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Instrumental Analysis of Volatiles in Air-and Nitrogen-Packed Peanut Butter

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ABSTRACT

Air- and nitrogen-packed samples from the same production lot of peanut butter, stored in the dark at 25°C for 1 yr, were analyzed periodically by direct gas chromatography. The ratio of methylbutanal to hexanal was consistently higher in nitrogen-packed than in equivalent air-packed samples and decreased throughout the storage period for both types of samples. Correlation coefficients, significant at 0.1%, were 0.99 for nitrogen-packed and 0.96 for air-packed samples. A total of 35 volatile components of peanut butter were identified by combined direct gas chromatography - mass spectrometry, and another 6 were tentatively identified.

Key Words: Peanut butter, volatiles, direct gas chromatography, mass spectrometry.

Since flavor is a major factor in determining the acceptability of peanut products, volatile components that may be related to flavor have been investigated extensively (2, 3, 4, 10, 11, 15, 16, 17, 18, 19, 20, 21, 23, 24, 26). Concentrates of peanut volatiles or their derivatives were prepared from peanut oil, ground peanuts or slurries of ground peanuts by solvent extraction, distillation or column chromatography. Concentrates of peanut volatiles were analyzed by gas chromatography (GC) combined with mass spectrometry (MS), or were separated into classes or individual compounds and then identified by a variety of methods. Such studies are expensive to conduct and require large quantities of sample, and hence cannot be used routinely. On the other hand, direct GC, a procedure where the original sample is placed in the inlet of a GC to distill volatiles that are collected on the GC column and then analyzed, requires 1 g or less of sample and offers a relatively rapid method for analyzing volatiles (5, 6, 7, 8, 13, 22). Effluents from the column can be passed through a separator into a MS for identification. The present study was undertaken to determine whether different kinds or amounts of volatiles develop in peanut butter samples stored under air and nitrogen.

Materials and Methods

Shelf Life

Jars from two cases each of air-and nitrogen-packed peanut butter from the same production lot were stored in the dark at about 25°C. Samples from each case of peanut butter were analyzed by direct GC at intervals of 1, 2, 4, 6, 8, 10, and 12 mo after production. To insure that only well-sealed samples were used for this study, partial pressure of oxygen and vacuum in the head space of each jar was determined just before the jar was opened. A Beckmann[2] head space sampler with model 777 oxygen analyzer was used. The head space in the jars was ca 50 ml.

The general procedure for direct GC analysis of peanut butter has already been described (7). For the current work, the published procedure was modified as follows: 1. To promote elution of volatiles, the inlet temperature was raised to 140°C, the rod holding the sample was wrapped with glass wool to increase the surface area of the peanut butter, and 20 ml of deionized water was placed on the glass wool over the sample rod. 2. To prevent interference with the methylpropanal peak by material bleeding from silicone septums and O-rings, a Teflon O-ring was used and a Teflon disk was placed beneath the septum and bound to it with Teflon tape. 3. To prevent premature elution of methanol and acetaldehyde a wet towel was wrapped around the column to maintain its temperature at about 20°C while the sample remained in the inlet and a lower carrier gas flow rate, 20 ml/min, was used. 4. After the sample was taken from the inlet, the wet towel was removed and the column oven was heated rapidly to 50°C, and held there for 2 min, then heated at 4°C/min for 30 min, 2°C/min for 15 min, and held at 200°C for 20 min.

Identification of Volatile Components

An air- and a nitrogen-packed peanut butter sample that had been stored for 18 mo in the dark at 25° and -15°C, respectively, were analyzed by GC-MS. The instruments used were a Tracor MT-222 gas chromatograph interfaced to a Hewlett Packard 5930 A (quadrapole) mass spectrometer via a silicone membrance separator, and an INCOS 2000 mass spectrometer data system (MS-DS).

