Application and Characteristics of Polymer Adsorption Method Used to Analyze Flavor Volatiles from Peanuts

L. L. Buckholz, Jr.,* D. A. Withycombe, and Henryk Daun

A method has been employed for the collection, characterization, and quantitation of headspace volatiles from roasted peanuts, using Tenax GC adsorption polymer. Two types of peanuts and three roasting conditions were used in the experiment. Collection time was 4 h, using 400 g of peanuts in a jacketed glass column held at 50 °C. Volatiles were swept by nitrogen into a $^1/_8$ in. o.d. glass trap packed with Tenax GC polymer. The trap was then inserted directly into the modified injection port of a gas chromatograph (GC) equipped with a flame ionization detector. Peaks were quantitated by a computing integrator, using an internal standard. Statistical analysis showed good reproducibility among runs as evidenced by the coefficient of variability which averaged 3.5%. Analysis of variance confirmed differences among roasting conditions. Conditions were established for the collection and transfer to a GC of aroma/flavor volatiles of roasted peanuts in proportions closely approaching their natural occurrence.

One of the most recent methods of flavor analysis which evolved with the development of sensitive gas chromatographic (GC) instrumentation is the headspace technique. In this procedure, the gaseous volatiles which are in equilibrium with the food are analyzed. Brown et al. (1972) developed a method of examining headspace volatiles of ground peanuts by gas extraction of volatile constituents directly onto a GC column. While this method offers the advantage of no loss of volatiles due to handling, the sample size is limited and no appreciable concentration of headspace volatiles can be achieved. In many instances, the concentration of volatiles in the headspace is too low for direct analysis. In these cases, collection and concentration of these substances are necessary.

ADSORPTION POLYMERS

In recent years, adsorption polymers have been used for collection, concentration, and subsequent GC analyses in a wide variety of applications. Novotny et al. (1974a) used a porous polymer adsorption precolumn for high-resolution GC analysis of the volatile constituents of body fluids. Murray (1977) described a technique for concentrating headspace, airborne, and aqueous volatiles on a porous polymer precolumn, and Zeldes and Horton (1978) used Tenax GC adsorbent polymer to trap volatiles in cigarette smoke. The use of adsorption polymers has become widespread in the testing of air pollutants (Murray, 1977). A recent symposium reviewed several uses of adsorption polymers for the headspace analysis of foods (Charalambous, 1978).

Sampling capacities depend on the adsorbates as well as the adsorbents. Adsorbents with the highest surface area will tend to have the highest sampling capacities. However, no single adsorbent will be best for every sampling application. The adsorbent must be chosen to fit a particular problem.

P-2,6-DIPHENYLENE OXIDE (TENAX GC) AS AN ADSORBENT

Tenax GC is a porous polymer based on *p*-2,6-diphenylene oxide. Murray (1977) showed that Tenax GC has a lower adsorption capacity than other polymers frequently used for headspace analysis because of its low specific surface area. According to Murray, Tenax GC also allowed breakthrough of some components of medium volatility which was attributed to selective adsorption of certain classes of compounds.

Murray agreed with Butler and Burke (1976) as to the low specific surface area of Tenax. Butler and Burke performed studies on capacities and efficiencies of various polymers, including Tenax, and concluded that "sampling capacities are determined by column capacities as well as column efficiencies". According to their studies, Tenax GC would be good for high boiling components due to its high thermal stability and low retention volume. This stability assures no bleed on GC columns during analysis and complete regeneration of the porous polymer by heating to 260 °C under a purge of helium gas. The polymer containing adsorbed headspace volatiles was found to be stable for up to 5 days at 0 °C with no decomposition of adsorbed volatiles. Early adsorption equilibrium and subsequent loss of some of the more volatile components were reduced by using three traps in series (Novotny, 1974b; Murray, 1977). Since the adsorbed volatiles are very stable on this polymer, concentration of headspace volatiles can be achieved by repeated adsorption of volatiles on the same trap (Mussinan, 1978). Water vapor does not affect Tenax GC performance (Novotny et al., 1974b).

Withycombe et al. (1978) used several polymers to trap the headspace volatiles from hydrolyzed vegetable protein (HVP) and found that, of the three polymers investigated, Chromosorb 105, Porapak Q, and Tenax GC, the volatiles trapped on Tenax GC contained the most characteristic HVP aroma. Since peanut headspace volatiles contain many notes similar to HVP, this was an important consideration in choosing Tenax GC for this study.

