Volatile "Fingerprint" Profile of Raw Peanuts as an Indicator of Quality

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ABSTRACT

The 1980 peanut crop suffered severe losses because of the drought in the United States, and in many cases, the peanuts that were harvested had off-flavors. Peanuts were imported from several foreign countries to offset crop losses. Many raw samples, both imported and US-grown, were examined by direct gas chromatography fingerprint method and by sensory techniques for flavor quality. The volatile profiles obtained were used as an indicator of quality. Based on the volatile profiles from numerous raw peanut samples examined, indicators of suspect peanuts were found that could provide a means of dividing the peanuts into several different groups, e.g. peanuts that had possibly undergone fermentation, oxidation, or external contamination. The volatile profiles of each of these groups and several high grade controls were correlated to peanut quality. In general, as the volatile profile increased, the quality decreased.

Key Words: Volatile profiles, quality indicators, rancidity, sensory evaluation, gas chromatography, mass spectrometry.

The 1980 peanut crop was probably the most disatrous harvest of our time. Approximately one-half of the crop was lost due to severe drought conditions and a heat wave. In the three years prior to 1980, the U.S. peanut crop averaged 1.76 billion kg of peanuts. These values can be compared to the 1980 figures of 1.05 billion kg. The 1980 total production represented a 43% reduction from the 1979 crop (22,26).

To off-set the shortage of high quality peanuts, former President Carter lifted the peanut import embargo and set the new quota at 90.9 million kg (21). Later, President Reagan increased the quota to 136.4 million kg (11). Of the 137.1 million kg permitted to enter the United States, approximately 57% were obtained from China, 18% from India, 12% from Sudan, 7% from Argentina, 2% from Brazil, and the remaining 4% from 11 other countries (12).

Whereas these statistics are of interest to many in the peanut industry, the purpose of this research was not to discuss the economic problems created by the 1980 crop, but to demonstrate the usefulness of the direct gas chromatographic (CG) fingerprint method for evaluating raw peanuts, and to show some of the results of our studies on the quality of the 1980 crop and of imported peanuts.

In 1971, a direct gas chromatographic method for the analysis of volatiles from vegetable oils was reported by Dupuy et al. (6). The method does not require enrichment of volatiles but yet, it is efficient and highly sensitive. Trace compounds can be detected at the parts per billion level. The original method was combined with mass spectrometry and used to separate and identify the volatiles from raw and roasted peanuts (3,17,18,20), peanut butter (8,10), vegetable oils (7), mayonnaise (9), and salad dressings (15). Several improvements on the original method allowed for further versatility in analyzing lipid oxidation products, whether they be found in food products (16), aqueous or non-aqueous media (14), or *in vitro* enzyme-catalyzed systems (23,24). Results from these investigations, showed that the data correlated well with flavor-scored samples, indicating, therefore, that the method is a practical instrumental means for measuring flavor quality.

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Materials and Methods

Samples of shelled peanuts, both domestic and imported, were obtained from several sources (breeders, shellers, brokers, and processors). The domestic peanuts were grown in the Southern section of the United States. Imported peanuts were from Argentina, Brazil, China, and India. After arrival at Southern Regional Research Center, the peanuts were stored in stoppered glass jars at 4 C until used.

The direct GC method developed by Dupuy et al. (3,6) and later modified by Lovegren et al. (17,20) was used to obtain the volatile profiles of raw peanuts. The compounds that comprise the volatile profile were identified with a Finnigan Model 4000 mass spectrometer interfaced with an INCOS data system.