Samples were analyzed on two different stainless steel columns, 0.125 in. OD, 0.085 in. ID, one 6 ft long, packed with Porapak P; and the other 8 ft. long packed with Tenax GC-Poly MPE (8). The same operating conditions were used with each column. A liner containing 1.0 g of peanut butter was sealed in the inlet (kept at 140°C) of the GC for 20 min, while volatiles that distilled from the sample collected on the cool (35°C) column of the chromatograph. After the liner with the spent sample was removed from the inlet, the column oven was heated to 90°C in 3 min, held there for 5 min, then heated to 190°C at 3°C/min and held there for 20 min. The flow rate for the helium carrier gas was 35 ml/min. For the mass spectrometer, ionization potential was 70 eV and the scan range was 29-235 AMU.

Volatiles were identified by comparing their gas chromatographic retention times and mass spectra with data for known compounds obtained on our instruments, or with published data (1, 12, 14, 24). Tentatively identified compounds could not be identified definitely because too many other compounds were present in the same peaks or because the amounts were too small to give suitable spectra. In general, the tentative identifications are based on detection of one or two characteristic ions at a reasonable retention time for the compound in question.

Results and Discussion

In earlier work (7) we showed that ratios of either methylpropanal or 2(3)-methylbutanal to hexanal tended to decrease as flavor quality of peanut butters decreased. In the current study, both of these ratios were found to be consistently higher in nitrogen-packed than in equivalent air-packed samples (Fig. 1 and 2). Measurements showed that 85% of the oxygen in the head space of the air-packed samples was depleted within 1 mo, and that none remained after 2 mo. This obser-

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[2]Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U. S. Department of Agriculture over others not mentioned.

vation is in accord with the data in Figures 1 and 2. Although no measurements were made, it is reasonable to assume that at 0 time ratios of methylpropanal and 2(3)-methylbutanal to hexanal were identical in the air- and nitrogen-packed samples. Therefore, ratios of methylpropanal and 2(3)-methylbutanal to hexanal must have decreased much more rapidly in the air- than in the nitrogen-packed samples during the first month of storage, the period when most of the oxygen in the air-packed sample was consumed. After the oxygen was depleted the rates of change for these ratios were not radically different for the two packing media. The natural logarithms of these ratios gave good correlations with time stored for both air- and nitrogen-packed samples for analyses made after storage periods of 1 to 12 mo (Table 1).

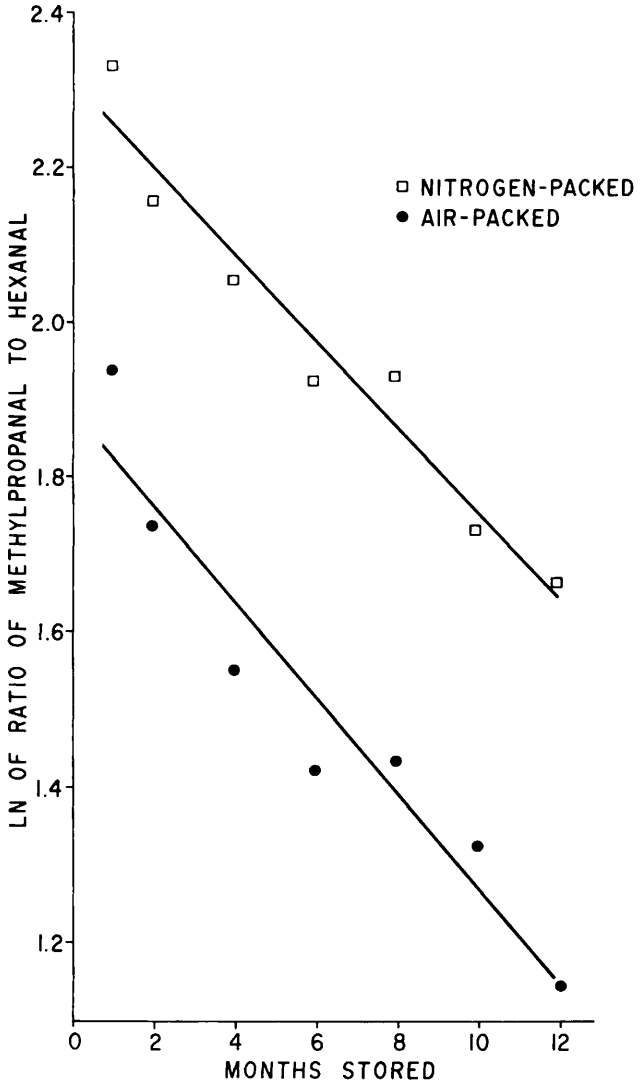

Fig. 1. Regression of natural logarithms of ratios of methylpropanal to hexanal on months stored for air- and nitrogen-packed peanut butter samples.

