JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

J. Agric. Food Chem. **2004,** *52,* 1735−1741 **1735**

Automated Dynamic Headspace/GC-MS Analyses Affect the Repeatability of Volatiles in Irradiated Turkey

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Although a dynamic headspace/gas chromatography−mass spectrometry (DH/GC-MS) method is an effective tool for determining volatiles of irradiated turkey meat, the profile of volatiles may be changeable depending upon the availability of oxygen in the sample vial and sample holding time before purge. The objective of this study was to evaluate the effects of helium flushing and sample holding time before purge on the volatiles profiles of irradiated raw and cooked turkey breast meat. Vacuum-packaged turkey breasts were irradiated at 2.5 kGy, and the volatiles of irradiated raw and cooked samples were analyzed using a DH/GC-MS with different holding times up to 280 min. The amounts of dimethyl disulfide and dimethyl trisulfide decreased as sample holding time in an autosampler (4 °C) before purge increased, whereas those of aldehdyes increased as holding time increased due to lipid oxidation. Helium flush of sample vials before sample loading on an autosampler retarded lipid oxidation and minimized the changes of sulfur volatiles in raw meat but was not enough to prevent oxidative changes in cooked meat. Although DH/GC-MS is a convenient method for automatic analysis of volatiles in meat samples, the number of samples that can be loaded in an autosampler at a time should be limited within the range that can permit reasonable repeatabilities for target volatile compounds.

KEYWORDS: Holding time; dynamic headspace/GC-MS; sulfur volatiles; aldehydes; irradiated turkey breast

INTRODUCTION

Several methods have been developed to determine volatile compounds in meat and meat products: direct injection of lipid fraction or distillate into a gas chromatograph, static headspace, dynamic headspace using a purge-and-trap, and solid phase microextraction (SPME) (*1*−*4*). Some of these methods require considerable sample preparation and exposure of samples to harsh conditions, which may induce changes in organic compounds (*5, 6*). Thus, the volatile components detected may not be the ones that produce odor in the original samples (*7*). Meat and meat products can easily be affected by environmental factors during processing and storage, and time-consuming sample preparation may change the original composition of volatiles because they are highly susceptible to oxidative changes and the volatile compounds from meat are reactive to other components surrounding them. SPME has been widely employed for volatiles analysis in recent years (*8*) because of its simplicity, mild extraction conditions, and low cost. However, SPME is a batch type method, and it is difficult to maintain even extraction conditions.

The dynamic headspace gas chromatography−mass spectrometry (DH/GC-MS) method described by us (*9*) is fast, effective, and easy because it uses an automated volatile extraction, trap, and concentration process using a purge-and-trap/cryofocusing unit and injects volatiles directly to a GC. Many samples (72 in a specific model) can be loaded to an autosampler at a time; volatiles are extracted by purging the headspace above the sample with an inert gas, such as helium, and then concentrated in an on-column trap. The extraction process uses only a minor temperature adjustment to facilitate volatility of compounds from sample. This method, therefore, can represent the most corresponding compounds to the natural volatile composition of the product.

The volatiles of meat and meat products have been successfully analyzed using the DH/GC-MS method (*9, 10*). The presence of oxygen, however, is one of the most critical environmental factors that influence lipid oxidation, which affects the volatile profile of meat sample during the dynamic headspace analysis. Ahn et al. (*5*, *11*) reported that sample holding before purge increased volatiles production in both raw and cooked meat because residual oxygen in sample vials accelerated lipid oxidation.

Irradiation is an efficient way to eliminate pathogens in meat (*12*) but generates a few sulfur-containing volatiles (*9, 10, 13*). In general, volatile sulfur compounds play a major role in the overall odor and flavor of many foods including irradiated meat (*13*−*15*). Although sulfur compounds are present in trace levels, the contribution of sulfur compounds to the flavor of food systems is very high due to their high volatility and low odor

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10.1021/jf034975p CCC: $27.50
Published on Web 02/24/2004

Table 1. Volatiles Profile of Irradiated Raw Turkey Breast without Helium Flush during Sample Holding Time in an Autosampler (4 °C) before Purge[a]

	sample holding time (min)								
volatile compound	0	40	80	120	160	200	240	280	SEM
hydrocarbons									
pentane	350 d	371 cd	414 bc	419 bc	409 bc	440 b	527 a	517 a	14
1-heptene	0	31	35	0	0	30	30	0	22
heptane	35	45	85	29	69	33	35	91	38
1-octene	72	104	117	134	100	135	96	119	27
2-octene	246	336	316	240	378	331	295	408	60
octane	227	264	231	283	293	250	234	280	27
benzene	184	167	199	184	191	179	196	222	13
toluene	512	587	644	586	584	647	553	607	48
alcohols									
ethanol	3715	3984	4576	3972	4054	4177	3727	3954	283
2-propanol	5369	3943	4348	3680	3943	4560	4258	4726	514
1-pentanol	371	894	973	1037	678	770	1040	609	340
sulfur volatiles									
dimethyl sulfide									
dimethyl disulfide					see **Figure 1**				
dimethyl trisulfide									
ketones									
2-propanone	12094	11254	14625	14031	12976	13965	10513	13765	1823
2-butanone	348	380	410	376	404	373	368	379	43
aldehydes									
hexanal	1005	894	973	1037	678	770	1040	609	340
nonanal	270	304	367	354	221	243	147	188	60
total	52215 a	44349 ab	48664 ab	42771 ab	41722 ab	42500 ab	36862 b	40286 ab	2741

