Influence of Curing Temperature on the Volatile Components of Peanuts

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Profiles of volatiles produced by peanuts cured at 22°, 35°, 45°, and 50° C were determined by gas-liquid chromatography and analyzed in relation to evaluation of flavor and aroma by a taste panel. Acetaldehyde, ethanol, and ethyl acetate were the compounds found that might indicate flavor deterioration. An increase in acetaldehyde concentration was detected with each increase in curing temperature. Ethyl acetate was not detected in peanuts cured at 22° C; however, all three compounds increased considerably at 50° C. All panelists preferred peanuts cured at the lower temperatures, and found the 50° C sample to be the most objectionable. Since ethyl acetate was detected in peanuts cured at 50° C, the presence of this compound could indicate flavor deterioration in cured peanuts. Ratios between certain peaks of the volatile profile also showed consistent trends that might be related to curing temperature.

During processing and handling of food products, objectionable flavors can develop. Improper curing of peanuts can produce objectionable flavors and render the products undesirable for human consumption (Beasley and Dickens, 1963).

Numerous investigators have used gas-liquid chromatography (glc) profiles as a means of assessing aroma and flavor. Teranishi and Buttery (1962) found that glc profiles could be used effectively to analyze the vapor above food products and related this information to the quality of the product. Bengtsson and Bosund (1964) used the volatile profile technique to evaluate changes in the flavor of frozen peas. Coffman *et al.* (1960) suggested that aroma profiles could be used as quality control standards. Buttery and Teranishi (1963) used glc to detect off-flavors due to different types of food deterioration.

The use of glc peak ratio data is becoming one of the best tools to effectively correlate glc profile data to differences in a wide range of foodstuffs due to flavor, variety, and treatment of the sample. In many instances, the flavor of a food material not only depends on the qualitative nature of the odoriferous compounds present, but also on the quantity present. Changes in the ratios of the compounds present may very well alter the aroma and flavor of the product. Rhoades (1960) suggested that the degree of roast in coffee could be indicated by the ratio of diacetyl to acetyl propionyl, and Rohan (1965) used the ratios of two peaks to properly classify the chocolate aroma of unroasted cocoa beans. Powers and Keith (1968), investigating coffee aroma, used a more sophisticated type of peak ratio analysis to properly classify different blends of coffee, and Biggers *et al.* (1969) used a detailed examination of peak ratio data to increase the reliability of differentiating among different coffee blends.

In this study, peak ratios were used in conjunction with sensory evaluation to correlate glc profile data to curing treatments of peanuts.

EXPERIMENTAL

Sample Treatment to be Used. Freshly harvested peanuts are normally cured to moisture level from 5–10% in bins equipped with fans. The normal curing temperature is 22° C at 50% relative humidity. However, improper curing does occur primarily due to elevated temperatures resulting in the production of an off-flavor product.

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Peanuts that had been freshly harvested (Variety NC-2) were placed in chambers equipped with fans and cured for 72 hr. Curing temperatures and their corresponding relative humidities (R.H.) were as follows:

°C	R.H., %
22 ± 2	50 ± 5
35 ± 1	55 ± 3
45 ± 1	65 ± 3
50 ± 1	70 ± 3

Following the curing treatment the peanuts were stored in an area known to be relatively free from any volatile solvent contamination until the product could be analyzed.

Preparation of Sample for Glc and Mass Spectral Analysis. The volatiles were collected for glc and mass-spectral analysis by subjecting a slurry of the peanuts consisting of 500 g of seeds and 1 l. of distilled water to a vacuum of 5×10^{-3} torr for 3 hr with a distilling-pot temperature of 25° C. The volatiles were collected in a trap cooled with liquid nitrogen (−196° C). In order to minimize the enzymatic formulation of volatile components during the grinding and vacuum extraction procedures, the following precautionary measures were used. The peanuts were separated into 100-g lots and ground in a small blender for 1 min. After grinding, the sample was immediately placed into the distilling pot, which had been previously evacuated and flushed with nitrogen. A previous paper describes the apparatus and techniques used along with the incorporated modifications (Pattee *et al.*, 1970a).

