

## Effects of Light on Concentrations of Some Volatile Materials in Milk

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### ABSTRACT

Gas chromatographic analyses of head-space vapors of steam distillates from milk enabled me to monitor part per billion changes in concentrations of acetaldehyde, propanal, methyl sulfide, acetone, butanone, n-pentanal, and n-hexanal before and after milks were exposed to sunlight in a clear glass flask and fluorescent light in a plastic jug. n-Pentanal and n-hexanal increased about the same under either light (19.6 to 68.5 ppb and 19.1 to 83.6 ppb, respectively). Acetaldehyde increased much more under sunlight than under fluorescent light. Methyl sulfide increased slightly in concentration under 44 h of fluorescent light (6.8 to 11.6 ppb) but did not change appreciably during exposure to 1 h of sunlight. Changes in concentrations of the same compounds, except acetone and butanone, were determined in raw; laboratory pasteurized; and plant pasteurized, homogenized, Vacu-Therm-treated milk exposed to sunlight for 20 min. Except for n-pentanal, all carbonyl compounds in pasteurized, homogenized, Vacu-Therm-treated milk changed less after exposure to 20 min sunlight than did the same compounds from either raw or laboratory pasteurized milk. n-Pentanal was relatively higher in exposed-pasteurized milk than in either raw or laboratory pasteurized milk. Differences between concentrations of volatile materials in exposed raw and in laboratory pasteurized milk were slight. Exposing skim milk to sunlight for 20 min produced more acetaldehyde than similarly treating homogenized-pasteurized milk, indicating that nonfat fractions are precursors of acetaldehyde. Increases in all other carbonyl compounds could be attributed to the fat.

The nature, significance, and prevalence of light-activated flavors in milk have been described recently (4, 6, 10). Barnard (1) reported that 86.1% of the fluid milk samples in blow mold, plastic containers from retail stores, during a 1970 survey were oxidized. Milk in other containers was likewise defective but less so (12.7-50%). The increasing incidence of oxidized flavor recently reported is attributed to increased use of all-plastic, translucent containers. In addition to the serious flavor problem cited, researchers have demonstrated the irradiation destruction of riboflavin, ascorbic acid, and tryptophan and significant nutritional losses (4, 5, 12).

Lack of a specific test for the defect probably deters fundamental studies of light-activated flavors. The 2-thiobarbituric acid test which effectively measures copper-induced, oxidized flavor, is totally unsuited to test for the light-activated off-flavor (12). Although in most studies flavor measurements have been used to indicate the severity of the light-induced off-flavor, such

measurements lack objectivity. Research reported here was designed to quantify changes in concentration of volatile materials in milk exposed to light. The simple, routine method developed can be used to study fundamental aspects of the oxidized flavor defect.

### MATERIALS AND METHODS

#### *Measuring volatile materials in milk*

Milk was steam distilled in micro-Kjeldahl equipment, and the head-space vapors of the distillate analyzed by GLC. Concentration of volatile materials in ppb were calculated from peak heights (3). GLC peaks were identified by using a combination of subtractive techniques (2) and peak retention times. Aldehydes were distinguished from ketones by treating the distillates with one drop of saturated aqueous potassium permanganate to oxidize the aldehydes (8) before GLC analysis. Two stainless steel columns were used: one (3.05 m × 3.18 mm) packed with 20% Carbowax 20 M on 60/80 mesh, acid-washed HMDS treated Chromosorb P; the other (a 152.4-m capillary column with an ID of .76 mm) coated with OV-101. The capillary column was used to confirm the identities of n-pentanal and n-hexanal.

Concentrations of compounds reported here were calculated with the aid of regression equations previously determined by converting peak heights from chromatograms obtained from the packed Carbowax column to ppb of each component.

#### *Exposure of milk to sunlight and fluorescent light*

About 500 ml of commercial pasteurized-homogenized milk at 5 C was exposed to direct sunlight for up to 1 h in a ground-glass, stoppered, liter Erlenmeyer flask. Radiant energy during exposure ranged from 0.91 to 1.09 ly/min (1 ly = 1 g cal/cm<sup>2</sup>) and the ambient temperature was 7-10 C. At intervals of 0, 5, 10, 20, 30, and 60 min, aliquots were removed and analyzed for volatile materials, and TBA tests for fat oxidation were conducted by King's method (9).

Two, two-liter aliquots of pasteurized-homogenized milk were transferred into clean, sterilized, disposable, capped plastic jugs. One jug was placed below a GE 40-watt, cool, white-fluorescent bulb in a vertical milk display case at 5 C storage, with the milk 21 cm below the light; the other jug, into a refrigerator at the same temperature. Samples were drawn from each plastic jug at 4.5, 18, and 44 h and analyzed for volatile materials as described. Milk exposed for 18 h also was analyzed for TBA.

