Headspace Gas Analysis as a Measure of Rancidity in Corn Chips

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Headspace analysis by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) has been used to identify and quantify volatiles formed in the oxidative deterioration of corn chips. The effect of light and temperature on the formation of propanal, pentanal and hexanal in stored chips was examined and the data correlated with the results of sensory evaluation. The procedure is suitable for determining concentrations of pentanal and hexanal below one ppm, which is below the level where rancidity based on sensory evaluation is detected. Problems associated with solute partitioning and sample decomposition in the analysis also were investigated.

Methods of quantifying rancidity in edible oils and fatty foods are based on sensory evaluation or chemical methods which measure one or a class of lipid oxidation products. Established procedures, such as peroxide value (1), thiobarbituric acid test (2, 3), rate of oxygen uptake (4) or free fatty acid (5) are widely used, but generally are indirect and must be empirically related to quality in the tested products. Chromatographic methods, particularly GC, are eminently suitable for direct determination of individual compounds responsible for rancid flavors (e.g., low molecular weight aldehydes) at ultra-trace levels. Thus, a simple or complex relationship between the concentration of such flavor components and sensory evaluation may be established.

This paper, as an extension of previous work on potato chips (6-9), examines the use of GC for the analysis of oxidation volatiles in corn chips. The latter are a deep fried snack food similar in appearance to potato chips but are prepared from groundcorn and have a characteristic flavor and yellowish appearance. They are marketed either plain or with added flavor, e.g., bacon, cheese, barbecue, etc. In the U.S., such products together with tortilla chips accounted for 5.9% of the snack food market in 1985 (10) or about one-half that of potato chips. The development of rancidity in corn chips is expected to be similar to that in potato chips and to be strongly influenced by the type of frying oil used as well as a variety of other factors. In the headspace procedure described here, conditions for proper equilibration and sampling are examined and the concentration of pentanal and hexanal correlated to sensory evaluation scores. The effects also are examined on the formation of propanal, pentanal and hexanal of storage under various conditions.

EXPERIMENTAL PROCEDURES

Materials and sample preparation. Chemicals were purchased from Tokyo Kasei Kogyo (Japan) and were used without further purification. Frying oils and commercial corn chips were obtained from local industrial sources or stores.

Raw, unflavored corn chip slices (APD Snack Foods, Sydney, Australia) were fried in fresh oils at 190 C in a mini frier for five min. The cooked chips (60 g) were allowed to drain and then packed in glass jars with loosely fitting screw top lids. The jars were then divided into three groups to be stored at (i) −20 C in the dark; (ii) 60 C in the dark (Schaal oven test), or (iii) exposed to 1000 lux of fluorescent light at 25 C.

Headspace analysis procedure. For chromatographic analysis, a sample (10.0 g) of the chips was removed and pulverized in a polyethylene bag. A portion (3.00 g) of this material was weighed into a glass vial (30 ml; Supelco type 3-3106), 4-heptanone (0.20 μl) added and the vial immediately sealed with a foil-lined rubber stopper (Alltech type 95305). A second portion of the pulverized chips was subjected to sensory evaluation on the same day as the analyses.

The vial containing the sample was placed, together with a gas syringe, in an air oven (90 ± 0.1 C) for one hr. A portion (250 μl) of the headspace gases was sampled with the syringe and injected directly into a Perkin Elmer Sigma 3B Gas Chromatograph equipped with a flame ionization detector and programmed integrator.

Columns were either stainless steel (1.8 m × 3.00 mm) packed with 10% OV-1 on Gas Chrom Q (100/120 mesh) or fused silica wall-coated open-tubular with SE 54 (25 m × 0.22 mm) (Scientific Glass Engineering, SGE, Melbourne, Australia).

Operating conditions were 65 C isothermal, 30 ml/min nitrogen carrier gas for the OV-1 column or 40 C programmed to 240 C at 10 C/min with carrier gas velocity of 50 cm/sec for the SE-54 column. Injection port and detector temperatures were constant at 200 C and 200 C, respectively. A splitless injection system (SGE) was used for the capillary column.

