Oilseed Volatile Analysis by Supercritical Fluid and Thermal Desorption Methods

Janet M. Snyder* and **Jerry W. King**
Food Quality & Safety Research Unit, NCAUR, ARS, USDA, Peoria, Illinois 61604

A knowledge of the volatile components present in an oil sample can provide important information relative to supercritical fluid extraction (SFE) process design, the current oxidative state of the oil, as well as the concentration and presence of important flavor volatiles in the oil. Volatile compounds from supercritical fluid-extracted oils were analyzed by headspace gas chromatography (GC) methods to determine if there were differences in the volatile profiles when two different methods of desorption were used. Canola, corn, soybean and sunflower seeds were extracted with supercritical carbon dioxide at 8000 psi and 50°C. Tenax porous polymer traps, attached at the exhaust port of the SFE apparatus, were utilized to collect the volatile components during the extractions. The volatile compounds on the Tenax trap were desorbed onto a GC column by both thermal and supercritical fluid techniques. Desorption temperature for the thermal method was 150°C, while conditions for the SFE technique were 50°C and 2000 psi. The lower-boiling volatiles from each oilseed were greater when desorbed by thermal means from the Tenax than by SFE; however, SFE desorbed the higher-molecular weight compounds that were not removed by the thermal desorption method. Hexanal tended to be desorbed in comparable amounts by both methods. The SFE-based desorption technique provides a unique analysis method for the determination of both volatile and semi-volatile compounds, as well as executing desorption under nonoxidative, low-temperature conditions that do not contribute to the degradation of lipid components.

KEY WORDS: Canola oil, corn oil, soybean oil, sunflower oil, supercritical CO_2, supercritical desorption, thermal desorption, volatiles.

Headspace analysis of seed oil volatiles is dependent on the analysis technique (1,2). Static headspace analysis of volatile compounds depends on the equilibrium that exits between the sample and the gas phase in the sampling vessel; hence, lower-boiling components in mixtures are preferentially detected by this technique (2,3). Dynamic headspace techniques produce a different volatile profile because the volatile sample is concentrated as the headspace gas passes through a porous polymer adsorbent (2–4).

Temperature also has an effect on the composition of the volatile compounds collected during the purge cycle of dynamic headspace sampling. Higher concentrations of these compounds can be measured as the temperature is increased (5,6). However, unsaturated compounds produced by lipid oxidation are heat-labile compounds (7,8); therefore, nondestructive methods are needed for the evaluation of the volatiles to prevent further degradation of the compounds during the analysis procedure.

Research has demonstrated the advantage of supercritical (SC) fluids to extract flavor compounds from a variety of foods when followed by direct transfer of the volatiles onto gas-chromatographic capillary columns (9,10). Desorption of volatiles from sorbent resins by supercritical fluid extraction (SFE), with subsequent analysis by gas chromatography (GC), offers the advantage of improved sensitivity, less degradation of the analytes and short analysis times (10–12). King *et al.* (13) have investigated the conditions for the SFE desorption of identified seed oil volatiles from sorbents used in the analytic sampling and/or cleanup of extraction fluid gas streams.

In the present study, we report the development of an SFE technique for recovery of seed oil volatiles as a mild method to analyze lipid samples that are easily decomposed.

EXPERIMENTAL PROCEDURES

Canola, corn, soybean and sunflower seeds were extracted by a previously reported SFE method (14) with SC-carbon dioxide (CO_2) as the extraction fluid. Canola, dry-milled corn germ and soybeans were flaked, while sunflower seeds were ground in a small grinder before extraction. Twenty grams of prepared oilseed was loaded into a high-pressure extraction vessel (1.43 cm i.d. × 61 cm), which was then inserted into the oven of a laboratory-built extraction apparatus (15). Each oilseed type was extracted twice with SC-CO_2 for 30 min at 8000 psi and 50°C. The extracted oil was collected in a receiver, which consisted of a bolted autoclave, in which the oil could be collected, and an exit line that permitted venting of the depressurized CO_2. A trap (0.6 cm i.d. × 18 cm), containing 0.8 g Tenax 20/35 mesh sorbent (Alltech Associates, Inc., Deerfield, IL) that was conditioned to remove any foreign compounds, was then positioned at the exit end of the receiver vessel (Fig. 1). The adsorbent-conditioning process included heating the trap at 200°C for 30 min with a helium flow of 40 mL/min through the trap. Compounds present during the extraction process were collected on the trap.

