Rapid Analysis of Vegetable Oil Flavor Quality by Dynamic Headspace Capillary Gas Chromatography

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A rapid capillary gas chromatographic headspace technique using a multiple purge and trap system was developed and applied for the determination of vegetable oil flavor quality. Oil volatiles were purged at 150°C for 20 min, collected over a Tenax trap and subsequently desorbed and reconcentrated in a series of two smaller traps. From the gas chromatographic profile, three compounds, t-2-heptenal, t-2-octenal and t,t-2,4-decadienal were selected for computation of the flavor score of individual oil samples. Analysis of the flavor quality of soybean oil by this technique demonstrated a very good correlation to the traditional sensory evaluation procedure. Good correlation was also observed for the flavor evaluation of corn oils. Precision, based on multiple analyses of known standard aldehydes, was shown to be better than 6%. The degree of chromatographic efficiency obtained by this multiple concentration technique permitted the use of a short 25-min chromatographic run in the resolution of these aldehydes of interest. This approach reduced the overall analysis time of existing instrumental oil flavor techniques significantly.

The analysis of headspace volatiles by gas chromatography is rapidly becoming an important tool for determining the flavor quality of a wide range of food products (1). Application of this technique to the objective quality evaluation of vegetable oils has generated extensive interest in the food industry, particularly in quality assurance programs where large sample volumes and minimal production delays are of prime consideration. Since its introduction many investigators have attempted to improve both the reliability and speed of this procedure (2,3). Although considerable advances in the reliability were made, a lack of instrumental versatility resulted in individual analysis that often exceeded two hours in duration (4,5).

Early designs of oil sampling devices lacked the accuracy and precision for product quality applications. Marginal correlations between gas chromatographic scores and taste panel evaluations were reported during this period particularly when speed in the instrumental operation was emphasized (6). With the gain in instrumental sophistication, reliability was considerably improved though often at the cost of analysis time. The advent of modern dynamic purge devices along with high resolution chromatographic technology further enhanced the reliability and afforded an overall reduction in individual oil analysis times to under two hours per sample. However, the number of analytical runs that could be performed in a single day was still limited.

Many published reports have linked individual compounds isolated from oil volatiles with flavor panel scores (6-9). Good correlations have been observed for a number of these gas chromatographic components including pentane, 2,4-decadienal, as well as total volatiles. Recently, Fraser and Khayat (10) reported the measurement of t-2-heptenal, t-2-octenal and t,t-2,4-decadienal as an indication of flavor quality in unhydrogenated soybean oil. Their studies demonstrated a precise correlation between the levels of these breakdown products of lipid hydroperoxides and taste panel ratings. Current instrumental procedures require lengthy chromatographic separation times to effectively resolve the complex headspace volatile mixture despite the use of high resolution capillary columns that offer superior reliability and speed. Such techniques rely on the preconcentration of oil volatiles at the head of the column at subambient temperatures with gradual release into the column at incremental temperature rates (11,12). More recently headspace enrichment adsorbant traps with cryogenic focusing have been used for sample preconcentration to maintain efficient separations (13). Adsorbants such as Tenax, activated charcoal and Ambersorb, packed in large stainless steel cylindrical traps, permitted the retention of organic compounds of a wide molecular weight range. These traps allowed the sample size and purge time to be maximized for trace level analysis. High temperature tolerance and efficient desorption of the polymers further extended the overall applicability, particularly towards the retention and volatilization of the high boiling, polar oil fractions. However, entrapped volatiles from large stainless steel traps, possessing relatively poor heat transfer efficiencies, desorb into the capillary column as broad input bands.

Optimization of input band width in the sampling system is one of the most critical factors in maintaining high column efficiency in capillary gas chromatography (14). The equation

$$N_t = \frac{N_{max}}{1 + b^2}$$

where N_t and N_{max} are the observed and maximum plate numbers and $b = \frac{i}{c}$ (where i and c are the input band width and chromatographic peak broadening respectively), shows that a narrower input band width generates a larger observed plate number. Because peak broadening is directly proportional to the analysis time in chromatographic separations, it follows that input band width is also proportional to the analysis time. Thus, for a maximum column efficiency in a minimal analysis time, regulation of the input band width as a narrow plug is significant. Sampling devices that enable the minimization of the input band width, while allowing the introduction of a maximum sample volume, are best suited for high efficiency rapid analyses.