For quantitative determination of headspace volatiles, fresh corn chips, prepared as above, served as standards by injection with 0.20 μl or other suitable volume of each aldehyde and 0.20 μl of heptan-4-one as internal standard prior to equilibration in the oven. Samples were treated similarly but were injected only with internal standard. Following GC analysis of the headspace, the concentration (ppm or $mg \bullet kg^{-1}$) of each component was calculated from Eqn 1.

$$C_S = k\,C_{IS}(A_S/A_{IS}) = k'(A_S/A_{IS}) \qquad [1]$$

where k′ is an empirical constant evaluated for each component under a fixed set of operating conditions (see Discussion), A_S and A_{IS} are blank-corrected areas calculated for GC peaks of the component of interest and internal standard, respectively, and C_S and C_{IS} are the corresponding concentrations calculated from the volumes injected, the densities of the compounds and the mass of sample taken. Based on repeated injections

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of standard samples, reproducibility for this procedure was established as 7% relative.

Gas Chromatography - Mass Spectrometry. A VG Analytical MM 12-12 quadrupole GC-MS instrument equipped with a directly coupled BP5 fused silica column (25 m × 0.25 mm) (SGE), electron impact ionization (70 eV) and a computer data system was used to identify the oxidation volatiles. Headspace sampling, helium carrier gas flow and temperature programming were similar to those in the GC-only studies. To reduce the interference of the air peak on early eluting species such as acetaldehyde, a helium atmosphere was utilized in the vials during temperature equilibration of samples, although samples equilibrated under air were also run for comparison. Compound identification was based on retention data, specific ion monitoring and a manual comparison of EI fragmentation patterns (11-13) of expected (14) and related compounds.

Sensory evaluation. Samples were evaluated for flavor (15) on the same day as the GC analyses by a fixed team of six panelists using a triangular test. Hence, the panelists were presented with three coded samples, one of which was a control, and instructed to rate these according to the hedonic scale: 0, bland; 1, suspicion of off-flavor; 2, noticeable but very slight off-flavor; 3, noticeable off-flavor; 4, distinct off-flavor; 5, disagreeable unpleasant off-flavor (rancid); 6, markedly disagreeable off-flavor (very rancid).

RESULTS AND DISCUSSION

Oxidation volatiles and compound identification. Freshly fried corn chips gave relatively "clean" headspace chromatograms as seen in Figure 1a, and contained less than one ppm of oxidation volatiles (Table 1). At this stage, there was no discernible rancidity flavor (flavor score 0), with the corn chips displaying a mild flavor reminiscent of popcorn. However, we could not detect the characteristic aroma constituents (16-18) by the direct sampling procedure, even though Legendre (16) has used a similar procedure to identify a variety of volatiles in corn breakfast cereal. Commercial corn chips containing added flavoring (bacon, cheese, barbecue or sour cream with chives), on the other hand, displayed a variety of small peaks in the headspace chromatogram, although these did not interfere in the detection of n-pentanal or n-hexanal. Evidently, the oxidation volatiles have a higher detection threshold than other flavor components, which is compatible with their detection by a direct headspace sampling procedure. The type and relative proportion of individual volatiles in corn chips is determined largely by the fatty acid composition of the frying oils used (Table 2) (19). For example, chips fried in the cottonseed - sunflower oil, which has a high linoleate content (Table 2), produced much higher concentration of pentanal and hexanal than those fried in either peanut or olive oil. Chips fried in the latter produced significant quantities of nonanal consistent with autoxidation of oleate (19), the major fatty acid moiety of these oils.