A flow rate of 500 mL/min CO_2 gas through the trap was maintained during the extraction of the oil. The Tenax trap was changed after 10 L of CO_2 had eluted through each trap. During development of the method, a second trap was added immediately after the first to determine if there was elution of any compounds from the initial trap. The flow rate of the CO_2 and the extraction time were also adjusted to avoid the elution of the more volatile compounds off the Tenax trap. A sample of oil was removed from the receiver as the trap was changed; four oil and volatile samples were collected during the extraction period.

The volatiles collected on the Tenax traps were desorbed by both thermal and SFE methods. Thermal desorption was accomplished in a modified Tekmar 4000 headspace Concentrator (Tekmar, Cincinnati, OH) (2,5). The volatiles were desorbed from a Tenax trap (0.8 g) at 150°C for 1 min at a helium flow rate of 40 mL/min and were injected onto a DB-1701 capillary column (0.32 mm × 30 m) (J&W Scientific, Folsom, CA); the split ratio for helium was 50:1 during injection. The Perkin-Elmer Sigma 3B GC (Perkin-Elmer, Norwalk, CT) was held at −50°C for 1 min to allow for cryogenic focussing, and then the oven temperature was ramped at 5°C/min to 250°C. The volatile

*To whom correspondence should be addressed at NCAUR, ARS, USDA, 1815 N. University St., Peoria, IL 61604.

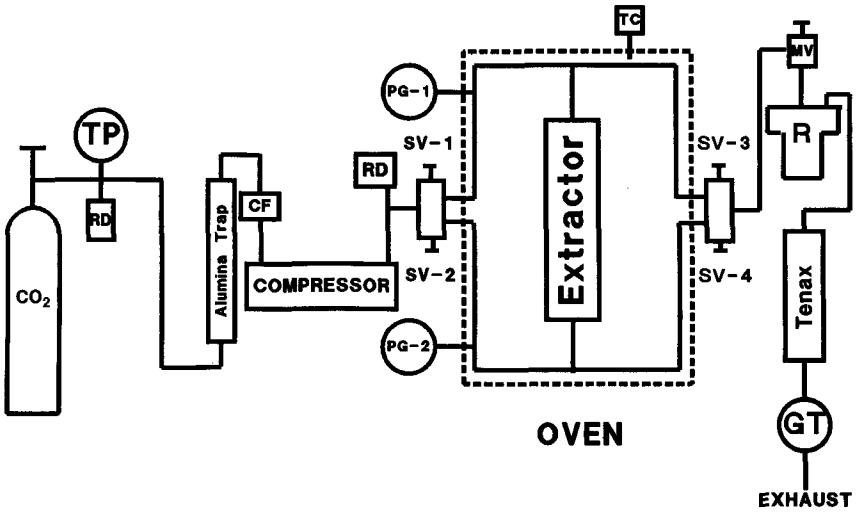

FIG. 1. Diagram of supercritical fluid extraction apparatus with Tenax trap (Alltech Associates, Inc., Deerfield, IL) at the exit port of the receiver. TP—total-pressure gauge; RD—rupture disc; CF—filter; PG—pressure gauge; SV—shut-off valves; TC—thermocouple; MV—micro-metering valve; R—receiver; Tenax—trap filled with Tenax sorbent; GT—gas totalizer.

compounds were measured and identified with a Finnigan Mass Spectrometer OWA 1050 (San Jose, CA). Mass spectra were obtained in the electron impact mode at an ionization voltage of 70 eV over the mass range of 20–450 amu.

Volatiles were also desorbed from the Tenax sorbent by an SFE method. Each trap, containing approximately 0.8 g Tenax adsorbent, was placed into a high-performance liquid chromatography column oven (Bio-Rad Laboratories, Richmond, CA) to maintain the desorption temperature. The extraction pressure was generated by connecting one end of the trap to an Isco high-pressure syringe pump (Model SFC-500 Microflow Pump; Isco, Lincoln, NE) and installing a 19-μm i.d. fused-silica back pressure restrictor at the exit end of the trap. The tip of the restrictor was then inserted into the septum of the GC injection port so that the end of the restrictor was positioned close to the capillary column.

