

- Scala, J., Abstract 28, Division of Agricultural Food Chemistry, American Chemical Society Centennial Meeting, New York, N.Y., April 5-8, 1976.
- Sweely, C. C., Bentley, R., Makele, R., Wells, W. W., *J. Am. Chem. Soc.* **85**, 2497 (1963).
- Van Soest, P. J., McQueen, R. W., *Proc. Nutr. Soc.* **32**, 123 (1973).
- Wardi, A. H., Allen, W. S., Varma, R., *Anal. Biochem.* **57**, 268 (1974).
- Yamagishi, T., Matsuda, K., Watanabe, T., *Carbohydr. Res.* **43**, 321 (1975).

- Yamagishi, T., Matsuda, K., Watanabe, T., *Carbohydr. Res.* **50**, 63 (1976).

Received for review November 22, 1977. Accepted April 7, 1978. Presented at the Symposium on Nutrients and Flavor Quality of Plant Foods, Division of Agricultural and Food Chemistry, 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977. Use of trade names does not imply endorsement by the U.S. Department of Agriculture over other products of equal value.

## Instrumental Analysis of Volatiles from Rice and Corn Products

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Profiles of volatiles of whole rice, brown rice, polished rice, rice bran, rice breakfast cereal, whole corn, and corn breakfast cereal were obtained by direct gas chromatography without prior enrichment of volatiles. Some of the volatiles were identified by combined gas chromatography-mass spectrometry. Methanol, acetaldehyde, ethanol, acetone, pentanal, hexanal, and hexanol were found in volatiles of whole rice, brown rice, polished rice, rice bran, and whole corn. In addition, 2-methylpropanal, 2-methylpyrazine, furfural, 2,5-dimethylpyrazine, benzaldehyde, and 2,6-dibutyl-4-methylphenol were found in rice and corn breakfast cereals. This unconventional gas chromatographic technique in combination with mass spectrometry should provide a rapid means of analyzing volatiles that might impart desirable flavor or undesirable off-flavor in new cultivars and in raw and processed cereal products, before and after storage. Even at this early stage of development, the methodology is being used by industry to monitor raw materials.

In recent years, much research has been devoted to measurements of the flavor characteristics of rice, corn, and other foods. Relatively little work, however, has been done on these products in the raw state. Obata and Tanaka (1965) analyzed 50 g of polished rice and identified carbon dioxide, ammonia, hydrogen sulfide, and acetaldehyde. In 1966, Yatsumatsu et al. analyzed the volatile carbonyl compounds from 100 g of boiled rice and found that propanal (or acetone), pentanal, and hexanal seemed to be responsible for the stale flavor of cooked rice stored at elevated temperatures. Pyridine, hexanal, methylpropanal, and crotonaldehyde were reported by Inglett et al. (1968) as being among the flavor components they found in corn and corn products. Mitsuda et al. (1968) analyzed the volatiles from 3 kg of rice bran by gas chromatography (GC) and identified several compounds, among them methanol, ethanol, *n*-hexanol, acetaldehyde, acetone, methylpropanal, pentanal, and hexanal. Fifty grams of ground corn kernels were examined by Hougen et al. (1971), who found that different species and varieties of grain appeared to produce largely the same volatile components. Tsuzuki et al. (1975) analyzed the headspace gas from 20 g of cooked rice and found that the longer the cooking time, the more volatiles were produced. Bullard and Holguin (1977) analyzed the volatiles from 3 kg of unprocessed rice by combined capillary-column gas chromatography-mass spectrometry (GC-MS) and showed

that the volatile flavor components of unprocessed rice are attractive to Philippine rice field rats.

Direct GC was used to analyze volatile flavor components from less than 1 g of raw and roasted peanut products (Brown et al., 1972; Fore et al., 1973) and of vegetable oils (Dupuy et al., 1971, 1976) and neutral volatiles in mayonnaise were examined and identified by direct GC-MS (Fore et al., 1976).

This paper presents the application of a direct, rapid, and simple GC-MS method for detecting and characterizing flavor-producing compounds in raw and processed rice and other cereal products. Less than 1 g of sample is used, without prior enrichment of volatiles.