[a] $n = 4$, total ion counts ($\times 10^4$). Different letters (a–d) within a row indicate significant differences ($P < 0.05$). SEM, standard error of the means.

threshold (*16*, *17*). The isolation and quantification of sulfur volatiles are difficult because they are highly volatile and susceptible to change under aerobic conditions. Thus, sample handling, exposure to environment, and sample holding time before purge are critical for the repeatability of sulfur compounds. Although DH/GC-MS is a convenient and reproducible method for volatiles analysis, dramatic changes in the amounts of certain volatiles were observed when holding time was increased (*5*, *11*).

The objective of this study was to evaluate the effects of helium flushing and sample holding time before purge on the volatiles of irradiated raw and cooked turkey breast meat using an automated DH/GC-MS, which will be important for improving the repeatability of volatiles in meat samples and determining an acceptable maximum number of samples that can be loaded in an autosampler at a time.

MATERIALS AND METHODS

Samples. Fresh turkey breast muscles (*pectoralis major* plus *minor*) were ground through a 3-mm plate twice, and a total of 128 patties (each ~50 g) were made. The patties were individually vacuum-packaged in high oxygen barrier bags (nylon/polyethylene, 9.3 mL of $O_2/m^2/24$ h at 0 °C; Koch, Kansas City, MO) and irradiated. Analyses were replicated using four samples from different birds. Standard sulfur compounds (dimethyl sulfide, dimethyl disulfide, and carbon disulfide; Sigma Chemical Co., St. Louis, MO) were also analyzed.

Ionizing Radiation. The vacuum-packaged turkey patties were irradiated at 2.5 kGy using a Linear Acceleration Facility (LAF, Circe IIIR; Thomson CSF Linac, St. Aubin, France) with 10 MeV of energy and a 10.2 kW power level. The average dose rate was 83.5 kGy/min. Alanine dosimeters were placed on the top and bottom surfaces of a sample and were read using a 104 electron paramagnetic resonance instrument (Bruker Instruments Inc., Billerica, MA) to check the absorbed dose. The dose range absorbed at meat samples was 2.449−2.734 kGy (maximum/minimum ratio was 1.11). After irradiation, samples were immediately returned to a 4 °C cold room and stored for at least 1 day. For cooked meat samples, samples were cooked in the bag in a water bath (90 °C) for 15 min, cooled with cold tap water, and then used for analysis.

Holding Time in Autosampler before Purge-and-Trap. Sample (3 g for raw meat and 2 g for cooked meat) was placed in a 40 mL sample vial and then capped with an airtight Teflon septum (fluorocarbon resin/silicone; I-Chem Co., New Castle, DE). To determine the effects of headspace air on lipid oxidation and volatiles production of samples, half of the samples were flushed with helium for 3 s at 40 psi before capping. Immediately after capping, eight samples were placed in a refrigerated autosampler tray (4 °C), and each sample was analyzed at a 40 min interval. Therefore, each sample (first to eighth vials) has a different holding time (0, 40, 80, 120, 160, 200, 240, and 280 min) in the autosampler (4 °C) before purge.

Volatiles Analysis by Automated Purge-and-Trap/GC-MS. The meat sample was purged with He (40 mL/min) for 15 min at 40 °C using a Solatek 72 multimatrix-vial autosampler/sample concentrator 3100 (Tekmar-Dohrmann, Cincinnati, OH) connected to a GC-MS (model 6890/5973, Hewlett-Packard Co., Wilmington, DE) according to the method of Ahn et al. (*9*). Volatile compounds were trapped using a Tenax/charcoal/silica column (Tekmar-Dohrmann) and desorbed for 2 min at 225 °C, focused in a cryofocusing module (−80 °C), and then thermally desorbed into a column for 60 s at 225 °C. An HP-624 column (7.5 m, 0.25 mm i.d., 1.4 μm nominal), an HP-1 column (60 m, 0.25 mm i.d., 0.25 μm nominal), and an HP-Wax column (7.5 m, 0.250 mm i.d., 0.25 μm nominal) were connected using zero dead-volume column connectors (J&W Scientific, Folsom, CA). A ramped oven temperature was used to improve volatile separation. The initial oven temperature of 0 °C was held for 1.5 min. After that, the oven temperature was increased to 15 °C at 2.5 °C/min, increased to 45 °C at 5 °C/min, increased to 110 °C at 20 °C/min, then increased to 210 °C at 10 °C/min, and then held for 2.25 min at that temperature. A constant column pressure at 22.5 psi was maintained. All mass spectra were acquired in the electron impact (EI) mode. The ionization potential of MS was 70 eV, and the scan range was m/z 19.1−350. Tentative identification of volatiles was achieved using the Wiley library (Hewlett-Packard Co.). The area of each peak was integrated using ChemStation software (Hewlett-Packard Co.), and the total peak area (total ion counts $\times 10^4$) was reported as an indicator of volatiles generated from the samples.

