Direct Sampling Capillary Gas Chromatography of Volatiles in Vegetable Oils

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ABSTRACT

Direct sampling gas chromatography used for determining volatiles and, indirectly, the flavor of vegetable oils, has been improved by a capillary column in place of the usual packed columns. Data on two good vegetable oils from a supermarket, and on one of these samples after intentional deterioration, are presented. Use of the capillary column provides a more efficient technique to differentiate between the better oils than did the previously used packed columns.

INTRODUCTION

The introduction in 1971 by Dupuy et al. (1) of a direct, unconventional gas chromatographic procedure for the detection of volatiles in vegetable oils provided a quick, simple method of effectively assessing the quality of many oil-based materials. The method has been modified and improved over the years by many researchers (2-8) and was extended for the assessment of deterioration of many types of food products, frequently in comparison with the flavor scores of taste panels on the same products (2, 3, 5-13). This research area recently has been reviewed by Waltking and Goetz (14). The purpose of this paper is to describe an improved procedure for the direct gas chromatographic analysis of volatiles, using a capillary column to resolve the volatiles, and an external inlet device to increase the initial size of the sample without concentrating it.

EXPERIMENTAL PROCEDURES

Materials

Oils A and B were commercial brands of hydrogenated soybean oil taken off a supermarket shelf and analyzed promptly. Oil C was similar to Oil A but had been left standing in the laboratory at ambient temperature and exposed to light for six mo.

Gas Chromatography

The gas chromatograph used was a Hewlett Packard (HP) 5790A series equipped with flame ionization detector. Flow rates for hydrogen and air were 30 and 240 ml/min, respectively. Nitrogen flow rates were 1.2 ml/min through the column and 30 ml/min for the auxiliary make-up gas. A HP ultra performance capillary column was used (50 m × 0.31 mm ID column coated with 0.52 micron film of crossedlinked 5% phenyl methyl silicone). An external closed inlet device (Scientific Instrument Service) designed from the inlet system previously described (15) was interfaced at the carrier gas arm of the insert Weldment assembly of the GC to facilitate direct gas chromatography. The inlet temperature of this device was set at 200 C, and the six-port rotary valve was set at 180 C. The detector was set at 275 C. The column oven was lowered to −30 C with dry ice during an intial hold period of three min, and the six-port valve was positioned in the "inject" mode to direct the carrier gas through the sample and purge the volatiles onto the head of the cold column. The six-port valve was then positioned in the "run" mode to divert the carrier gas directly into the column. The oven temperature was programmed immediately from −30 to 30 C at 10 C/min, from 30 to 150 C at 2.5 C/min, and from 150 to 250 C at 5 C/min. Final hold was 250 C for 10 min.

A HP Lab Automation System 3356 was used for data acquisition and analysis. A HP 7221T Plotter was used to plot the GC curves.

Sample Preparation

An 85 mm length of 9mm OD borosilicate glass tubing was packed with volatile-free glass wool (conditioned for 16 hr at 200 C) loose enough to permit diffusion of oil, yet tight enough to prevent oil seepage from liner onto GC column. Clearance of about six mm was allowed at the bottom of the liner and 20 mm at the top. About 300 mg of the oil sample was added on top of the glass wool plug, and the liner with sample was secured in the heated inlet device for three min.

Capillary GC/MS

A Finnigan-Mat Model 4000 Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS) was used in the identification of the volatile components of the oils. A SE-54 capillary column having the same physical dimensions and characteristics as the column described above was used for the GC/MS analysis. The external inlet was interfaced to the capillary injector via the carrier flow supply about an inch before entering the capillary injection port. The injector was run in the "split" mode, and the split ratio was adjusted to 5:1. The GC oven was cooled to −30 C with dry ice. The glass liner containing 500 mg of oil was secured in the external inlet, and the six-port valve was switched to the inject mode. The data system and GC were started, while keeping the oven at −30 C for a five-min injection. After the injection time, the valve was switched to the run mode and the GC oven was heated to 30 C at 10 C/min, to 150 C at 2.5 C/min, then to 250 C at 5 C/min. The mass spectrometer was scanned from 33 to 450 amu in one sec. The acquisition was carried out for 80 min

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resulting in 4800 scans. The peaks were identified by comparision with library spectra and retention times. Mass spectra were confirmed by chromatographing authentic standards.