### MATERIALS AND METHODS

**Materials.** Standards used for determination of retention time and mass spectra were obtained from reliable sources. Silicone O-rings and poly-MPE (poly-*m*-phenoxylene) were purchased from Applied Science Laboratories, State College, Pa. (O-rings conditioned at 200 °C for 2 h). Pyrex glass wool was obtained from Corning Glass Works, Corning, N.Y. (conditioned at 200 °C for 16 h). Tenax-GC was obtained from TekLab, Inc., Baton Rouge, La., and Porapak P was obtained from Waters Associates, Framingham, Mass.

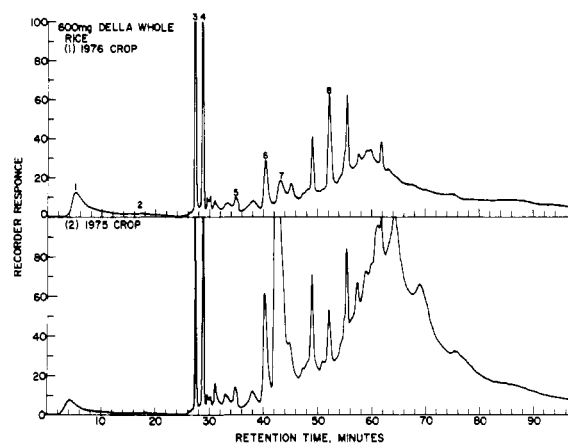
**Gas Chromatography.** The GC analyses were carried out on a Tracor MT-220 gas chromatograph with dual independent hydrogen flame detectors, a Westronics MT22 recorder, and a Hewlett-Packard 3380A integrator. The column used was 1/8 in. by 9 ft stainless steel packed with 60/80 mesh Tenax-GC that had been coated with approximately (by weight) 7% poly-MPE (Novotny et al., 1975; Williams and Wille, 1976). The flow rate of the helium carrier gas was 40 mL/min. The inlet temperature was 120 °C, and the detector was kept at 250 °C. Hydrogen flow was 60 mL/min and air flow 470 mL/min.

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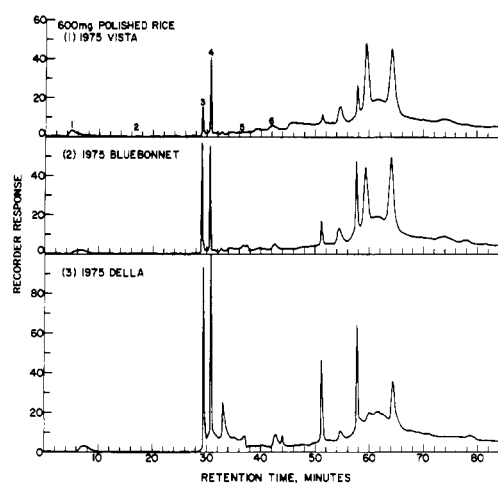
**Mass Spectrometry.** A Hewlett-Packard 5930A mass spectrometer was interfaced to a Tracor 222 gas chromatograph via a silicone membrane helium separator. The transfer line was heated to 220 °C, and the ionization voltage used was 70 eV. An INCOS 2000 mass spectrometer data system was interfaced to the combined unit for data acquisition and processing. The  $m/e$  (mass to charge ratio) scan range used was 21–300.

**Sample Preparation and Analysis for GC.** Samples of rice and corn products were ground in a Waring blender. The bottom end of a  $3\frac{3}{8}$  in. length of  $\frac{3}{8}$  in. O.D. borosilicate glass tubing was packed with a plug of volatile-free glass wool, with a clearance of  $\frac{1}{4}$  in. at the bottom. The sample material (200 mg for rice bran, rice breakfast cereal, and corn breakfast cereal; 500 mg for corn; and 600 mg for whole, brown, and polished rice) was weighed directly into the glass liner, then another plug of glass wool was inserted on top of the sample. Two drops of distilled water was applied to the top of the glass wool to "steam distill" the volatiles from the sample. The septum nut, septum, and retainer nut of the GC inlet were removed and the sample liner was inserted into the inlet assembly (Dupuy et al., 1976) on top of a silicone O-ring which fitted in the bottom of the GC inlet. When the retainer nut was tightened above the upper lip of the liner, a seal was formed between the base of the inlet and the lower lip of the liner. On closing the inlet system with the septum and septum nut, the carrier gas was forced to flow down through the sample. Volatiles were rapidly eluted from the heated sample and transferred to the upper portion of the GC column which was cooled to room temperature during the 30-min elution period. The liner with the spent sample was removed, the inlet system was closed, and the temperature of the oven was raised to 100 °C and temperature programmed to 190 °C at 3 °C/min. The final temperature was maintained at 190 °C until all volatiles were eluted, and the oven was then cooled to 30 °C in preparation for the next sample.