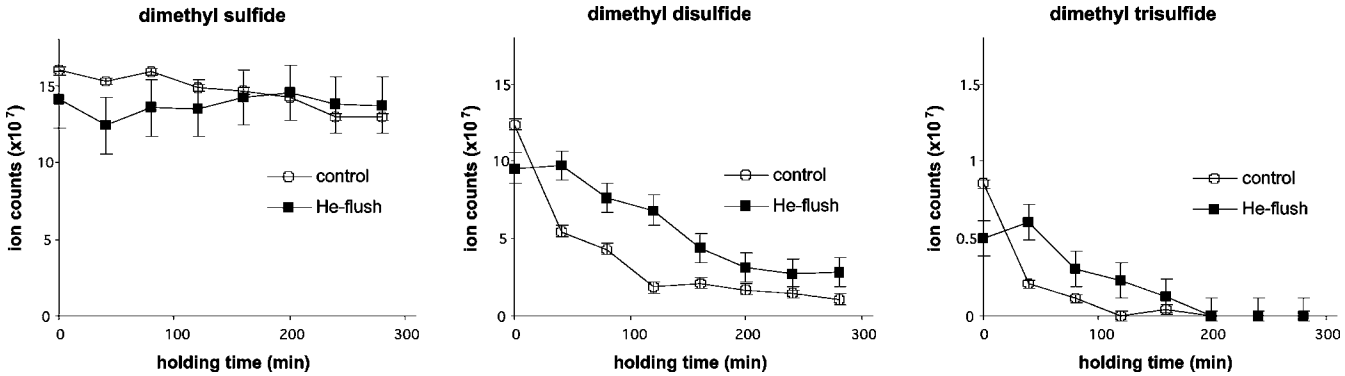

Figure 1. Production of sulfur volatiles from irradiated raw turkey breast during sample holding time in an autosampler (4 °C) before purge.

Table 2. Volatiles Profile of Irradiated Raw Turkey Breast with Helium Flush during Sample Holding Time in an Autosampler (4 °C) before Purge[a]

	sample holding time (min)								
volatile compound	0	40	80	120	160	200	240	280	SEM
hydrocarbons									
pentane	590 b	1078 ab	1456 ab	1321 ab	1390 ab	1432 ab	1841 a	1369 ab	224
1-heptene	0	33	31	0	0	0	65	0	19
heptane	0 b	67 ab	134 a	111 a	134 a	132 a	159 a	124 a	22
1-octene	0	0	198	47	30	60	74	38	76
2-octene	120	255	438	344	357	405	452	372	86
octane	150	186	471	261	246	266	280	167	112
benzene	53	123	191	191	173	181	205	127	44
toluene	439	565	592	618	582	590	684	547	68
alcohols									
ethanol	3873	4978	5132	4684	4736	4461	4630	4211	268
2-propanol	3529	4551	4655	4767	4872	4479	4494	3641	608
1-pentanol	211	430	484	418	381	345	552	413	130
sulfur volatiles									
dimethyl sulfide									
dimethyl disulfide					see **Figure 1**				
dimethyl trisulfide									
ketones									
2-propanone	7855	13777	11556	12485	12707	10228	14151	9713	2511
2-butanone	330	407	439	434	447	404	441	363	37
aldehydes									
hexanal	281	259	307	240	358	261	334	256	53
nonanal	239	219	238	215	197	191	170	166	43
total	41815	49681	47796	46730	45339	41131	44960	38036	2726

[a] $n = 4$, total ion counts ($\times 10^4$). Different letters (a, b) within a row indicate significant differences ($P < 0.05$). SEM, standard error of the means.

2-Thiobarbituric Acid-Reactive Substances (TBARS). Lipid oxidation was determined using a TBARS method (*11*). Minced sample (5 g) was placed in a 50 mL test tube and homogenized with 15 mL of deionized distilled water (DDW) using a Brinkman Polytron (type PT 10/35, Brinkman Instrument Inc., Westbury, NY) for 15 s at high speed. The meat homogenate (1 mL) was transferred to a disposable test tube (13 × 100 mm), and butylated hydroxytoluene (7.2%, 50 μL) and a thiobarbituric acid/trichloroacetic acid [20 mM TBA and 15% (w/v) TCA] solution (2 mL) were added. The sample was mixed using a vortex mixer and then incubated in a 90 °C water bath for 15 min to develop color. After cooling for 10 min in cold water, the samples were vortex mixed and centrifuged at 3000*g* for 15 min at 5 °C. The absorbance of the resulting upper layer was read at 531 nm against a blank prepared with 1 mL of DDW and 2 mL of TBA/TCA solution. The amounts of TBARS were expressed as milligrams of malonedialdehyde (MDA) per kilogram of meat.

