.9)	184 (12.9)	187 (7.9)	NA	NA	NA
phorate	260.4	11.93	75	121 (44.5)	260 (25.3)	97 (26.1)	5	50–5000	1.000
phosalone	367.8	29.67	182	367 (18.4)	121 (42.1)	184 (32.9)	5	50–5000	0.999
phosmet	317.3	28.52	160	161 (10.9)	77 (6.9)	93 (6.2)	5	50–5000	0.998
procymidone	284.1	21.97	96	283 (67.8)	285 (44.1)	67 (40.6)	10	50–5000	1.000
profenophos	373.6	23.89	208	339 (60.4)	139 (100.0)	206 (79.6)	5	50–5000	0.998
prometryn	241.4	17.34	241	184 (70.8)	226 (55.3)	105 (21.6)	5	50–5000	0.999
propargite	350.3	27.70	135	150 (14.0)	231 (12.6)	64 (8.4)	10	50–5000	0.999
propazine	229.7	13.39	214	229 (64.3)	172 (53.0)	58 (34.4)	5	50–5000	0.999
propetamphos	281.3	13.91	138	194 (45.9)	236 (29.9)	222 (22.8)	5	50–5000	0.999
propiconazole I	342.2	26.91	173	259 (94.6)	69 (68.4)	175 (64.3)	5	50–5000	1.000
propiconazole II	342.2	27.12	173	259 (90.7)	69 (66.8)	175 (62.6)	5	50–5000	1.000
propyzamide	256.1	13.98	173	175 (64.8)	145 (28.0)	255 (23.5)	5	50–5000	0.998
pyridaben	364.9	31.50	147	148 (12.1)	117 (11.7)	132 (10.3)	5	50–5000	0.999
pyrimethanil	199.3	14.16	198	199 (46.7)	77 (4.7)	200 (5.6)	5	50–5000	0.999
simazine	201.7	13.03	201	186 (58.2)	173 (34.3)	68 (24.0)	5	50–5000	0.998
tebuconazole	307.8	27.47	125	250 (100.7)	70 (42.2)	83 (42.3)	10	50–5000	0.999
tecnazene	260.9	11.40	203	261 (70.3)	215 (78.9)	201 (77.8)	5	50–5000	0.996
terbufos	288.4	13.74	231	57 (81.6)	103 (29.5)	153 (26.2)	5	50–5000	1.000
terbuthylazine	229.7	13.83	214	173 (36.9)	216 (33.4)	229 (30.3)	5	50–5000	0.999
terbutryn	241.4	17.97	226	185 (68.1)	241 (66.5)	170 (51.3)	5	50–5000	0.999
tetrachlorvinphos	366.0	22.96	329	331 (92.8)	109 (83.7)	333 (32.1)	5	50–5000	0.995
thiometon	246.3	12.35	88	125 (51.3)	89 (28.2)	93 (27.3)	50	100–5000	1.000
triadimefon	293.8	19.40	57	208 (76.5)	85 (30.6)	210 (26.1)	5	50–5000	1.000
triadimenol	295.8	21.70	112	168 (93.7)	128 (65.6)	70 (24.3)	10	50–5000	1.000
triallate	304.7	14.91	86	268 (54.8)	270 (37.8)	128 (26.8)	5	50–5000	0.999
triflumizole	345.7	22.34	73	278 (83.8)	206 (65.1)	179 (38.8)	5	50–5000	0.999
trifluralin	335.3	11.61	306	264 (72.1)	290 (13.2)	307 (12.7)	5	50–5000	0.998
uniconazole	291.8	24.05	234	236 (34.6)	70 (18.5)	235 (17.7)	10	50–5000	0.999
vinclozolin	286.1	16.62	212	198 (91.0)	187 (81.1)	285 (75.7)	5	50–5000	1.000

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

Table 2. SIM Programs (SIM-1, SIM-2, and SIM-3) Used to Analyze and Confirm Pesticides in Malt Beverages