Duplicate distillations were made for each curing treatment and analyzed by glc. Volatile components were separated on a Micro-Tek 2000R Research Gas Chromatography, equipped with dual flame ionization detectors.

Columns used in this study and the operating parameters are as follows: a $^1/_8$ in. × 12 ft stainless steel column packed with 15% Carbowax 20M on 60–80 mesh acid-washed DMCS treated Chromosorb W and programmed from 70° C to 140° C at 2° C per min; a $^1/_4$ in. × 6 ft stainless steel column packed with 60–80 mesh Chromosorb 102 programmed from 125° C to 200° C at 2° per min. These two columns differ greatly in their degrees of polarity.

Mass spectral analysis was used to confirm identification using a TOF mass spectrometer (Pattee *et al.*, 1969).

Flavor Profile Data Collection and Analysis. Integration of the aroma profiles was done using a digital readout system. The output from the glc electrometer was fed directly into the integrator, and the retention times and their corresponding

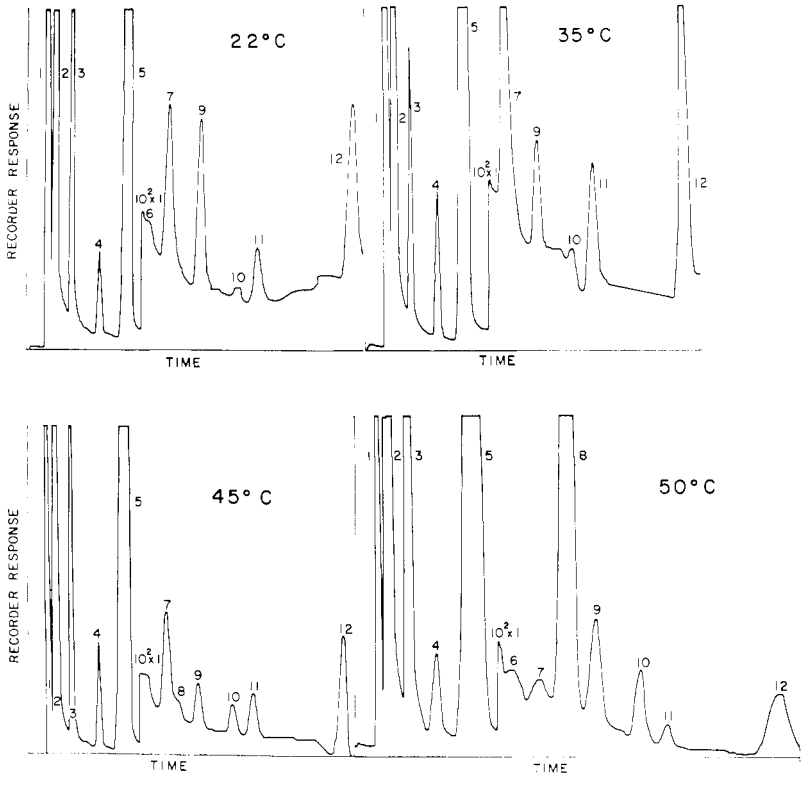

Figure 1. Chromatograms of peanuts cured at different temperatures

peak areas were recorded by a Victor printer. These data were punched on IBM cards and read into a computer for analysis. The techniques for computer handling of the data are described elsewhere (Pattee *et al.*, 1970b).

Functions computed were total area, relative retention time, relative percent, peak area on a per/g basis, and peak ratio comparisons.

Flavor Panel Evaluation to Be Used. The panel used to evaluate off-flavor in peanuts was selected from staff members and students. In strict terminology, the panelists were untrained but were familiar with the aroma and flavor of good and off-flavored peanuts and tasting techniques.

