Direct Gas Chromatographic Examination of Volatiles in Salad Oils and Shortenings[1]

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ABSTRACT

A simple, rapid and direct gas chromatographic technique was developed for the examination of volatiles in salad oils and shortenings at the 10 ppb level without prior enrichment. The liner of the inlet of the gas chromatograph is carefully packed with volatile-free glass wool to allow slow diffusion of the sample on the glass wool, but to prevent seepage onto the gas chromatographic column. The liner with sample is inserted in the heated inlet, and the volatiles are eluted rapidly from the samples as the carrier gas flows through the liner and sweeps the volatiles onto the column, which is temperature-programed between 55 and 190 C to resolve the volatiles. Numerous samples of salad oils and shortenings were examined, and the better quality oils had only small amounts of volatiles.

INTRODUCTION

Several enrichment techniques have been used by various investigators to provide from food products volatiles in sufficient concentration for analysis by gas chromatography and mass spectrometry. Unfortunately most of these methods are time consuming or have limitations. Solvent extraction and distillation have been used frequently (1,2); however solvent extraction is not quantitative and may in some instances result in contamination arising from impurities in the solvent used. Distillation is a tedious procedure that often promotes chemical changes in the analytical sample. Although high vacuum distillation minimizes these chemical changes (3-5), the technique is nonetheless complex and time consuming. Analysis of headspace vapors (6) provides a simpler and more rapid analytical approach; however the detection of trace volatiles by this technique is somewhat limited by the large volume of headspace gas required to detect such trace components.

Low temperature precolumns have been used with limited success to concentrate volatiles from headspace vapors before their chromatographic separation (7). The degree of concentration achieved is limited by diffusion on the precolumn. Activated charcoal has been used to concentrate volatiles by adsorption for subsequent analysis (8,9), but this technique is also complex and time consuming.

This paper reports a simple, rapid and direct gas chromatographic technique for the examination of volatiles in salad oils and shortenings at the 10 ppb level without prior enrichment.

[1]Presented at the JOCS-AOCS Joint Meeting, Los Angeles, April 1972.

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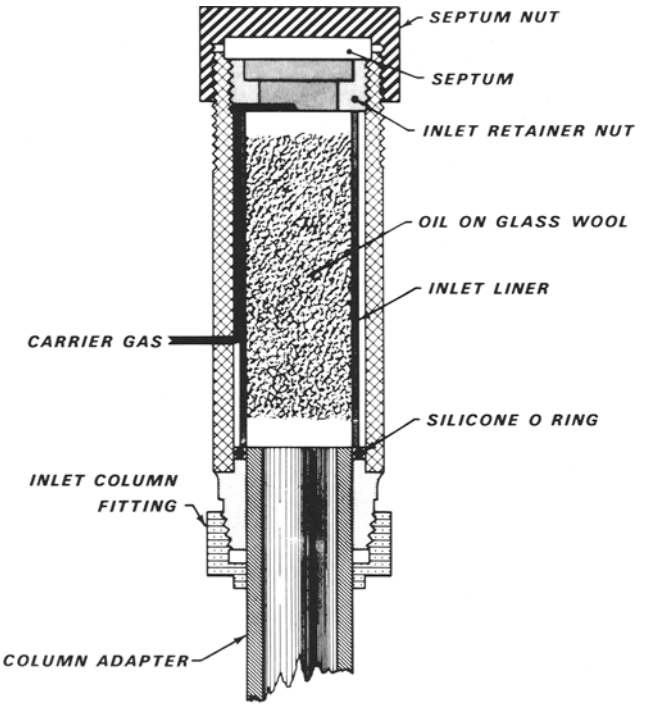

FIG. 1. Schematic drawing showing inlet liner and sample of oil diffused on glass wool.

EXPERIMENTAL PROCEDURES

Materials

Porapak P, 80-100 mesh, was obtained from Waters Associates (Framington, Mass.). Silicone O-rings were obtained from Applied Science Laboratories (College Station, Pa.), and were conditioned for 2 hr at 200 C before use. Pyrex brand glass wool manufactured by Corning Glass Works (Corning, N.Y.), was heated at 200 C for ca. 16 hr to remove volatiles. Specially processed samples of vegetable oils or shortenings were obtained from five sources.