group	time (min)	pesticides and ISs	ions (amu)	dwell time (ms) scan rate (cycles/s)
		SIM-1		
1	7.00	acenaphthlene-d_{10} (IS)	80, 160, 162, 164	50
				3.77
2	10.75	tecnazene	201, 203, 215, 261	50
				3.77
3	11.65	BHC-α, diallate I and II, dicloran, hexachlorobenzene	86, 128, 176, 178, 181, 183, 206, 208, 217, 219, 234, 236, 282, 284, 286, 288	30
				1.38
4	13.15	lindane	111, 181, 183, 219	50
				3.77
5	13.63	phenanthrene-d_{10} (IS), propyzamide	145, 173, 175, 184, 187, 188, 189, 214, 237, 249, 255	40
				1.50
6	14.40	BHC-δ	181, 183, 217, 219	50
				3.77
7	16.00	alachlor, heptachlor, vinclozolin	45, 100, 146, 160, 187, 188, 198, 212, 270, 272, 274, 285	40
				1.50
8	18.00	aldrin, dichlofluanid	66, 123, 167, 224, 226, 261, 263, 265	50
				1.90
9	18.88	4,4′-dichlorobenzophenone, fenson	51, 77, 111, 139, 141, 250, 268	50
				1.90
10	20.29	heptachlor epoxide	351, 353, 355, 357	50
				3.77
11	21.05	captan, chlozolinate, tolyfluanid	63, 77, 79, 80, 106, 137, 151, 186, 187, 188, 238, 259	40
				1.50
12	21.62	allethrin, chlorbenside, *trans*-chlordane, folpet, procymidone	67, 76, 79, 96, 104, 107, 123, 125, 127, 136, 147, 260, 268, 270, 283, 285, 371, 373, 375, 377	30
				1.10
13	22.45	*cis*-chlordane, endosulfan-α	195, 237, 239, 241, 371, 373, 375, 377	50
				1.90
14	23.50	dieldrin	79, 263, 277, 279	50
				3.77
15	24.35	endosulfan-β, endrin, nitrofen	195, 202, 207, 237, 241, 253, 263, 283, 285, 315, 317, 319	40
				1.50
16	25.54	o,p′-DDT, endrin aldehyde	67, 165, 235, 236, 237, 250, 345, 347	50
				1.90
17	26.85	p,p′-DDT	165, 235, 236, 237	50
				3.77
18	27.30	captafol	77, 79, 80, 151	50
				3.77
19	27.95	chrysene-d_{12} (IS), endrin ketone, iprodione, methoxychlor	67, 113, 152, 183, 187, 189, 227, 228, 236, 238, 240, 241, 244, 314, 315, 317, 319, 339, 341, 343	30
				1.10
20	29.20	mirex	237, 270, 272, 274	50
				3.77
21	31.15	*cis*- and *trans*-permethrin	163, 165, 183, 184	50
				3.77
22	32.00	cyfluthrin I–IV	163, 165, 199, 206, 227	50
				3.03
23	34.00	fenvalerate I and II, fluvalinate τ-I and τ-II	125, 152, 167, 181, 199, 209, 250, 252	50
				1.69
		SIM-2		
1	7.00	acenaphthlene-d_{10} (IS)	80, 160, 162, 164	50
				3.77
2	10.00	ethalfluralin	276, 292, 316, 333	50
				3.77
3	11.40	benfluralin, trifluralin	264, 276, 290, 292, 293, 306, 307	50
				2.17
4	12.50	atrazine, carbofuran, propazine, simazine	44, 58, 123, 131, 149, 164, 172, 173, 186, 200, 201, 202, 214, 215, 229	30
				1.47
5	13.50	phenanthrene-d_{10}, pyrimethanil, terbuthylazine	77, 173, 184, 187, 188, 189, 198, 199, 200, 214, 216, 229	40
				1.50
6	14.50	chlorothaonil, triallate	86, 128, 264, 266, 268, 270	50
				2.53
7	15.50	desmetryn	58, 171, 198, 213	50
				3.77
8	16.50	carbaryl	115, 116, 144, 145	50
				3.77
9	17.05	metalaxyl, prometryn	45, 89, 105, 116, 160, 184, 194, 206, 223, 226, 241, 249	40
				1.50
10	17.70	terbutryn	170, 185, 226, 241	50
				3.77
11	18.50	metolachlor, fenpropimorph	117, 128, 129, 146, 162, 238, 240, 303	50
				1.90

Table 2. (Continued)

