Volatiles and Oil Quality[1]

H.W. JACKSON and **D.J. GIACHERIO**, Kraft, Inc., Research & Development, Glenview, IL 60025

ABSTRACT AND SUMMARY

A simple, rapid, and versatile procedure for collecting and measuring volatiles from edible oils is presented. The technique involves direct sampling, can be used with all gas chromatographs having adequate sensitivity, does not require special valving, and is not limited to a specific sample size. Correlation of volatiles with flavor panel scores was excellent with soybean oils aged at room temperature under normal fluorescent lighting. Identification of the major volatiles from aged soybean oil using this technique was accomplished using gas chromatography-mass spectrometry (GC-MS).

INTRODUCTION

The procedure presented here for oil volatiles is a modification of the Dupuy procedure (1) in that it involves direct sampling using glass wool, and a Porapak P column for trapping and separation of volatiles.

The method differs in that it does not require a special sample inlet, uses an internal standard, and the sample collection is carried out external to the gas chromatogram (GC). This allows one to use any type of GC with adequate sensitivity and gives a 30 to 40% increase in samples run per day.

This method has shown good correlation with flavor of soybean oil samples and could serve as an objective measure of quality for specific oils under known processing and storage conditions.

Most of the volatiles collected and measured are probably formed by the thermal breakdown of peroxides, etc. As the oil ages, an increasing amount of volatiles will exist in the free state and will be included with that formed from precursors. The advantages of running oil volatiles at the present time as compared to peroxide values are specificity, sensitivity, and reliability.

EXPERIMENTAL PROCEDURES

Principle

Vegetable oil, distributed over glass wool in a heated aluminum U-tube, is purged with a flow of helium. Volatiles from the oil are swept out of the tube and trapped on a gas chromatographic column of Porapak P, which is kept at room temperature. When the purge is finished, the column is disconnected from the U-tube and connected to a gas chromatograph; temperature programmed GC then affords a chromatogram of the volatiles.

Reagents

Reagents are n-nonane (high purity) and fresh, partially hardened liquid (PHL) vegetable oil.

Apparatus

(a) *Gas chromatograph:* Varian model 1440 or equivalent, equipped with a linear temperature programmer and a flame ionization detector. The instrument should be equipped to handle 1/8 in. columns.

(b) *GC columns (two matched columns are necessary for rapid analyses):* 6 ft x 1/8 in. stainless steel columns packed with 80-100 mesh Porapak P. Condition the columns for 24-36 hr at 235 C. The temperature at which the columns are conditioned is critical: higher temperatures cause the column resolution to deteriorate; lower temperatures result in excessive column bleed during the analyses.

(c) *Syringes (for sample handling):* a 1 ml glass syringe equipped with a 20 gauge needle; a 100 µl syringe equipped with a removable 25 gauge needle.

(d) *Aluminum tubing,* 1/4 in. outside diameter.

(e) *Swagelok fittings:* 1/4 in. (stainless steel) nuts; 1/4 in. to 1/8 in. (stainless steel) adapters; 1/4 in. (aluminum) front and back ferrules.

(f) *Silanized glass wool.*

(g) *Oven:* A Blue M model no. 472 forced air oven, or the equivalent. Modify the oven to accommodate a U-tube by cutting a 5 in. x 1 in. rectangular hole in the top. The oven may be further modified by drilling two small (ca. 1/4 in. diameter) holes in the top. The holes serve as inlet and exit ports for the tubing which delivers helium to the U-tube. Thus, the helium flow to the U-tube can be preheated.

(h) *Source of helium:* A tank of Zero Gas Grade, or the equivalent, equipped with a pressure regulator, a flow controller, and sufficient 1/8 in. (copper or stainless steel) tubing to reach the oven.

Procedure

Preparation of internal standard: 10 µl of n-nonane are added to 200 ml of fresh oil.

Preparation of glass wool: Silanized glass wool is soaked in reagent grade petroleum ether for at least 2 hr. The solvent is then drained off. The glass wool is dried for several minutes under a stream of high purity nitrogen; it is then dried overnight in an oven. After drying, it is stored at room temperature in a clean jar. Each batch of washed glass wool should be checked for residual volatiles by subjecting a 0.6-0.65 g portion of it to the entire procedure, omitting only the oil sample and the internal standard solution.

Preparation of U-tubes: Aluminum tubing (1/4 in. diameter) is cut into 2 ft lengths. These are then bent into U-tubes (ca. 3 in. in width). The tubes are rinsed thoroughly, first with distilled water, and then with reagent-grade acetone; they are dried for several hours in an oven at 170 C.

Packing the U-tubes: A 0.60-0.65 g sample of the prepared glass wool is packed loosely and evenly into one side of a U-tube (partially crimping that side of the U-tube very near the bottom with pliers is helpful). A thin, metal rod is used to force the glass wool into the tube. The packing should extend from the crimp to within 1/2 to 1 in. of the top. Swagelok fittings (i.e., nuts, front and back ferrules, and adapters) are then fitted to both ends of the U-tube. (To avoid leaks, the fittings must be tightened well.)