In our work, a simple inexpensive polymer adsorption method was employed and characterized for the collection and quantitation of headspace volatiles from fresh roasted peanuts.

EXPERIMENTAL SECTION

The two types of peanuts used for this study were "Runner no. 1" and "Spanish". Roasting was conducted under controlled parameters to obtain light, medium, and dark roasted peanuts. Details of the roasting conditions were described in a separate communication (Buckholz et al., 1979). The whole roasted peanuts were stored prior to analysis in glass containers at −32 °C in a nitrogen atmosphere.

Extraction and Collection. Extraction of headspace volatiles was conducted in a glass chromatographic column, 3.8 × 55.9 cm (1.5 × 22 in.), fitted with a fritted glass disk at the base and a 24/40 joint at the top. The column was

International Flavors and Fragrances, Union Beach, New Jersey 07735 (L.L.B., D.A.W.), and Rutgers–The State University, Cook College, Department of Food Science, New Brunswick, New Jersey 08902 (H.D.).

0021-8561/80/1428-0760$01.00/0

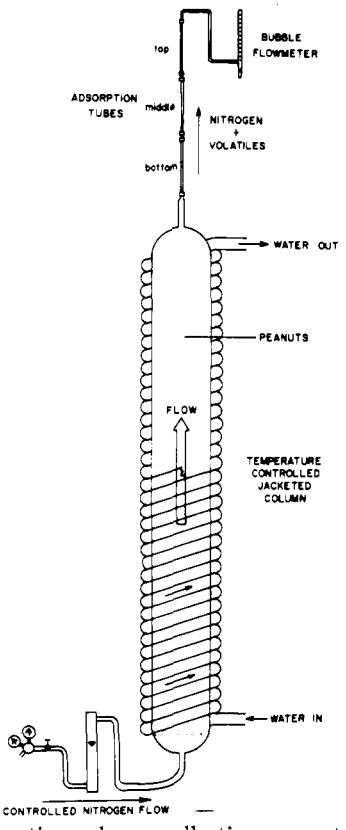

Figure 1. Adsorption polymer collection apparatus. Reprinted from *J. Food Sci.* **45**, 547 (1980). Copyright 1980 by Institute of Food Technologists.

wrapped with flat faced rubber tubing through which 50 °C water was circulated from a Lauda-Thermostat K-2 constant temperature bath (see Figure 1). A Teflon thermometer adapter was fitted in the 24/40 joint into which a $^1/_8$ in. o.d. × 4 in. glass adsorption tube assembly was secured. Each adsorption tube contained 40 mg of 60–80 mesh Tenax GC (Enka N.V.) contained between two plugs of silanized glass wool. Three traps in a series were used (Figure 2). Teflon Swagelok fittings were used to connect all traps. Nitrogen gas was used to sweep the volatiles onto the traps at a constant flow rate of 40 mL/min. The traps were preconditioned before use by holding them at 260 °C for 24 h in a heating manifold while purging with helium gas at a 12 mL/min flow rate.

Nitrogen Sweep Rate and Collection Time. In order to establish the nitrogen sweep rate and collection time, a series of preliminary experiments were performed. Single trap collections were used for all preliminary experiments. Nitrogen gas flow rates of 10, 20, 30, 40, 50, and 60 mL/min were evaluated. Collection times of 0.25, 0.5, 1, 2, 4, 8, and 12 h at the 40 mL/min nitrogen flow rate were also evaluated. These experiments were carried out with Runner no. 1 medium roast peanuts. (As a result of the preliminary experiments, the 4-h collection time was chosen for further experiments at a nitrogen sweep rate of 40 mL/min.)

Internal Standard. Two standard curves were developed to determine if there were losses of peanut volatiles due to incomplete recovery from the adsorption polymer.

Table I. General Experimental Design

1. Influence of flow rate
2. Influence of collection time
3. Influence of traps in series
4. GC analysis
   A. Method of quantitation
   B. Application of internal standard
5. Statistical analysis

Response factors were obtained by plotting peak area vs. concentration. Ethyl nonanoate was chosen as the internal standard, and a series of dilutions of this standard was made in anhydrous methanol. One standard curve was developed from the dilution series as recovered from the adsorption polymer and the second from direct injection of the dilution series as follows.