group	time (min)	pesticides and ISs	ions (amu)	dwell time (ms) scan rate (cycles/s)
		SIM-2 (Continued)		
12	19.32	nitrothal-isopropyl	68, 194, 212, 213, 214, 236, 254	50 2.17
13	20.20	cyprodinil	77, 210, 224, 225	50 3.77
14	21.05	furalaxyl	95, 146, 152, 242	50 3.77
15	22.20	triflumizole	73, 179, 206, 278	50 3.77
16	23.00	napropamide	72, 100, 128, 271	50 3.77
17	23.80	fludioxinil, oxadiazon	127, 154, 175, 177, 182, 248, 258, 260	50 1.90
18	24.55	oxyfluorfen	252, 302, 331, 361	50 3.77
19	25.30	oxadixyl	45, 105, 132, 163	50 3.77
20	26.20	benalaxyl, norflurazon	55, 91, 97, 102, 145, 148, 177, 204, 206, 237, 272, 301, 303, 305, 307, 309, 371, 387, 389, 417	30 1.10
21	27.40	propargite	64, 135, 150, 231	50 3.77
22	27.95	chrysene-d_{12} (IS), nitralin	236, 238, 240, 241, 274, 300, 316, 317	50 1.90
23	28.70	fenpropathrin	97, 125, 181, 265	50 3.77
24	30.15	cyhalothrin, fenarimol, pyridaben	107, 117, 132, 139, 147, 148, 181, 197, 208, 209, 219, 251	35 1.65
25	32.05	cypermethrin I–IV, flucythrinate I and II	44, 77, 157, 163, 165, 181, 199, 207, 209	45 1.83
26	35.00	azoxystrobin, dimethomorph 1 and 2	165, 301, 303, 344, 372, 387, 388, 403	50 1.90
		SIM -3		
1	7.00	demeton-O, acenaphthlene-d_{10} (IS)	60, 80, 88, 89, 160, 162, 164, 171	45 2.06
2	11.50	phorate	75, 97, 121, 260	50 3.77
3	12.15	demeton-S, dimethoate, thiometon	60, 87, 88, 89, 93, 125, 143, 170	50 1.90
4	13.00	fonophos, terbufos, phenanthrene-d_{10} (IS), propetamphos	57, 103, 109, 110, 137, 138, 153, 184, 187, 188, 189, 194, 231, 222, 236, 246	30 1.38
5	14.20	diazinon, disulfoton	88, 89, 97, 137, 142, 152, 179, 199	50 1.90
6	15.85	chlorpyrifos-methyl, malaoxon, parathion-methyl	79, 99, 109, 125, 127, 139, 149, 263, 275, 286, 288, 290	50 1.27
7	17.75	fenitrothion, malathion	93, 109, 125, 127, 173, 260, 277	50 1.90
8	18.95	chlorpyriofos, fenthion, parathion, triadimefon	57, 85, 97, 109, 125, 139, 169, 197, 199, 208, 210, 278, 291, 314	30 1.57
9	19.85	bromophos-methyl	125, 329, 331, 333	50 3.77
10	20.65	Penconazole	159, 161, 248, 250	50 3.77
11	21.45	chlorvinfenphos, triadimenol	58, 70, 112, 121, 128, 168, 213, 255, 267, 269, 323, 325	35 1.65
12	21.95	bromophos-ethyl, methidathion, pachlobutrazol	85, 93, 125, 127, 145, 167, 236, 238, 301, 303, 357, 359	35 1.65
13	22.75	tetrachlorvinphos	109, 329, 331, 333	50 3.77
14	23.30	fenamiphos, hexaconazole	82, 83, 154, 214, 216, 217, 288, 303	40 2.25
15	23.70	profenophos, uniconazole	41, 70, 139, 173, 206, 208, 215, 217, 234, 235, 236, 339	45 1.38
16	24.25	cyproconazole, myclobutanil	82, 125, 139, 150, 179, 181, 222, 224	50 3.77
17	25.75	ethion	97, 125, 153, 231	45 2.06
18	26.40	carbophenothion, propionconazole	69, 97, 121, 153, 157, 173, 191, 259	50 3.77
19	27.30	tebuconazole	70, 83, 125, 250	35 1.65

Table 2. (Continued)

group	time (min)	pesticides and ISs	ions (amu)	dwell time (ms) scan rate (cycles/s)
			SIM -3 (Continued)	
20	28.15	chrysene-d_{12} (IS), EPN, phosmet	77, 93, 141, 157, 160, 161, 169, 185, 236, 238, 240, 241	35 1.65
21	29.25	azinphos-methyl, phosalone	77, 105, 121, 132, 160, 182, 184, 367	40 2.25
23	31.50	coumaphos, dioxathion	70, 97, 109, 125, 153, 180, 210, 226, 271, 308, 310, 362	45 1.38
24	32.00	fenbuconazole	125, 127, 129, 198	50 3.77

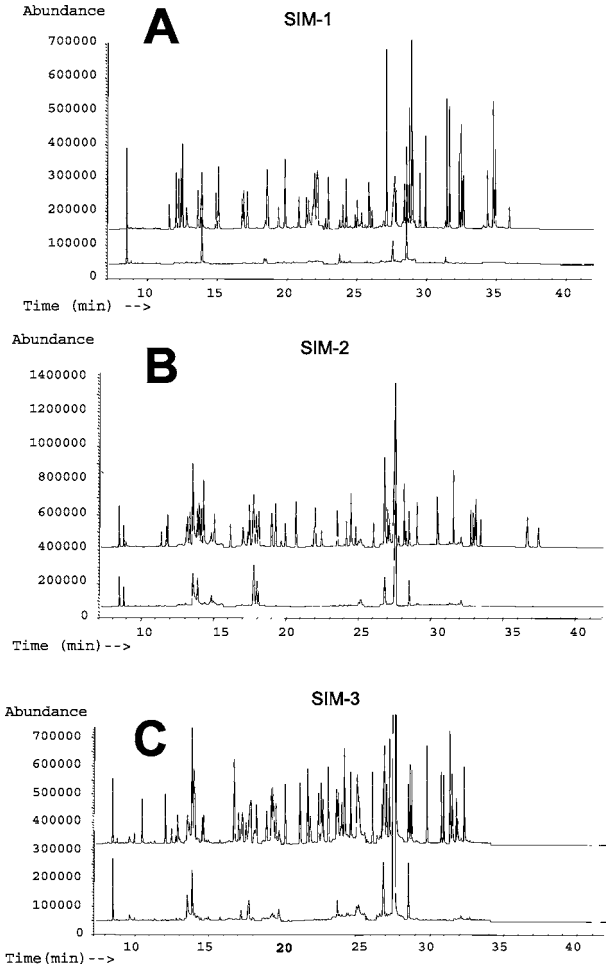

Figure 2. Reconstructed GC-MS(SIM) chromatograms from the three SIM programs used to screen pesticides in a malt beverage extract. Results from the three SIM programs: (**A**) SIM-1, (**B**) SIM-2, and (**C**) SIM-3 as described in **Table 2**. Each chromatogram shows a malt beverage blank extract (bottom) and an extract from a 50 mL malt beverage sample fortified at 10 ng/mL. See the Materials and Methods for extraction details and GC-MS conditions.