Gas Chromatography

The following gas chromatographic conditions were employed for rapid elution of trace amounts of volatiles in refined vegetable oils and shortenings: instrument–a Microtek 2000 MF gas chromatograph (GC) with dual independent hydrogen flame detectors, a Westronics LD 11B recorder and an Infotronics CRS-100 integrator; columns–1/8 in. OD stainless steel U-tubes, 6 ft long, packed with Porapak P; flow rates–helium carrier gas (60 ml/min in each column), hydrogen (60 ml/min to each flame), air (1.2 ft^3/hr [fuel and scavenger gas for both flames]); temperature–inlet at 120 C, detector at 250 C, column oven programed between 55 and 190 C, initial hold at 55 C for 20 min, programed at 5 C/min for 27 min, final hold at 190 C for ca. 30 min; attenuation–1 x 4, Auto X1 for integrator; chart speed–15 in./hr. A silicone O-ring was

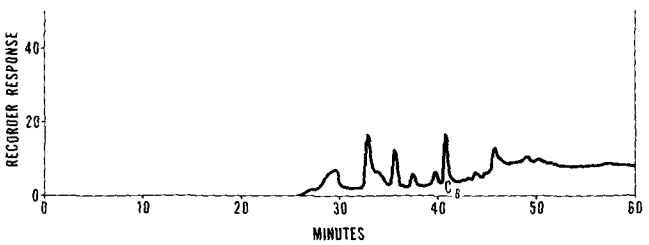

FIG. 2. Gas chromatogram of volatiles eluted from an oil with a high flavor score.

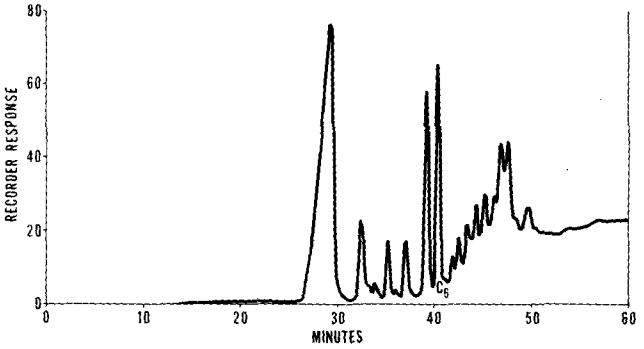

FIG. 3. Gas chromatogram of volatiles eluted from an oil with a medium flavor score.

positioned around the 1/4 in. stainless steel adapter, which projected into the bottom of the inlet of the GC.

Sample Preparation and Analysis

The lower portion of a 3 and 3/8 in. length of 3/8 in. OD borosilicate glass tubing was packed firmly with glass wool and the upper portion packed somewhat more loosely with glass wool, allowing a 1/4 in. clearance at the bottom and a 1/2 in. clearance at the top. A 500 mg portion of salad oil or shortening was added on top of the loose plug of glass wool and covered with a small plug of glass wool, allowing a 1/4 in. clearance above the glass wool plug. The septum nut, septum, and retainer nut of the GC were removed, and the liner with sample was inserted in the inlet of the GC on top of the silicone O-ring. A seal was formed between the base of the inlet and the lower lip of the liner as the retainer nut was tightened above the upper lip of the liner. On closing the inlet system with the septum and septum nut, the carrier gas was forced to flow upward and then down through the sample as shown in Figure 1. The integrator and programer were turned on immediately. Volatiles were rapidly eluted from the sample as the carrier gas swept through the heated liner. The volatiles were swept onto the top portion of the column, which was maintained at 55 C during the initial hold period of 20 min. The liner containing the spent sample was then removed from the inlet, and the volatiles were resolved by temperature programing the column oven between 55 and 190 C. After the chromatographic run was completed, the oven was cooled at 55 C for the next run.

RESULTS AND DISCUSSION

To achieve rapid and maximum elution of volatiles from salad oils and shortenings by direct gas chromatographic analysis with minimum oil decomposition, it was necessary to force the carrier gas to flow through the sample in the liner of the properly heated inlet of the GC. For best resolution of volatiles, it was necessary to concentrate the volatiles on the top portion of a cool column, remove the spent liner with sample from the inlet after an initial hold period of 20 min, and then temperature program the column oven.

In preliminary experiments (10,11), the liner with sample was left in the inlet throughout the chromatographic run. Consequently a special liner with a protruding inner lip at the bottom was used to accommodate a 500 mg sample of oil and prevent seepage of oil onto the column. However it was difficult to produce a good seal between the base of the inlet and the lower lip of the special liner, even though a silicone O-ring was inserted between the two surfaces. As a result, the elution of volatiles was not rapid enough to produce quantitative elution and good resolution of volatiles.