Flavor characteristics from samples that were used to obtain the fingerprint profiles were identified by a trained sensory panel comprised of SRRC employees, 13 males and 7 females, ranging in age from 22 to 62, with an average of 42. The training was conducted over a period of 3 months using modified roasted peanut samples. The raw peanuts were roasted in a rotisserie oven equipped with a heavy gauge, stainless steel basket. The oven was preheated for 20 min. to an average temperature of 185 C. A minimum of 200 g of raw peanuts were roasted at one time. Time and temperature of roasting varied from 22 to 28 min. and from 167 to 177 C to obtain a uniform degree of roasting as judged visually. The roasted color was masked by the use of a red light when presenting the peanut samples to the panel. After roasting, the peanuts were cooled for 5 min. with forced air. Testae and hearts were removed by hand, and the peanuts were then ground with an Oster Blender for 2 min. A 28-gram portion of each sample was then presented to the panel for sensory evaluations as described by the American Society for Testing and Materials (1). A 4x4 selected Latin Squares Plan was used as the basis for sample distribution (5). The panel rated the roasted peanuts for overall quality and designated character notes using a modification of the descriptive analysis method with structured scaling (13). Descriptive analysis is a valuable method used in difference testing and in product development research. It provides a complete description of sample differences. The character notes described were the following: peanutty, sweet, beany, bitter, musty, rancidity, sulfur and metallic tastes. Results, derived from statistical analysis of the panel responses using analysis of variance, indicated that the differences among the peanuts were statistically significant. An overall quality score ranged from 1 to 9 (excellent to very poor). Significant differences were determined by Duncan's Multiple Range Test (25), and comparison of treatment means (4).

Results and Discussion

Samples of the 1980 domestic crop and several imported peanuts were analyzed and ranked from best to worst according to quality by the direct GC volatile profile fingerprint method correlated with sensory evaluations according to the method of Lovegren et al. (20). When plotted on the same scale, profiles of off-flavor peanuts and those of high quality were easily observed. In Figure 1, the volatile profile of one of the best samples, 415, US-grown, and the worst, 397, a peanut imported from China, were plotted on the same scale to

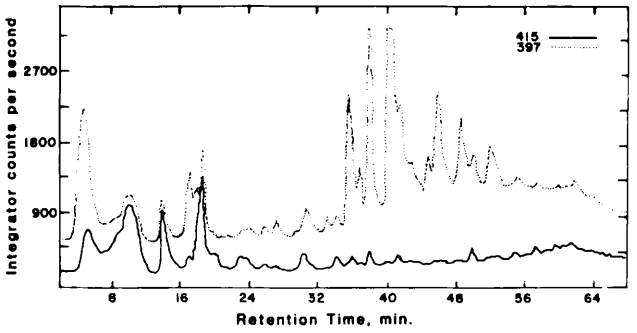

Fig. 1. Volatile profiles of two samples of peanuts that were judged one of the worst, sample 397, and one of the best, sample 415. The bottom curve begins at ca. 200 counts and the top curve is offset 400 counts for clarity.

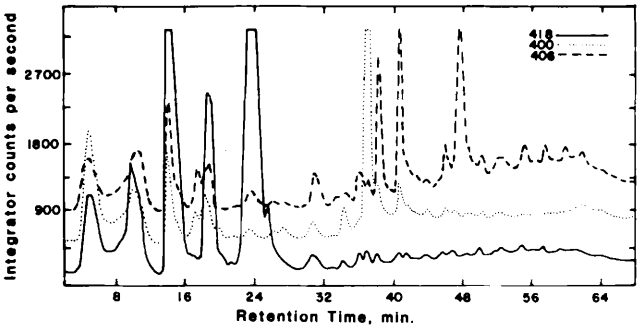

Fig. 2. Volatile profiles that indicate unusual compounds found in three particular peanut samples. Sample 406, from Brazil; 400, from China; 418, U.S. Southern-grown Spanish. The bottom curve begins at ca. 200 counts and the other curves are off-set 400 counts for clarity.

illustrate the type of differences that can be observed by the direct GC method. In comparing the profiles, a recorder response for the upper limit of the graph is approximately 3600 counts per second, which is about twice as high as the scale used by Lovegren et al. (20). In general, if a volatile component exceeded 2300 counts, those peanuts usually have an off-flavor. If the component is hexanal or hexanol and sometime pentane, secondary products of lipid oxidation, the sample is usually rancid. The rancid flavor can be detected by the sensory panel at levels over 1500 counts (approximately 2 ppm of hexanal, 3 ppm of hexanol, and 2 ppm pentane). As observed in the peanuts from China, two of the components, hexanal (38 min.) and hexanaol (40.5 min.), were both off scale. The pentane peak (17 min.) was not off scale in this sample. In addition to the high hexanal and hexanol contents, sample 397 also had several volatiles that eluted past 45 min. This section of the profile is referred to as the "mound" area, and is comprised of higher molecular weight volatile compounds, such as saturated hydrocarbons and substituted benzenes. Peanuts that have an unusually high mound area also have an off-flavor, but different flavor characteristics than that detected in rancid peanuts. Another exceptionally abundant compound observed in sample 397, was N-methyl pyrrole (36 min.).