1. A curve was developed by injecting a series of dilutions (5, 10, 25, 50, 75, and 100% by weight) of ethyl nonanoate in methanol individually onto preconditioned Tenax GC traps. The traps were then inserted into the gas chromatograph, and the individual peak areas were recorded. The amount of each dilution injected onto the traps was 0.1 μL.

2. A second curve was developed by directly injecting a 0.1-μL quantity of the same series of dilutions into the gas chromatograph and recording these individual peak areas.

Linear regression was then used to plot the two curves for the internal standard dilution series, illustrating peak area vs. concentration. One curve was developed for the adsorption polymer dilution series and one curve for direct injection.

The following formulas were used for the regression analysis:

$$\text{slope } b = Sxy/Sx^2$$

$$\text{coefficient of determination} = R^2 = \frac{S(xy)^2}{(Sx^2)(Sy^2)}$$

$$\text{regression equation} = \hat{y} = \bar{y} + b(x - \bar{x})$$

where Sx^2 = sum of squares of x, Sy^2 = sum of squares of y, Sxy = sum of cross products of x and y, $\bar{x}$ = mean of x, $\bar{y}$ = mean of y, and $\hat{y}$ = predicted values for y.

GC Analysis. Table I illustrates the general experimental outline of the preliminary experiments performed in order to characterize the method.

The traps containing adsorbed volatiles were inserted directly into the modified injection port of the Varian 2700. A bypass line containing a toggle valve was inserted into the carrier gas line leading into the injector block. By throwing the toggle valve, the carrier gas could be diverted from the injector block into a flexible line containing a Swagelok fitting at the end. The adsorption polymer trap could be inserted into this fitting and locked. The trap was then inserted into the injector port through a previously bored, sized septum (sized to accept the trap with a tight fit), and the toggle valve was thrown. This directs the carrier gas through the trap, thus sweeping the entrapped volatiles through the injector port and onto the column. A 400 ft × 0.032 in. i.d. glass capillary column, coated with SE30, was used. The column temperature was programmed from 50 to 190 °C at 2 °C/min. Percent

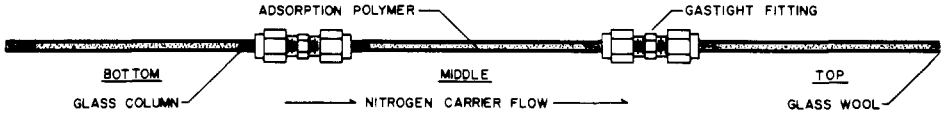

Figure 2. Illustration of the three traps in series. Reprinted from *J. Food Sci.* **45**, 547 (1980). Copyright 1980 by Institute of Food Technologists.

composition was calculated by a computer (Craven et al., 1971). Peak areas were determined through integration by peak area normalization, using a Varian 220L chromatography data system. Thirty-two peaks of 0.1% or more of the total peak area were selected for quantitative consideration in the GC profiles. The same peaks were present in all samples. Percent composition was determined by using the normalization formula of McNair and Bonelli (1969): % A = (area A/total area) × 100. Six collections and subsequent GC analysis were performed on each roast sample or a total of 36 collections and GC analyses for all roast samples and both types. Quantitation was done by internal standard, using the formula from Bills et al. (1963): weight unknown = (weight standard)/(area standard) × (area unknown)/(response factor). The internal standard was applied to each peanut charge (400 g) as described below.

The peanuts were spread out in a stainless tray. Four grams of a 0.5% methanolic solution of ethyl nonanoate was then sprayed onto the peanuts by using a standard chromatographic spray reagent applicator. This application applied 50 ppm of ethyl nonanoate to the surface of the peanuts. The portion of internal standard which was volatilized and adsorbed onto the adsorption polymer trap with the peanut headspace volatiles could be calculated from the response curves. The internal standard peak areas were averaged for the 36 collections and subsequent GC analyses. This average peak area was then plotted on curve 1 (adsorption polymer standard curve) and the corresponding concentration obtained. This concentration was then subsequently traced on curve 2 (direct injection standard curve) to obtain the peak area corresponding to it. The difference in peak areas between the adsorption polymer standard curve and the direct injection standard curve produced a factor which compensated for losses of peanut headspace volatiles due to incomplete recovery from the adsorption polymer collection method.

Statistical Analysis. 1. Precision of the adsorption polymer method was determined statistically using the six largest peak areas found in the GC profiles. These were peaks 4, 6, 7, 13, 18, and 20. The peak areas were averaged individually for each of the six GC analyses and the standard deviation, standard error, and coefficient of variability determined. This was done for all conditions and types. The coefficient of variability was used as a measure of precision.