After 20 days of the Schaal oven test, corn chips fried in cottonseed-sunflower oil became highly rancid (flavor score 6), sticky and noticeably lighter in color. Headspace analysis of these chips revealed a striking increase in the number and intensity of peaks (Fig. 1b). From the GC-MS data, the main components were iden-

TABLE 1

Concentration of Major Volatile Components in Fresh Corn Chips

Oil	Concentration (ppm)			
	Propanal	Pentanal	Hexanal	Nonanal
Cottonseed/ sunflowerseed blend	0.08	0.15	0.28	0
Peanut	0.23	0.08	0.16	0.02
Olive	0.04	0.07	0.15	0.10
Palm olein	0.03	0.08	0.11	0.01

TABLE 2

Fatty Acid Composition of the Frying Oils[a]

Oil	Fatty acid Content (g/100 g)					
	Myristic	Palmitic	Stearic	Oleic	Linoleic	Others
Cottonseed + sunflowerseed (50 + 50 by volume)	0.67	15.4	3.6	21.9	55.6	2.8[b]
Peanut	trace	7.2	4.1	58.3	24.9	5.5[c]
Olive	trace	14.6	2.3	64.9	15.7	2.5[b]
Palm olein[e]	0.9-1.4	37.7-41.7	4.0-4.8	40.7-43.9	10.4-13.4	[d]

[a] As determined by GC of the fatty acid methyl esters formed by boron trifluoride catalyzed transesterification.

[b] Includes 2% palmitoleic acid.

[c] Includes 2% arachidic acid and 2% behenic acid.

[d] Includes 0.1-0.6% lauric acid, 0.2-0.5% arachidic acid, 0.1-0.4% palmitoleic acid and 0.1-0.6% linolenic acid.

[e] Data provided by supplier.

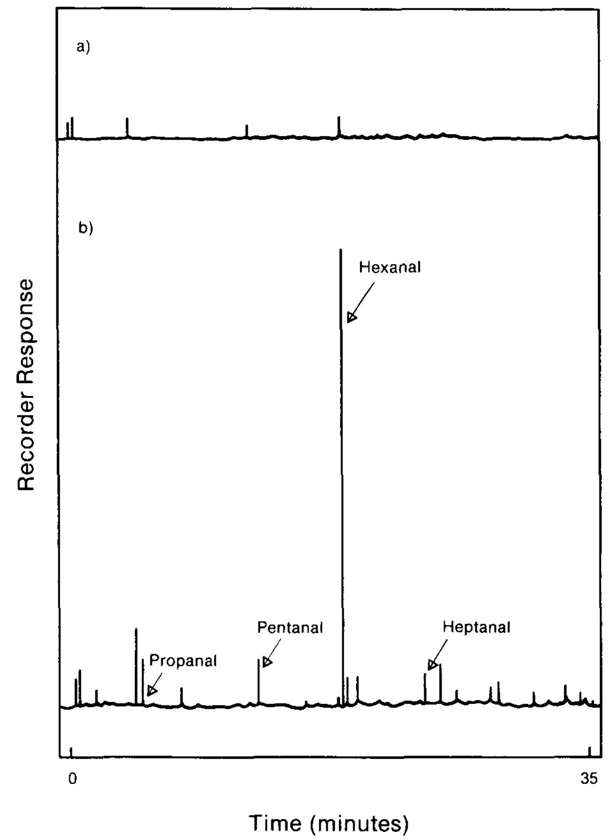

FIG. 1. Chromatograms of headspace vapors from corn chips fried in a 50:50 blend of cottonseed and sunflower oils. In a, samples were analyzed one hr after frying and in b after storage for 20 days in the dark at 60 C. Conditions: 25 m SE-54 WCOT column programmed at 10 C/min from 40 C to 240 C. (Detection sensitivity is 10 times greater in a.)