The Porapak P column used for quantitive analysis (Fig. 3, curve B) of peanut butter volatiles was not entirely satisfactory for GC-MS. Excessive bleeding at the higher temperatures overloaded the data system and made it difficult to identify some peaks, hence,

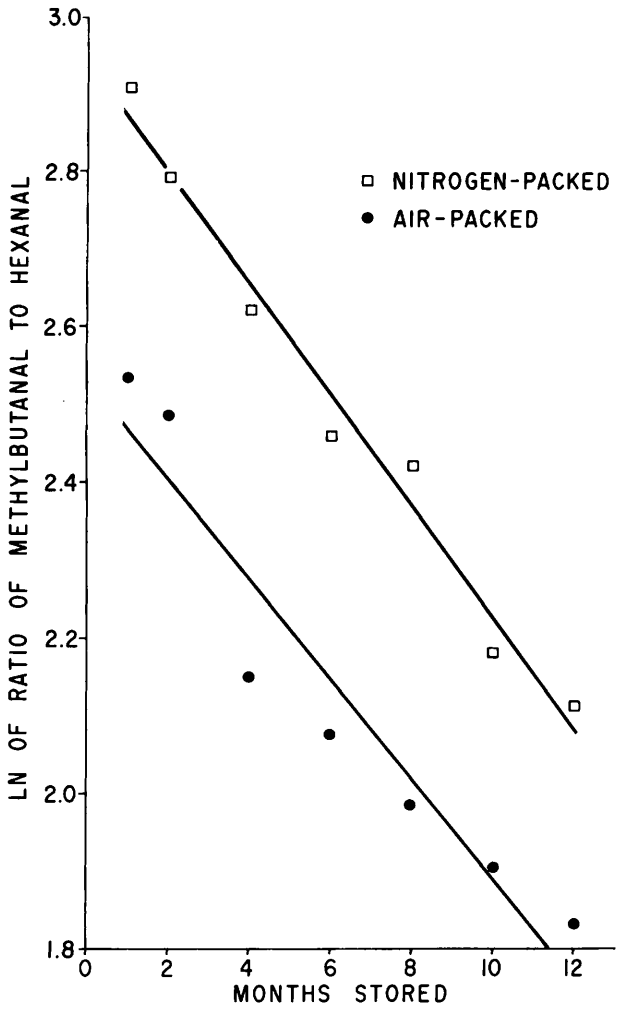

Fig. 2. Regression of natural logarithms of ratios of methylbutanal to hexanal on months stored for air- and nitrogen-packed peanut butter samples.

Table 1. Linear regression of natural logarithms of peak area ratios with months stored.

Packed in	Ratios	Correlation coefficients[1/]	Coefficient of variation of regression
Nitrogen	Methylpropanal/hexanal	- 0.97	2.51
	Methylbutanal/hexanal	- 0.99	1.58
Air	Methylpropanal/hexanal	- 0.96	4.42
	Methylbutanal/hexanal	- 0.96	3.45

1/ Significant at 0.1%.

the samples were also analyzed on a Tenax GC-Poly MPE column (Fig. 3, curve A). This column packing

is similar to Porapak P in resolving powder, but is more heat stable (25). Its lower bleed rate reduced the MS background and permitted use of higher MS-DS sensitivities.