2. Reproducibility of the adsorption polymer method was determined by comparing the six (same) largest peak areas of the five subsequent GC analyses to the peak areas of the first analysis on a percent basis.

The overall percent differences for types were then determined in the following steps: (A) The average peak areas minus the percent differences of the individual peaks for the five subsequent runs were determined by the formula (subsequent GC peak area)/(initial GC peak area) × 100 = % difference. (B) The results of step A were then averaged for each condition within types. (C) The results in step B were then averaged for types.

RESULTS AND DISCUSSION

Extraction Rate. Figure 3 shows a comparison of GC profiles for 10, 40, and 60 mL/min nitrogen flow rates. From this figure it is evident that with the low flow rate (10 mL/min) the highly volatile front end components constitute the major fraction adsorbed, whereas with the high flow rate of 60 mL/min, the back end or least volatile components mainly remain and the highly volatile components in the front end are lost by desorption. The 40 mL/min experiment showed a balance between the more volatile and less volatile components. Examination of the extractions utilizing various nitrogen flow rates found a rate of 40 mL/min to be optimal. One-hour collections were used in the flow rate experiments.

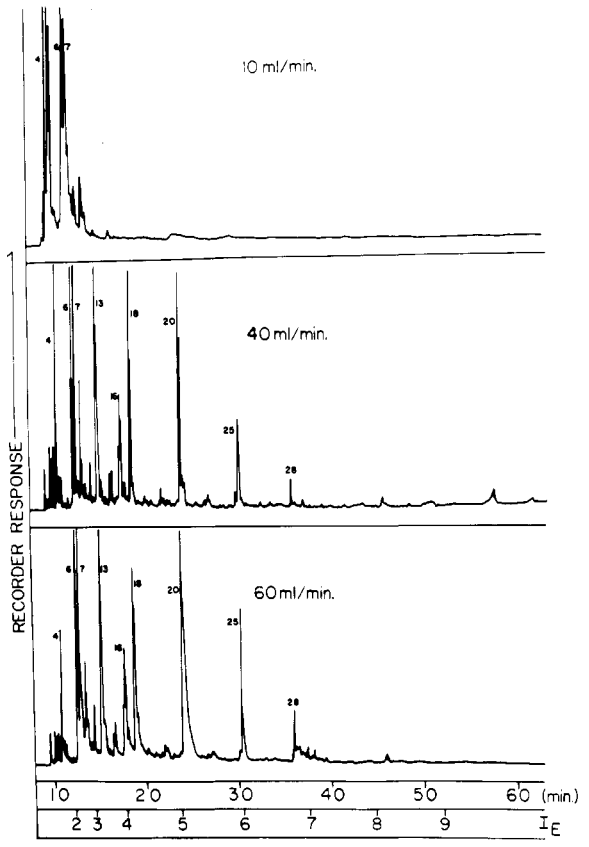

Figure 3. A comparison of GC profiles for 10, 40, and 60 mL/min of nitrogen gas flow rates, using Runner no. 1 medium roast peanuts.

Table II. Total Volatiles Collected for the Most (I), Middle (II), and Least (III) Volatile Zones of the GC Profiles for the 4-, 8-, and 12-h Collections (400 g of Peanuts Was Used per Collection)

GC chromatogram sections	4 h, 10^{-6} g	2 h, 10^{-6} g	8 h, 10^{-6} g	12 h, 10^{-6} g
most volatile peaks 1-10	130.8	210.6	152.3	94.3
medium volatile peaks 11-19	99.0	42.7	132.8	120.7
least volatile peaks 20-32	43.2	18.3	92.7	119.1
total volatile components	273.0	271.6	377.8	334.1

Sensory Quality Criteria of the Flow Rate. The flow rate of 40 mL/min was selected on the basis of sensory analysis as most resembling the headspace of peanuts in their natural state. Headspace volatiles collected for the 10, 40, and 60 mL/min were evaluated organoleptically. These volatiles samples were previously described under the sensory quality criteria for the collection time.