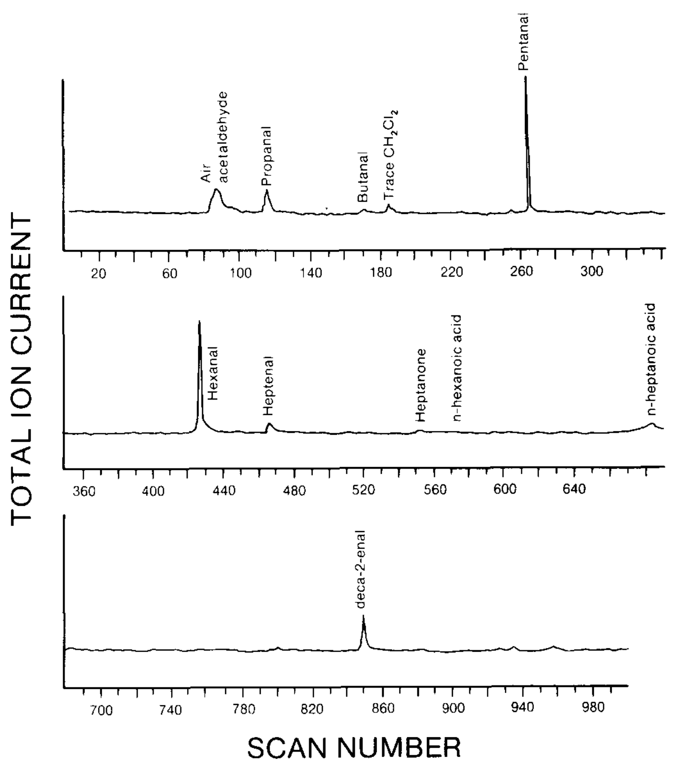

FIG. 2. Chromatogram of headspace vapors as identified by GC-MS. Conditions are described in Experimental.

tified as propanal, n-pentanal, n-hexanal and 2-decenal. Minor components identified were acetaldehyde, n-butanal, n-butenal, n-heptanal and 2-heptanone. The formation of these products appears (19) consistent with the autoxidation of linoleate, the main component of the frying oil incorporated in the chips (corn chips contain 20–30% by mass of oil). Also detected in the headspace were the polar n-hexanoic and n-heptanoic acids which eluted from the inert fused silica column (Fig. 2) but not from the more adsorptive packed columns. The occurrence of these low molecular weight acids, which seems characteristic of advanced rancidity, is attributed to the oxidation of the corresponding aldehyes. The possibility that these acids were produced by hydrolytic rancidity accompanying the oxidative process is unlikely in the absence of detectible levels of n-octanoic acid expected from the autoxidation and hydrolysis of linoleate (20). The absence of 2,4-decadienal, a major autoxidation product of linoleate, is attributed to its further ready oxidation to n-hexanal (21) and ultimately to n-hexanoic acid. Unexpectedly, pentane (which co-elutes with propanal) was not positively identified in this highly rancid sample, although it could have been present in trace amounts and obscured by propanal in the chromatogram. In Figure 2, selective ion monitoring of the propanal peak indicated essentially one component with the mass spectrum (peaks at m/z 58, 57, 29, 28, 27 in decreasing order of intensity) unequivocally indicating the species as propanal. Hence, n-pentane as a measure of rancidity evidently depends for detection on its selective concentration either during sample preparation (22) or quantification using an adsorptive column (9) to retain other components.

Although relative concentrations varied significantly for chips cooked in the other three oils, hexanal was the major oxidation volatile in each case.

Quantitative aspects. The application of headspace GC in quantitative analysis requires that solute concentrations in the sample be determined from measurements of their corresponding concentrations in the vapor phase. It has been shown (23), for a fixed sample size and equilibration temperature, that the area of a GC peak of component i is proportional to the vapor pressure of the pure solute P_i^o at that temperature and mole fraction x_i of solute in the matrix [Eqn 2]. Substitution for P_i^o from the Clausius Clapeyron equation also gives the temperature dependence of the response [Eqn 3].

$$A_i = kx_i\gamma_i P_i^o \qquad [2]$$

$$A_i = kx_i\gamma_i 10^{[(-\Delta H_v/2.303RT) + B]} \qquad [3]$$

where k and B are constants, γ_i is the activity coefficient $\cong 1$, and ΔH_v is the molar heat of vaporization of the solute.