The objective of this study was primarily to enhance the speed of oil volatiles analysis by introducing an efficient preconcentration step for sample enrichment. A multiple trapping scheme was utilized offering a twofold gain: 1) Cyrogenic conditions were eliminated while maintaining column sample introduction in a narrow band, and, a rapid temperature program rate was attained under these conditions without any loss in chromatographic resolution of the key compounds; and 2) Independent stripping and concentration/separation stages allowed

overlap between these steps. Consequently, continuous operation for high volume multiple analyses was possible and resulted in total analysis time reductions by one-half to one-third that of existing methods. The focus was on determining the flavor quality of vegetable oils that were both freshly processed and aged for periods exceeding six months.

EXPERIMENTAL

Sample Preparation. Vegetable oils were obtained from a supermarket, sampled in 100-cc capped vials that were blanketed with a nitrogen headspace and stored in a -10°C freezer. Freshly processed oils were obtained directly from the plant and sampled again in 100-cc vials. Individual vials were thawed at room temperature prior to analysis.

One gram of oil was placed in a clean 20-cc glass vial, flushed with nitrogen at room temperature and purged at 150°C for 20 min in the Dynamic Thermal Stripper Model 1260 (Envirochem) with nitrogen flowing at 50 cc per minute. Tenax was the trapping medium employed. Reference aldehyde standards were purchased from Aldrich Chemicals, Inc. Methyl nonanoate (Aldrich) was added at a concentration of 1050 ppb to the one gram of oil as an internal standard.

GC Analysis. A Varian 6000 gas chromatograph fitted with a flame ionization detector was employed. Nitrogen was used as the carrier gas (1.5 ml/min) and the make-up gas (30ml/min). Flow rates of air and hydrogen in the flame ionization detector were established at 300 and 30 ml/min respectively. All separations were performed with a 60m × 0.32 mm DX-1 fused silica column (J&W Scientific) having a one micron coating of a 10% polyethylene glycol liquid phase. To the Varian 6000 was coupled a Unacon Concentrator Model 810A (Envirochem).

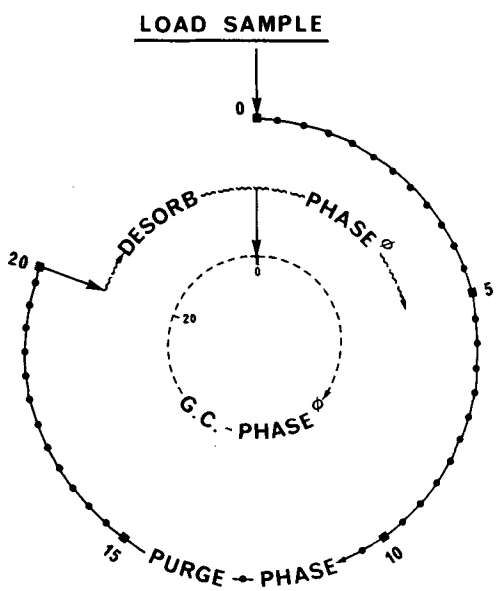

FIG. 1. Sequence of timed events (in minutes) for the isolation of oil volatiles. Desorb phase (Sorbant tube = 3 min.; Trap 1 = 2 min., Trap 2 to Column transfer = 5 min.) G.C. phase (G.C. run time = 20 min.; G.C. oven cool time = 5 min.)

Desorption temperature was set at 250°C for 3 min. Individual trap desorption temperatures were factory preset at 230°C. A 10:1 split ratio was employed in the initial desportion step. The column oven was held at 50°C for one minute and programmed at 10°C/min, to a final temperature of 210°C. Where it was held for another three minutes, data was acquired and integrated with the Hewlett-Packard Model HP3359 Laboratory Automation System and plotted on a Hewlett-Packard HP9872C plotter.