Collection Time. Figure 4 shows a comparison of the 4-, 8-, and 12-h GC profiles. Examination of total volatiles collected and the balance between the low, medium, and high boiling point constituents showed that the 4-h collection was optimum. This is shown in Table II. This was also established by sensory criteria. The high concentrations of the most volatile components tapering off with the gradual increase of the least volatile components with time is evident. Table III also demonstrates this trend by comparing the major peak areas for the various

Table III. Comparison of the Major Peaks of Various Collection Times to the 4-h Collection Time on a Percent Basis

	4 h		0.25 h		0.5 h		1 h	
peaks	area[a]	%	area	%	area	%	area	%
4	7.450	100.00	30.076	403.70	15.989	214.62	22.358	300.11
6	9.460	100.00	5.981	63.22	7.448	78.73	22.005	232.61
7	26.271	100.00	12.987	49.43	6.232	23.72	52.944	201.53
13	9.779	100.00	1.156	11.82	1.580	16.16	7.057	72.16
18	6.615	100.00	0.171	2.57	0.273	4.13	1.781	26.92
20	9.181	100.00	0.311	3.39	0.435	4.74	3.556	38.73
25	2.451	100.00	0.00	0.00	0.273	11.14	0.925	37.74
	4 h		2 h		8 h		12 h	
peaks	area[a]	%	area	%	area	%	area	%
4	7.450	100.00	14.263	191.45	9.242	124.05	5.025	67.44
6	9.460	100.00	14.770	156.13	14.655	154.92	8.316	87.91
7	26.271	100.00	38.308	145.82	28.034	106.71	22.275	84.79
13	9.779	100.00	5.902	60.35	21.351	218.34	23.801	238.06
18	6.615	100.00	1.672	25.28	13.656	206.44	14.859	224.63
20	9.181	100.00	3.371	36.72	19.377	211.06	30.760	335.04
25	2.451	100.00	1.132	46.19	5.856	238.92	10.220	416.97

[a] Area ÷ 10^5.

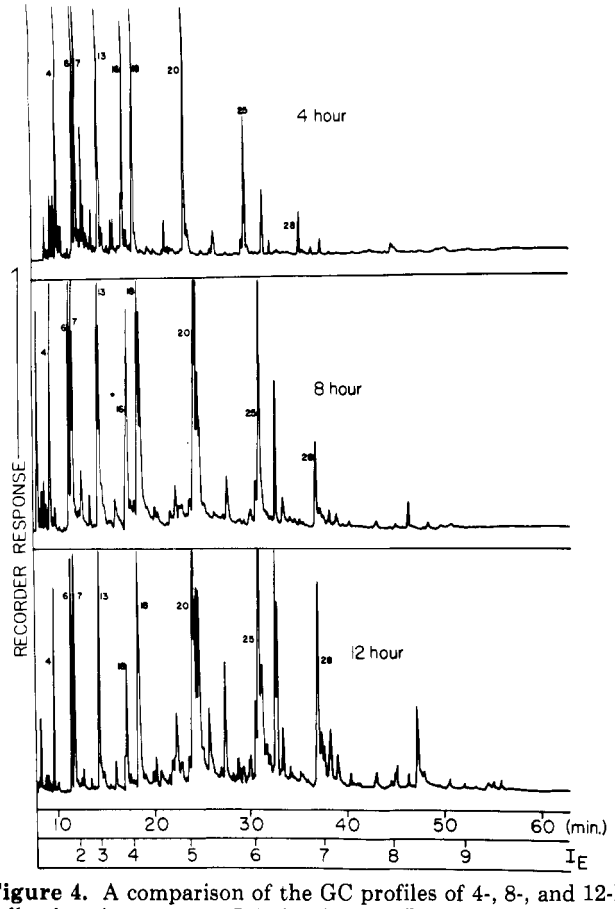

Figure 4. A comparison of the GC profiles of 4-, 8-, and 12-h collection times at 40 mL/min nitrogen flow rate. Runner no. 1 medium roast peanuts were used.

collection times to those of the 4-h collection time on a percent basis.

The six major peak areas chosen for comparison throughout this experiment were peaks 4, 6, 7, 13, 18, and 20.

The identity of these peaks by mass spectrometry is as follows: 4, isobutyraldehyde; 6, isovaleraldehyde; 7, 2-methylbutanal; 13, 1-methylpyrrole; 18, 2-methylpyrazine; and 20, 2,5-dimethylpyrazine.