For reasonable values of ΔH_v it can be shown that near 100 C, A_i changes by ca. 1% for each degree change in temperature, so careful control of the vial

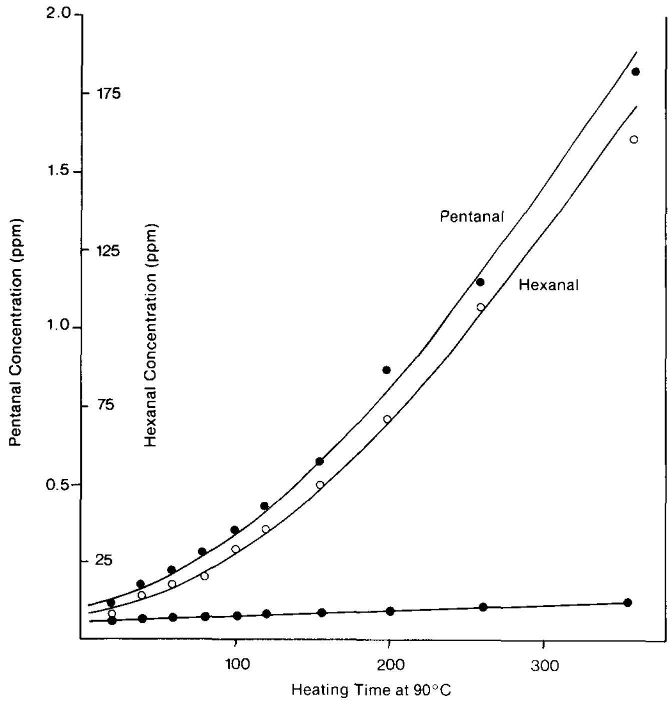

FIG. 3. Effect of equilibration time on the concentration of aldehydes in rancid (flavor score 4) corn chips. Equilibration temperature was 90 C.

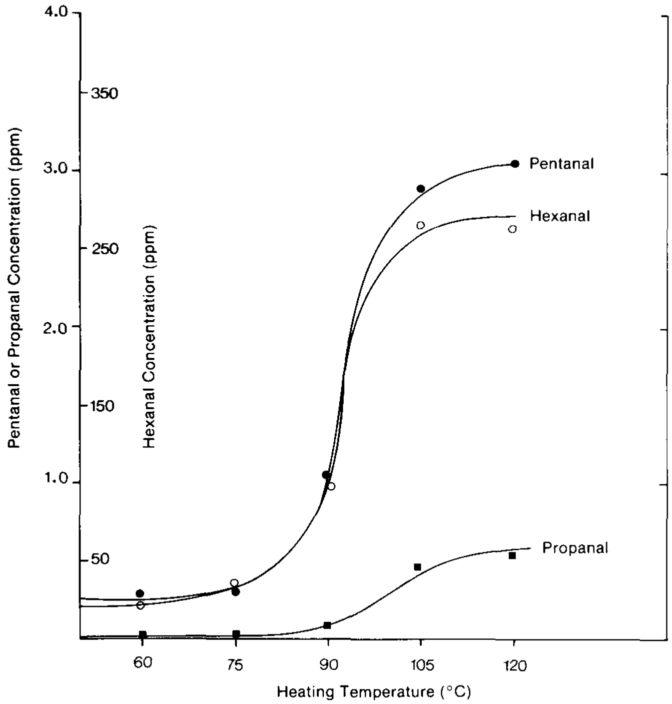

FIG. 4. Effect of equilibration temperature on the concentration of aldehydes in rancid (flavor score 4) corn chips. All analyses were performed after one hr at the specified temperature.

temperature (± 1-3 C) is required. A linear calibration curve should be possible if the temperature is thus controlled. Indeed, calibration plots for pentanal and hexanal added to fresh corn chips were linear in the range 0-100 ppm. For practical purposes, an internal standard procedure was preferred to minimize the effects of small variations in temperature and sample aliquot injected (re Experimental).

