Comparison of Solid-Phase Microextraction and Dynamic Headspace Methods for the Gas Chromatographic–Mass Spectrometric Analysis of Light-Induced Lipid Oxidation Products in Milk

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Abstract

A sensitive, rapid procedure for testing lipid oxidation products in milk is developed using solid-phase microextraction (SPME) and gas chromatography–mass spectrometry. SPME is as sensitive as dynamic headspace (DH) analysis for measuring the pentanal and hexanal produced in milk after exposure to light. Furthermore, compared with DH, SPME is less expensive and demonstrates better precision and accuracy. In addition, SPME does not exhibit carryover or septa artifact peaks. The linearity of calibration curves (based on the method of additions technique with an internal standard) is consistently better for SPME than for DH. Furthermore, replicate analyses of pentanal and hexanal spiked in skim milk and 2% milk at 2 ng/mL demonstrate significantly lower coefficients of variation using SPME. To further test the practicality of SPME for measuring light-induced chemical changes in milk, 2% milk and skim milk samples are exposed to fluorescent light (200 foot-candles) for 0, 3, 6, 9, 12, 17, 24, and 48 h and analyzed by SPME and DH. Pentanal and hexanal in all samples are measured by SPME and DH. Correlation coefficients of resulting plots indicate that SPME is more accurate than DH in measuring the quantity of lipid oxidation products in milk.

Introduction

Light-induced off-flavors in milk are common and of major concern to the dairy industry. It has been estimated that exposure of milk in high-density polyethylene (HDPE) jugs to fluorescent lights in supermarket dairy cases is responsible for the development of light-induced off-flavors in some 80% of samples sold in supermarkets (1).

Light-induced off-flavors have two distinct components. Initially, a burnt, oxidized flavor develops and predominates for approximately two or three days. Dairy technologists and dairy chemists refer to this off-flavor note as light-activated flavor (LAF) (2). Degradation of sulfur-containing amino acids of the serum (whey) proteins is probably responsible for this reaction (3). The exact reaction products responsible for this so-called light-activated flavor have not been clearly elucidated. Methional [3-(methylthio)propanal], however, has been implicated as a possible contributor (4). Understanding the true impact that methional has on LAF is difficult to determine because it is relatively unstable and breaks down into more stable components, including mercaptans, sulfides, and disulfides. Samuelsson (5) and Forss (6) have suggested that methanethiol, dimethyl disulfide, and dimethyl sulfide also contribute to LAF. A recent dynamic headspace/multivariate analysis study of off-flavors in milk showed a correlation between increasing levels of dimethyl disulfide with increasing exposure time of milk to fluorescent light (7). In two recent studies, when light-exposed samples with LAF were analyzed by dynamic headspace gas chromatography–mass spectrometry (GC–MS), methional was not detected at measurable levels (7,8). Jung et al. (9) recently postulated a new mechanism for the formation of dimethyl disulfide by singlet oxygen oxidation of methionine.

In addition to the poorly understood LAF off-flavor, a second type of light-induced off-flavor occurs in milk and is attributed to lipid oxidation. This off-flavor, often characterized as metallic or "cardboard-like", usually develops after two days and does not dissipate. Aldehydes (especially pentanal and hexanal) and, to a lesser degree, ketones (e.g., 1-hexen-3-one and 1-nonen-3-one), alcohols, and hydrocarbons have been observed to form in milk as a result of light-induced lipid oxidation reactions (3,8). The unsaturated aldehydes and ketones have the lowest sensory thresholds and are usually considered the primary sources of oxidized off-flavors. When milk is exposed to light, various carbonyl compounds form from the reaction of light and oxygen with unsaturated fatty acids in the milk fat triglycerides and other milk fat components. Autoxidation of unsaturated fatty acids involves a free radical reaction, forming fat hydroperoxides which degrade to various malodorous compounds (e.g., hexanal, the predominant lipid reaction byproduct in light-exposed milk in the case of linoleic acid) (3).

Because it is a sensitive technique, dynamic headspace GC (DHGC) is usually the method of choice for analyzing lipid oxidation products that occur in light-exposed milk in the ng/mL range. The DHGC technique, however, is not routinely used in quality control testing because it can be time-consuming and can involve relatively expensive equipment. Furthermore, DHGC methods sometimes suffer from other annoying problems. For example, analyte carryover from one GC run to the next sometimes occurs when analyte concentrations are high, and this can lead to erroneous quantitative results. Also, the occurrence of artifact peaks originating from GC septa, thermal degradation of trapping media (e.g., Tenax), and other components of the dynamic headspace instrumentation can be troublesome (11).