An extraction pressure of 2000 psi and temperature of 50°C were used to elute the volatiles onto the GC column over a 1-min desorption period. In addition, an SFE desorption temperature of 150°C was used to elute the volatiles from the Tenax traps, used during extractions of soybeans, to compare the volatile profiles obtained at two different desorption temperatures. As before, the split ratio for the injector was 50:1 during the desorption step. The GC analysis conditions were the same as for the thermal desorption method. The concentrations of the volatile compounds obtained by each desorption method were calculated from an average of four analyses, two extractions from two traps for each extraction.

Volatile component standards were obtained from Bedoukian Chemicals (Danbury, CT). All dilutions of the standards were prepared in hexadecane. Concentrations of the components varied from 50 ppb to 500 ppm and were determined from the ion current for the most prominent amu peak for each standard. From the calibration curves determined over the above concentration ranges with hexadecane as an internal standard, concentrations were determined for each standard compound for both methods of desorption. The response curves for eight of the volatile components were found to be linear.

Tenax traps from each oilseed extraction were reprocessed three times by each desorption method to determine if the volatile compounds were completely desorbed from the Tenax by each method. Hexanal concentration was measured to demonstrate completeness of the removal of the volatile components from the Tenax sorbent.

RESULTS AND DISCUSSION

The volatile profiles for corn oil in Figure 2 demonstrate the recorded differences between the two desorption methods; many of the major compounds were identified. As indicated in Figure 2A, desorption by SFE permits determination of higher-molecular weight components that are not observed in the thermal desorption-derived chromatogram. Higher-molecular weight compounds, determined by SFE, that were positively identified, included 2,4-decadienal isomers, hexadecanol, oleic acid and octadecanol. Thermal desorption permitted the analysis and characterization of the indicated lower-molecular weight compounds (Fig. 2B). Many compounds, such as the C3 and C4 saturated and unsaturated aldehydes as well as C2-C4 hydrocarbons, were present in the thermal desorption-derived chromatograms. Only trace amounts of propanal are evident in the chromatograms from SFE. Similar volatile components were also identified in the chromatograms obtained from canola and sunflower oil.

Chromatograms of the volatiles from soybean oil that were obtained by SFE desorption at temperatures of 50 and 150°C are illustrated in Figure 3. The peaks have been computer-enhanced for the scans from 300 to 850 in both chromatograms. This enhancement was performed with the aid of an off-line computer, MODCOMP Model 32-85 (Modular Computing Systems, Inc., Fort Lauderdale, FL) to show in greater detail the differences in volatiles