Conditioning the U-tubes: The U-tube is connected to the helium line and then lowered (entirely) into the oven. Oven temperature is 170 C; helium flow, 40 ml/min; purge time, 20 min. The tube is then removed and allowed to cool to room temperature.

Purging the sample: The GC column is connected to that end of the U-tube which does not contain glass wool. A 30 µl aliquot of the internal standard solution is added with a syringe to the other end of the U-tube. A 0.6 ml sample of the oil to be analyzed is immediately added in a similar fashion. (Do not clean the syringes with solvent after each

[1]Presented at the AOCS Meeting, New Orleans, April 1976.

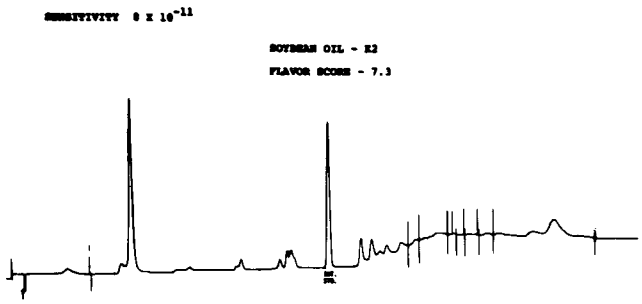

FIG. 1. Gas chromatogram of volatiles eluted from a soybean oil with a good flavor score.

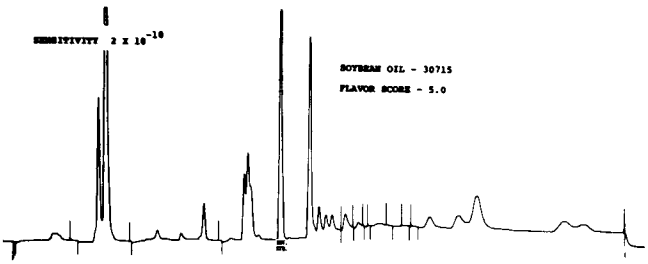

FIG. 2. Gas chromatogram of volatiles eluted from a soybean oil having a fair flavor score.

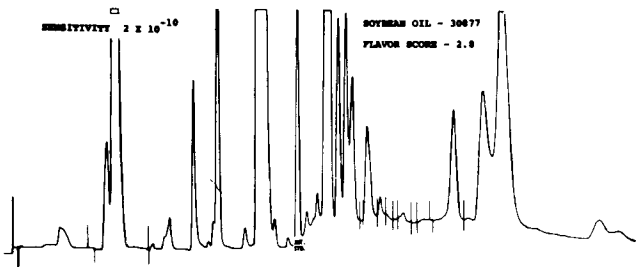

FIG. 3. Gas chromatogram of volatiles eluted from a soybean oil having a poor flavor score.

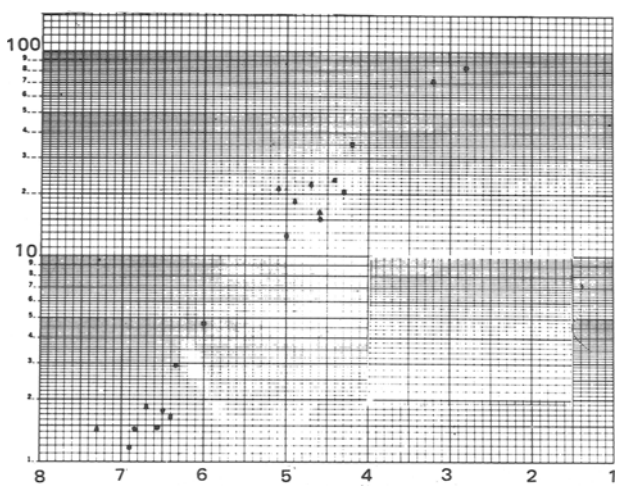

FIG. 4. Total volatiles vs. flavor scores.

ture.). The U-tube-GC column assembly is then connected to the helium line at the oven. It is allowed to purge at room temperture (40 ml He/min) for 5 min, to remove traces of oxygen from the system. During this time, one should (a) check all joints for leaks, and (b) check the flow rate of helium with a bubble meter. After 5 min at room temperature, the U-tube should be lowered into the oven

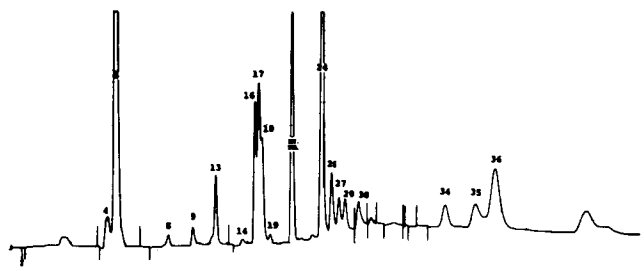

FIG. 5. Gas chromatogram of volatiles eluted from a soybean oil. See Tables II, III, and IV.