Headspace Analysis. Headspace volatiles were initially purged onto a large-bore Tenax collection trap. This unit was dismantled from the stripper and desorbed. The volatiles were transferred onto a smaller Tenax trap and finally reconcentrated in a narrow bore trap. Contents of the smaller trap were then swept into the capillary column where chromatographic separation followed.

The scheme of analysis with such a multiple-trap concentration procedure involved a 5-min preconcentration phase followed by the 20-min gas chromatographic run and cool cycles (Fig. 1). Separation of the purge device from the concentrator/gas chromatograph permitted their concurrent operation. Subsequently, an overall 25-min cycle was attained. Decreasing the purge time from the current 20 minutes has no effect on the total number of analyses that can be achieved, as long as the chromatographic step is maintained at its current 25-min duration. However, further time reductions are possible when both gas chromatographic and purge times are reduced. This is not recommended for determination of flavor scores by the procedure outlined here, as a loss in chromatographic resolution is encountered for the three aldehydes selected.

RESULTS AND DISCUSSION

Headspace volatiles of vegetable oils from lipid hydroperoxide decomposition have been extensively studied in the past decade. An extensive list of oil breakdown products has been characterized (15,16). Included in this list are the aldehydes t-2-heptenal, t-2-octenal and t,t-2,4-decadienal formed from the oxidation of linoleic acid. Measured levels of these aldehydes in soybean oil were correlated to taste panel scores, according to a procedure reported recently (10) based on the studies of Min (7,8) and others. Oil flavor scores (FS) were computed according to the equation:

$$FS = 17.85 - (1.12 \log A_C^H + 1.04 \log A_C^O + 0.95 A_C^D)$$

where A_C^H, A_C^O, and A_C^D are values of the peak areas observed for t-2-heptenal, t-2-octenal and t,t-2,4-decadienal respectively, normalized to the internal standard methyl nonanoate and individual response factors under these analytical conditions. Initially, response of these aldehydes under the rapid multiple-trapping conditions employed in this study was investigated based on the addition of known concentrations of each component in a freshly deoderized, unhydrogenated soybean oil (Fig. 2). In the range of 50 to 2000 ppb, the regression values (R^2) exceeded 0.99 (N = 5) with relative standard deviations of under 2% for heptenal, octenal and methyl nonanoate and 5.8% for decadienal (see Table 1).

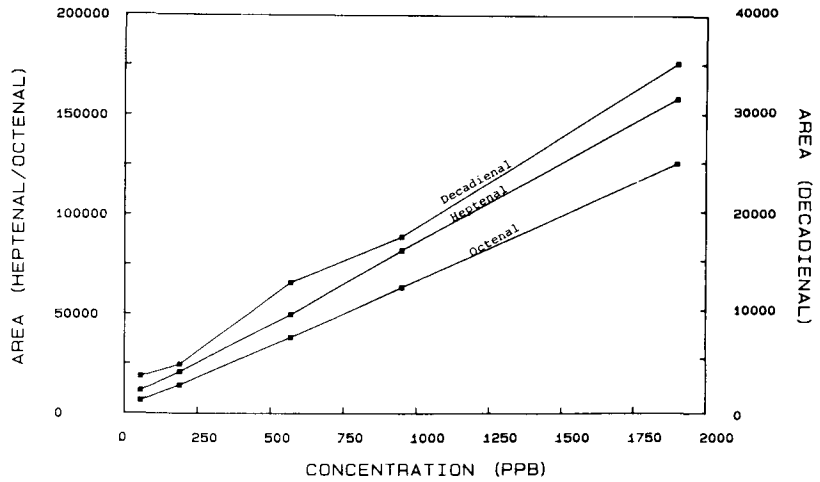

FIG. 2. Instrumental response for octenal (R^2 = 0.99), heptenal (R^2 = 0.99), and decadienal (R^2 = 0.99) in the concentration range between 57 and 1900 ppb.