Sensory Quality Criteria of the Collection Time. One of the most important considerations for choosing the 4-h collection time was the result of a sensory evaluation

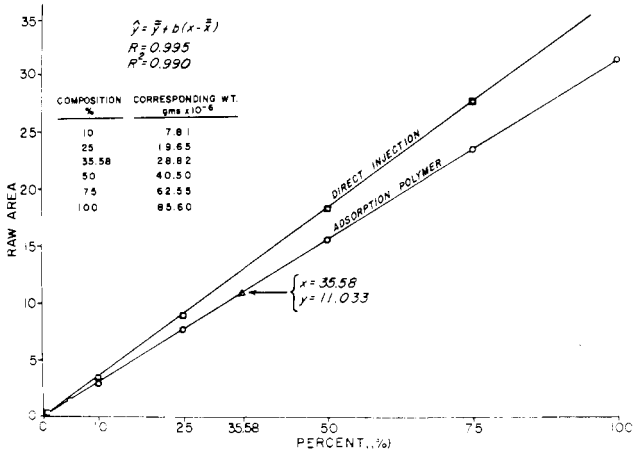

Figure 5. Graph of the concentration curves developed for the internal standard. Curve 1 is the adsorption polymer curve and curve 2 is the direct injection curve.

of the collected headspace volatiles. The 2-, 4-, 8-, and 12-h collections were evaluated organoleptically by desorbing the volatiles from the adsorption polymer traps (placed in a heating manifold) into glass U traps cooled in liquid nitrogen. The desorbed volatiles were swept into the glass U-shaped traps by a helium gas flow rate of 12 mL/min. The traps were sealed, brought to room temperature, and opened, and the aroma was evaluated by a team of three experienced flavorists. It was agreed upon by all judges that the aroma of the 4-h sample was most similar to a true roasted peanut aroma. Harsh green notes predominated in the 2-h sample and in the 12-h sample the burnt notes predominated.

"True Ratio". The porous polymer adsorption method offers the advantage of being able to approach a "true ratio" of volatiles adsorbed that represents the similar ratio as found in nature, whereas other methods do not offer this flexibility. The work done in this experiment shows that this ratio can be approximated by adjusting times and flow rates and evaluating organoleptically.

Internal Standard. Figure 5 illustrates the two concentration curves developed for the internal standard. (The internal standard peak would be at position 9 on the IE scale in GC profile figures.)

Curve 1 is the curve developed from application of the standard to the adsorption polymer traps prior to GC analysis.

Table IV. Comparison of Linear Regression Values for the Internal Standard Curves Developed for Both the Adsorption Polymer Collection Method and Direct Injection

	direct injection	adsorption polymer
slope	0.3635	0.3108
y intercept	−0.2076	−0.0262
coeff determ	0.903	0.992
regression eq	$\hat{y}$ = 0.3635 (concn − 0.2076)	$\hat{y}$ = 0.3108 (concn − 0.0262)

Table V. Total Volatiles Collected in Each Series Trap for Each Chromatogram Section (This Collection Represented 400 g of Peanuts)

GC chromatogram sections	bottom trap, 10^{-6} g	middle trap, 10^{-6} g	top trap, 10^{-6} g
most volatile peaks 1-10	61.8	56.0	66.0
middle volatile peaks 11-19	56.3	27.7	24.0
least volatile peaks 20-32	29.5	1.4	1.4
total	147.6	85.1	91.4

Table VI. Comparison of Statistical Results for Precision and Reproducibility of Headspace Volatiles Collected for Both Peanut Types

peak no.	4	6	7	13	18	20
			Runner			
SD[a]	5.37	6.20	13.87	8.03	1.90	4.27
SE[b]	1.71	2.49	3.49	3.19	0.76	1.69
coeff var[c]	6.00	3.53	3.80	4.30	2.36	3.21
			Spanish			
SD	1.63	3.11	11.53	8.70	3.10	3.14
SE	0.90	1.24	4.65	3.43	1.21	1.24
coeff var	2.48	2.80	3.50	3.52	2.94	2.92

[a] Standard deviation. [b] Standard error. [c] Coefficient of variation.

Curve 2 was developed from the direct injection series. Linear regression calculations are listed in Table IV.

It was observed that the peak areas obtained by direct injection were higher than by the adsorption polymer application. This indicated that not all the ester was recovered from the adsorption polymer application. To compensate for this in quantitating peak areas, a factor was developed as follows: the average area from 36 replicas of ethyl nonanoate plotted on curve 1 was 11.033×10^5, which corresponded to 28.82×10^{-6} g. The area corresponding to 28.82×10^{-6} g on curve 2 was 12.727×10^5, which resulted in the calculation of the factor 12.727/11.033 = 1.154. This factor was used to make adjustments in the quantitated volatiles obtained from the adsorption polymer series.