In contrast to sample 397, one of the best peanut samples, 415, produced a very low profile over the entire run. The few compounds that were eluted during the first 19 min. were too low in concentration to cause any flavor problems. In general, the volatile profiles of fair to good quality raw peanuts may show profiles slightly higher than that of the peanuts shown in Figure 1, sample 415, but significantly lower than the Chinese peanuts shown in Figure 1.

The volatile profiles of peanuts discussed above illustrate how the fingerprint of raw peanuts established by Lovegren et al. (17,20) can be used to evaluate quality. The method can also be used to detect volatile contaminants. For example, the volatile profiles of three samples judged fair to good by the sensory panel were plotted in Figure 2. Sample 418 was an immature domestic grown Spanish peanut and was rated fair. Samples 406 and 400 were rated by the sensory panel as good peanuts. When a curve was plotted in this expanded scale, the contaminants are easily seen as those being over the 1500 counts per second range. Two of the contaminants were identified as hexane (23 min.) and toluene (37 min.). Another compound identified was limonene (48 min.), a citrus oil component, which was detected in sample 406. Since limonene is not known to be in peanuts, no explanation can be presented for the presence of that compound in these particular peanuts, other than that the peanuts were obvisouly contaminated. Ethanol (14 min.), which is not a contaminant, was unusually high in the immature peanuts. This high ethanol content, observed in other (but not all) immature peanuts examined, may represent increased curing problems of immature peanuts. Beasley and Dickens (2) reported that immature peanuts are more severely damaged flavor-wise by improper curing treatment than mature peanuts. The combination of immaturity and improper curing probably caused some of the off-flavor in the domestic 1980 crop. Curiously, in all of the imported peanuts analyzed, the ethanol content was exceptionally lower than the normal range of good US-grown peanuts. Just as the high ethanol content in the immature peanuts would suggest some type of improper curing was done, the low ethanol content in the imported peanuts would suggest a more efficient manner of curing is done abroad.

The volatile profile curves of peanuts representing three different flavor problems are shown in Figure 3. Peanut sample 392, from Argentina, was judged rancid

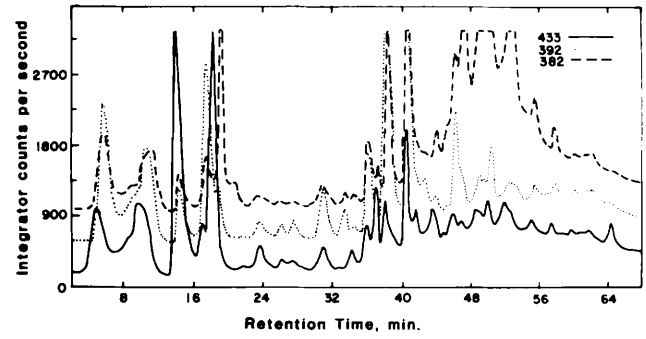

Fig. 3. Volatile profile of Chinese (382) peanuts demonstrating unusually high mound area; Argentina (392) peanuts, showing large oxidation products and above average mound area; Southern grown Spanish peanuts (433), classified immature and off-flavor. The bottom curve begins at ca. 200 counts and the other curves are off-set 400 counts for clarity.

by the sensory panel. In the volatile profile, the three largest peaks observed were pentane (17.5 min.), hex-

anal (38 min.) (over 4 ppm), and hexanol (40.5 min.) (over 5 ppm). The latter two compounds were off-scale, i.e., greater than 1500 counts. The mound area was somewhat higher than normal, which, when combined with the oxidation degradation products (pentane, hexanal, and hexanol), probably had a synergistic effect on the off-flavor.

The volatile profile from U.S. Southern-grown Spanish peanuts that were rated off-flavor by the panel is also shown, sample 433. Peanut butter made from these peanuts was also judged off-flavor. These peanuts were not judged rancid, which correlated with the low pentane, hexanal, and hexanol, but the off-flavor was described primarily as musty, metallic, and/or beany. The two largest peaks observed were ethanol (14 min.), and acetone (19 min.). The high ethanol content by itself probably does not cause an off-flavor, but the presence of a high ethanol content serves as an indicator of off-flavored peanuts. The mound area was somewhat higher than normal, compare sample 433 to 415 of Figure 1. In sample 433, the off-flavor is probably due to a synergestic effect of several volatiles of higher concentration than normally found. Whereas this profile, was observed in many so-called immature peanuts of the 1980 domestic crop, it was not found in all peanuts that were judged immature.