TABLE 1

Analysis of a Known Mixture of Aldehydes and Methyl Nonanoate (internal standard) Using the Multiple-Trap Volatiles Analyzer

	Corrected Area Counts			
Analysis No.	2-t-heptenal	2-t-octenal	2,4-t,t-decadienal	methyl nonanoate
1	36213	27876	7981	86117
2	36538	27720	7768	84288
3	37491	28624	8676	86818
Coefficient of variation (%)	1.8	1.7	5.8	1.5

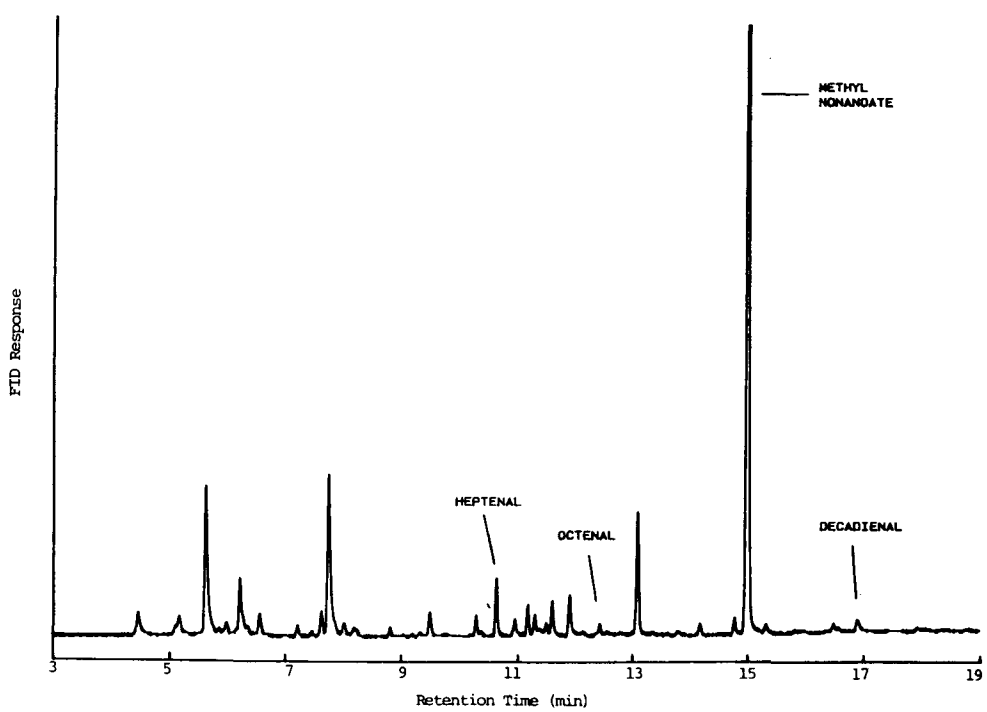

FIG. 3. Profile of soybean oil volatiles purged at 150°C for 20 minutes. (Methyl nonanoate added as an internal standard.)