**Sample Preparation and Analysis for MS.** The quantity of volatiles that permeates the silicone membrane separator and enters the mass spectrometer varies considerably depending on the temperature of the oven and the polarity of the compound. When small peaks from a volatile profile are to be analyzed by MS, the sample size must sometimes be increased to adequately supply the instrument with concentrations of volatiles that are sufficient for detection; therefore, sample sizes were increased by 50% for MS analysis. In making MS determinations, a slightly modified technique was used to elute volatiles from the sample because added water in the sample is incompatible with the operation of the MS. The modification consisted of eluting the volatiles from the sample onto a glass liner, similar to the above one, which is attached on the bottom of the GC inlet inside the column oven via a  $\frac{3}{8}$  in. Swage-lok adapter and two  $\frac{1}{4}$  in. silicone O-rings. This liner contained 0.4 g of Porapak P with a plug of volatile-free glass wool on both sides and was cooled by wrapping a damp towel around it. The volatiles were eluted from the sample onto the Porapak P for 30 min. The volatiles of the sample were thus trapped on the Porapak P, and the water originally needed for volatile elution was dissipated. The Porapak P liner was then inserted into the GC inlet, and the temperature of the inlet was increased to 160 °C. The carrier gas was allowed to sweep through the liner for 20 min, the liner was removed, and the column was temperature programmed as described. The liner must be inserted in a position that is reverse to the flow of gas used previously to adsorb the volatiles onto the Porapak P liner. If the Porapak P liner



**Figure 1.** Profiles of volatiles from whole rice (1975 and 1976 crop years): (1) methanol, (2) acetaldehyde, (3) ethanol, (4) acetone, (5) *n*-pentanal, (6) *n*-hexanal, (7) 1-hexanol, (8) *n*-dodecane.



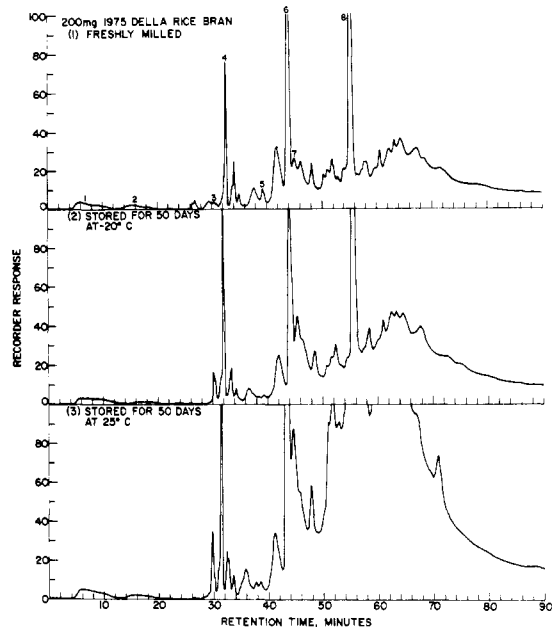
**Figure 2.** Profiles of volatiles from polished rice (1975 crop year, three varieties). Identifications same as in Figure 1.

cannot be used immediately, it may be stoppered with Teflon-covered corks, placed in a Teflon-lined screw-cap vial and stored in a freezer for as long as 3 days.