As evident in Figures 3 and 4, equilibration temperature and time are critical in the headspace analysis of corn chips. This behavior is ascribed to two effects, (i) thermal decomposition of hydroperoxides during equilibrium, and (ii) further autoxidation of sample by air in the headspace. The exact behavior of the sample will depend on temperature, the degree of rancidity and the presence or absence of air in the vial during equilibration. Fresh corn chips to which pentanal and hexanal were added equilibrated fairly rapidly (< 30 min), whereas rancid chips displayed behavior similar to that in Figure 3. Fresh chips were, in fact, stable for several hours in an inert argon atmosphere. These results suggest that the effects shown in Figures 3 and 4 are due to both hydroperoxide decomposition and further oxidation. The levelling effect in Figure 4 is thought to be due to oxygen depletion in the vial.

It has been suggested (24) that hydroperoxide decomposition is rapid and complete only at temperatures exceeding 200 C. However, in the latter report, one is dealing with on-column decomposition in oils injected directly into the gas chromatograph where rapid pyrolysis is required to produce discernible product peaks. In headspace analysis, slower decompositions occurring during equilibration (e.g., 10-60 min) will still contribute to peak intensity of the headspace volatiles without affecting peak shape. The behavior suggests that it may be difficult to distinguish between existing oxidation volatiles in the corn chips and identical products formed from the pyrolysis of hydroperoxides during thermal equilibration. To minimize this problem the lowest possible equilibration time and temperature must be used. Lowering the equilibration temperature, unfortunately, produces poorer partitioning of volatiles in the headspace, thereby decreasing the detection sensitivity. Indeed, the limited data available indicate poor partitioning for oxidation volatiles in the headspace even for relatively volatile species such as hexanal which has a partition ratio of 0.15 at 140 C between potato chips and helium. For the corn chips we have obtained a value of 0.11 for the partition ratio at 90 C. The response, per unit concentration, A_i/x_i, can be enhanced by increasing the vapor pressure which, in turn, can be achieved by raising the equilibration temperature. However, upper temperature limits apply where thermally unstable samples are involved because of the risk of thermal or autoxidative degradation. In this study, sampling was conducted at 90 C for one hr as a compromise between hydroperoxide decomposition and the requirement for producing sufficient solute in the vapor phase for detection.

Of relevance to the quantitative determination of hexanal and other aldehydes, Schieberle and Grosch (21) have shown that the hexanal concentration in oxygen at 38 C diminishes fairly rapidly, presumably due to oxidation to hexanoic acid, as previously discussed. Therefore, the need to use an inert rather than air atmosphere during equilibration is apparent. On the other hand, monitoring headspace volatiles at elevated temperatures (100-140 C) in air may be suitable for accelerated stability testing of corn chips (26).

Effect of storage. The analysis of headspace volatiles proved a sensitive means of monitoring oxidative changes in corn chips under various storage conditions. Thus, control samples of chips fried in the cottonseed-sunflower oil and stored at -20 C showed no change in volatiles profile for over one year. Identical samples kept at 60 C in the dark or exposed to normal fluorescent lighting showed increases in the concentrations of pentanal and hexanal as shown in Figures 5 and 6. In particular, the heated samples demonstrated an exponential buildup in the aldehyde concentrations after the induction period of 15 days. Surprisingly, no buildup was detected in the concentration of propanal under either set of conditions.

Because the particular glass containers used for storage were relatively opaque in the UV region (% transmittance < 1% at wavelengths less than 310 nm), photoxidation may have been impeded in those samples exposed to light. For this reason, light exposure tests were also conducted on corn chips stored in commercial polypropylene film packaging which transmits appreciably below 300 nm (20% T at 270 nm for 0.1-mm film). Under these conditions, only marginally larger increases in the concentrations of propanal, pentanal and hexanal were observed (Table 3). The increased production of propanal was most pronounced.