($n = 5$ replicates performed) ranged from 5 to 116% among the three malt beverages evaluated (**Table 4**). While it may be possible to further optimize the SPE and elution technique for individual pesticides, the purpose here was to effectively screen for a broad array of compounds and this method was successful in this regard. A closer inspection showed recoveries in excess of 70% for 85 of the 142 pesticides, good agreement of recoveries between the three representative malt beverages, and decent precision for six replicates performed for each pesticide and malt beverage (generally below 8% relative standard deviation). The similarity in recoveries obtained for a given pesticide in the three malt beverages indicates that different properties listed in **Table 3** likely to be encountered in real samples would have little impact on method performance and is indicative of the robustness of this method.

Table 3. Chemical and Physical Properties of Three Beers (Beers 1–3) Used in This Study[a]

	beer		
	1	2	3
alcohol (% weight)[b]	4.5	4.5	3.9
total acids (g/100 mL)[c]	0.27	0.26	0.14
real extract (% weight)[d]	4.6	4.5	3.3
specific gravity (20 °C/20 °C)[e]	1.0098	1.0097	1.0075
fusel oil (mg/L)[f]	118	176	85
bitterness units[g]	45	32.5	10
color	dark brown	amber	light amber

[a] References to methods are listed with their corresponding subscripts. Fusel oil is the total amount of high molecular weight alcohols (propyl, butyl, and pentyl alcohols). Bitterness units are unitless values used to determine the amount of hops present. The color was determined by visual observation of the beer. [b] Ref *11*, Section Beer-4: Alcohol: Section B. Beer and Distillate Measured Gravimetrically. [c] Ref *11*, Section Beer-8: Total Acidity: Section A. Potentiometric Titration. [d] Ref *11*, Section Beer-5: Real Extract: Section B. Beer Measured Gravimetrically. [e] Ref *11*, Section Beer-2: Specific Gravity: Section B. Digital Density Meter. [f] Ref *12*. [g] Ref *11*, Section Beer-23: Beer Bitterness: Section A. Bitterness Units (BU).

Certain deviations and trends were apparent in the recovery data, which warrant some discussion. The organophosphates fonofos and phosmet gave markedly higher recoveries (102 and 83%, respectively) for beer 2 than for beers 1 and 3 (68 and 70% for fonofos and 55 and 54% for phosmet) (**Table 4**). Unique constituents in beer 2, which were not apparent in the properties shown in **Table 3**, may promote retention to the NEXUS sorbent or vice versa for the other two malt beverages. Likewise, an examination of the pyrethroid data showed a similar although less significant trend of higher recoveries for beer 2. The lowest recoveries were obtained for the organohalogens endrin aldehyde (5−7%), folpet (35−39%), and chlozolinate (32−49%); the organitrogens kresoxim-methyl (22−23%) and fenpropimorph (18−52%); and the organohalogen/organonitrogen chlorothalonil (34−42%). Low recoveries such as these may be attributed to ineffective adsorption to and/or incomplete elution from the sorbent phase. Analyte instability and/or thermal decomposition at GC temperatures may also have contributed to low recoveries. Quantitative recoveries were obtained for the majority of organonitrogen and azole pesticides, indicative of the compatibility of these with the NEXUS sorbent. Similarly, recoveries in slight excess of 100% were observed for the organophosphates azinphos-ethyl, azinphos-methyl, and fenamiphos and the organonitrogen pesticides carbaryl, carbofuran, and bitertanol. However, in consideration of the standard

Table 4. Recoveries of Organochlorine, Pyrethroid, Organonitrogen, and Organophosphorus Pesticides Extracted from Three Different Malt Beverages (Chemical and Physical Properties Listed in **Table 3**) at a Fortification Concentration of 10 ng/mL[a]