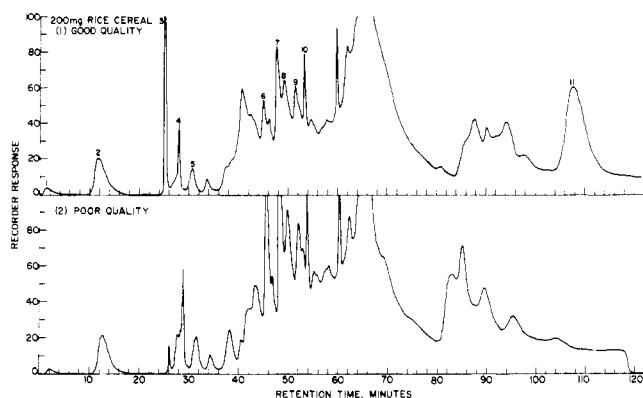
## RESULTS AND DISCUSSION

Investigations indicate that volatiles from less than 1 g of ground cereal products (whole rice, brown rice, polished rice, rice bran, rice breakfast cereal, whole corn, and corn breakfast cereal) can be effectively analyzed by direct GC without prior enrichment of volatiles. This was accomplished by adding 100  $\mu$ L of water to the GC liner containing the sample and heating the assembly in the injection port at about 120 °C to promote rapid distillation of volatiles (Fore and Dupuy, 1972). Water was necessary to effectively elute and analyze the volatiles by GC. Before making the MS determinations, however, the water had to be separated from the volatiles. The technique of Fore et al. (1976) was used to effect the separation.

As shown in Figures 1 and 2, as little as 600 mg of ground unprocessed rice or polished rice was sufficient to provide volatiles for the analysis by direct GC. The sample size was increased by 50% for identification of volatiles by combined GC-MS. Since volatiles appeared to be more concentrated in the bran layer of rice or in ready-to-eat cereals, 200 mg of these products was enough to produce a meaningful profile of volatiles (Figures 3 and 4). Similar analyses were made on corn and a commercial corn breakfast product, shown in Figures 5 and 6.

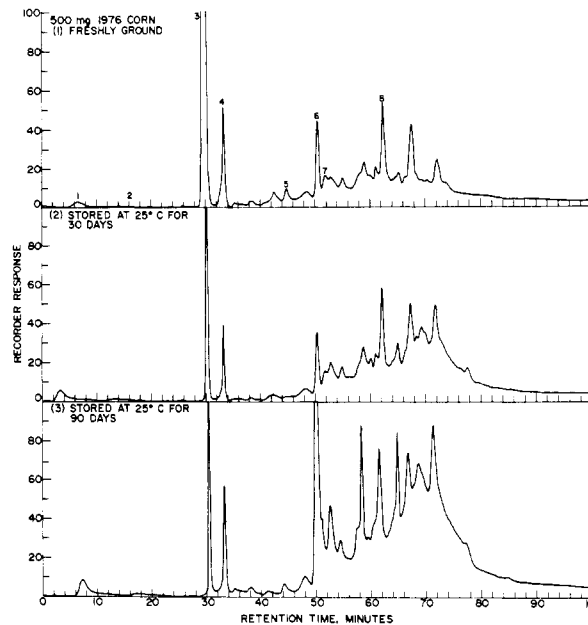


**Figure 3.** Profiles of volatiles from rice bran (1975 crop year) freshly milled and stored for 50 days at  $-20$  and  $25^{\circ}\text{C}$ . Identifications same as in Figure 1.

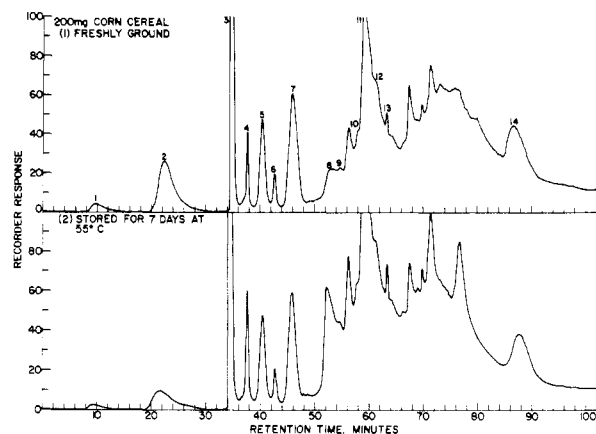


**Figure 4.** Profiles of volatiles from commercial rice breakfast cereals of good and poor quality: (1) methanol, (2) acetaldehyde, (3) ethanol, (4) acetone, (5) 2-methylpropanal, (6) *n*-hexanal, (7) 2-methylpyrazine, (8) furfural, (9) 2,5-dimethylpyrazine, (10) benzaldehyde, (11) butylated hydroxytoluene (BHT).