TABLE 3

Effect of Exposure to Fluorescent Light at 25 C on Formation of Propanal, Pentanal and Hexanal in Corn Chips

	Concentration (ppm)			
	Days exposure			
	14		35	
Solute	glass[a]	plastic pack[b]	glass[a]	plastic pack[b]
Propanal	0.09	0.58	0.12	0.67
Pentanal	0.19	0.42	0.40	0.83
Hexanal	0.68	1.31	1.38	4.72

[a] Sealed containers opaque to radiation below 300 nm.

[b] Commercial polypropylene packaging with an absorbance maxima at 280 nm.

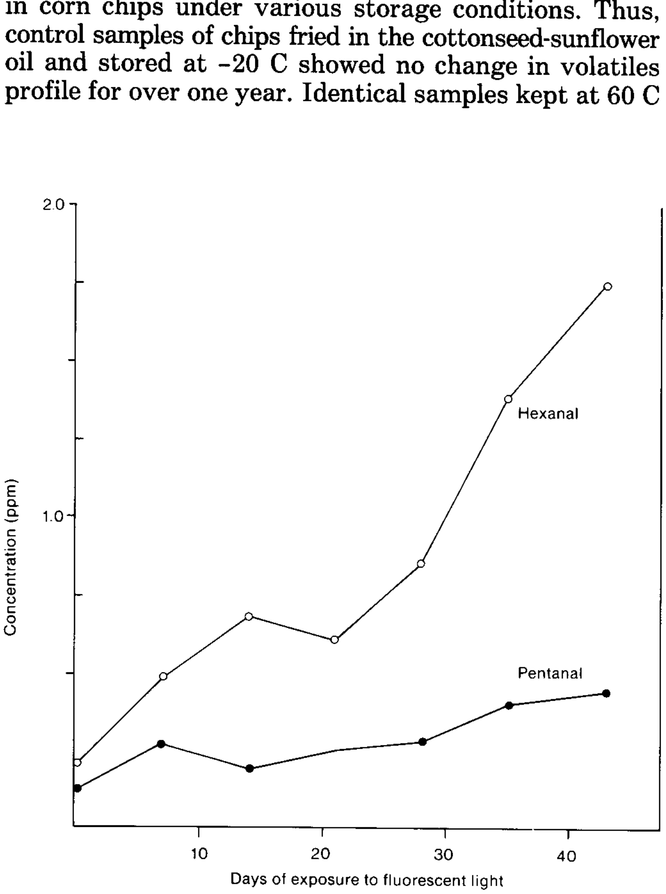

FIG. 5. Pentanal and hexanal concentration in corn chips exposed to fluorescent light at 25 C in glass containers.

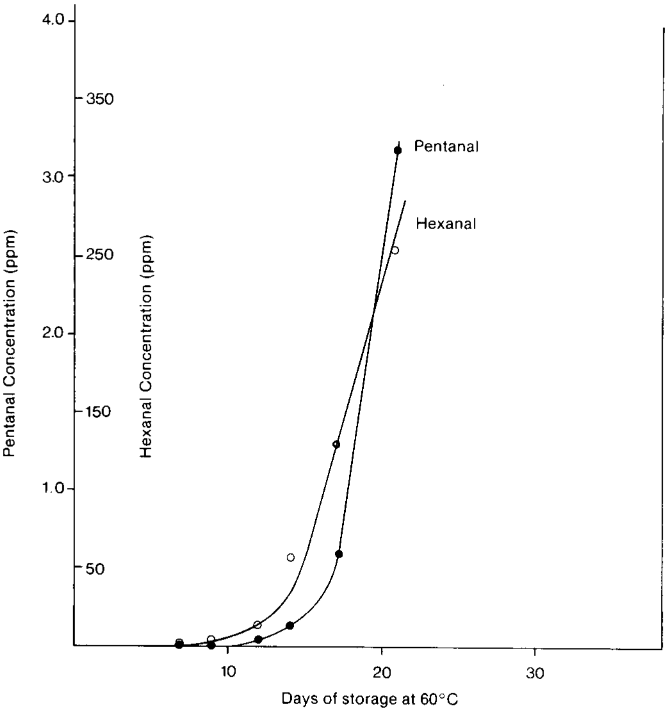

FIG. 6. Pentanal and hexanal formation in corn chips stored in the dark at 60 C.