Solid-phase microextraction (SPME), a solventless extraction technique developed in 1990 (12), has been shown to be a simple, effective tool for detecting low levels of flavor compounds in foods and beverages (13,14). New fibers recently developed for SPME have extended the usefulness of the technique for studying food off-flavors and malodors (15).

The goals of this study were to determine if SPME–GC is a suitable substitute for DHGC for measuring lipid oxidation products in milk. The present study compares the sensitivity, reproducibility, and accuracy of the two methods.

Evaluation of the suitability of SPME as an alternative sample preparation procedure for DH was accomplished by comparing the following analytical results obtained using both methods: the linearity of standard calibration curves, the precision demonstrated by replicate determinations of pentanal and hexanal in the same sample, and the correlation coefficients resulting from plots of pentanal and hexanal levels in milk versus length of time exposed to 200 foot-candles (ft-c) of fluorescent light. Also, an organoleptic evaluation of light-abused samples was conducted with 12 trained panelists to assess the degree of off-flavor development in light-abused milk and to see if a significant correlation could be made between flavor scores and aldehyde concentrations or between flavor scores and levels of light exposure.

Experimental

Source of milk samples

Four 1-gallon HDPE jugs of skim milk and four 1-gallon HDPE jugs of 2% milk were obtained directly from a local dairy the same day they were manufactured. The skim milk samples were composited, and the 2%-milk samples were composited. The two composite samples were judged to be free of off-flavors and malodors by an organoleptic taste panel.

Instrumentation

A CDS PeakMaster (CDS Analytical, Oxford, PA) concentrator was used for DH sampling. An SPME manual holder assembly and fibers were obtained from Supelco (Bellefonte, PA). GC–MS was performed with a Varian Saturn 3 system (Varian Analytical Systems, San Fernando, CA), which included a Varian Star 3600 CX GC. DHGC–MS and SPME–GC–MS conditions are provided in the folling sections.

MS conditions

The electron impact (EI) mode of the Saturn 3 Ion Trap Detector (ITD) was used. The mass range was set at *m/z* 33–300. The manifold temperature was 190°C, and the transfer line temperature was 200°C. These MS conditions were used for all DH and SPME analyses.

DHGC

Sample preparation

20.00 g of milk was placed in a 30-mL glass impinger bottle (CDS Part No. 4031-0333). Ten microliters of an internal standard solution (20 µg/mL 4-methyl-2-pentanone) were added to the sample with a GC syringe. Approximately 100 mg of 1-tetradecanol was added to skim milk samples prior to purging in order to prevent excessive foaming. The sample bottle was placed in a 45°C water bath. After allowing the sample to equilibrate to 45°C for 5 min, the sample was purged with helium at 25 mL/min for 20 min. Faster helium flow rates tended to cause excessive foaming in the milk samples, and shorter purging times resulted in lower detection levels for the quantitative determination of pentanal and hexanal.

The volatiles were trapped on a Tenax trap (CDS Part No. 30E35063) maintained at 40°C. After collection onto this trap, an additional dry-purge cycle was used to reduce the water vapor that may have accumulated on the trap during stripping. The volatile components were then desorbed onto the analytical column by heating the trap to 200°C for 10 min and cryofocused at –100°C with liquid nitrogen prior to column injection. The analytical column was fed through a GC injection port, fed through a 1.5-m heated transfer line (230°C), and connected to the CDS PeakMaster valve oven. Cryofocusing was accomplished with the standard cryofocusing unit that is a component of the CDS PeakMaster. Volatiles were cryofocused near the front of the analytical capillary column, approximately 10 cm outside of the GC oven and after the CDS PeakMaster transfer line. At the start of the GC run, the cryofocused volatiles were released into the analytical column inside the GC oven (which was at an initial temperature of 50°C) by rapidly heating the cryofocusing unit to 225°C.

Additional DH parameters

The valve oven was 230°C. The dry purge temperature was 40°C for 2 min. The bake temperature was 240°C for 4 min.

GC column and conditions

The analytical column was a 30-m × 0.25-mm-i.d. DB-5 fused-silica capillary column with a 1-µm film thickness (J&W Scientific, Folsom, CA). The initial column temperature was 50°C for 1 min, heated to 180°C at a rate of 6°C/min, held at 180°C for 4 min, heated to 240°C at a rate of 6°C/min, and held at 240°C for 8 min. All injections were made in the splitless mode. Helium carrier gas was used at a flow rate of 2.0 mL/min.