	recovery (%)				recovery (%)		
pesticide	beer 1	beer 2	beer 3	pesticide	beer 1	beer 2	beer 3
			organochlorine				
alachlor	92 ± 2	94 ± 2	93 ± 2	endosulfan-β	71 ± 3	68 ± 2	73 ± 4
adrin	62 ± 4	67 ± 3	49 ± 7	endrin	80 ± 3	88 ± 5	74 ± 6
BHC-α	72 ± 5	79 ± 5	76 ± 4	endrin aldehyde	7 ± 1	5 ± 0.3	5 ± 0.2
BHC-δ	92 ± 5	84 ± 3	81 ± 3	endrin ketone	67 ± 3	78 ± 1	79 ± 2
captafol	55 ± 9	60 ± 8	65 ± 8	fenson	86 ± 3	93 ± 1	92 ± 3
captan	59 ± 13	74 ± 9	76 ± 16	folpet	35 ± 1	37 ± 3	39 ± 3
chlorbenside	76 ± 3	81 ± 4	63 ± 8	heptachlor	68 ± 2	74 ± 3	56 ± 7
cis-chlordane	68 ± 3	74 ± 3	56 ± 7	heptachlor epoxide	71 ± 2	79 ± 2	68 ± 5
trans-chlordane	66 ± 3	73 ± 3	54 ± 7	hexachlorobenzene	60 ± 3	64 ± 2	53 ± 6
chlorothalonil	34 ± 2	36 ± 3	42 ± 11	iprodione	70 ± 13	87 ± 10	82 ± 15
chlozolinate	32 ± 20	48 ± 8	49 ± 20	lindane	84 ± 3	95 ± 2	86 ± 2
diallate I	76 ± 4	81 ± 2	76 ± 3	methoxychlor	71 ± 7	85 ± 3	74 ± 6
diallate II	75 ± 4	80 ± 1	76 ± 3	metolachlor	103 ± 3	98 ± 5	98 ± 4
dichlofluanid	47 ± 16	73 ± 7	73 ± 6	mirex	59 ± 4	68 ± 4	48 ± 7
4,4′-DCBP[b]	83 ± 3	89 ± 4	84 ± 3	nitrofen	72 ± 3	79 ± 2	69 ± 2
dicloran	86 ± 3	86 ± 1	82 ± 2	procymidone	89 ± 3	94 ± 4	92 ± 3
o,p′-DDT	53 ± 3	61 ± 5	35 ± 8	quintozene	67 ± 3	73 ± 1	64 ± 3
p,p′-DDT	75 ± 3	83 ± 5	65 ± 7	tecnazene	71 ± 4	73 ± 1	70 ± 2
dieldrin	86 ± 17	80 ± 2	66 ± 6	vinclozolin	83 ± 8	99 ± 6	95 ± 8
endosulfan-α	68 ± 2	76 ± 2	70 ± 8				
			pyrethroid				
allethrin	87 ± 1	94 ± 2	88 ± 4	fenpropathrin	59 ± 7	72 ± 9	55 ± 9
cyfluthrin I	67 ± 4	77 ± 6	56 ± 7	fenvalerate I	70 ± 5	75 ± 5	57 ± 7
cyfluthrin II	66 ± 3	76 ± 5	55 ± 7	fenvalerate II	71 ± 5	82 ± 12	63 ± 5
cyfluthrin III	69 ± 4	81 ± 7	56 ± 8	flucythrinate I	61 ± 9	78 ± 10	56 ± 9
cyfluthrin IV	71 ± 6	84 ± 8	57 ± 7	flucythrinate II	63 ± 9	79 ± 10	57 ± 9
cyhalothrin	66 ± 8	80 ± 11	58 ± 9	fluvalinate τ-I	72 ± 4	80 ± 6	59 ± 6
cypermethrin I	77 ± 9	103 ± 11	70 ± 10	fluvalinate τ-II	71 ± 4	78 ± 6	57 ± 7
cypermethrin II	67 ± 9	85 ± 11	60 ± 10	permethrin I	81 ± 4	92 ± 5	57 ± 8
cypermethrin III	67 ± 8	93 ± 9	63 ± 9	permethrin II	70 ± 4	81 ± 6	58 ± 7
cypermethrin IV	56 ± 9	74 ± 9	52 ± 9				
			organonitrogen				
atrazine	96 ± 1	93 ± 6	97 ± 4	nitralin	69 ± 2	69 ± 3	65 ± 1
azoxystrobin	93 ± 2	92 ± 5	94 ± 4	nitrothal-isopropyl	88 ± 2	90 ± 4	85 ± 3
benalaxyl	89 ± 1	92 ± 5	96 ± 4	norflurazon	92 ± 2	91 ± 6	91 ± 4
benfluralin	64 ± 3	69 ± 6	57 ± 4	oxadiazon	78 ± 1	85 ± 3	87 ± 3
bitertanol I	110 ± 10	112 ± 9	113 ± 5	oxadixyl	76 ± 5	70 ± 5	84 ± 5
bitertanol II	87 ± 14	111 ± 9	114 ± 5	oxyfluorfen	78 ± 2	83 ± 3	72 ± 2
carbaryl	101 ± 15	116 ± 12	89 ± 8	pachlobutrazol	102 ± 5	97 ± 7	99 ± 4
carbofuran	110 ± 8	108 ± 6	113 ± 4	prometryn	98 ± 1	95 ± 5	97 ± 4
cyproconazole	86 ± 9	86 ± 12	94 ± 5	propargite	62 ± 5	79 ± 8	70 ± 7
cyprodinil	92 ± 2	96 ± 4	96 ± 4	propazine	102 ± 2	99 ± 4	99 ± 5
desmetryn	90 ± 9	92 ± 7	95 ± 5	propionconazole I	102 ± 8	96 ± 3	77 ± 4
dimethomorph I	89 ± 3	87 ± 6	92 ± 4	propionconazole II	91 ± 8	99 ± 2	96 ± 4
dimethomorph II	90 ± 3	88 ± 6	92 ± 4	propyzamide	94 ± 3	95 ± 2	92 ± 2
ethalfluralin	72 ± 2	75 ± 5	65 ± 3	pyridaben	77 ± 7	93 ± 9	84 ± 10
fenarimol	90 ± 2	89 ± 5	97 ± 4	pyrimethanil	95 ± 2	94 ± 5	94 ± 3
fenbuconazole	83 ± 6	94 ± 7	99 ± 5	simazine	100 ± 4	94 ± 6	101 ± 4
fenpropimorph	18 ± 25	28 ± 35	52 ± 34	tebuconazole	89 ± 19	105 ± 14	93 ± 8
fludioxinil	84 ± 2	92 ± 6	93 ± 4	terbuthylazine	94 ± 2	93 ± 5	94 ± 4
furalaxyl	92 ± 1	90 ± 6	95 ± 4	terbutryn	95 ± 2	95 ± 5	96 ± 4
hexaconazole	78 ± 11	92 ± 4	103 ± 10	triadimefon	93 ± 6	97 ± 2	94 ± 4
kresoxim-methyl	22 ± 1	22 ± 1	23 ± 1	triadimenol	109 ± 11	97 ± 3	108 ± 7
metalaxyl	92 ± 3	91 ± 6	95 ± 4	triallate	74 ± 1	78 ± 4	74 ± 1
metolachlor	103 ± 3	98 ± 5	98 ± 4	triflumizole	62 ± 24	86 ± 13	88 ± 8
myclobutanil	109 ± 5	88 ± 6	95 ± 5	trifluralin	65 ± 3	69 ± 6	58 ± 4
napropamide	90 ± 1	93 ± 5	96 ± 4	uniconazole	99 ± 6	97 ± 7	100 ± 4
			organophosphorus				
azinphos-ethyl	101 ± 5	105 ± 2	103 ± 3	fenamiphos	104 ± 6	102 ± 6	110 ± 6
azinphos-methyl	103 ± 5	109 ± 2	105 ± 4	fenitrothion	93 ± 5	94 ± 2	86 ± 3
bromophos	70 ± 3	75 ± 3	60 ± 5	fenthion	82 ± 4	90 ± 3	85 ± 4
bromophos-methyl	77 ± 3	82 ± 2	72 ± 2	fonophos	68 ± 8	102 ± 5	70 ± 6
carbophenothion	78 ± 8	83 ± 4	70 ± 5	isofenphos	89 ± 3	92 ± 2	90 ± 3
chlorfenvinphos	95 ± 5	95 ± 2	96 ± 4	malathion	101 ± 5	103 ± 3	96 ± 4
chlorpyrifos	80 ± 8	87 ± 3	74 ± 3	methidathion	96 ± 4	97 ± 1	92 ± 3
chlorpyrifos-methyl	73 ± 3	81 ± 2	73 ± 4	parathion	85 ± 4	89 ± 1	82 ± 3