#### *Effects of processing on susceptibility to light-activated changes in milk*

A liter of raw milk was collected from the surge tank of the De Laval Vacu-Therm pasteurizer at the University Dairy plant during routine milk processing. Another sample of about 500 ml was collected a few minutes later after pasteurization at 76.5 C, homogenization in a CP homogenizer using a single-service, conical homo valve and Vacu-Therm treatment. About half of the raw milk was transferred to a liter Erlenmeyer flask and was laboratory pasteurized at 63 C for 30 min with gentle agitation. Each was divided into two equal parts: a control and a sample at 5 C exposed in clear-glass Erlenmeyer flasks to mid-morning sunlight of 0.97-1.16 ly/min for 20 min. The ambient

<sup>1</sup>Contribution 906, Department of Dairy and Poultry Sciences, Kansas Agricultural Experiment Station, Manhattan.

temperatures of the samples were 4-7 C.

Distillations for GLC analyses were made within 3 h after exposure. GLC analyses were the same day.

#### *Effect of sunlight on fortified skim and whole homo milk*

Commercial Vacu-Therm-pasteurized, homogenized milk and commercial skimmilk (0.13% fat) fortified with 1% NFM solids and Vacu-Therm pasteurized were each exposed to mid-morning sun 20 min in a 250 ml, glass stoppered Erlenmeyer flasks. Unexposed samples of the same milks were the controls. Distillations and GLC analyses again were done within 3 h of exposure.

## RESULTS AND DISCUSSION

Subtractive techniques (2) proved that all peaks except one were from compounds with carbonyl functional groups. The peak that was not from a carbonyl compound was eliminated with mercuric chloride and had a retention time identical to methyl sulfide. Other researchers have identified methyl sulfide in normal milk (11).

Acetaldehyde, propanal, acetone, and butanone are among the carbonyl compounds that have been identified as normal constituents in milk (7). GLC peaks with retention times close to five and six carbon chain carbonyl compounds were scrutinized with the aid of an OV-101 capillary column. Because these compounds had the same retention times on the capillary column as n-pentanal and n-hexanal (and differed from the corresponding ketones) and because their corresponding GLC peaks were eliminated when the distillates were treated with saturated permanganate, I identified them as such and calculated their concentrations from n-pentanal and n-hexanal standard curves. Standard curves obtained from the analysis of milks spiked with

measured ppb of the compounds identified in milk provided regression equations to use in calculating concentrations of compounds in experimental samples.

Exposing pasteurized, homogenized milk to sunlight increased concentrations of most of the volatile materials found after only 5 min (Table 1). Acetaldehyde increased from 6.1 to 35.5 ppb during 1-h exposure, whereas methyl sulfide did not change appreciably. n-Pentanal reached a maximum of 142.8 ppb after a 20-min exposure then decreased to 110.4 ppb at 1 h. N-Hexanal increased steadily from 19.1 to 83.6 ppb throughout the 1-h exposure to sunlight. All TBA values were relatively low (Table 1). It is generally agreed that TBA does not reflect light-activated flavor defects, but TBA increased slightly from 0.020 to 0.022 for up to 30-min exposure and to 0.034 for 1-h exposure.

Changes in volatile materials in milk in a plastic jug exposed to fluorescent light are shown in Table 2. A similar pattern of changes in volatile materials occurred in milk exposed to sunlight and fluorescent light, although times of exposure and light intensities were different. The principal difference was the methyl sulfide increased slightly in milk exposed to fluorescent light but not in milk in a clear glass flask exposed to sunlight. Acetaldehyde concentrations were not so pronounced in milk that was fluorescently treated as in that exposed to sunlight.

Susceptibilities to light activation by raw, laboratory pasteurized, and plant pasteurized milks from the same milk supply are compared in Table 3. Concentrations of each chemical component in all control milks were

TABLE 1. *Changes in concentrations of indicated chemical constituents of pasteurized, homogenized milk after exposure to direct sunlight<sup>a</sup>*

Compounds	Times exposed (min)					
	0	5	10	20	30	60
	(conc ppb)					
Acetaldehyde	6.1	14.3	14.1	20.8	28.3	35.5
Methyl sulfide	7.2	7.4	6.8	6.4	6.2	6.5
Propanal	2.6	3.6	4.2	4.2	6.2	5.7
Acetone	311.0	351.0	346.0	355.0	390.0	365.0
Butanone	23.3	29.3	29.5	29.5	30.3	29.9
n-Pentanal	11.8	65.8	105.4	142.8	130.0	110.4
n-Hexanal	19.1	32.1	54.0	68.0	75.8	83.6
TBA values	(0.020)	(0.020)	(0.020)	(0.022)	(0.027)	(0.034)

<sup>a</sup>At 11 A.M. standard time (0 exposure time) sun energy was 0.91 g cal/cm<sup>2</sup>/min; at noon 1.09 g cal/cm<sup>2</sup>/min.