SPME–GC

Three grams of milk sample, 10 µL of internal standard solution (20 µg/ml 4-methyl-2-pentanone), and a micro-stirring bar (Fisher, Itasca, IL, cat. no. 09-312-102) were placed in a 9-mL

glass GC vial (height, 46 mm; diameter, 20 mm) and capped with PTFE/Grey Butyl Molded Septa (Pierce Chemical, Rockford, IL). SPME was performed with a 75-µm Carboxen-1006/polydimethylsiloxane (PDMS) fiber mounted in an SPME manual holder assembly (Supelco). The Carboxen/PDMS has a combination of micro-, meso-, and macro-pores ranging from 6 to 50 Å. The Carboxen/PDMS fiber was selected because, according to the SPME manufacturer, it is the fiber best suited for the analysis of low-molecular-weight volatiles such as pentanal and hexanal. Previous experiments in our laboratory using 100-µm and 30-µm PDMS fibers failed to detect low-ppb levels (< 10 ppb) of pentanal and hexanal in milk samples. The SPME fiber was conditioned according to the manufacturer's recommendations (280°C for 30 min in the GC injector).

The SPME device consisted of a holder and a replaceable fiber assembly. The assembled unit looks much like a syringe, but in place of the hollow needle is a fiber inside a protective sheath. The fiber is attached to the holder plunger, so that it may be exposed by moving it out of the sheath. The fiber itself consists of a piece of fused-silica rod coated with an adsorbent.

The sample vial was placed in a 45°C water bath and stirred at high speed. After allowing 2 min for the sample to equilibrate to 45°C, the septum piercing needle of the SPME device was inserted through the vial septum, and the plunger on the SPME apparatus was pushed down to expose the Carboxen/PDMS fiber to the headspace above the sample. The setting on the SPME holder assembly scale was adjusted to 1.0 scale units to ensure that the fiber was positioned in the headspace above the sample exactly identically from run to run.

After a 15-min exposure time with constant stirring, the fiber was retracted into the needle assembly and removed from the vial. The setting on the SPME holder assembly was changed to 3.4 scale units prior to injection into the GC injector port, which was fitted with a special insert for SPME analysis (Varian, part no. 03-925330-00). The injector temperature was 250°C, and all injections were made using the splitless mode. The fiber was left in the injection port for 5 min before removing.

The salting-out effect has been used as a way to increase sensitivity with headspace testing. However, the addition of 0.20 g or 0.70 g NaCl to the sample prior to SPME extraction did not improve sensitivity of the method for the analysis of pentanal or hexanal in milk samples.

GC column and conditions: The analytical column was a 30-m × 0.32-mm-i.d. Supel-Q PLOT fused-silica capillary column (Supelco). The column temperature was initially 70°C for 2 min, heated to 140°C at a rate of 6°C/min, and held at 140°C for 2 min, heated to 220°C at a rate of 6°C/min, and held at 220°C for 5 min. Helium was used as the carrier gas at a flow rate of 2.0 mL/min.

Selection of analytical capillary columns

Imhof and Bosset (16) studied the performance of eight different types of capillary columns for the analysis of volatile chemicals in milk by dynamic headspace GC. Of the columns studied, the column that provided the best resolution of milk volatiles (including pentanal and hexanal) was a 30-m × 0.25-mm-i.d. DB-5 fused-silica capillary column with a film thickness of 1 µm. Therefore, this column has been routinely used in our laboratory for analyzing milk volatiles by DHGC.

One problem with the DB-5 column, however, is that it does not provide adequate resolution of extremely volatile sulfur compounds (e.g., hydrogen sulfide and methyl sulfide), which can be important contributors to off-flavor problems in dairy products. The Supel-Q PLOT fused-silica capillary column used for SPME-GC analyses is able to resolve these important odor-impact compounds. Therefore, the SPME-GC method was developed with this column instead of the DB-5 column. If the Suple-Q PLOT column could accurately quantitate pentanal and hexanal in milk, it would be a good column to use for studying malodors caused by volatile sulfur compounds in milk as well as malodors generated by light oxidation.

Also, the Carboxen/PDMS fiber is well suited to the analysis of the volatile sulfur compounds that are likely responsible for LAF. Low-molecular-weight sulfur gases were nearly impossible to extract using SPME until the Carboxen/PDMS fiber was developed. The Carboxen/PDMS fiber was found to efficiently extract hydrogen sulfide and other volatile sulfur compounds from beer and wine (17).