These preliminary studies indicate that the volatiles profiles for different varieties of rice and corn are qualitatively similar. In general, the profiles for rice varieties contained methanol, acetaldehyde, ethanol, acetone, pentanal, hexanal, and 1-hexanol, but individual component concentrations differed among varieties. This appeared to be true for analyses of whole rice, brown rice, rice bran, and corn. With the exception of 1-hexanol, these compounds were also found in polished rice. Figures 3 and 5 show that the volatiles obtained from rice and corn products increased greatly after storage of the products, particularly the hexanal, hexanol, and some uncharacterized components of higher molecular weight. Figure 4 shows the profiles of volatiles from samples of commercial rice breakfast cereals of good and poor quality. The hexanal peak (no. 6) which has been described in connection with rancidity (Dupuy et al., 1976) was larger in the poor quality sample, which may be due to the very low concentration of BHT (butylated hydroxytoluene). Conversely, a smaller hexanal peak was noted in the good quality product which contained more BHT. Figure 6 shows the effect of storage on a sample of corn breakfast



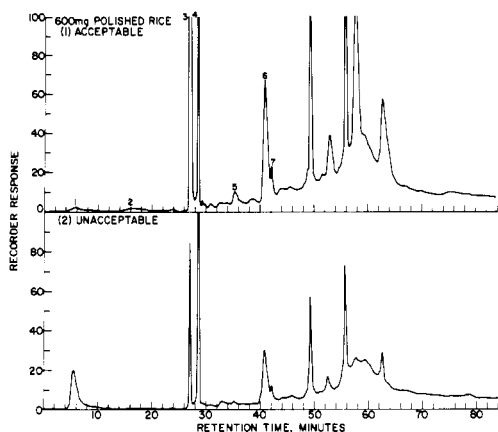
**Figure 5.** Profiles of volatiles from corn (1976 crop year) freshly ground and stored at  $25^{\circ}\text{C}$  for 30 and 90 days. Identifications same as in Figure 1.



**Figure 6.** Profiles of volatiles from a commercial corn breakfast cereal, freshly ground and stored for 7 days at  $55^{\circ}\text{C}$ : (1) methanol, (2) acetaldehyde, (3) ethanol, (4) acetone, (5) 2-methylpropanal, (6) diacetyl, (7) 2-methylbutanal, (8) pyrazine, (9) *n*-hexanal, (10) 2-methylpyrazine, (11) furfural, (12) 2,5-dimethylpyrazine, (13) benzaldehyde, (14) butylated hydroxytoluene (BHT).

cereal. In chromatogram 1, the freshly ground corn cereal indicates a very small concentration of hexanal (peak no. 9). After storage at  $55^{\circ}\text{C}$  for 7 days (chromatogram 2), there is a slight increase in the hexanal content, apparently related to the conditions of storage.

This technique was applied to resolve a flavor problem in two rice lots which comprised the raw materials available to a manufacturer of breakfast cereals. One lot of rice produced an acceptable product with good flavor, whereas the product of the other lot had undesirable off flavors. Samples of both rice were examined by the direct GC method; the profiles of their volatiles are shown in Figure 7. The upper chromatogram, which represents the acceptable sample, shows greater total volatiles than were obtained for the unacceptable sample in the lower chromatogram. Based on the observation of total volatiles alone, a reverse result might have been anticipated since it was reasonable to suspect the sample with greater volatiles to contain the off flavor compound(s). Upon analysis by GC-MS, however, the lower chromatogram



**Figure 7.** Profiles of volatiles from polished rice used in acceptable and unacceptable breakfast cereals: (1) methanol, (2) acetaldehyde, (3) ethanol, (4) acetone (upper chromatogram), acetone and dimethyl sulfide (lower chromatogram), (5) *n*-pentanal, (6) *n*-hexanal, (7) 1-hexanol.