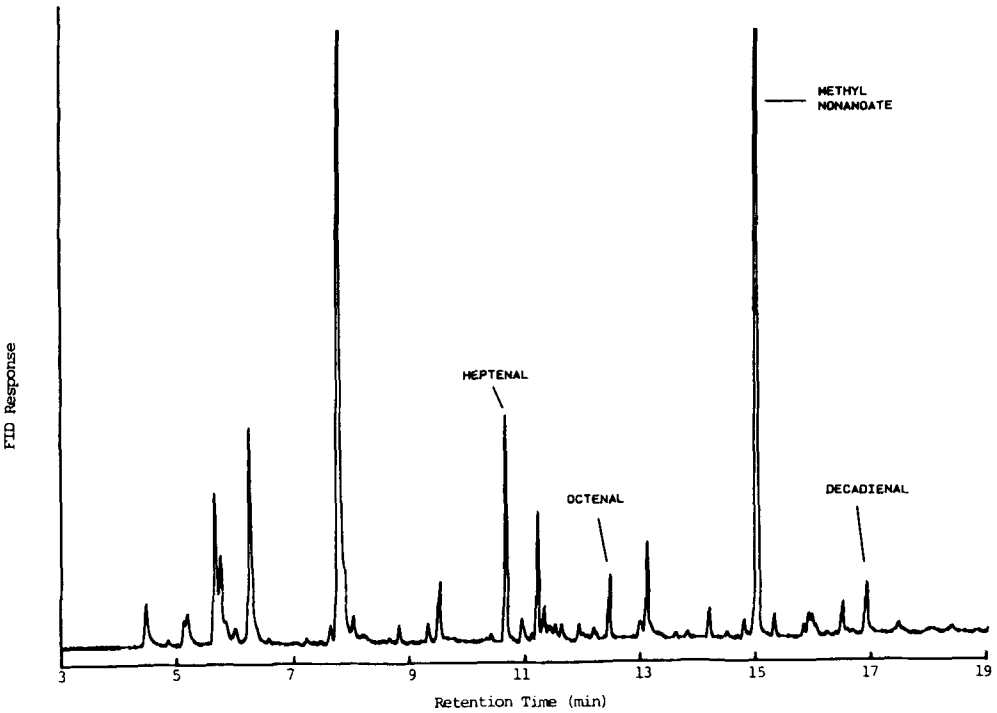

FIG. 4. Profile of corn oil volatiles purged at 150°C for 20 minutes.

TABLE 2

Concentration of Heptenal, Octenal and Decadienal in Twelve Randomly Selected Soybean Oils With the Instrumental and Sensory Flavor Scores

	Concentration (ppb)			Flavor Score	
Sample	Heptenal	Octenal	Decadienal	Sensory	G.C. (σ)
1	92	40	94	6.7	6.8 (± 0.2)
2	83	18	65	6.8	7.0 (± 0.2)
3	124	30	91	6.9	6.7 (± 0.1)
4	184	48	126	6.9	6.2 (± 0.1)
5	87	19	52	6.9	7.0 (± 0.3)
6	207	25	93	6.9	6.6 (± 0.2)
7	224	21	108	6.4	6.6 (± 0.2)
8	217	74	157	6.5	5.9 (± 0.1)
9	185	34	206	6.6	6.2 (± 0.1)
10	75	10	69	6.7	7.0 (± 0.3)
11	96	14	113	6.7	7.0 (± 0.2)
12	88	22	132	6.8	6.9 (± 0.2)
$\bar{X}$				6.73	6.66

The extent of the loss of volatiles during the deoderization process in soybean oil dictates the final blandness of the flavor of the oil. Freshly processed, soybean oil, purged extensively at 150°C, exhibited relatively low levels of such volatiles. Aldehydes in these oils were measured at levels under 40 ppb. The blandness of this oil was verified by trained oil taste panelists who rated the product on a scale of 7.0 (excellent) to 4.0 (poor). Gas chromatographic profiles of freshly processed soybean and corn oil volatiles under rapid, multiple-trapping analyses illustrated this apparent absence of major components in these oils (Figs. 3 and 4). Unique characteristics were observed in each profile as can be expected from flavor distinctions between soybean and corn oils. For our purpose, it is important to note the excellent separation of heptenal, octenal and decadienal. More volatile compounds, particularly the abundant hydrocarbons pentane and hexane, eluted in the first ten minutes of the run. At best, only partial resolution can be expected in this region where extended temperature programs are necessary. However, these early eluting components of the chromatographic profile were not necessary in our oil flavor-score computation. Heptenal, octenal and decadienal, eluting at temperatures of 145, 160 and 205°C respectively were sufficiently retained in the column to provide separation from the more volatile short-chain hydrocarbons. Hexane, the major product of linoleic decomposition, demonstrated lower correlations to the sensory rat-