A total of five panelists were used, and 20 judgments were made on each sample. The degrees of significance of the preference data are listed.

Representative samples from each curing treatment were ground into meal and presented to the panel in dark colored bottles. Samples were coded, and the panelists were instructed to consider both aroma and taste. A balanced triangular-type organoleptic procedure was used; the panel was instructed to match the duplicate samples and to indicate the sample (duplicate or odd) with the preferred aroma and taste.

RESULTS AND DISCUSSION

Identification of Volatile Components. Typical chromatograms (Chromosorb 102) of the peanuts cured at the four temperatures used are shown in Figure 1. Table I identifies the volatile components. Some of these compounds have been shown to be present in good quality kernels (Pattee *et al.*, 1969). Acetaldehyde, acetone, ethanol, hexanal, and ethyl acetate were found in off-flavored peanuts by Pattee *et al.* (1965) using glc and functional group data.

Quantity of Selected Components from Peanuts Cured at Different Temperatures. Previously, Pattee *et al.* (1965) found that volatiles concentrated in the −196° C fraction isolated from off-flavor peanuts nearly duplicated the aroma and off-flavor. They also suggested that off-flavor in peanuts might be due in part to an increase in acetaldehyde and ethanol concentration coupled with the presence of ethyl acetate. As shown from data listed in Table II, these compounds exhibit a considerable increase in concentration at 50° C when com-

Table I. Volatile Components Identified in Peanuts Cured at Different Temperatures

Peak No.	Compound
1	Methanol
2	Acetaldehyde[a]
3	Ethanol[a]
4	Acetone
5	Pentane
6	Ethyl ether[b]
7	Methyl formate
8	Ethyl acetate[a]
9	Unknown
10	Chloroform[b]
11	Pentanal
12	Hexanal

[a] Previously identified in off-flavor peanuts. [b] Contaminant.

Table II. Quantities of Selected Components from Peanuts Cured at Different Temperatures

°C Curing Temperature	Component	Area counts/g
22	Acetaldehyde	1033
	Ethanol	79
	Ethyl acetate	0
35	Acetaldehyde	1212
	Ethanol	58
	Ethyl acetate	Trace
45	Acetaldehyde	1214
	Ethanol	80
	Ethyl acetate	Trace
50	Acetaldehyde	2024
	Ethanol	207
	Ethyl acetate	315

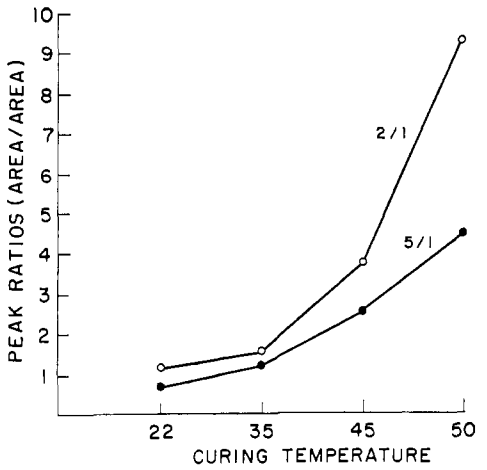

Figure 2. Effect of curing temperature on the peak ratios for acetaldehyde to methanol (2 to 1) and pentane to methanol (5 to 1)

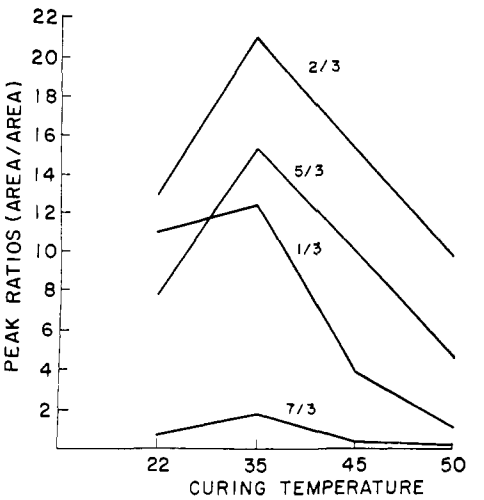

Figure 3. Changes in selected peak ratios using the anaerobic indicator ethanol as the denominator