RESULTS AND DISCUSSION

The close correlation of taste panel flavor scores with total volatiles (TV) and with some of the individual volatile compounds as determined by the direct GC method of Dupuy et al. (1-3) has been demonstrated and has become a useful tool for determining the degree of deterioration of vegetable oils (3, 5, 8, 11). Previous findings showed that pentane, TV and *trans*-2, *trans*-4-decadienal gave higher correlation coefficients for flavor score on six oils than did the results of 12 industrial taste panels on the same oils (5). Though the method originally published by Dupuy et al. (1) and later modified (2-8) is a rapid method, the packed columns used in the method have much poorer separation capability than do capillary columns. The latter are known to have 10-100 times the resolving capability of packed columns (16-19). However, the amount of sample that can be added is a limiting factor. Also, in the original method, the sample purge time was 20 min, compared to three min for the method presented herein.

In the present work, three oils were examined by the direct GC method for volatiles using a commercial capillary column equipped with an external inlet device. Two of these oils were the best (lowest in volatiles) of a number of commercial brands taken from supermarket shelves and examined promptly. The third oil is a sample that was low in volatiles initially, but which had been allowed to stand in the laboratory for six mo prior to GC analysis. The GC curves for these three samples, called Oils A, B and C, respectively, are shown in Figures 1, 2 and 3. Table I lists the compounds identified by GC/MS from the curves and shows the relative amounts of each material in the three samples. Based on earlier findings (3, 5, 8, 11), the TV, as well as amounts of several of the major components, are highly correlated with the degree of deterioration of the vegetable oil as measured by flavor score. The large number of compounds and amounts of individual components and TV shown in Figure 3 are typical of the gradual deterioration of a vegetable oil with the passage of time when it is allowed to stand exposed to air and light. The data also show that oil A is obviously a better oil than B.

In conclusion, these studies indicate that the direct gas chromatographic method for determination of volatiles in vegetable oils is improved by use of capillary gas chromatography coupled with the external inlet device in the gas chromatograph. Furthermore, judging from the data shown in Figures 1-3, this method gave increased sensitivity and better resolution when compared to results previously published.

Plans are to examine a series of flavor-scored vegetable oils and compare flavor scores and instrumental data. Other areas being investigated with this cryogenic direct inlet/capillary technology include assessment of quality in meat, fish, poultry, peanuts and sugars, and identification of fungal and plant mediated volatiles.