Statistical Analysis. The experiment was designed to determine the effect of sample holding time before purging and trapping on volatiles production in irradiated raw and cooked meat. Data were analyzed using the Generalized Linear Model procedure of SAS software (*18*). Student−Newman−Keul's multiple-range test was used to determine the significant differences between the mean values of treatments. Mean values and standard error of the means (SEM) are reported in all tables and figures. When necessary, a *t* test also was separately performed. Significance was defined at $P < 0.05$.

RESULTS AND DISCUSSION

Volatiles of Raw Meat. Irradiated raw turkey breast had various volatile compounds including hydrocarbons, alcohols, carbonyls (ketones and aldehydes), and sulfur-containing volatiles (**Table 1**). Ahn et al. (*9*, *10*) reported that irradiation accelerated lipid oxidation, increased the production of ketones and aldehdyes, and produced sulfur compounds responsible for the characteristic irradiation off-odor in meat. Carbonyls and sulfur volatiles accounted for 26 and 56%, respectively, of the total volatiles in irradiated raw turkey breast, and dimethyl sulfide, dimethyl disulfide, and 2-propanone were among the most predominant volatile compounds.

The amounts of hydrocarbons, alcohols, and carbonyls of irradiated raw turkey were not much affected by holding time and remained stable during sample holding time in an autosampler at 4 °C. Pentane was the only alkane that increased during the sample holding time and could be related to lipid oxidation accelerated by the headspace oxygen in sample vials.

Sulfur compounds, however, were significantly affected by sample holding time (**Figure 1**). The amount of dimethyl sulfide was significantly reduced after 120 min of sample holding in the 4 °C autosampler (fourth sample), and the amount at 280

Table 3. Volatiles Profile of Irradiated Cooked Turkey Breast without Helium Flush during Sample Holding Time in an Autosampler (4 °C) before Purge[a]

	sample holding time (min)								
volatile compound	0	40	80	120	160	200	240	280	SEM
hydrocarbons									
pentane	1399 c	1470 c	1922 b	2312 ab	2797 a	2608 a	2831 a	2878 a	141
heptane	203	165	221	222	224	202	195	226	12
2-octene	203	265	268	233	164	186	251	208	106
octane	236	264	274	269	266	291	273	279	46
benzene	233	242	226	216	200	218	246	230	9
toluene	775	860	813	782	655	668	663	712	61
alcohols									
ethanol	4711	4483	4392	4253	4108	4085	3924	4085	306
2-propanol	3613	3347	3382	3359	3132	3450	3342	3428	144
1-pentanol	741 c	655 c	953 bc	1184 bc	1561 abc	1907 ab	1924 ab	2209 a	232
sulfur volatiles									
dimethyl sulfide									
dimethyl disulfide					see **Figure 2**				
dimethyl trisulfide									
ketones									
2-propanone	14632	12910	14589	12034	14105	14774	15201	15415	1081
2-butanone	571	495	515	511	497	509	491	500	53
aldehydes									
3-methylbutanal	456	443	467	458	136	447	412	410	75
2-methylbutanal	334	386	335	409	394	325	369	362	44
propanal									
pentanal					see **Figure 3**				
hexanal									
heptanal									
octanal	174	184	200	278	333	361	330	394	49
nonanal	239	219	238	215	197	191	170	166	43
total	81257 c	80314 c	89604 bc	88605 bc	95163 b	110194 a	111079 a	117550 a	2983

[a] $n = 4$, total ion counts ($\times 10^4$). Different letters (a–c) within a row indicate significant differences ($P < 0.05$). SEM, standard error of the means.

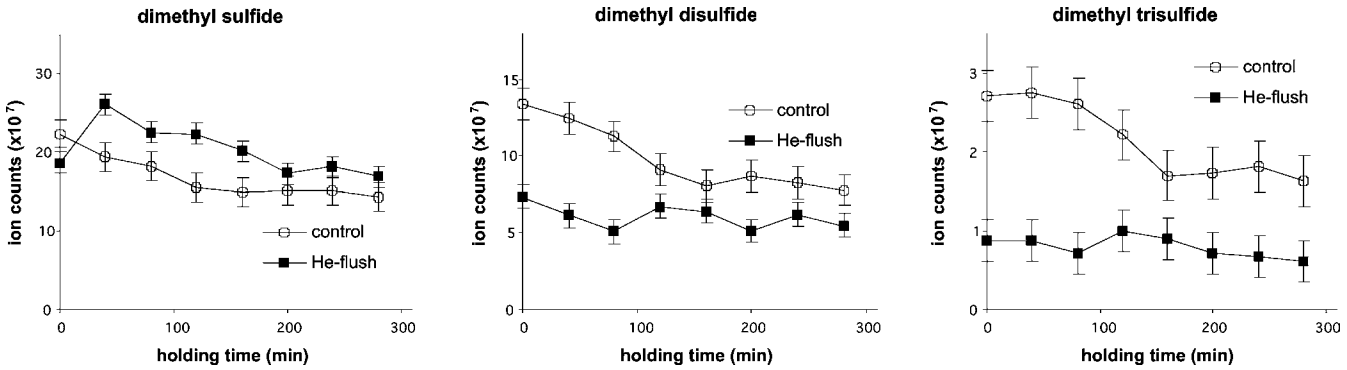

Figure 2. Production of sulfur compounds from irradiated cooked turkey breast during sample holding time in an autosampler (4 °C) before purge.