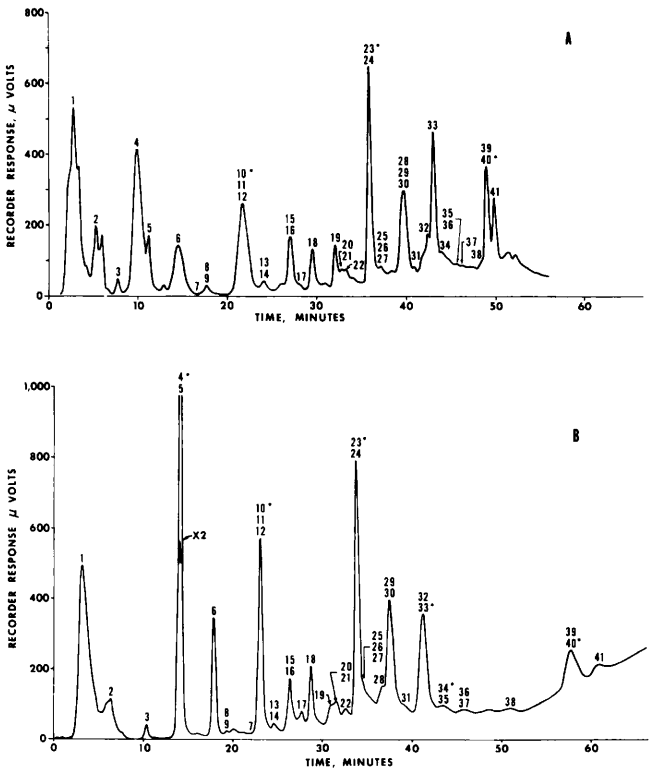

Fig. 3. Components identified in 18 mo old air-packed peanut butter by GC-MS. A, Tenax GC - Poly MPE column; B, Porapak P Column. (1) Methanol, (2) Acetaldehyde, (3) Ethanol, (4) Pentane, (5) Acetone, (6) Methylpropanal, (7) Acetic Acid, (8) Butanal (t), (9) Butanone (t); (10) 2-Methylbutanal, (11) 3-Methylbutanal, (12) Benzene, (13) Pentanal, (14) 2-Pentanone, (15) N-Methylpyrrole, (16) Dimethyldisulfide, (17) Toluene, (18) Hexanal, (19) 2-Methylpyrazine, (20) Furfural (21) Ethylbenzene, (22) Xylene (t), (23) 2,5-Dimethylpyrazine, (24) 2,3-Dimethylpyrazine, (25) Ethylmethylbenzene (t), (26) 2-Heptenal (t), (27) 2,4-Hexadienal (t), (28) Benzaldehyde, (29) 2-Ethyl-5-methyl-pyrazine, (30) 2, 3,5-Trimethylpyrazine, (31) 2-Isopropenylpyrazine, (32) 2-Ethyl-3, 6-dimethylpyrazine, (33) Phenylacetaldehyde, (34) Methylisopropenylpyrazine (35) 2-Acetylpyrrole, (36) 2,5-Diethyl-3-methylpyrazine, (37) 6,7-Dihydro-5H-cyclopentapyrazine, (38) 2-Methyl-6,7-dihydro *5H*-cyclopentapyrazine, (39) *trans*-2, *cis*-4-Decadienal, (40) 4-Vinylphenol, (41) *trans*-2, *trans*-4-Decadienal. (t) = Tentative. *designates major component of complex GC peak.

Compounds identified with the Tenax GC-Poly MPE column are given in the legend of Figure 3. Once these identifications were made, sufficient spectral data could be extracted from the Porapak P runs to permit assignment of the compounds to the proper peaks (Fig. 3, curve B). With the exception of ethylmethylbenzene, all of these compounds have been reported in peanut products (2-5, 9, 14, 15, 20, 24). In addition to the compounds that were identified, MS data revealed several broad hydrocarbon peaks that could not be identified. Their retention times correspond fairly well to C_8 to C_{15} normal hydrocarbons, with C_{12} emerging at about 42 min (Fig. 3, curve A). The same compounds were identified in both air- and nitrogen-packed samples.

One of the greatest advantages of the MS-DS in this type of work is its ability to function as a selective detector. For example, with the flame ionization detector and Tenax GC - Poly MPE column, a single peak (Fig. 3, curve A) was observed at 40 min. However, the mass spectra (scans 362 to 382, Fig. 4) for this peak could not be interpreted in terms of a single compound. Use of a DS program which plotted intensities of individual ions, as well as total ion intensity, against scan number showed that the total ion intensity and some of the individual ion intensities had maximums in scans 371-373, but that there were two other groups of ions with maximum intensities in scans 368 and 376. Another DS program gave spectra for each peak, corrected for the overlapping of adjacent peaks, which matched published spectra.