The overall quality of sample 382, from China, was rated one of the worst. Some of the off-flavor may be attributed to the off-scale hexanol and the nearly off-scale hexanal, since the sensory panel did identify a slightly rancid taste. More likely, the off-flavor could be attributed to the volatiles that were found in the mound area, from 43 to 63 min. Not only were three of these compounds greatly off-scale, but the over-all mound area showed a very high total volatile content. Undoubtedly, these compounds were largely responsible for the bad flavor. The compound found at 19 min. was acetone, which has not been known to contribute of off-flavor at the observed level.

That the mound area contributes to off-flavor was best determined by comparing volatiles from two samples obtained from Argentina. One of the samples, 451, was rated by our sensory panel to be fairly good peanuts, whereas the other sample, 452, was rated to be peanuts with very bad quality. Peanut butter made from sample 452 peanuts also had a very bad flavor, described as musty, petroleum-like, phenol, iodine, oily. The two volatile profile curves were practically superimposible, except for the mound area from 45 to 63 min, which was exceptionally larger in sample 452. Obviously, the flavor differences caused by volatiles has to be attributed primarily to the compounds found in the mound area. Results from GS/MS analysis of 452 showed that the mound area is comprised of various saturated hydrocarbons, substituted benzene derivatives, and secondary products of lipid oxidation, (Table 1). These results strongly suggest that the mound area is at least partially responsible for the musty flavor.

Peanuts that were analyzed by direct GC were also evaluated by sensory means. Data presented in Table 2 describe the intensity values of flavor characteristics of roasted peanuts as detected by the taste panel. The roasted peanut flavor, described as peanuttiness, was

Table 1. Identified compounds of the mound area.

Elution time (min)	Compound
43	Decane, Ethylbenzene
46	2-Pentylfuran, 3-CSB*
47	Undecane, 3-CSB
48.5	4-CSB
50.5	Dodecane
51	4-CSB
52	Tridecane
53.5	4-CSB
55	Tetradecane
57.5	Naphthalene, Pentadecane
62	Methylnaphthalene

* 3-or 4-Carbon Substituted Benzene

Table 2. Flavor characteristics of roasted peanuts. Intenstiy values*.

SAMPLE NO.	SOURCE	PEANUTTY	SWEET	BEANY	BITTER	MUSTY	RANCID	SULFUR	METALLIC
397	CHINA	3.44	0.83	1.81	1.88	3.11	2.50	0.88	1.11
382	CHINA	3.90	0.52	1.62	3.00	1.62	1.76	0.57	1.62
393	CHINA	3.45	1.27	1.81	1.73	1.95	1.77	0.77	1.36
390	INDIA	3.52	1.71	3.38	1.57	2.14	2.00	1.00	1.24
392	ARGENTINA	4.52	1.52	1.00	2.62	1.67	1.14	0.76	1.33
452	ARGENTINA	3.00	2.00	3.07	3.00	2.75	4.00	3.00	1.92
418	USA	4.55	0.68	1.09	2.14	1.50	1.14	0.45	1.05
433	USA	4.62	1.76	1.80	1.86	1.71	0.95	0.71	1.24
400	CHINA	4.30	1.15	1.35	1.60	0.50	0.50	0.25	0.55
434	CHINA	4.65	1.94	1.71	0.94	0.94	0.88	0.12	0.41
415	USA	5.27	1.27	1.27	0.86	0.41	0.54	0.41	0.50
373	ARGENTINA	4.35	2.15	1.15	0.65	0.35	0.60	0.30	0.50
451	ARGENTINA	5.60	2.50	1.80	0.00	1.50	3.00	0.41	0.91

*0, None; 1, Just Detectable; 2, Very Slight; 3, Slight; 4, Slightly Moderate; 5, Moderate; 6, Moderately Strong; 7, Strong; 8, Very Strong.