Table 4. (Continued)

pesticide	recovery (%) beer 1	beer 2	beer 3	pesticide	recovery (%) beer 1	beer 2	beer 3
				organophosphorus (Continued)			
coumaphos	77 ± 3	93 ± 2	93 ± 3	parathion-methyl	94 ± 5	93 ± 2	85 ± 3
demeton-O	60 ± 8	56 ± 6	44 ± 3	phorate	63 ± 11	66 ± 6	64 ± 5
demeton-S	86 ± 8	86 ± 4	77 ± 6	phosalone	81 ± 2	94 ± 2	93 ± 2
dialifos	65 ± 4	83 ± 6	76 ± 6	phosmet	55 ± 12	83 ± 4	54 ± 8
diazinon	80 ± 6	94 ± 4	73 ± 7	profenphos	72 ± 5	83 ± 3	78 ± 5
dioxathion	106 ± 9	101 ± 3	96 ± 5	propetamphos	94 ± 5	97 ± 2	85 ± 5
disulfoton	67 ± 9	70 ± 5	65 ± 5	terbufos	65 ± 7	67 ± 4	61 ± 4
EPN	78 ± 3	85 ± 2	78 ± 3	tetrachlorvinphos	96 ± 4	102 ± 3	98 ± 2
ethion	83 ± 2	86 ± 3	78 ± 4	thiometon	65 ± 12	69 ± 6	67 ± 5

[a] The number of replicates for each beer type (beers 1–3) is $n = 5$ samples. Each % recovery is an average ± standard deviation. [b] 4,4′-DCBP, 4,4′-dichlorobenzophenone.