Calibration of methods

For both DHGC and SPME–GC, calibration was based on peak-area results for 5 standard solutions using the method of additions technique and an internal standard (4-methyl-2-pentanone). The 5 standards contained both pentanal and hexanal at concentrations of 0.0, 1.0, 5.0, 10.0, and 30.0 ng/mL. Calibration was based on total ion measurement. Inspection of numerous scan numbers in the upslope, apex, and downslope regions of the pentanal, hexanal, and internal standard peaks was made for all injections by DHGC and SPME–GC to ensure that co-elution of interfering peaks did not occur.

Table I. Comparison of the Principal Analytical Parameters for Pentanal and Hexanal Analyzed by DHGC–MS and SMPEGC–MS

Compound	Sample	Analytical technique	Detection limit (ng/mL)	Repeatability of 4 replicates at 2 ng/mL (coefficient of variation, %)	Linear least squares correlation coefficient*
Pentanal	skim	DH	0.1	8.0	0.966
		SPME	0.1	1.9	0.990
Hexanal	skim	DH	0.3	21.1	0.910
		SPME	0.5	7.1	0.995
Pentanal	2% milk	DH	0.3	7.6	0.996
		SPME	0.3	2.1	0.999
Hexanal	2% milk	DH	0.8	8.3	0.982
		SPME	0.8	4.9	0.993

*Calibration curve of 5 standards ranging from 0 to 30.0 ng/mL.

Validation of methods

Table I shows the principal analytical parameters for pentanal and hexanal in standard calibration samples analyzed by DHGC and SPME–GC. Detection limits were determined by analyzing decreasing concentrations of pentanal and

hexanal in 2% milk and skim milk. The lowest concentration was established as that for which all the ions selected for a given compound could be differentiated from the background. Repeatability was assessed by calculating the coefficient of variance obtained by analyzing in quadruplicate the same sample of either 2% milk or skim milk spiked with 2 ng/mL of pentanal and hexanal. The linear correlation coefficients of the standard calibration curves were used as an estimate to compare the accuracy of each technique for each analyte in 2% milk and skim milk.

Application example: subjecting milk to varying levels of light

To test the feasibility of using SPME–GC as a tool for studying a practical problem, a study was conducted in which fresh 2% milk and skim milk were bottled in half-gallon HDPE milk jugs and exposed to 200 ft-c of fluorescent light (F40WW/RS/EW, 34 watt, Philips Lighting Co., Somerset, NJ) for varying time periods (3, 6, 9 12, 17, 24, and 48 h). The light exposure level of 200 ft-c was chosen because this is approximately the level of light exposure that milk is subjected to in supermarket dairy cases. Samples were maintained at 4.0 ± 0.1°C during light exposure.

The light-exposed series of milk samples was also subjected to organoleptic taste paneling in order to assign flavor scores to each sample as a way of estimating the level of off-flavor formation in each sample.

Results and Discussion

Comparison of analytical parameters: standard calibration curves

Results for standard calibration curves prepared by the method of additions technique and employing an internal standard were compared for SPME and DH methods. Five standard solutions were prepared from the skim milk, and 5 were prepared from the 2% milk. Concentrations (i.e., spike levels of pentanal and hexanal added to either skim milk or 2% milk) were 0.0 ng/mL, 1.0 ng/mL, 5.0 ng/mL, 10.0 ng/mL, and 30 ng/mL. The results in Table I show that the linear correlation coefficients are closer to unity for SPME results than for DH results. The trend for more linear calibration curves for SPME versus DH occurs in all cases (i.e., for both pentanal and hexanal and in both skim and 2% milk).

The SPME calibration curves for pentanal and hexanal demonstrated excellent linearity, even when the standard with the highest concentration level was extended to 500 ng/mL. Linear correlation coefficients for SPME with 7 standards (the 5 standards from 0 ng/mL to 30 ng/mL plus a 200 ng/mL standard and a 500 ng/mL standard) were as follows: pentanal in 2% milk, 0.982; hexanal in 2% milk, 0.990; pentanal in skim milk, 0.989; and hexanal in skim milk, 0.985.

Table I also shows that SPME was more precise than DH. The coefficient of variation for four replicate determinations of a 2 ng/mL standard is significantly lower for SPME than for DH. This is true for both pentanal and hexanal analytes in both skim milk and 2% milk.

The improvement in precision with SPME versus DH is not surprising. As a general rule, fewer steps and sample manipulations in a sample preparation scheme often result in better recoveries of analytes and better precision. The purging/stripping, trapping, and desorbing steps associated with DH can be inefficient and significantly contribute to analytical errors.

The detection limits (as defined in the Validation of methods section) were approximately the same for pentanal and hexanal in skim milk and 2% milk.