characteristic of all test samples. The intensity values suggested that peanuttiness was perceived as slight to moderately strong. Sample 452, as reflected by the intensity value of 3.00, had the weakest peanut flavor, whereas sample 451, with an intensty value of 5.60, had the strongest peanut flavor. A sweet flavor was detected in some of the roasted peanuts examined. The sweet taste in samples 452, 434, 451, and 373 was categorized very slight. Sweetness was judged below the detectable level in the other samples examined. Intensity ratings indicated the presence of detectable levels of a raw, beany peanut taste in some roasted peanut samples. Results suggested that samples 390 and 452 had the highest levels of beaniness that was described as slight, but clearly detectable. In samples 397, 393, and 390, the beany flavor was very slight. The most intense bitter tastes were recognized in samples 382, 392, and 452, whose intensity values identified the bitterness as either very slight or slight. Bitter taste was not detectable in samples 434, 415, 451, and 373. A musty taste was characterized in some of the 13 samples evaluated by the panel, but it was clearly recognizable in samples 397 and 452. Rancidity was also perceived in some of the samples, but sample 452 had the highest intensity value, which was characterized as slightly moderate. The panel described a slightly moderate sulfur taste in sample 452. A metallic taste was just detectable in some of the roasted samples, as reflected by intensity values below 2.00.

Each of the 8 flavor characteristics evaluated were assigned an intensity value as shown in Table 2. These

values reflect the overall quality ratings that were determined by analysis of variance, followed by Duncan's Multiple Range Test. Data presented in Table 3 represent the overall quality of the roasted imported and domestic peanuts, whose intensity values were shown in Table 2. The differences detected among the 13 samples were statistically significant at the 0.05 level. As shown in Table 3, the overall quality of samples 397, 382, and 393 was significantly different from samples 390 through 451. Sample 390 was significantly different from samples 434, 415, 373, and 451, but similar to those whose intensity values were above 5.9. Thse results also showed no significant differences, but similarities among samples 418, 433, 400, 434, 415, 373, and 451. All of those samples were categorized as having a "good" overall quality. In general, the results indicated that sample 397 was rated the poorest and was significantly different from 415, 373, and 451, which were rated good to fair.

Table 3. Overall quality of imported and domestic roasted peanuts.

SAMPLE NO.	SOURCE	OVERALL QUALITY RATING			
		QUALITY SCORE*	SIGNIFICANT DIFFERENCE**		
397	CHINA	6.72	A		
382	CHINA	6.48	A		
393	CHINA	6.18	A		
390	INDIA	6.00		B	
392	ARGENTINA	5.90		B	
452	ARGENTINA	5.86		B	
418	USA	5.41		B	C
433	USA	5.33		B	C
400	CHINA	4.60		B	C
434	CHINA	4.47			C
415	USA	4.36			C
373	ARGENTINA	4.30			C
451	ARGENTINA	3.31			C

*1, excellent; 3, good; 5, fair; 7, poor; 9, extremely poor.

**Scores with the same letter are not significantly different ($\alpha = 0.05$).

Conclusion

In analyzing off-flavor peanuts, at least three major indicators of off-flavor were identified. The first indicator was the presence of secondary products of lipid oxidation, hexanal, hexanol, and pentane, in concentrations that exceed 1500 counts per sec. (Figure 3). When these volatiles were off-scale (approximately 5 ppm) the peanuts were judged rancid by the sensory panel.

The second main indicator of peanuts that had an off-flavor problem was ethanol. In the immature domestic peanuts that were off-flavor, Figure 2, sample 418, the ethanol content was higher than normal (8 ppm compared to a normal range of 1-2 ppm). These results would suggest that more research is needed to develop curing or drying practices for immature peanuts to determine if the off-flavor problem can be minimized in event another "drought" year occurs.

The third indicator of off-flavor was the mound area, which occurs past 43 min. (Figures 1 and 3), and is comprised of saturated hydrocarbons, substituted benzenes, and secondary products of lipid oxidation, (Table 1). That those compounds contribute significantly to off-flavor in peanuts was well supported by sensory examination and direct GC analysis of samples 451 and 452. The mound area was observed in ground raw peanuts that were stored for two weeks at 40 C (19). Their results showed that the series of saturated hydrocarbons were from 10 to 16 carbons in length. They further concluded that the products were probably caused by some enzymatic reaction. This research is presently being pursued.

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