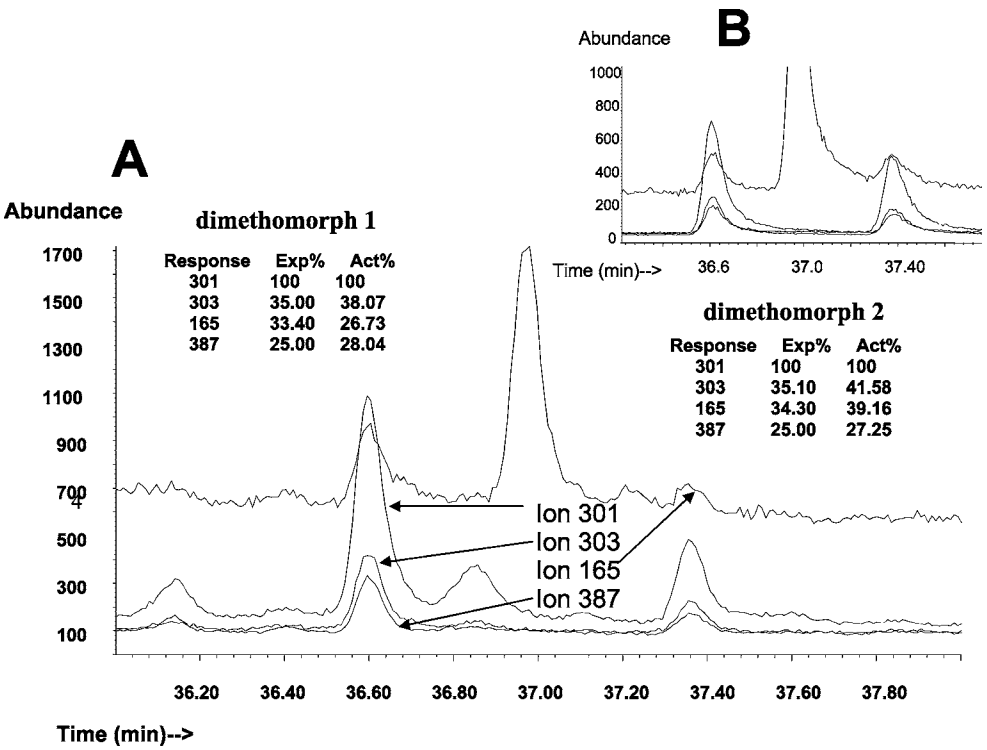

Figure 3. (**A**) Extracted ions for dimethomorph isomers, *m*/*z* 301 (target), 303, 165, and 387 (qualifier ions) at retention times of approximately 36.60 and 37.36 min. Additional information includes the comparison between the actual qualifier-to-target % (obtained from the malt beverage extract) and the expected qualifier-to-target % (obtained from a dimethomorph standard) results. (**B**) Reconstructed chromatogram of a dimethomorph standard at 50 ng/mL.

deviations obtained, no matrix enhancement was evident for most of the pesticides studied for the three different beer types. In a previous work involving multiresidue pesticide screening in wines, another polymer-based SPE sorbent, OASIS, was used to extract similar pesticides from wine matrices (*9*). Essentially the same pesticides were tested in wines as in the malt beverages of this study, and similar results with recoveries (>70%) were achieved for most of the analytes, suggesting that both the NEXUS and the OASIS sorbents have similar adsorption and retention characteristics.

Analysis of Malt Beverage Samples. Of the 42 prepared malt beverages screened, the fungicide demethomorph was identified in one sample and 26 samples were found to contain the carbamate insecticide carbaryl. Overlayed extracted chromatograms for dimethomorph and carbaryl in two different malt beverage samples are shown in **Figures 3** and **4**, respectively. In both cases, the t_R values of the target ions and qualifier-to-target ratios were consistent with authentic pesticide standards. Chromatograms from sample extracts were processed, and ions extracted for dimethomorph (*m*/*z* 301, 303, 165, and 387) from one of the samples are shown in **Figure 3A** (with an accompanying GC of a dimethomorph standard in **Figure 3B**). Two isomers of the fungicide dimethomorph (*E*- and *Z*-forms) were found in the malt beverage sample at a total concentration of 1 ng/mL (**Tables 1**−**4** and **Figure 2** list the two dimethomorph isomers as 1 and 2 since the *E*- and *Z*-isomers have not been distinguished by GC-MS). The criteria for identification of dimethomorph were determined based on the retention time (36.60 and 37.36 min for both isomers, respectively) and the target-to-qualifier ion ratios using *m*/*z* 301 as the target ions and *m*/*z* 303, 165, and 387 as the qualifier ions as shown in **Figure 3**. An extraneous peak of *m*/*z* 165 is shown at approximately 37.0 min in both the malt beverage extract (**Figure 3A**) and the standard (**Figure 3B**) but does not seem to interfere with the confirmation of the fungicide. Dimethomorph is registered in the United States for use on a variety of