TABLE I

Linear Regression Analysis

Peak no.	Correlation coefficient
5	−.96
8	−.96
9	−.97
13	−.97
16	−.98
24	−.97
26	−.88
34	−.94
35	−.96
36	−.97
Total peaks	−.97

(maintained at 170 C). The entire U-tube, including the joints, should be in the oven. The hole in the oven should be covered with insulating material in order to keep the remainder of the GC column as close as possible to room temperature. The sample is purged for 20 min; the GC column is then disconnected from the U-tube and connected to the gas chromatograph (connect the injector end first). After the purge, the aluminum U-tube is discarded. The stainless steel fittings are saved, however.

GC Conditions: Carrier (helium) flow–30 ml/min
H_2 flow–27 ml/min
Air flow–350 ml/min
Injector temperature control–off
Detector temperature–265-275 C
Oven temperature–Programmed from 60 C at 4°/min to 205 C.
Attenuation–fresh oils: 8×10^{-11} amps/mv
aged oils: 2×10^{-10} amps/mv

Notes

(a) Integration of GC data was performed with a Varian model 220 L Chromatography Data System. Levels of various peaks were reported in parts per billion relative to the n-nonane internal standard.

(b) Columns should be stored overnight in a gas chromatograph at 200 C.

(c) In the method presented here, peaks eluting beyond PK36 (See Fig. 5) were not used in statistical analyses. Recent work suggests that immediately after PK36 is integrated, the column temperature should be raised to 230 C and the higher boiling components, if any, eluted prior to cooling the column. This will avoid a higher background than normal in subsequent runs. Approximately 25 min is allowed after PK36 is eluted to carry out the above procedure.

Identification of Volatiles

Soybean oil was aged 5 wk at room temperature under normal fluorescent lighting. This oil was then subjected to the volatile technique presented here and the volatiles

TABLE II

Multiple Regression Analysis

Variable entered	Multiple R
Pk. 16	.97
Pk. 35	.98
Pk. 8	.98
Pk. 24	.98
Pk. 34	.98
Pk. 5	.98
Pk. 36	.98
Pk. 13	.98
Pk. 9	.98

TABLE III

Predicted Flavor Scores Based on Multiple Regression Using Pk. 16, 35, 8, 24, 34, 5, 36, 13, & 9

Case number	Y Flavor panel	Y Computed
1	6.5	6.5
2	6.8	6.9
3	6.5	6.5
4	6.3	6.3
5	6.0	6.0
6	7.3	7.1
7	6.9	6.8
8	6.4	6.5
9	6.7	6.7
10	4.2	4.5
11	5.1	4.4
12	2.8	3.2
13	4.8	4.7
14	4.4	4.5
15	4.1	3.8
16	5.0	4.9
17	4.7	4.4
18	4.5	4.7
19	4.5	4.8
20	3.2	3.2

eluted into a mass spectrometer (Hitachi RMU6E). The mass spectra and retention times were compared to known standards run under the same conditions.

RESULTS

Typical chromatograms of soybean oils of varying flavor scores are shown in Figures 1 through 3. The flavor scores would range from a high of 9 to a low of 1, 9 corresponding to the highest quality. The flavor scores were obtained from an expert panel.

The precision of this technique for both fresh and aged oils, based on total area of all peaks, gives a relative standard deviation of 8% at the 95% confidence level. The sensitivity level for individual components is on the order of 10 ppb using a Porapak P column.

To verify that the technique for measuring oil volatiles correlated with flavor, twenty samples of soybean oil of varying age, stored at room temperature under normal room fluorescent lighting, were analyzed and submitted to statistical analyses using linear and multiple regression.

A plot of voltailes data (calculated as ppb relative to nonane) versus flavor score gave an exponential curve. Plotting the data as logarithms or using semi-logarithmic paper gave the best fit with our data (Fig. 4).

All statistical correlations were calculated on the logarithms of the ppb volatiles. Linear correlations were calculated using some of the major peaks (Peaks 5, 8, 9, 13, 16-17-18, 24, 26, 34, 35, and 36. See Fig. 5) and also on the total of all peaks (Table I). Multiple regression analysis on the same peaks, excluding peak 26, gave a slightly better correlation (Table II).

The predicted flavor scores vs. actual scores using multiple regression on the peaks above are shown in Table III.

The major volatiles produced and measured using this technique have been identified using GC mass spectrometry and are shown in Table IV. Peak numbers refer to those shown in Figure 5. Those peaks listed as tentative had the correct retention times by GC, and mass spectra compatable with these compounds, but known standards were not available for final confirmation.

TABLE IV

Major Volatiles Produced and Measured Using Multiple Regression Technique

Peak number	Soybean oil volatiles	Identification	
		Tentative	Positive
4	Butane		X
	Butene	X	
5	Pentane		X
8	Hexane	X	
	N-Butanal	X	
9	Butenal		X
13	N-Pentanal		X
14	2-Pentenal	X	
16	Octane		X
17	2-Octene		X
18	Octadiene	X	
19	2 Hexenal	X	
24	2-Heptenal		X
27	2-4 Heptadienal		X
28	Octenal	X	
30	Benzyl Alcohol	X	
	Nonanal	X	
34	2-Decenal		X
35	2-4 Decadienal		X
36	2-4 Decadienal		X

REFERENCES

1. Dupuy, H.P., S.P. Fore, and L. Goldblatt, JAOCS 50:340 (1973).