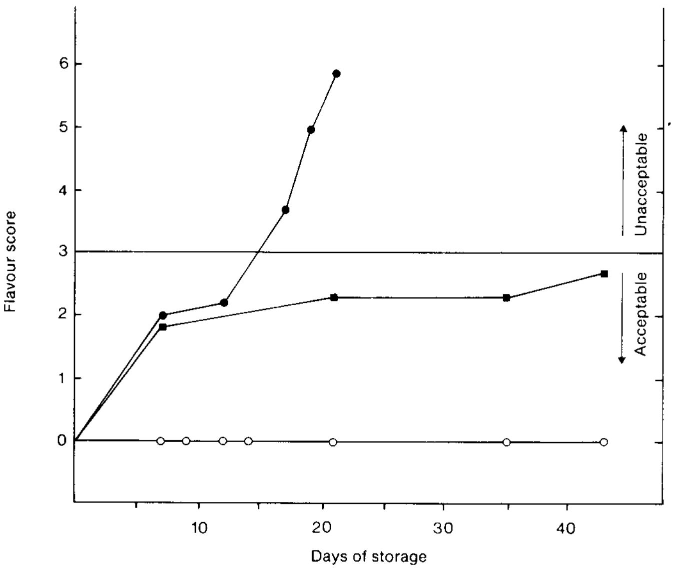

FIG. 7. Effect of standing time (days) on the flavor score of corn chips stored under various conditions. O——O, control, -20 C; ■——■, fluorescent light exposure at 20 C; ●——●, 60 C in the dark.

TABLE 4

Correlation of Pentanal and Hexanal Concentration with Flavor Score of Corn Chips[a]

	Concentration (ppm)	
Flavor score	Pentanal	Hexanal
0	0.22	0.28
1	0.23	0.72
2	0.23	1.04
3	0.85	5.00
4	2.60	18.5
5	6.60	67.5
6	35.00	270.0

[a]Stored at 60 C in the dark.

Corn chips fried in the other three oils were more resistant to autoxidation. Thus, the induction period at 60 C for samples fried in palm olein oil (preferred by commercial snack food manufacturers) was 59 days. After this period, however, the samples oxidized in the normal way with exponential rises in the concentrations of pentanal, hexanal and nonanal.

Sensory evaluation. Data for sensory evaluation of the corn chips under various conditions are given in Figure 7. Overall, the trends in the GC data in Figure 5 and 6 are reflected here also. For example, the accelerative effect at 60 C seen in Figure 6 is clearly apparent. Analysis of the data of Table 4 shows there is a good correlation between flavor scores and GC data. Thus, a nearly linear relationship exists between the logarithm of the pentanal and hexanal concentrations and the flavor score for corn chips stored at 60 C ($r \cong 1.0$ for scores in the range 2-6 inclusive). Therefore, it appears these aldehydes are a major contributor to the rancid aroma of oxidized corn chips. Indeed, fresh corn chips spiked with a mixture of pentanal and hexanal (ca. 10 ppm and 100 ppm respectively) had a flavor similar to that of actual rancid samples. From Table 3 it is also evident that the headspace analysis procedure can detect aldehyde concentrations for the entire range of rancidity flavor scores. Thus, for a flavor score of zero, pentanal and hexanal concentrations of about 0.2 and 0.3 ppm, respectively, were calculated.

Samples with flavor scores exceeding 3 (and unacceptable according to the hedonic scale used) correspond to concentrations of pentanal and hexanal exceeding 0.9 and 5 ppm, respectively. The GC method of determining rancidity, therefore, appears as a sensitive and more precise alternative to sensory evaluation in this application. A further advantage of the GC method is that it may be more suitable for detecting rancidity in flavored corn chips where strong flavorings may interfere in the sensory evaluation of rancidity.

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