Chemical changes in milk caused by light exposure: SPME versus DH

To further evaluate the suitability of SPME as an alternative sample preparation procedure to DH for measuring light-induced chemical changes in milk, skim milk and 2% milk were exposed to 200 ft-c of fluorescent light (F40WW/RS/EW, 34 watt, Philips Lighting Co.) for varying times at 4.0 ± 0.1°C and analyzed by both techniques. Results for both methods with both 2% milk and skim milk compared fairly well, as shown in Figures 1–4. The production of hexanal from 0 to 48 h of light exposure tended to

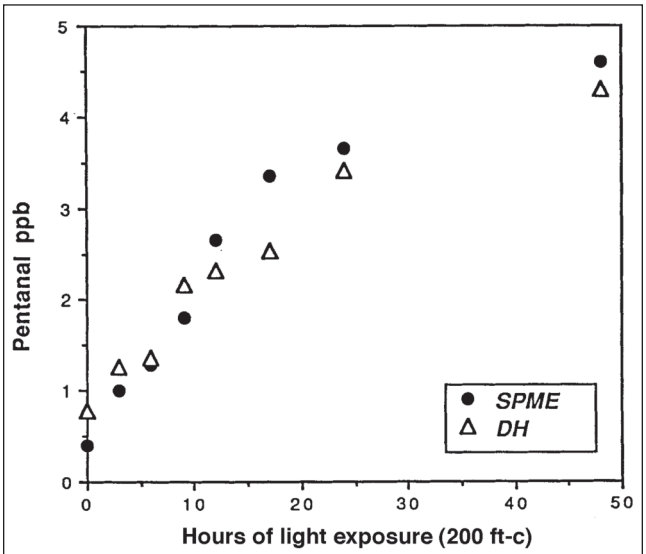

Figure 1. Formation of pentanal in 2% milk as a function of hours fluorescent light exposure (200 ft-c) by SPME–GC–MS and DHGC–MS. Also shown are the second order polynomial regression equations for each method and the corresponding correlation coefficients (r^2).

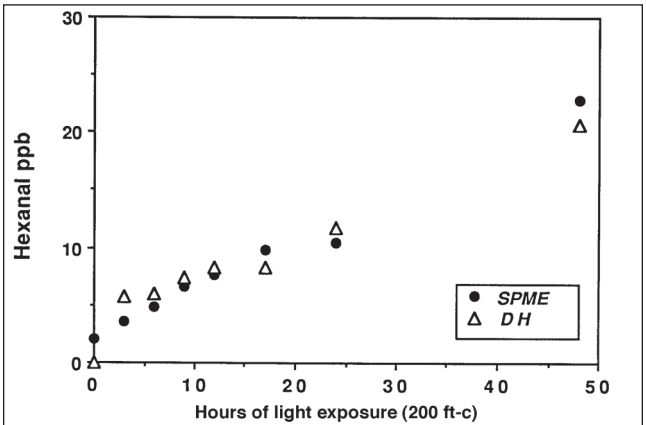

Figure 2. Formation of hexanal in 2% milk as a function of hours fluorescent light exposure (200 ft-c) by SPME–GC–MS and DHGC–MS. Also shown are the linear regression equations for each method and the corresponding correlation coefficients (r^2).

increase linearly. However, the plot of increasing pentanal concentration with increasing time of exposure more accurately fit a second-order polynomial equation. Reaction kinetics are apparently different for pentanal formation in comparison with hexanal formation, perhaps because the substrate for pentanal is limiting, whereas linoleic acid, the substrate for hexanal, is present at significantly higher levels in milk.

Calculations of pentanal and hexanal concentrations in the milk samples exposed to light were based on the linear regression equations for the low-range standard curves (from 0 to 30 ng/mL), because linear correlation coefficients tended to be closer to unity in comparison with the extended range calibration curves and because the levels of pentanal and hexanal in all light-exposed samples were less than 30 ng/mL.

As in the case of calibration curve data, correlation coefficients were better for SPME than for DH. SPME linear correlation coefficients for hexanal were closer to unity than were DH linear correlation coefficients, and second-order polynomial correlation coefficients for pentanal were closer to unity for SPME than for DH. These trends were observed for both skim milk and 2% milk.