It was soon found that a regular liner could be used for a 500 mg oil sample without seepage of oil onto the column.

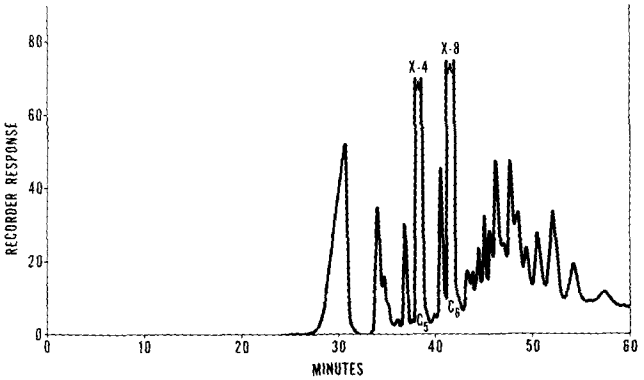

FIG. 4. Gas chromatogram of volatiles eluted from an oil with a low flavor score.

The lower portion of the liner was firmly packed with glass wool, and a looser plug was inserted on top to diffuse the oil sample. Removal of the liner with spent sample after the 20 min hold period further precluded the likelihood of oil seepage onto the column. Thus, by using a regular liner as shown in Figure 1, it was possible to produce a very good seal between the base of the inlet and the lower lip of the liner, resulting in rapid and more quantitative elution of volatiles. Increasing the inlet temperature from the previously reported 100 C (10) to 120 C also enhanced the rate of elution of volatiles onto the gas chromatographic column. Increasing the initial hold period from 2 to 20 min and lowering the column temperature from 70 to 55 C during the hold period concentrated the volatiles on the top portion of the column. Much better resolution was obtained when the liner with spent sample was removed from the inlet and the column was temperature-programed between 55 and 190 C, than when the liner with sample was left in the inlet throughout the chromatographic run.

Numerous samples of oils and shortenings were examined by this simple and rapid direct gas chromatographic technique. Because it does not require prior enrichment of volatiles, any possible side reactions are minimized. The sample is taken directly from the container and placed in the glass liner, which is immediately inserted into the inlet in the presence of an inert atmosphere of helium and secured into position. Most volatile profiles can be obtained within 1 hr.

Although volatiles profile and flavor score have not yet been correlated, the oils with a relatively high flavor score had only small amounts of volatiles, as shown by a representative chromatogram in Figure 2. As the quality of the oil decreased, the concentration of volatiles increased, as shown by a representative chromatogram in Figure 3. Oils with a relatively low flavor score had a much higher concentration of volatiles, as shown by a representative chromatogram in Figure 4.

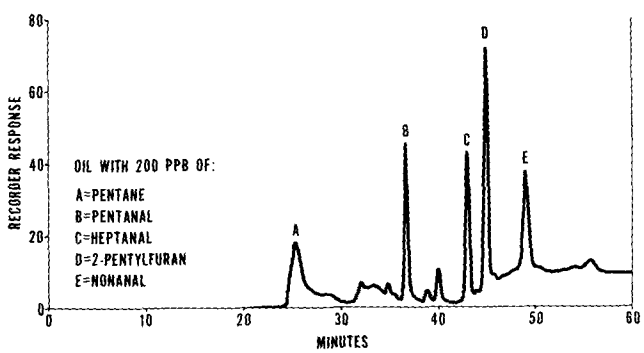

FIG. 5. Gas chromatogram of volatiles eluted from a good oil supplemented with 200 ppb of pentane, pentanal, heptanal, 2-pentylfuran and nonanal.

The technique is very sensitive, as shown in Figure 5, for a representative chromatogram of a very good oil supplemented with trace amounts of volatile components: pentane, pentanal, heptanal, 2-pentylfuran and nonanal. Based on the area for the small peak with retention time of 39 min, volatiles can be examined at the 10 ppb level without prior enrichment.

Additional studies are in progress to correlate flavor score with volatiles profile of salad oils. This simple and rapid technique should help to provide the oil industry with an objective measure of flavor quality and possible prediction of shelf life.

ACKNOWLEDGMENT

J.H. Conkerton drew the figures.

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[Received March 20, 1973]