Table III. Peak Ratios of Volatile Components from Peanuts Cured at Different Temperatures

Glc Peak Ratio No.	Curing Temperature, °C 22	35	45	50
2/1	1.150	1.660	3.830	9.490
4/1	0.043	0.032	0.067	0.122
5/1	0.702	1.230	2.580	4.570
7/1	0.060	0.143	0.098	0.046
1/2	0.862	0.600	0.261	0.105
3/2	0.077	0.048	0.066	0.102
5/2	0.606	0.738	0.675	0.481
7/2	0.052	0.086	0.026	0.005
1/3	11.200	12.400	3.950	1.020
2/3	12.900	20.700	15.100	9.750
5/3	7.870	15.300	10.200	4.690
7/3	0.673	1.780	0.386	0.047
1/4	23.300	31.300	14.800	8.170
2/4	27.100	52.200	57.000	7.600
3/4	2.800	2.510	3.760	7.960
7/4	1.400	4.480	1.450	0.038
1/5	1.420	0.812	0.386	0.218
2/5	1.640	1.350	1.480	2.070
3/5	0.127	0.065	0.098	0.212
7/5	0.086	0.116	0.038	0.010

pared to the concentrations produced at the other curing treatments used. A slight increase in acetaldehyde concentration is shown at 35° C and 45° C.

Alcohols such as methanol and ethanol, both present in peanuts, have received very little attention as flavor contributors. However, Anderson and Day (1965) and Day and Anderson (1965) stated that methanol and ethanol may affect the overall flavor of a product *per se*, as well as through interactions and ester formation. Since both esters (Table I, Figure 1) of the above mentioned alcohols are found in peanuts cured at 50° C, these compounds may be of significance in the overall aroma and flavor of high-temperature cured peanuts.

According to Keith and Powers (1968), ethyl acetate has a threshold value of 3 ppm which is intermediate between ethanol and acetaldehyde. The odor of ethyl acetate has been described by Wenger *et al.* (1956) as being fruity. Since this compound does not appear in the aroma profile of peanuts cured at 22° C, ethyl acetate alone could be an indicator of deterioration of aroma and flavor due to high temperature curing.

CORRELATION OF GLC PEAK RATIO DATA TO CURING TREATMENT OF PEANUTS

The glc peaks ratioed by the computer are listed in Table III. Powers and Keith (1968) have stated that, for peak ratio data to be of discriminatory value for samples known to differ in treatment, the ratios should progressively increase or decrease. Two peak ratios were found which should be of major discriminatory value for quality evaluation of raw peanuts using this assumption. When the ratios 2 to 1 (acetaldehyde to methanol) and 5 to 1 (pentane to methanol) are plotted *vs.* their corresponding curing temperature, a progressive increase results with regard to treatment (Figure 2). If one were to plot the inverse of these ratios, a progressive decrease would have resulted. Thus, respective high or low ratio values of 2 to 1, 5 to 1, or their inverses could be suggestive of improper curing treatment.