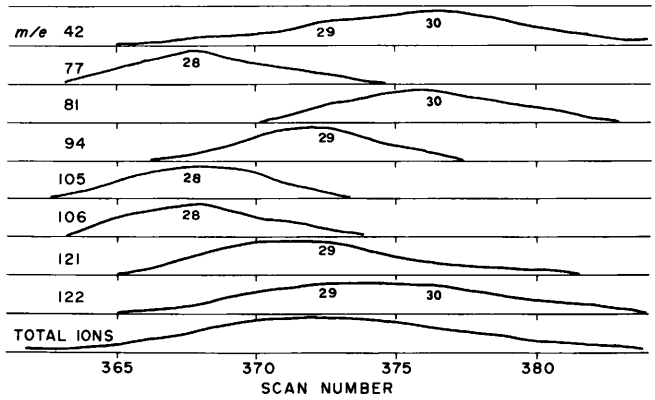

Fig. 4. Plots of intensities of total and characteristic individual ions against scan number from MS-DS analysis of a single GC Peak. (28) Benzaldehyde, (29) 2-Ethyl-5-methylpyrazine, (30) 2, 3, 5-Trimethylpyrazine.

The behavior of acetic acid during GC analysis is interesting. Although no peak was observed on the chromatograms for acetic acid (Fig. 3), it was identified by GC-MS. Apparently the acetic acid in the 0.2 g samples used for the chromatograms in Figure 3 was completely absorbed by the columns, but the 1.0 g samples used for GC-MS provided enough excess acetic acid to allow its identification. When no water was added to the peanut butter, as for GC-MS analysis, acetic acid eluted from the Tenax GC -Poly MPE column at 15 min instead of 17 min, thus a high acetic acid content may interfere with identification of methylpropanal on this column, but should not affect its quantitative analysis. On the other hand, on the Porapak P column, acetic acid occurs as a broad peak underlying the methylbutanal peak, whether or not water is added. Nevertheless, we did not encounter any serious interference with measurements or identification of methylbutanal on Porapak P colums.

Summary and Conclusions

No qualitative differences were found between

peanut butter samples from the same production lot that were packed in air and nitrogen. However, during storage for 1 yr, ratios of methylpropanal and methylbutanal to hexanal, determined by direct gas chromatography, were consistently higher for nitrogen- than for air-packed samples. Natural logarithms of these ratios, which have been shown to decrease as peanut butter flavor deteriorates (7), gave good negative correlations with storage time for both types of samples. Although peanut butter is a complex product, direct GC-MS, a relatively simple analytical tool, identified 35 of its volatile components, and tentatively identified 6 others. Furthermore, multiple components were identified in apparently simple peaks of the chromatograms.

Acknowledgement

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Literature Cited

1. A. S. T. M. Committee E-14 on Mass Spectrometry, Subcommittee on Data and Information Problems, 1969. Index of Mass Spectral Data. A. S. T. M., Philadelphia, Pa.

2. Ballschmieter, H. M. B., and A. W. Dercksen, 1970. Alcohols in Peanut Aroma. Fette Seifen Anstrichm. 72:719-722.

3. Brown, B. A., K. S. Konigsbacher, F. E. Ellison, and G. E. Mann, 1968. Separating and Isolating Aroma and Flavor Constituents of Roasted Peanuts. J. Food Sci. 33:625-627.

4. Brown, D. F., V. J. Senn, F. G. Dollear, and J. B. Stanley, 1971. Concentrations of Some Aldehydes and Ketones found in Raw and Roasted Peanuts. J. Am. Peanut Res. and Educ. Assoc., 3:208-216.

5. Brown, M. L., J. I. Wadsworth, H. P. Dupuy, and R. W. Mozingo, 1977. Correlation of Volatile Components of Raw Peanuts with Flavor Score. Peanut Sci. 4:54-56.

6. Dupuy, H. P., E. T. Rayner, J. I. Wadsworth, and M. G. Legendre, 1977. Analysis of Oils for flavor quality by Direct Gas Chromatography. J. Am. Oil Chem. Soc. 54:445-449.

7. Fore, S. P., H. P. Dupuy, and J. I. Wadsworth, 1976. Correlation of Volatile Components of Peanut Products with Flavor Score I. Shelf Life Studies on Peanut Butter. Peanut Sci. 3: 86-89.