Chromatograms of 2% milk samples exposed to light for 0 and

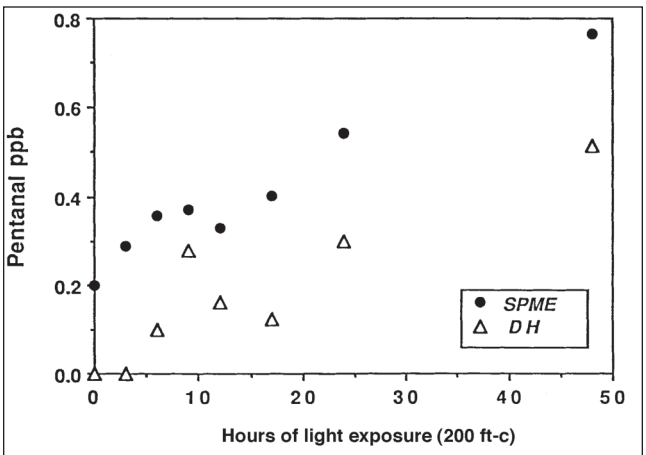

Figure 3. Formation of pentanal in skim milk as a function of hours fluorescent light exposure (200 ft-c) by SPME–GC–MS and DHGC–MS. Also shown are the linear regression equations for each method and the corresponding correlation coefficients (r^2).

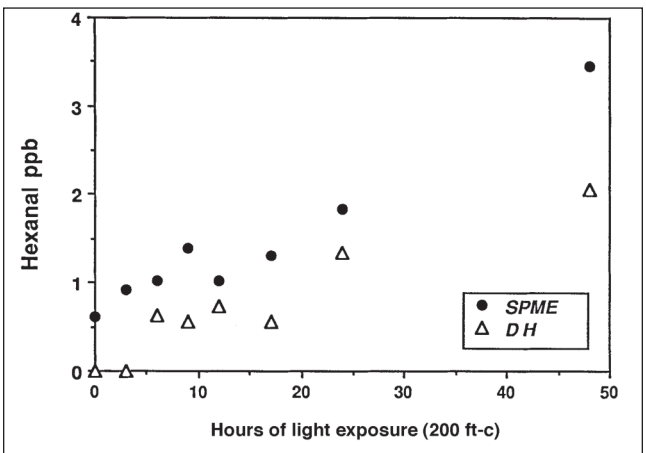

Figure 4. Formation of hexanal in skim milk as a function of hours fluorescent light exposure (200 ft-c) by SPME–GC–MS and DHGC–MS. Also shown are the linear regression equations for each method and the corresponding correlation coefficients (r^2).

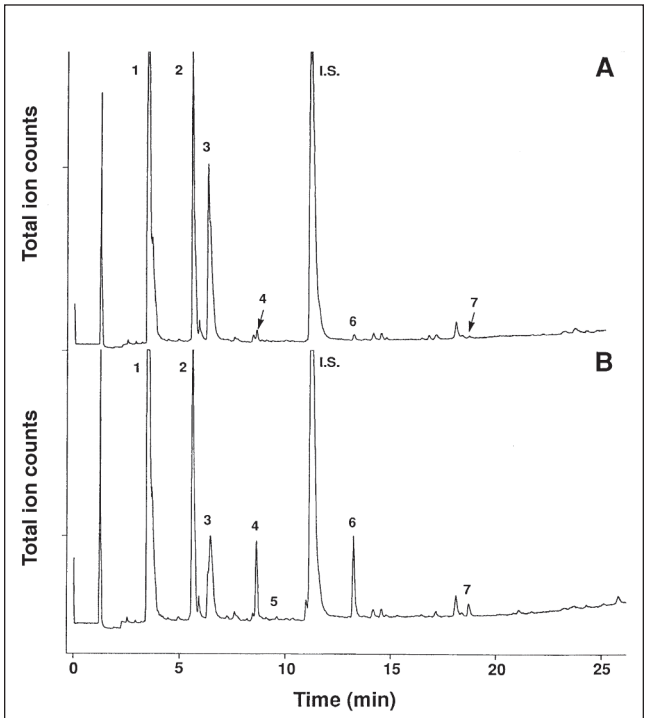

Figure 5. Examples of SPME total ion chromatograms of 2% milk samples exposed to fluorescent light (200 ft-c) for different exposure times: 0 (A) and 48 hours (B) light exposure. Peaks: 1, acetone; 2, 2-butanone; 3, methyl pentane; 4, pentanal; 5, dimethyl disulfide; 6, hexanal; 7, heptanal; and IS, internal standard (4-methyl-2-pentanone).