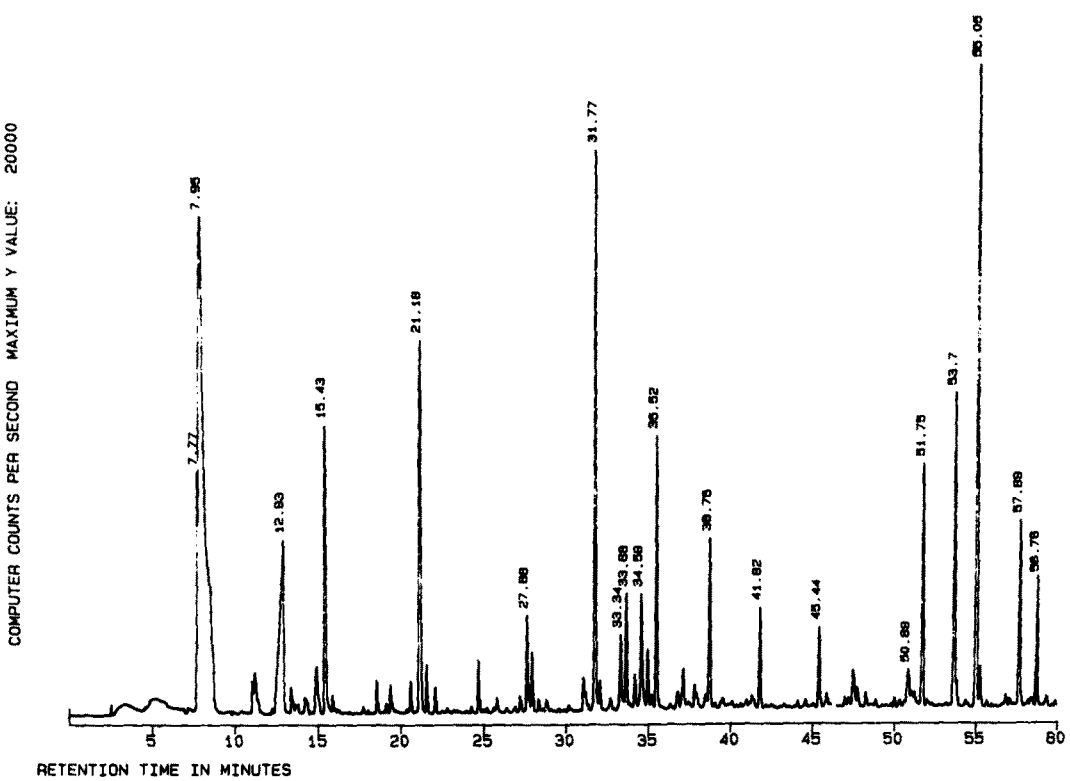

FIG. 1. GLC analysis of "Oil A," a "good" commercial oil as taken from the supermarket shelf. Chromatograms were run for 80 min, but only 60 min are shown.

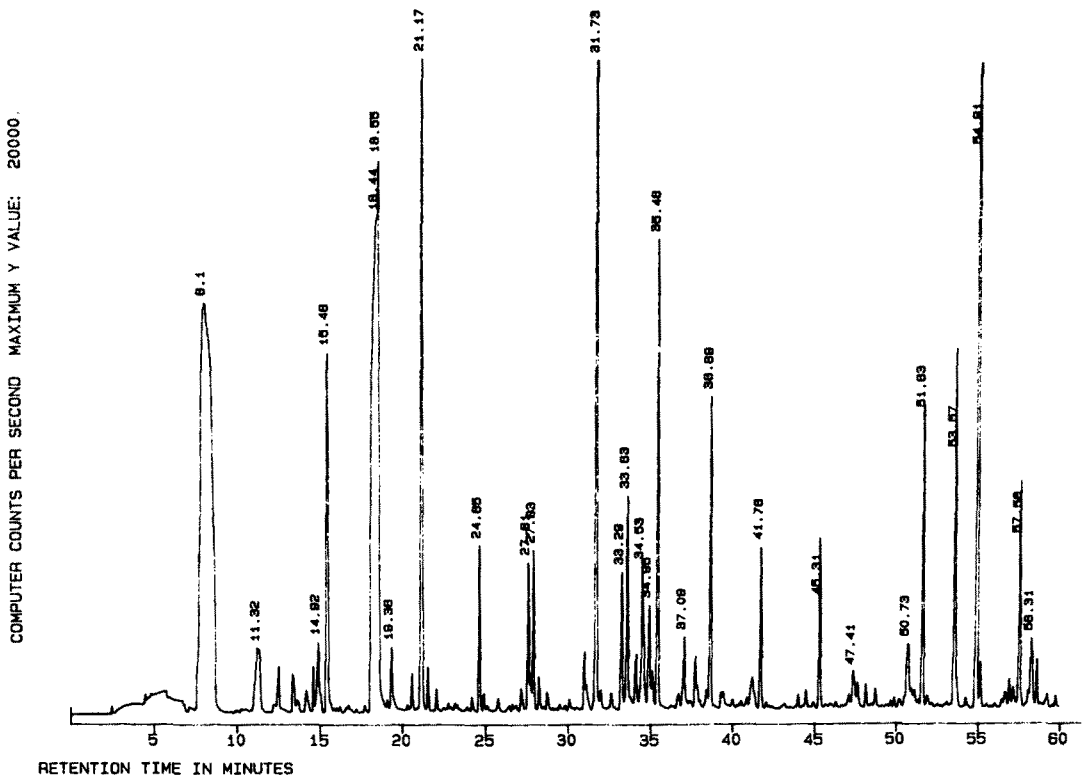

FIG. 2. GLC analysis of "Oil B," a second commercial oil as taken from the supermarket shelf.