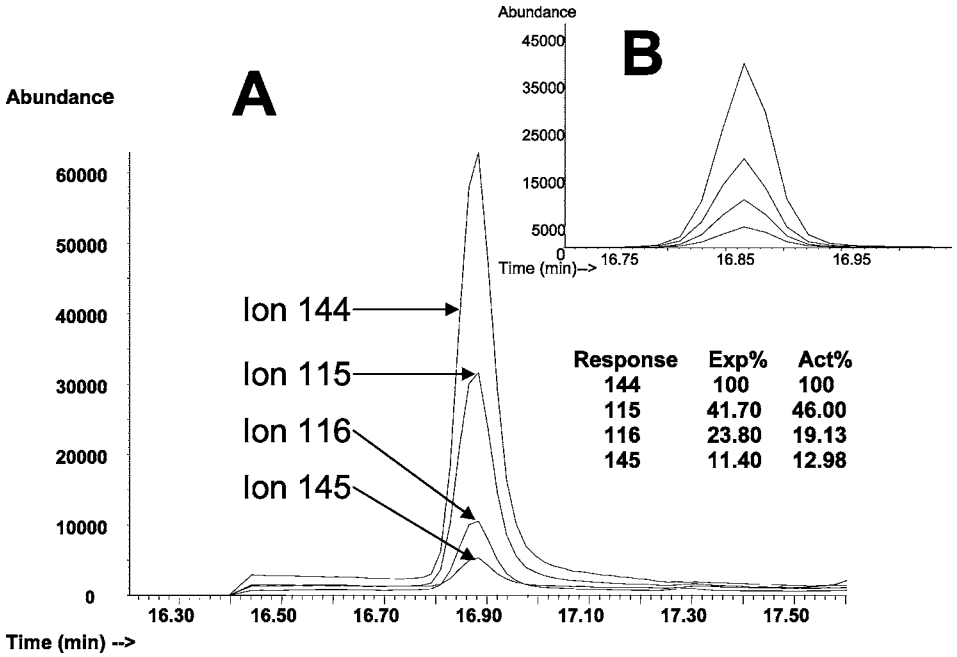

Figure 4. (**A**) Extracted ions for carbaryl, *m*/*z* 144 (target), 115, 116, and 145 (qualifier ions) at a retention time of approximately 16.88 min from a reconstructed GC-MS(SIM) chromatogram obtained from a malt beverage extract. Additional information includes the comparison between the actual qualifier-to-target % (obtained from the malt beverage extract) and the expected qualifier-to-target % (obtained from a carbaryl standard) results. (**B**) Reconstructed chromatogram of a carbaryl standard at 2500 ng/mL.

crops such as tomatoes, potatoes, grapes, tobacco, and hops to aid in the control of downy mildew and other fungi (*22*−*24*). Hengel and Shibamoto (*3*) performed a study that showed dimethomorph residues in treated hops could carry over into the malt beverage through the fermentation process. However, they showed that much of the dimethomorph level at the fermentation stage was significantly low (<8 ng/mL), considering the initial high levels of the pesticide applied to the raw hops (1000 ng/mL).

Carbaryl ranged from <20 ng/mL to approximately 36 ng/mL in 26 samples that tested positive for this analyte. **Figure 4** shows the reconstituted chromatogram of a SIM-2 program from the malt beverage sample containing ~36 ng/mL carbaryl, along with an accompanying chromatogram standard with extracted ions *m*/*z* 144, 115, 116, and 145. In the case of carbaryl, the t_R of 16.88 min for the target ion *m*/*z* 144 and the qualifier-to-target ratios using the qualifier ions *m*/*z* 115, 116, and 145 provided identification of carbaryl in the malt beverage samples. The concentration of carbaryl may not be quantitated accurately because its r^2 value (0.989) does not meet the acceptable criterion for quantitation ($r^2 \geq 0.990$) for this study. This is most likely due to the thermal lability of carbaryl and its degradation to its breakdown product, 1-naphthol, under GC conditions (*4*). The low r^2 value for carbaryl may influence the fortification results for the three malt beverage types shown in **Table 4**, which lists high recoveries for two beverages (101 ± 15 and 116 ± 12%) and a relatively lower recovery (89 ± 8%) for the third beverage.

However, such estimations of carbaryl indicate that the levels of the pesticides in malt beverages are significantly lower than the tolerance levels allowed for the starting ingredients, such as malt barley, rice, corn, wheat, and hops. Carbaryl is used to control insects affecting grain crops and for postharvest application for the protection of stored grains (*4*). In the United States, carbaryl is not registered for use for malt barley but it can be used on other grain ingredients used in beer making such as rice, wheat, and corn, with U.S. EPA limits set at 5, 3, and 5 ppm, respectively (*24*). The European Union also permits the use of carbaryl on cereal grains, including barley, but at levels lower than those established by the United States: barley, 0.5 ppm; rice, 1.0 ppm; corn, 0.5 ppm; and wheat, 0.5 ppm (*25*). The presence and persistence of carbaryl in the final liquid product can also be attributed to its high water solubility (120 mg/L at 20 °C) (*26*, *27*). Otherwise, the carbaryl concentration in the malt beverage was approximately 10−100 times lower than the limits set for the grain products. None of the other 140 analytes were identified above the LOD in the 42 beer samples, which may be attributed to dilution of the pesticides when all other ingredients are combined and dissipation during the brewing process (*2*, *4*, *6*−*8*).

Future efforts will involve expansion and improvement of the sample preparation scheme and the analysis of additional pesticides. Better means of quantitating carbaryl and other thermally sensitive pesticides require the use of HPLC methods, rather than GC methods (*4*, *6*, *7*, *28*−*31*). Presently, work is being conducted in our laboratories on adapting the extraction and cleanup procedures proposed in this work to LC-MS analysis for the identification and quantitation of thermally labile pesticides, such as the carbamates, in beverage alcohol products (such as wines and malt beverages). In addition, the current GC-MS(SIM) method proposed in this work has been shown to be effective for screening over 100 pesticides and can be further expanded by adding other pesticides amenable to GC analysis in either of the three SIM programs.

In conclusion, an effective, comprehensive screening method for organohalogen, organonitrogen, and organophosphate pesticides in malt beverages using SPE with GC-MS(SIM) has been presented. Fortification data showed good correlation among three representative malt beverages, excellent overall recoveries, and decent precision for replicate analyses, all of which indicated the suitability of this method for analyzing all types of malt beverages. The method is robust and flexible and can also be expanded to include the screening of additional pesticides.

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