Buttery and Teranishi (1963) and Jennings *et al.* (1962) have suggested that chromatographic analysis could help resolve the sources of off-flavor when several different types of food deterioration may be involved. It has been suggested by Whitaker and Dickens (1964) that anaerobic respiration is the source of off-flavor in high-temperature-cured peanuts. Under anaerobic conditions it is well established that acetaldehyde and ethanol accumulate. Eriksson (1968) has suggested that for peas under anaerobic conditions the NAD to NADH ratio would favor the alcohol partner. Swaisgood and Pattee (1968) have shown peanut alcohol dehydrogenase to have kinetic properties similar to those of the pea alcohol dehydrogenase. Ratio analysis using ethanol as the denominator should indicate if anaerobic conditions occur with increasing curing temperature. When acetaldehyde, pentane, methanol, and methyl formate are ratioed with ethanol and plotted against curing temperature (Figure 3), it is noted that the ratio increases in all cases between the 22° C and 35° C curing temperature, thus indicating that an aerobic type of respiration was predominating. However, between the 35°, 45°, and 50° C curing, it is noted that the ratios progressively decrease. This would indicate that ethanol is the most rapidly increasing component and that anaerobic respiration became the predominate type of respiration. These results thus support the suggestion by Whitaker and Dickens (1964) that anaerobic respiration does occur during high-temperature curing and indicate that ratio analysis can also be used to determine if changes are occurring in the metabolic processes by which the volatiles arise.

Table IV. Flavor Panel Evaluation and Peak Ratio Differences for Peanuts Cured at Different Temperatures

Curing Temperature of Sample	Peak Ratio Differences 2/1	5/1	% of Panel that Detected Difference	% Preference of Panel for Lower Curing Temperature Treatment
22 *vs.* 35	0.510	0.528	85	66[b]
22 *vs.* 45	2.680	1.878	75[c]	83[c]
22 *vs.* 50	8.340	3.868	100	100
35 *vs.* 45	2.170	1.350	87	58[a]
45 *vs.* 50	5.660	1.990	100	100

[a] Significant at 0.05 level. [b] Significant at 0.01 level. [c] Significant at 0.001 level.

CORRELATION OF GLC PEAK RATIO DIFFERENCE FACTORS TO SENSORY EVALUATIONS

A triangle-type test was used for sensory evaluation because it lends itself more readily to correlation with peak ratio differences than the quality or flavor indices used by Biggers *et al.* (1969). They ranked coffee samples organoleptically and correlated this ranking to quality based on peak ratio summations. However, evidence of two possible mechanisms for the production of volatile compounds, as mentioned in the previous section, precludes the mathematical development of a flavor index based on peak ratio summations for each curing treatment. For these reasons peak ratio differences were used to correlate the analytical data to the organoleptic evaluation.

Organoleptic evaluation and the differences for peak ratios 2 to 1 and 5 to 1 are given in Table IV. Peak ratios 2 to 1 (acetaldehyde to methanol) and 5 to 1 (pentane to methanol) were selected for correlation purposes, since these two ratios progressively increased throughout the temperature range, and they had previously been suggested as being of discriminatory value for quality evaluation. When the peanut sample cured at 22° C is compared to samples cured at the higher temperatures, the peak ratio differences increased with increasing temperature. It is seen that the larger the peak ratio difference, the higher the percent preference for the lower temperature cured sample. The data suggest that a peak ratio difference of approximately 2.5 for 2 to 1 and 1.5 for 5 to 1 must be achieved before the taste panel is able to establish a definite preference. This is pointed out by the decline of the percent preference of the panel for the lower curing temperature when the 35° C cured sample was compared to the 45° C cured sample, thus indicating that the peak ratio difference between these treatments may not be large enough for the panel to state a preference for the lower temperature treated sample with the same degree of confidence as in the 22 *vs.* 45, 22 *vs.* 50, and 45 *vs.* 50 sample comparisons. The similarity of the 35° and 45° C samples is also reflected in the analytical data given for selected components in Table II. When the 45° C cured sample was compared to the 50° C cured sample, 100% of the panel preferred the sample cured at the lower temperature. It is felt that in addition to the peak ratio difference given in Table III, the quantity of ethyl acetate present in the 50° C sample (Table II) also enabled the panel to detect the difference in these samples more readily.

Results of this study suggest that peak ratio data can be used effectively to correlate glc profile data to curing treatments of peanuts and to organoleptic evaluation of the product. Further refinement of this technique of analysis could possibly serve as a basis for an objective evaluation method for quality rating of food products.

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