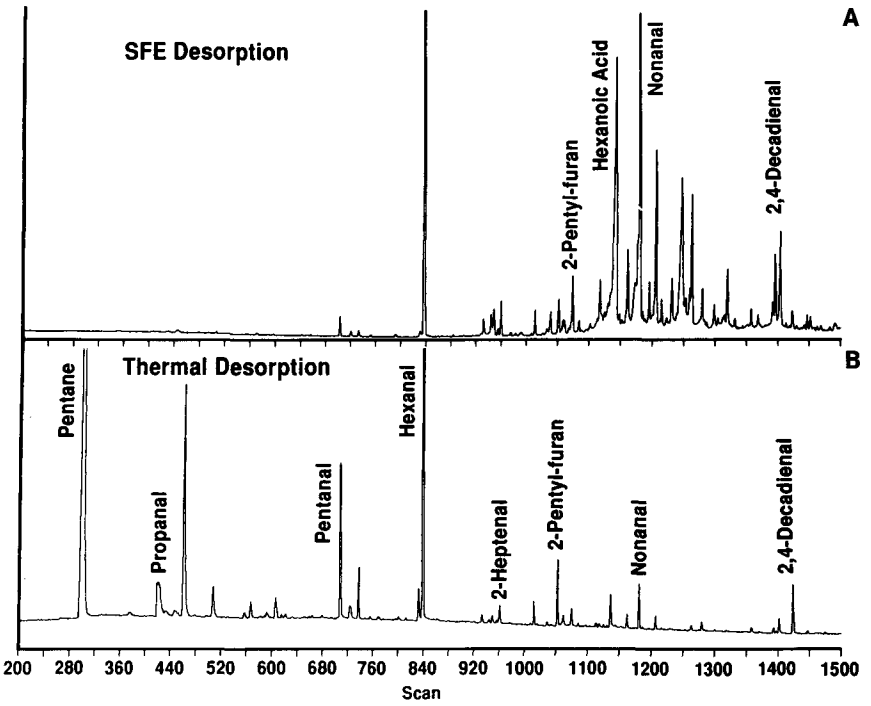

FIG. 2. Gas chromatography/mass spectrometry ion current chromatograms of volatiles and semi-volatiles from supercritical fluid extraction (SFE) corn oil extracted at 8000 psi and 50°C: A, SFE desorption at 50°C for 1 min; B, thermal desorption at 150°C for 1 min.

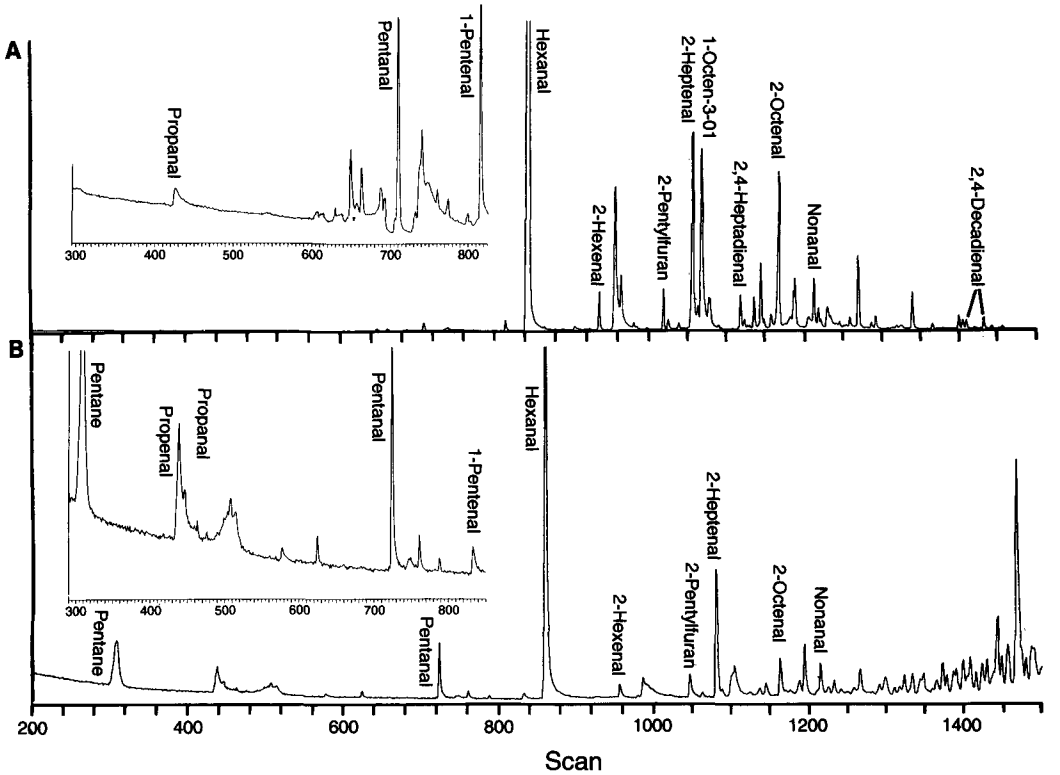

FIG. 3. Gas chromatography/mass spectrometry ion current chromatograms of volatiles and semi-volatiles from soybean oil extracted at 8000 psi and 50°C. Insets are the enhanced chromatograms for scans 300–850: A, supercritical fluid extraction (SFE) desorption at 50°C for 1 min; B, SFE desorption at 150°C for 1 min.

obtained at the two desorption temperatures. Degradation products, such as pentane and propanal, were greater when the SFE desorption temperature was 150°C (Fig. 2B) than when the temperature was 50°C (Fig. 2A). The concentration of the unsaturated aldehyde pentenal was smaller at 150°C, due to its decomposition at the higher temperature. The volatile profiles obtained at the two temperatures were different; however, the hexanal concentration was still the largest of all compounds present at both desorption temperatures. Peaks between scans 1300 and 1500 in Figure 3B were artifacts that were formed when a temperature of 150°C was used during SFE desorption.