8. Fore, S. P., M. G. Legendre, and G. S. Fisher, 1978. Analysis of Neutral Volatiles of Mayonnaise by Direct Gas Chromatography and Mass Spectrometry. J. Am. Oil Chem. Soc. 55: 482-485.

9. Hoffman, G., and J. G. Keppler, 1960. The Stereo-configuration of 2,4-Decadienals Isolated from Oils Containing Linoleic Acid. Nature 185:310-311.

10. Johnson, B. R., G. R. Waller, and A. L. Burlingame. 1971. Volatile Components of Roasted Peanuts: Basic Fraction. J. Agric. Food Chem. 19:1020-1024.

11. Johnson, B. R., G. R. Waller, and R. L. Foltz. 1971. Volatile Components of Roasted Peanuts: Neutral Fraction. J. Agric. Food Chem. 19:1025-1027.

12. Kinlin, T. E., R. Muralidhara, A. D. Pittet, A. Sanderson, and J. P. Walradt, 1972. Volatile Components of Roasted Filberts J. Agric. Food Chem. 20:1022-1027.

13. Legendre, M. G., H. P. Dupuy, R. L. Ory, and W. O. McIlrath, 1978. Instrumental Analysis of Volatiles in Rice and Corn Products. J. Agric. Food Chem. 26:1035-1038.

14. Maga, J. A., and G. E. Sizer, Pyrazines in Foods, 1973. Crit. Rev. Food Technol. 4:457-505.

15. Mason, M. E., B. R. Johnson, and M. C. Hamming. 1966. Flavor Components of Roasted Peanuts. Some Low Molecular Weight Pyrazines and Pyrrole. J. Agric. Food Chem. 14:454-460.

16. Mason, M. E., B. Johnson, and M. C. Hamming, 1967. Volatile Components of Roasted Peanuts. The Major Monocarbonyls and Some Noncarbonyl Components. J. Agric. Food Chem. 15:66-73.

17. Pattee, H. E., E. O. Beasley, and J. A. Singleton, 1965. Isolation and Identification of Volatile Components from High-Temperature-Cured Off-Flavor Peanuts. J. Food Sci. 34:388-392.

18. Pattee, H. E., J. A. Singleton, and W. Y. Cobb. 1969. Volatile Components of Raw Peanuts: Analysis by Gas-Liquid Chromatography and Mass Spectrometry. J. Food Sci. 34:625-627.

19. Pickett, T. A., and K. T. Holley. 1952. Peanut Roasting Studies. Georgia Agr. Expt. Sta. Tech. Bull. No. 1, Athens, Ga.

20. Shu, C. K., and G. R. Waller. 1971. Volatile Components of Roasted Peanuts: Comparative Analysis of the Basic Fraction. J. Food Sci. 36:579-583.

21. Singleton, J. A., H. E. Pattee, and E. B. Johns. 1971. Influence of Curing Temperatures on the Volatile Components of Peanuts. J. Agr. Food Chem. 19:130-133.

22. Rayner, E. T., J. I. Wadsworth, M. G. Legendre, and H. P. Dupuy, 1978. Analysis of Flavor Quality and Residual Solvent of Soy Protein Products. J. Am. Oil Chem. Soc. 55:454-458.

23. Shu, C. K., and G. R. Waller, 1971. Volatile Components of Roasted Peanuts: Comparative Analyses of the Basic Fraction. J. Food Sci. 36:579-583.

24. Walradt, J. P., A. O. Pittet, T. E. Kinlin, R. Muraldihara, and A. Sanderson, 1971. Volatile Components of Roasted Peanuts. J. Agric. Food Chem. 19:972-979.

25. Williams, J. L., and H. J. Wille, 1976. Improvement of the Direct GC Analysis of Vegetable Oils' Volatile Profile by a Poly MPE - Tenax GC Column. J. Am. Oil Chem. Soc. 53: 634-635.

26. Young, C. T. and K. T. Holley. 1965. Comparison of Peanut Volatiles in Storage and Roasting. Georgia Agr. Expt. Sta. Bull. N. S. 41, Athens, Ga.

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