min (eighth sample) was ~80% of the first sample. The production of dimethyl disulfide and dimethyl trisulfide was more sensitive to holding time in the autosampler before purge than that of dimethyl sulfide. The amounts of dimethyl disulfide and dimethyl trisulfide began to decrease even from the second sample (40 min of holding), and only 44 and 24% of the first sample, respectively, were detected after 40 min of holding time. After 280 min of holding, the amount of dimethyl disulfide detected was only 9% of that at 0 min, and dimethyl trisulfide was not detected after 120 min of sample holding. Therefore, we believe that analysis of sulfur volatiles using an automated DH/GC-MS is highly dependent upon sample holding time, and their amounts can be severely underestimated if sample holding time is long (number of samples loaded at one time). If sulfur compounds are the volatiles of interest, therefore, *irradiated* raw meat samples should be loaded one at a time.

In general, sulfur volatiles have very high volatility and low odor threshold compared to other volatile compounds. The instabilities of sulfur volatiles during sample holding may be attributed to their high reactivity with headspace oxygen. Thus, to know the effect of headspace oxygen on the sulfur volatiles, samples were flushed with helium before loading (**Table 2**). The volatile composition of irradiated raw turkey breast flushed with helium was not much different from that of nonflushed sample at 0 min of holding time. Helium-flushed samples had lower amounts of hexanal than nonflushed samples ($P < 0.05$), but helium flush was effective in improving the repeatability of sulfur volatiles during sample holding time (**Figure 1**). The amounts of sulfur volatiles in helium-flushed samples were lower than those of nonflushed from 0 min, indicating that some of the sulfur compounds were lost during helium flush. The amounts of dimethyl disulfide and dimethyl trisulfide decreased during the holding time as in nonflushed samples but to a lesser degree. After 280 min of sample holding, the amount of dimethyl disulfide left in the helium-flushed sample was 29% (nonflushed, 9%) of that of the 0 min sample, and dimethyl trisulfide was not detected after 200 min of sample holding (after 120 min in nonflushed sample). Therefore, helium flushing

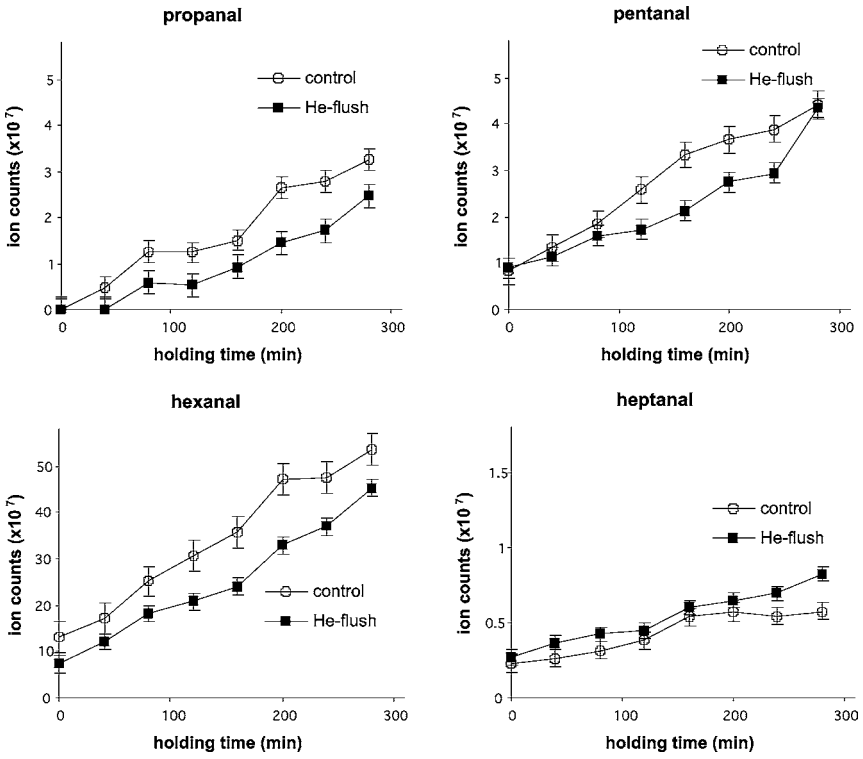

Figure 3. Production of aldehdyes from irradiated cooked turkey breast during sample holding time in an autosampler (4 °C) before purge.