showed that the off-flavor sample contained dimethyl sulfide. This material, which eluted with the acetone, was detected by computer analysis of the mass spectral data and appeared only in the unacceptable sample of polished rice and the breakfast cereal manufactured from it. This finding was confirmed by the manufacturer. The rapid and successful resolution of a serious raw materials problem prompted this major food processor to adopt the direct GC-MS method for analysis of incoming bulk raw materials and to incorporate it into their product specifications. Profiles of volatiles obtained by direct GC-MS analysis, therefore, can be an invaluable tool for assessing food product quality, but the technique requires critical evaluation and careful interpretation to properly identify the flavor-related materials, either desirable or undesirable.

This rapid and efficient GC-MS method, when fully developed, could be an indispensable technique for plant breeders in expediting production of new, better breeding lines for food products. It could provide food processors with a rapid and accurate means of monitoring the quality of raw materials. Agronomists should be able to assess the effects of agricultural practices on commodity improvement, and engineers should be able to effectively determine how flavor quality of a product is affected by different

methods of processing. Objective and definitive flavor evaluation of this type should ensure the consumer of a higher quality product.

#### ACKNOWLEDGMENT

The authors wish to thank G. E. Inglett, Northern Regional Research Center, SEA, USDA, Peoria, Ill., for supplying us with the corn samples, G. I. Pittman for drawing figures, J. J. Berquist for photographing figures, and E. T. Rayner for his advice in preparing this manuscript.

#### LITERATURE CITED

- Brown, D. F., Dollear, F. G., Dupuy, H. P., *J. Am. Oil Chem. Soc.* **49**, 81 (1972).  
 Bullard, R. W., Holguin, G., *J. Agric. Food Chem.* **25**, 99 (1977).  
 Dupuy, H. P., Fore, S. P., Goldblatt, L. A., *J. Am. Oil Chem. Soc.* **48**, 876 (1971).  
 Dupuy, H. P., Rayner, E. T., Wadsworth, J. I., *J. Am. Oil Chem. Soc.* **53**(10), 628 (1976).  
 Fore, S. P., Dupuy, H. P., *J. Am. Oil Chem. Soc.* **49**, 129 (1972).  
 Fore, S. P., Dupuy, H. P., Wadsworth, J. I., Goldblatt, L. A., *J. Am. Peanut Res. Educ. Assoc.* **5**(1), 59 (1973).  
 Fore, S. P., Legendre, M., Fisher, G., *J. Am. Oil Chem. Soc.* **55**(5), 482 (1978).  
 Hougen, F. W., Quilliam, M. A., Curran, W. A., *J. Agric. Food Chem.* **19**(1), 182 (1971).  
 Inglett, G. E., Blessin, C. W., Bookwalter, G. N., *Food Prod. Dev.* **2**(2), 66-67, 74 (1968).  
 Mitsuda, H., Yasumoto, K., Iwami, K., *Agric. Biol. Chem.* **32**(4), 453 (1968).  
 Novotny, M., Hayes, J. M., Bruner, F., Simmonds, P. G., *Science* **189**, 215 (1975).  
 Obata, Y., Tanaka, H., *Agric. Biol. Chem.* **29**(3), 191 (1965).  
 Tsuzuki, E., Morinaga, K., Shida, S., Danjyo, T., Shimokawa, K., *Bull. Fac. Agric. Miyazaki Univ.* **22**, 197 (1975).  
 Williams, J. L., Wille, J. H., *J. Am. Oil Chem. Soc.* **52**(10), 634 (1976).  
 Yatsumatsu, K., Moritaka, S., Wada, S., *Agric. Biol. Chem.* **30**(5), 478 (1966).

Received for review November 22, 1977. Accepted April 10, 1978. Presented at the Symposium on Nutrients and Flavor Quality of Plant Foods, Division of Agricultural and Food Chemistry, 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977. Use of a company or product name by the U.S. Department of Agriculture does not imply approval or recommendation of the product to the exclusion of others that may also be suitable.