TABLE 3

Concentration for Heptenal, Octenal and Decadienal in Twelve Randomly Selected Corn Oils With the Instrumental and Sensory Flavor Scores

	Concentration (ppb)			Flavor Score	
Sample	Heptenal	Octenal	Decadienal	Sensory	G.C. (σ)
1	366	68	283	5.3	5.4 (± 0.2)
2	1425	145	970	4.4	3.9 (± 0.3)
3	531	76	596	5.3	4.8 (± 0.2)
4	413	101	384	5.1	5.0 (± 0.2)
5	419	53	366	5.6	5.3 (± 0.1)
6	611	57	289	5.2	5.2 (± 0.2)
7	641	53	444	5.5	5.0 (± 0.3)
8	338	49	279	5.7	5.6 (± 0.1)
9	807	120	2026	4.2	3.9 (± 0.4)
10	420	71	311	5.1	5.2 (± 0.2)
11	752	64	340	4.9	5.0 (± 0.2)
12	685	60	285	5.4	5.1 (± 0.3)
$\bar{X}$				5.14	4.95

ings under these conditions. This could be attributed to the influence of a coeluting peak as a shoulder on its tailing edge (Figs. 3 and 4).

Aged processed soybean and corn oils exhibited significantly increased levels of each of the three aldehydes. Formation of the hydroperoxide precursors have been demonstrated to correlate to storage conditions, the presence of processing aids such as citric acid and the inclusion of antioxidants such as BHT and tBHQ (17). Quantitation of the observed aldehyde levels allowed direct comparisons with organoleptic evaluations of these oils by trained taste panelists. The flavor scores as determined by gas chromatography of both soybean and corn oils are presented along with taste panel scores in Tables 2 and 3. Instrumental flavor scores were determined by the equation presented earlier. In the reported flavor range between 4.0 and 7.0, average difference between the two techniques was under 0.3 points. These results clearly demonstrated the close agreement between predicted flavor scores of instrumental and sensory analyses by this technique.

Statistical evaluation using multiple regression analysis of soybean volatiles indicated a marginal improvement in the correlation coefficients with the incorporation of additional compounds in the volatiles profile beyond the current three aldehydes. Other studies have demonstrated close correlations between total oil volatiles and the taste panel flavor scores (9). Our objective focused on the need for reliable and rapid analyses. The short chromatographic run time employed in this study was well suited for complete separation of these aldehydes from the remaining headspace gases for both soybean and corn oils. Inclusion of additional components resulted in resolution difficulties for corn oil volatiles and subsequently this approach was disfavored. The potential for a more rapid analysis based on the measurement of total volatiles has been attempted in these studies. The Unacon Concentrator, fitted with an independent flame ionization detector, has the capability of monitoring oil volatiles eluting from the small bore trap prior to entry in the gas chromatographic system. This process is completed in under five minutes. However, without a concurrent decrease in the purge time, the overall procedure cannot be further reduced from its present 25-minute duration.

Much has been written on the importance of sample introduction in the overall efficiency of the separation process in chromatography (14,18,19). In general, it is desirable for the purged volatiles to be introduced into the column in a narrow band thereby minimizing peak spreading and leading to an increase in the plate number. Initial trapping of purged organics demand large bore traps. With a large amount of packing material, extended collection periods from large samples are possible. These traps enable the capture of compounds at trace levels that are frequently important in the overall characteristic of the sample, as evident in many food and flavor investigations. Such large bore traps are typically stainless steel tubings with internal diameters ranging from 50 mm to 80 mm. Transferring captured volatiles to narrow bore traps, particularly at low capillary flow rates, results in a concentration of the headspace gases. This process provides efficient desorption onto the capillary column where high resolution at high speed is maintained.

Although resolution in gas chromatography can be enhanced by lowering the column temperature, the practical limit to low temperature separations is a lengthy analysis time. Headspace preconcentration with polymer adsorbants affords the advantage of a considerable time savings. Additionally, significant cost savings are realized when cooling gases such as liquid carbon dioxide or liquid nitrogen are eliminated.

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