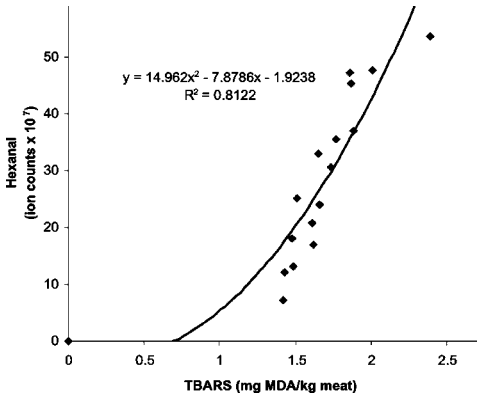

Figure 4. Relationship between TBARS values and the production of hexanal in irradiated cooked turkey breast.

improved the stability of sulfur volatiles but was not enough to prevent changes during sample holding time.

Volatiles of Cooked Meat. Irradiated cooked turkey breast produced a greater number of volatiles and more carbonyls and sulfur compounds than irradiated raw meat (**Table 3**). The amount of aldehydes was greatest among the volatile groups, and hexanal was the most predominant among the aldehydes. Volatile hydrocarbons, alcohols, and ketones were not much affected by holding time, whereas the amounts of sulfur volatiles and a few aldehydes changed significantly during holding time. The amounts of sulfur volatiles decreased as holding time increased, and the changes were the most distinct in dimethyl disulfide and dimethyl trisulfide (**Figure 2**). However, the rates of decrease were not as steep as those in irradiated raw meat. The amounts of dimethyl disulfide and dimethyl trisulfide detected after 280 min of sample holding were 58 and 60% of that of the 0 min sample, respectively.

The changes of aldehydes in irradiated cooked meat were totally different from those of sulfur compounds (**Figure 3**). The amounts of propanal, pentanal, hexanal, and heptanal in cooked meat increased proportionally with holding time. The amounts of hexanal and pentanal, the representative lipid oxidation products, rapidly increased with holding time, indicating that lipid oxidation in cooked meat developed rapidly during sample holding due to oxygen in the headspace and posed a huge problem in the accuracy of the volatile analysis.

Dimethyl disulfide and dimethyl trisulfide in helium-flushed cooked meat were more stable than in nonflushed samples, but the absolute amounts of those volatiles were lower than those of nonflushed samples (**Figure 2**). The amounts of aldehydes in helium-flushed cooked meat also increased in proportion to the holding time, but their rates were slower than those in nonflushed ones (**Figure 3**). This indicated that helium flush alone was not effective enough to prevent lipid oxidation and changes in sulfur compounds in irradiated cooked meat during the holding time (**Table 4**). When irradiated cooked meat is analyzed using a DH/GC-MS, therefore, aldehydes and sulfur volatiles are either overestimated or underestimated depending on the sample holding time in an autosampler. Ahn et al. (*5*) tested both helium flush and oxygen absorber in sample vials to prevent oxidative changes, but hexanal was masked by a volatile (2,6-dimethylheptane) when an oxygen absorber was used. Therefore, the number of samples loaded in an autosampler at a time should be limited to one, and more efficient methods to prevent the changes of volatiles are needed.

TBARS Values. According to TBARS values (**Table 5**), irradiated cooked turkey breast developed lipid oxidation rapidly during the holding time, whereas lipid oxidation in irradiated raw meat was slow. A significant increase in TBARS values in irradiated cooked meat was observed after 200−240 min of sample holding and was highly correlated with the amounts of hexanal detected by DH/GC-MS (**Figure 4**). Shahidi et al. (*19*) reported that hexanal was a representative volatile compound for lipid oxidation, and Ahn et al. (*20*) showed that propanal, pentanal, hexanal, 1-pentanol, and total volatiles correlated highly ($P < 0.01$) with TBARS values of cooked meat. The increases of propanal, pentanal, and hexanal in cooked meat

Table 4. Volatiles Profile of Irradiated Cooked Turkey Breast with Helium Flushing during Sample Holding Time in an Autosampler (4 °C) before Purge[a]

	sample holding time (min)								
volatile compound	0	40	80	120	160	200	240	280	SEM
hydrocarbons									
pentane	1181 f	2009 e	2105 e	2584 de	2930 cd	3483 c	4255 b	4938 a	190
heptane	173	173	171	228	296	319	265	284	30
2-octene	0	0	0	151	234	175	271	345	73
octane	190 b	252 ab	225 ab	219 ab	449 a	344 ab	362 ab	379 ab	48
benzene	66	65	66	0	231	161	148	252	57
toluene	683	701	680	724	740	727	713	715	57
alcohols									
ethanol	23769 a	11646 b	11233 b	8604 b	8442 b	7485 b	7732 b	7039 b	2729
2-propanol	4565	4759	4550	4505	4753	4488	4422	4588	111
1-pentanol	398 c	524 bc	690 bc	845 bc	944 bc	1369 ab	1685 a	1998 a	201
sulfur volatiles									
dimethyl sulfide									
dimethyl disulfide					see **Figure 2**				
dimethyl trisulfide									
ketones									
2-propanone	14295	15093	11369	12521	14939	14422	14555	15820	1996
2-butanone	517	502	510	527	565	559	553	608	34
aldehydes									
3-methylbutanal	657	687	597	567	648	611	604	664	33
2-methylbutanal	483	511	433	402	469	437	436	474	31
propanal									
pentanal					see **Figure 3**				
hexanal									
heptanal									
octanal	127 b	98 b	88 b	243 b	339 ab	336 ab	543 a	551 a	63
nonanal	494	582	485	496	649	743	689	756	88
total	83003 c	84380 c	82382 c	86266 c	91866 bc	96594 bc	104567 ab	115451 a	4508

[a] $n = 4$, total ion counts ($\times 10^4$). Different letters (a–f) within a row indicate significant differences ($P < 0.05$). SEM, standard error of the means.