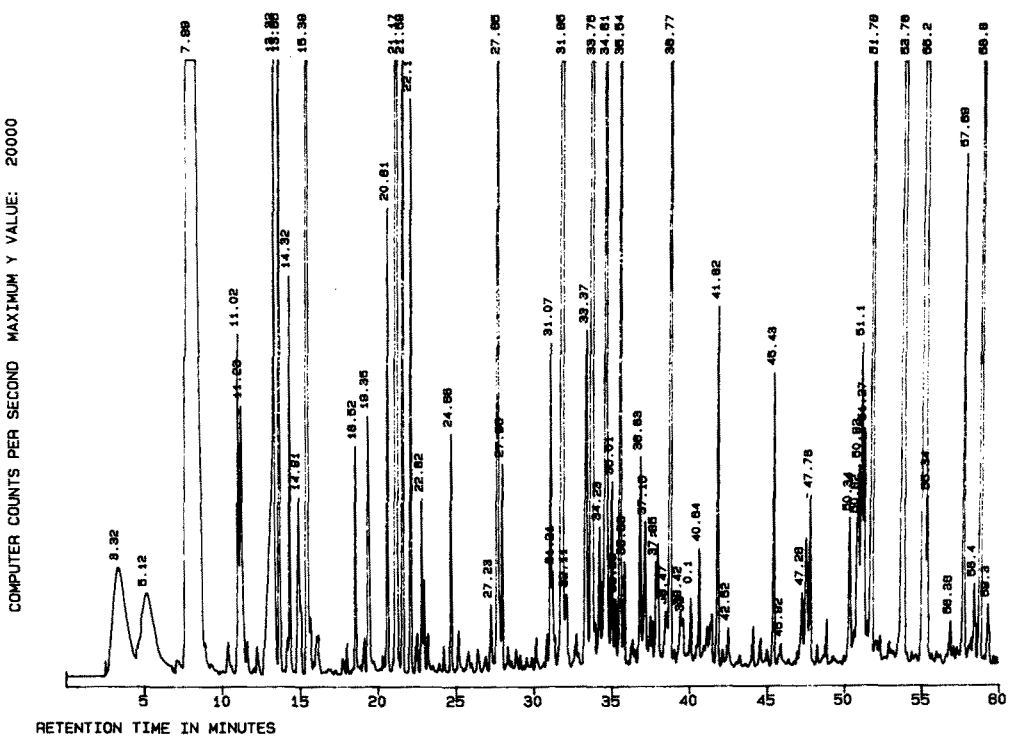

FIG. 3. GLC analysis of "Oil C." a sample of Oil A brand allowed to deteriorate by standing at ambient temperature exposed to light for 6 mo.

TABLE I

Analysis of Volatiles in Vegetable Oils

Volatile compound	Retention time in min	Integrator count × 10^{-3}		
		Oil A	Oil B	Oil C
Acetaldehyde	3.32	2	3	8
Acetone + Pentane	7.99	180	260	1835
Hexane + 2-Butanone	11.02	3	7	30
Butanal	11.23	7	9	40
2-Butenal	13.32	3	5	115
Benzene	13.65	1	2	90
3-Penten-2-one	14.32	1	3	29
Acetic acid	14.91	7	10	24
Pentanal + Heptane	15.39	28	40	195
Ethylfuran	15.66	1	1	7
2-Pentanol	18.52	3	65	19
1-Pentanol	19.35	4	9	35
Toluene	19.75	—	—	2
1-Octene	20.61	3	4	38
Hexanal + Octane	21.17	42	65	340
2-Octene	21.59	4	4	75
3-Octene	22.1	2	2	46
2-Hexenal	24.68	4	13	19
Octatriene	25.8	2	3	4
Nonane	27.80	—	2	5
Heptanal	27.96	5	13	18
2-Butylfuran	31.07	6	6	30
t-2-Heptenal	31.85	47	85	540
1-Hepten-3-ol	33.37	9	14	50
2, 3-Octanedione	33.75	11	22	440
2-Pentylfuran + 2-octanone	34.23	7	7	20
t, c-2, 4-Heptadienal	34.61	15	21	160
Octanal	35.01	1	3	21
t, t-2, 4-Heptadienal	35.54	25	40	90
Limonene	36.83	3	3	25
2-Octenal	38.77	16	26	130
3, 5-Octadien-2-one	40.1	2	2	10
Nonanal	41.82	10	14	36
2-Nonenal	45.43	10	15	30
Benzothiazole	50.34	2	2	23
2-Decenal	51.78	23	30	190
t, c-2, 4-Decadienal	53.78	35	36	485
t, t-2, 4-Decadienal	55.2	70	95	885
Tetradecane	58.8	12	12	160
Pentadecane[a]	63.5	1	2	2
Hexadecane[a]	67.3	7	7	10
Heptadecane[a]	70.45	3	3	8
Octadecane[a]	73.95	9	25	10
Total Volatiles		910	1400	6980

[a]To present more detailed curves, Figs. 1, 2 and 3 were cut off at 60 min retention time. These four minor components, therefore, do not appear in the GC curves, but were identified by GC/MS.

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