GC Analysis. *Traps in Series.* One limitation found with this adsorption polymer is the partial loss of some of the highly volatile compounds. Usually these compounds

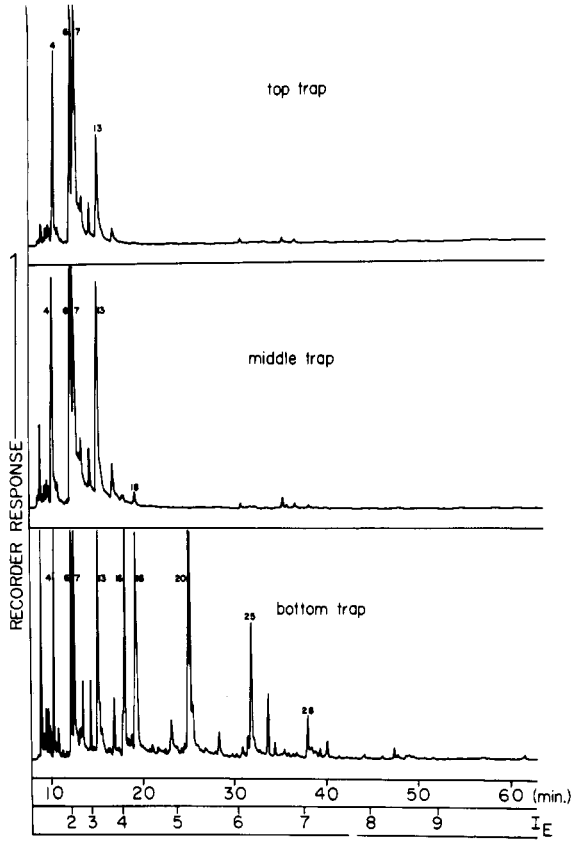

Figure 6. A comparison of GC profiles for the three traps in series showing the bottom trap, middle trap, and top trap. The breakthrough of more volatile components is illustrated in the upper two traps.

are not significant components of flavor to peanuts. To compensate for these losses due to early adsorption and desorption, three traps were used in a series as recommended in the literature. Figure 6 shows GC profiles of the three traps in series as discussed by Novotny et al. (1974) and Murray (1977). The first trap in the series collected volatiles in all three zones, most, medium, and least volatile components, while the second and third traps collected predominantly the most volatile and some medium volatile components. Table V shows the total volatiles collected by each trap and for each section of the chromatogram. The peak areas of the corresponding numbered peaks in traps 1, 2, and 3 were totaled. The totaled peak areas for the individual peaks were then quantitated as 10^{-6} g via the internal standard. Some volatiles in the front end of the chromatogram reach a very early adsorption-desorption equilibrium and break through into the second and third traps. This was observed after only 15 min of collection as shown in Figure 7.

Statistical Analysis. The standard deviation, standard error, and coefficient of variability for repetitive GC analyses for each roasting condition are listed in Table VI.

Table VII. Major Peak Areas for the Five Subsequent GC Analyses Compared to the Initial Analysis on a Percent Basis

	Runner no. 1			Spanish		
peaks	light	medium	dark	light	medium	dark
4	92.54	99.29	98.93	103.22	103.37	104.12
6	100.30	96.67	101.41	99.37	101.02	101.00
7	95.31	97.84	101.16	98.58	102.83	101.21
13	100.36	100.10	96.00	102.99	100.83	98.79
18	97.89	103.83	100.96	103.19	100.90	102.20
20	95.05	98.60	100.50	102.03	98.20	96.87