Table 5. TBARS Values of Irradiated Raw and Cooked Turkey Breast Affected by Helium Flushing during Holding Time in an Autosampler (4 °C) before Purge[a]

	sample holding time (min)								
	0	40	80	120	160	200	240	280	SEM
raw meat									
control	0.31	0.34	0.33	0.35	0.35	0.34	0.33	0.37	0.02
He flush	0.30	0.35	0.34	0.34	0.35	0.38	0.35	0.33	0.02
SEM	0.01	0.02	0.03	0.02	0.02	0.01	0.02	0.01	
cooked meat									
control	1.49 d	1.62 cd	1.51 d	1.74 cd	1.77 cdx	1.86 bcx	2.01b	2.39 ax	0.07
He flush	1.42 b	1.43 b	1.48 b	1.61 b	1.66 by	1.65 by	1.89a	1.87 ay	0.06
SEM	0.03	0.11	0.05	0.06	0.02	0.03	0.05	0.08	

[a] $n = 4$, mg MDA/kg meat. Different letters (a–d) within a row indicate significant differences ($P < 0.05$). Different letters (x, y) in a column indicate significant difference ($P < 0.05$). SEM, standard error of the means.

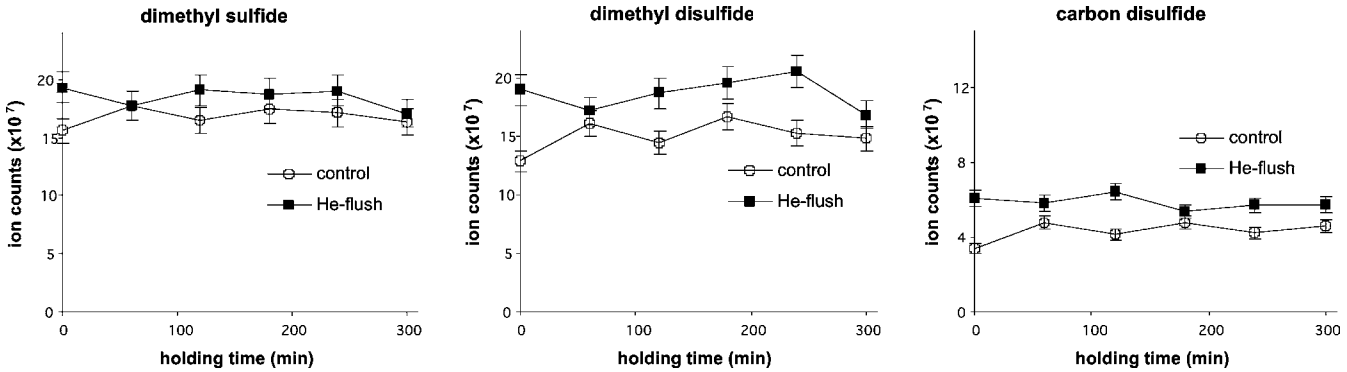

Figure 5. Repeatability of standard sulfur volatile compounds without and with helium flushing during the sample holding time in autosampler (4 °C) before purge.

were distinct during the short stay in an autosampler, and they were more sensitive to the holding time than the TBARS values (**Figure 3**). This indicated that the amounts of aldehydes could be more informative for lipid oxidation in irradiated cooked meat than TBARS values.

Standard Sulfur Compounds. When a few standard sulfur compounds were analyzed instead of irradiated meat samples, they were stable during the holding time (**Figure 5**), indicating that the sulfur compounds produced by irradiation in turkey meat were much less stable than standards, probably due to the

presence of many other reactive compounds from meat samples. Irradiation generates free radicals such as hydrated electrons, superoxide anions, and hydroxyl radicals (*21*). Therefore, the sulfur volatiles produced from meat are exposed to many other volatile compounds, aqueous electrons, and free radicals and have greater chances to react with other compounds (*21*).

Conclusion. Automated DH/GC-MS is a useful system to analyze volatile compounds in meat samples continuously. As the holding time for a sample in an autosampler before purge increased, however, the profile and amounts of volatiles changed due to the instability of sulfur compounds and development of lipid oxidation. Therefore, the number of samples loaded in an autosampler at a time should be limited depending on sample type and targeted volatile species, and standard curves for the changes in certain volatiles over sample holding time may be needed for accurate measurements of sulfur compounds and aldehydes in irradiated raw and cooked meats.

LITERATURE CITED

(1) Girard, B.; Nakai, S. Static headspace gas chromatographic method for volatiles in canned salmon. *J. Food Sci*. **1991**, *56*, 1271−1274.