TABLE 2. *Concentrations of indicated constituents compared in unexposed milk and in pasteurized, homogenized milk exposed to fluorescent light*

Compounds	Refrigerator			Display case <sup>a</sup>		
	Storage time (h) <sup>b</sup>			Storage time (h) <sup>b</sup>		
	4.5	18	44	4.5	18	44
	(conc ppb)					
Acetaldehyde	5.8	7.5	4.8	7.4	8.3	12.0
Methyl sulfide	6.8	8.2	7.4	7.2	8.3	11.6
Propanal	2.4	2.8	2.7	2.7	3.1	5.4
Acetone	390.0	406.0	363.0	365.0	398.0	414.0
Butanone	51.0	51.6	44.2	48.6	48.8	48.6
n-Pentanal	8.2	14.6	13.2	37.0	48.5	114.0
n-Hexanal	19.6	26.4	24.4	30.0	32.1	68.5

<sup>a</sup>Exposed to 40W fluorescent bulb at 21 cm distance.

<sup>b</sup>At 18 h, TBA values of both refrigerator and display case samples are .014.

TABLE 3. Changes in concentrations of indicated constituents of raw, laboratory pasteurized, and plant pasteurized, homogenized milk exposed to sunlight

Time exposed	Raw milk	Lab past. <sup>a</sup>	Plant past. milk <sup>b</sup>
		<i>Acetaldehyde</i> (ppb)	
0	6.3	6.4	6.4
20 min	14.9	19.9	13.6
		<i>Methyl sulfide</i> (ppb)	
0	10.0	8.8	7.4
20 min	10.2	10.2	8.2
		<i>Propanal</i> (ppb)	
0	2.2	2.2	2.2
20 min	3.9	3.9	3.6
		<i>n-Pentanal</i> (ppb)	
0	4.6	10.3	7.4
20 min	40.6	44.9	80.2
		<i>n-Hexanal</i> (ppb)	
0	12.9	14.4	13.9
20 min	55.5	60.2	30.6
		<i>TBA values</i>	
0	.019	.019	.013
20 min	.023	.024	.027

<sup>a</sup>63C for 30 min.

<sup>b</sup>Vac-Therm, HTST pasteurized, homogenized.

similar; n-pentanal varied most. Those in the exposed plant pasteurized milk (Vacu-Therm) increased least for all components, except for n-pentanal, which increased the most. Again methyl sulfide did not increase upon exposure to sunlight.

TBA values were poor measures of the volatiles in light-activated milk. Surprisingly, TBA values changed most in the plant pasteurized milk (0.013 to 0.027), despite lower concentrations of volatiles produced. The .027 TBA indicates acceptable milk.

TABLE 4. Changes in concentrations of indicated chemical constituents of commercial skim milk and whole homo milk exposed to sunlight

Time exposed	Skim milk <sup>a</sup>	Plant past. milk <sup>b</sup>	
		<i>Acetaldehyde</i> (ppb)	
0	8.3	9.0	
20 min	26.6	20.2	
		<i>Methyl sulfide</i> (ppb)	
0	7.6	8.4	
20 min	5.9	7.3	
		<i>Propanal</i> (ppb)	
0	2.4	3.2	
20 min	3.5	6.5	
		<i>n-Pentanal</i> (ppb)	
0	2.4	26.2	
20 min	15.4	179.5	
		<i>n-Hexanal</i> (ppb)	
0	11.8	28.0	
20 min	21.2	66.4	

<sup>a</sup>Commercial skim milk fortified with 1% NFDM solids.

<sup>b</sup>Homo milk from the same source as the skim milk.

Table 4 shows changes in concentrations of chemical compounds from skim milk and whole homogenized milk exposed to sunlight 20 min. Higher concentrations of acetaldehyde from skim milk than from whole homogenized milk, both exposed to sunlight, show that acetaldehyde originates from the nonfat milk fraction. n-Pentanal also increased significantly in the exposed skimmilk, and though the increase was much less than in the exposed homogenized milk, the ratios of the increases were similar. Precursors of all other carbonyl compounds apparently were from the lipids. Their concentrations did not differ appreciably between control skim milk and homogenized milk.

Changes in concentration of several carbonyl compounds in milk exposed to sunlight or to fluorescent light are in the part-per-billion range. The same chemical compounds produced in sunlight-exposed milk were observed in milk exposed to fluorescent light, but in somewhat different proportions. Whether the observed changes cause the typical light activated flavor still needs to be investigated. The origin and mechanism of acetaldehyde formation merits additional study. Lower concentrations of n-pentanal after 20 min exposure to sunlight suggests that it may interact or be altered.

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