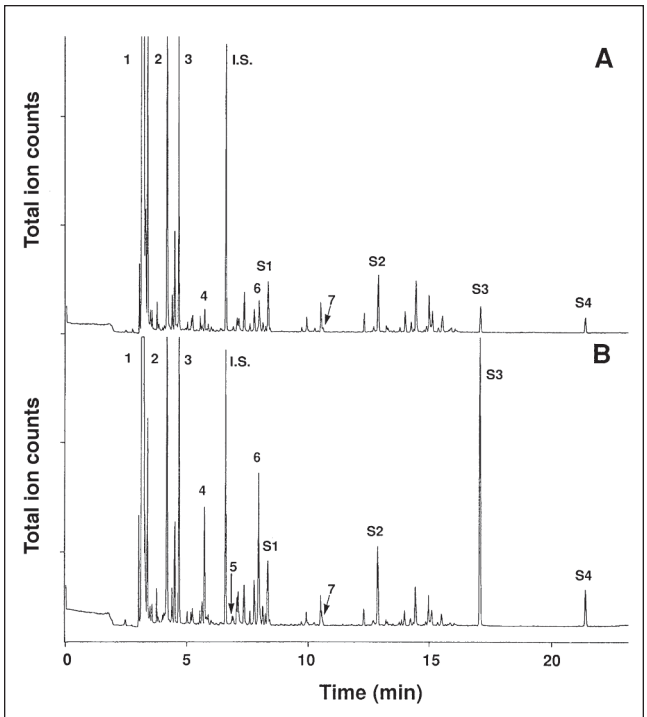

Figure 6. Examples of DH total ion chromatograms of 2% milk samples exposed to fluorescent light (200 ft-c) for different exposure times: 0 (A) and 48 hours (B) light exposure. Peak identities are the same as in Figure 5. Peaks labeled with an "S" prefix are artifact peaks from GC septa, O-rings in the dynamic headspace analyzer, or from other components of the headspace analyzer: S1, hexamethylcyclotrisiloxane; S2, octamethylcyclotetrasiloxane; S3, decamethylcyclopentasiloxane; S4, dodecamethylcyclohexasiloxane.

48 h and then analyzed by SPME and DH are shown in Figures 5 and 6, respectively. A dimethyl disulfide peak is noted in both the SPME and DH 48-h samples. Samples of 2% milk and skim milk exposed to light for 17 h or less did not reveal detectable levels of dimethyl disulfide using either SPME or DH.

The heptanal peak (peak 7 in Figure 6) in the DH chromatograms eluted as an unresolved shoulder peak on the downslope of a larger styrene peak. The styrene peak appears to be a contaminant in the milk and is likely a component of the milk jug.

In addition to chemical testing, light-exposed milks were subjected to organoleptic taste paneling. One dozen people were involved in the taste panel. Most of the panelists had considerable experience with tasting off-flavors in dairy products. The panelists assigned each sample a score ranging from 0 to 8. A score of 0 was equivalent to no off-flavor detected, whereas a score of 8 indicated milk with an extremely strong off-flavor. One goal of this study was to see if there was a correlation between the extent of light exposure, aldehyde levels, and perception of off-flavors. If a significant correlation could be found between the degree of light exposure and flavor score, then the next step would be to see if a milk sample's flavor score could be predicted from pentanal and/or hexanal results obtained by SPME. Unfortunately, panelists were unable to determine flavor scores with any reasonable degree of precision, as evidenced by the large error bars in Figures 7 and 8. Error bars represent the standard deviation of flavor scores for the same sample evaluated by 12 taste panelists.

Potential SPME–GC–MS applications for measuring light-induced lipid oxidation products in milk

The intensity of light-induced off-flavor formation in milk is determined by several factors. One factor is the specific composition of the milk sample. For example, α-tocopherol and other natural antioxidants present in the sample tend to deter photooxidation, whereas elevated levels of linoleic acid and other polyunsaturated acids in the phospholipids of the milk fat globular membrane promote photooxidation. The number, position, and configuration of double bonds affect the rate of oxidation. The relative rates of oxidation for arachindonic, linolenic, linoleic, and oleic acids are approximately 40:20:10:1. Conjugated double bonds are more reactive than non-conjugated, and double bonds in the *cis* configuration are more reactive than *trans* (10).

The presence of elevated levels of prooxidant metals such as copper, iron, and nickel can significantly accelerate the rate of lipid oxidation off-flavor development. Other factors are the type, thickness, and color of the bottle or jug material used to store the milk. The intensity and wavelength of light, as well as the duration of exposure, are also critical factors.

The simple SPME–GC method presented in this work could be used to evaluate how well the various types of plastic bottling materials protect milk against photooxidation reactions. Because more protection usually means more packaging cost, the goal of this type of research would be to determine the least expensive type of packaging to use that would provide the necessary protection against light-induced off-flavor formation.