(2) Ramarathnam, N.; Rubin, L. J.; Diosady, L. L. Studies on meat flavor. 4. Fractionation, characterization, and quantification of volatiles from uncured and cured beef and chicken. *J. Agric. Food Chem*. **1993**, *41*, 939−945.

(3) Specht, K.; Baltes, W. Identification of volatile flavor compounds with high aroma values from shallow-fried beef. *J. Agric. Food Chem*. **1994**, *42*, 2246−2253.

(4) Brunton, N. P.; Cronin, D. A.; Monahan, F. J.; Durcan, R. A comparison of solid-phase microextraction (SPME) fibres for measurement of hexanal and pentanal in cooked turkey. *Food Chem*. **2000**, *68*, 339−345.

(5) Ahn, D. U.; Jo, C.; Olson, D. G. Headspace oxygen in sample vials affects volatiles production of meat during the automated purge-and-trap/GC analyses. *J. Agric. Food Chem*. **1999**, *47*, 2776−2781.

(6) Bezman, Y.; Mayer, F.; Takeoka, G. R.; Buttery, R. G.; Ben-Oliel, G.; Rabinowitch, H. D.; Naim, M. Differential effects of tomato (*Lycopersicon esculentum* Mill) matrix on the volatility of important aroma compounds. *J. Agric. Food Chem*. **2003**, *51*, 722−726.

(7) Benincasa, C.; De Nino, A.; Lombardo, N.; Perri, E.; Sindona, G.; Tagarelli, A. Assay of aroma active compounds of virgin olive oil from southern Italian regions by SPME-GC/ion trap mass spectrometry. *J. Agric. Food Chem*. **2003**, *51*, 733−741.

(8) Ruiz, J.; Ventanas, J.; Cava, R. New device for direct extraction of volatiles in solid samples using SPME. *J. Agric. Food Chem*. **2001**, *49*, 5115−5121.

(9) Ahn, D. U.; Nam, K. C.; Du, M.; Jo, C. Volatile production in irradiated normal, pale soft exudative (PSE) and dark firm dry (DFD) pork under different packaging and storage conditions. *Meat Sci*. **2001**, *57*, 419−426.

(10) Ahn, D. U.; Jo, C.; Du, M.; Olson, D. G.; Nam, K. C. Quality characteristics of pork patties irradiated and stored in different packaging and storage conditions. *Meat Sci*, **2000**, *56*, 203−209.

(11) Ahn, D. U.; Jo, C.; Olson, D. G. Volatile profiles of raw and cooked turkey thigh as affected by purge temperature and holding time before purge. *J. Food Sci*. **1999**, *647*, 230−233.

(12) Murano, E. A. Irradiation of fresh meats. *Food Technol*. **1995**, *49*, 52−54.

(13) Ahn, D. U. Production of volatiles from amino acid homopolymers by irradiation. *J. Food Sci*. **2002**, *67*, 2565−2570.

(14) Schulz, H.; Kruger, H.; Liebmann, J.; Peterka, H. Distribution of volatile sulfur compounds in an interspecific hybrid between onion (*Allium cepa* L.) and leek (*Allium porrum* L.). *J. Agric. Food Chem*. **1998**, *46*, 5220−5224.

(15) Kubec, R.; Velisek, J.; Dolezal, M.; Kubelka, V. Sulfur-containing volatiles arising by thermal degradation of alliin and deoxyalliin. *J. Agric. Food Chem*. **1997**, *45*, 3580−3585.

(16) Riha, W. E.; Hwang, C. F.; Karwe, M. V.; Hartman, T. G.; Ho, C. T. Effect of cysteine addition on the volatiles of extruded wheat flour. *J. Agric. Food Chem*. **1996**, *44*, 1847−1850.

(17) Silberstein, O.; Kahan, J.; Penniman, J.; Henzi, W. Irradiation of onion powder: effects on taste and aroma characteristics. *J. Food Sci*. **1979**, *44*, 971−974.

(18) SAS Institute. *SAS User's Guide*; SAS Institute, Inc.: Cary, NC, 1989.

(19) Shahidi, F.; Yun, J.; Rubin, L. J.; Wood, D. F. The hexanal content as an indicator of oxidative stability and flavor acceptability in cooked ground pork. *Can. Inst. Food Sci. Technol. J*. **1987**, *20*, 104−106.

(20) Ahn, D. U.; Olson, D. G.; Lee, J. I.; Jo, C.; Chen, X.; Wu, C. Packaging and irradiation effects on lipid oxidation and volatiles in pork patties. *J. Food Sci*. **1998**, *63*, 15−19.

(21) Swallow, A. J. Fundamental radiation chemistry of food components. In *Recent Advances in the Chemistry of Meat*; Bailey, A. J., Ed.; The Royal Society of Chemistry: Burlington House, London, U.K., 1984; Chapter 8, pp 165−177.

Received for review August 28, 2003. Revised manuscript received January 16, 2004. Accepted January 25, 2004.

JF034975P