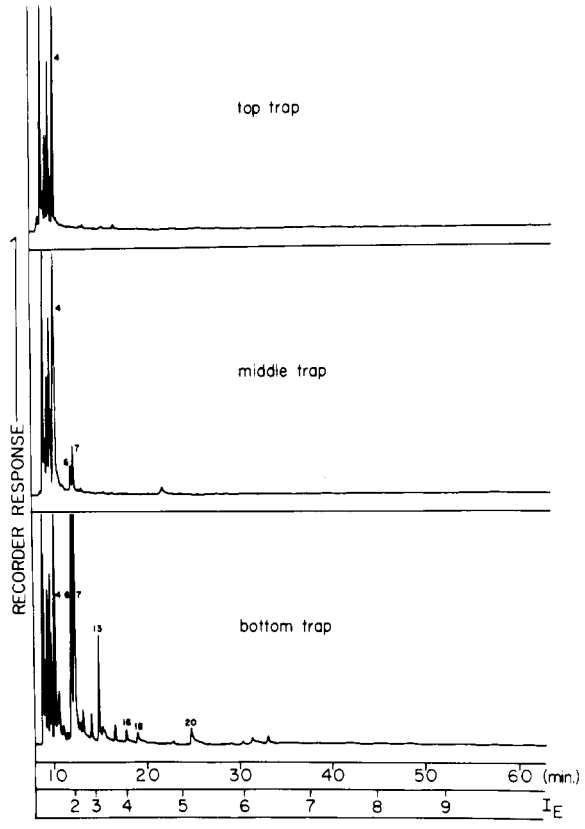

Figure 7. GC profiles showing breakthrough of highly volatile components in the peanut headspace after only 15 min of collection.

The six major peak areas were averaged for each roasting condition within types and statistically analyzed for each type. The coefficient of variability showed good precision for the analysis for both types. The average coefficient of variability for all 36 replications was 3.5%.

Reproducibility. To determine reproducibility, the selected peak areas for the five subsequent GC analyses were compared to the peak areas for the first analysis on a percent basis for each roasting condition (Table VII). These results were then averaged for types to produce the final percent difference among replicate peak areas: Runner no. 1 = 1.29% difference and Spanish no. 1 = 1.18% difference. These results indicate excellent reproducibility for the collection method and subsequent GC analysis.

Literature reports have claimed that one adsorption polymer is not suitable for all applications; the use of the proper adsorption polymer is almost a "customized" application. Withycombe et al. (1978) found that Tenax GC provided the most organoleptically characteristic hydrolyzed vegetable protein (HVP) isolate even though a greater number of constituents were provided from other polymers.

CONCLUSIONS

Tenax GC has been found very useful for adsorption of headspace volatiles that represent a GC profile ratio similar to that perceived by human senses in the original product. The use of the adsorption polymer technique proved to be a rapid, economical method for collecting headspace volatile components of roasted peanuts. Good reproducibility (1.24%) and precision (3.5%) were obtained with this method. One limitation found with the method is the low adsorption–desorption equilibrium of some of the more highly volatile components. However, the method offers many advantages with respect to both the size of sample to be extracted and extraction time and the reduced loss of volatiles due to isolate handling or transfer. Due to the similarity of the chemical composition, the polymer adsorption method should be applicable for other heat processed (roasted) foods such as cocoa and coffee.

LITERATURE CITED

Bills, D. D., Khatri, L. L., Day, E. A., *J. Dairy Sci.* **46**, 1342 (1963).
Brown, D. F., Dollear, F. G., Dupuy, H. P., *J. Am. Oil Chem. Soc.* **49**(1), 81 (1972).
Buckholz, L. L., Jr., Hruza, A., Daun, H., Chang, S., presented at the 13th Middle Atlantic Regional Meeting of the American Chemical Society, Monmouth College, West Long Branch, NJ, March 19–23, 1979.
Butler, L. D., Burke, M. F., *J. Chromatogr. Sci.* **14**, 117 (1976).
Charalambous, G., "Analysis of Foods and Beverages, Headspace Techniques", Academic Press, New York, 1978.
Craven, D. A., Everett, E. S., Rubel, M., *J. Chromatogr. Sci.* **9**, 541 (1971).
McNair, H. M., Bonelli, E. J., Basic Gas Chromatograph Varian Aerograph, Palo Alto, CA, 1969.
Murray, K. E., *J. Chromatogr.* **135**, 49 (1977).
Mussinan, C., private communication, International Flavors & Fragrances, Union Beach, NJ, 1978.
Novotny, M., McConnell, M. L., Lee, M. L., Farlow, R., *Clin. Chem.* **20**(9), 1105 (1974a).
Novotny, M., Lee, M. L., Bartle, K. D., *Chromatographia* **7**(7), 333 (1974b).
Withycombe, D. A., Mookherjee, B. D., Hruza, A., in "Analysis of Foods and Beverages, Headspace Techniques", Academic Press, New York, 1978, p 81.
Zeldes, S. G., Horton, A. D., *Anal. Chem.* **50**(6), 779 (1978).

Received for review September 28, 1979. Accepted February 25, 1980. Presented at the 1979 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, March 5–9, 1979.