Another use for this SPME–GC test would be to screen raw milk samples for their tendency for photodegradation. Compositional differences in raw milk samples resulting from the cow's diet sometimes account for the tendency of some milk samples to develop unusually strong light-induced off-flavors. For example, feeding cows high levels of soybeans has been shown to increase milk fat's linoleic acid content and increase the susceptibility of milk to photooxidation (2). SPME–GC could be used as a quick screening test for raw milk to help locate problem samples before processing and minimize customer complaints due to excessive lipid oxidation reactions.

Conclusion

Typically, DHGC with flame ionization detection or MS detection has been used to monitor production of lipid oxidation products

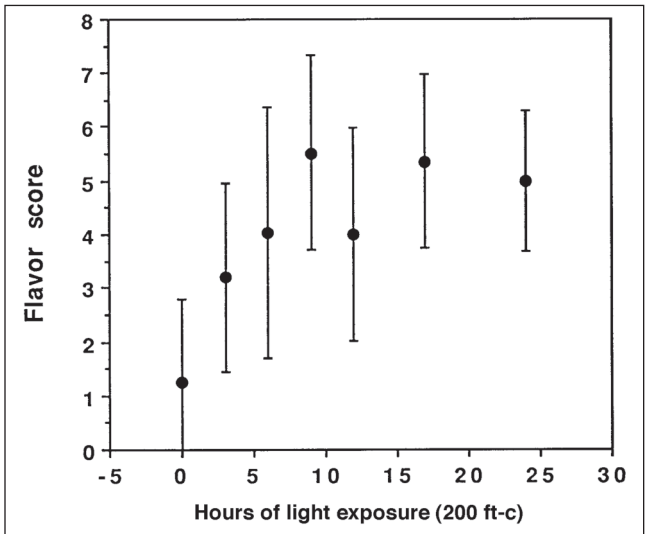

Figure 7. Plot of flavor score for 2% milk as a function of hours of fluorescent light exposure (200 ft-c), where 0 represents no detectable off-flavor and 8 represents extremely strong off-flavor. Error bars represent the standard deviations of flavor scores for the 12 panelists.

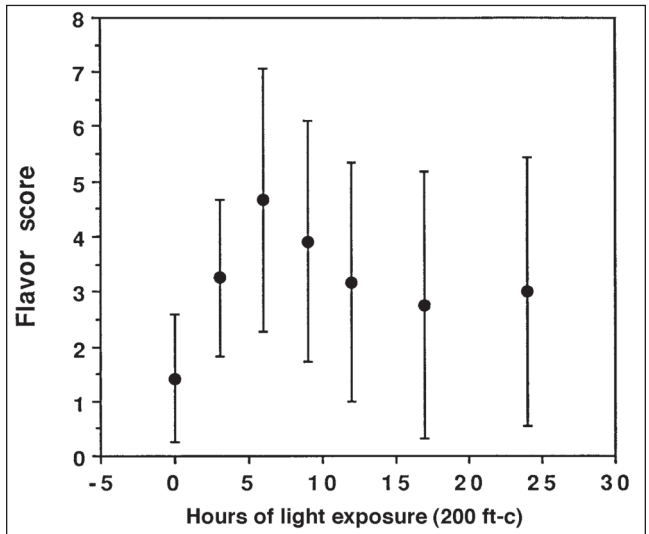

Figure 8. Plot of flavor score for skim milk as a function of hours of fluorescent light exposure (200 ft-c), where 0 represents no detectable off-flavor and 8 represents extremely strong off-flavor. Error bars represent the standard deviations of flavor scores for the 12 panelists.

in milk. However, commercially available DH instrumentation is substantially more expensive than SPME equipment and does not appear to offer any significant advantages with respect to improved sensitivity or precision in comparison with SPME for measuring pentanal and hexanal in milk. A test more amenable to routine quality control monitoring of milk samples could be a valuable tool for the dairy industry.

Using the instruments and experimental conditions specified in this work, SPME was shown to be a more desirable sample preparation technique than DH for monitoring light-induced lipid oxidation products in 2% milk and skim milk. SPME consistently demonstrated superior precision without a sacrifice in sensitivity. Furthermore, none of the problems with carryover, background, or artifact peaks that may occur with some DH systems was observed with the Carboxen/PDMS fiber used in this work. No carryover peaks were detected in milk samples, even when injecting the SPME fiber immediately after it was used to analyze a milk sample spiked with a 500 ng/mL mixture of aldehydes (butanal, isopentanal, pentanal, hexanal, heptanal, and octanal).

This work shows that SPME is a viable substitute for DH for studying oxidation off-flavors in milk, especially considering the cost advantage of SPME equipment compared to DH instrumentation.

Acknowledgments

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