The concentrations of eight major components found in the four vegetable oils by both adsorption techniques are compared in Table 1. The concentrations of pentane and pentanal compounds were larger when desorption was conducted by the thermal desorption method than with the SFE method. Decomposition of thermally labile compounds to low-molecular weight products has been reported (3), and the desorption temperature of 150°C can cause additional degradation of the volatile components. However, when lower temperatures were used for thermal desorption, many of the higher-boiling compounds were retained on the Tenax due to incomplete desorption.

The concentrations of pentane and pentanal, as determined by single ion monitoring (SIM) during mass spectrometry, were lower in all four oils by SFE. Hexanal concentrations were similar for all oils after using either method of desorption. However, the values for SFE desorption were slightly higher than those obtained from thermal desorption of the samples. As shown in previous studies (3), the quantity of hexanal was greatest in sunflower oil, which contains approximately 75% linoleic acid. Nearly equal concentrations of hexanal were measured for corn and soybean oils, which contain about 55% linoleic acid. Hexanal was lowest in canola oil, which contains 22% linoleic acid. Correspondingly, the concentrations of 2-heptenal and 2,4-decadienal, also formed from the decomposition of linoleic acid (8), were highest for sunflower oil, followed by soybean and corn oils, and then canola, which contained the least amount of linoleic acid. Concentrations of 2-heptenal, 2-pentylfuran, octanal, nonanal and 2,4-decadienal were all consistently higher when the compounds were desorbed from the Tenax by SC-CO_2. This indicates an advantage inherent in the SFE method over the thermal desorption technique.

The results of the evaluation of the completeness of the two desorption techniques are presented in Figure 4. For this evaluation, the desorption times were 1 min for all analyses. The samples were extracted a second and a third time to measure any residual analyte remaining on the Tenax sorbent after the initial extraction. As indicated, small amounts of residual hexanal were present as determined by the second desorption step of each method; however, no hexanal was found in the third desorption. Hexanal concentration was always higher for the second thermal desorption than for the second desorption with SFE. This shows that the SFE method is either more effective than the thermal desorption method for removing trace levels of analyte from the sorbent resin, or abates the formation of hexanal by preventing thermal decomposition of higher-molecular weight adsorbed components. Longer extraction times were also tried for the first thermal desorption. However, traces of hexanal were always present during the second analysis. Again, higher temperatures can be used to remove the hexanal, but this will induce decomposition of the unsaturated volatiles, thereby changing the composition of the total volatile profile.

In summary, both volatile and semi-volatile compounds were successfully collected on Tenax sorbent after decompression of the SC-CO_2 utilized during the extraction of several oilseeds. Volatile components were successfully desorbed and detected by the thermal desorption method. However, only SC fluid-based desorption permitted the analysis of semi-volatile species, which were not effectively desorbed by the thermal-based procedure. The reported results suggest that some improvement may be necessary in the SFE-based desorption method to recover the more volatile compounds if these compounds are in the seed oil and not artifacts of the thermal

TABLE 1

Volatile Concentration in Vegetable Oils

Volatile compound	Type of desorption	Concentration[a] (ppb)			
		Canola	Corn	Soybean	Sunflower
Pentane	Thermal	16.1	409.2	72.3	161.6
	SFE	8.5	24.9	7.4	97.3
Pentanal	Thermal	3.3	73.9	61.1	247.5
	SFE	0.7	3.9	13.9	80.3
Hexanal	Thermal	34.4	284.1	298.9	403.7
	SFE	38.7	317.8	328.9	425.4
2-Heptenal	Thermal	1.0	1.9	119.9	74.1
	SFE	3.7	128.0	179.1	216.8
2-Pentylfuran	Thermal	2.7	14.2	71.7	30.9
	SFE	24.1	95.5	44.8	61.3
Octanal	Thermal	0.5	4.5	0.3	9.9
	SFE	3.2	37.6	1.8	36.6
Nonanal	Thermal	20.6	18.6	18.9	24.8
	SFE	111.5	201.2	76.9	115.6
2,4-Decadienal	Thermal		23.4	11.4	31.5
	SFE	1.2	113.1	62.8	316.2

[a]Each value is the average of two analyses from two individual extractions. SFE, supercritical fluid extraction.

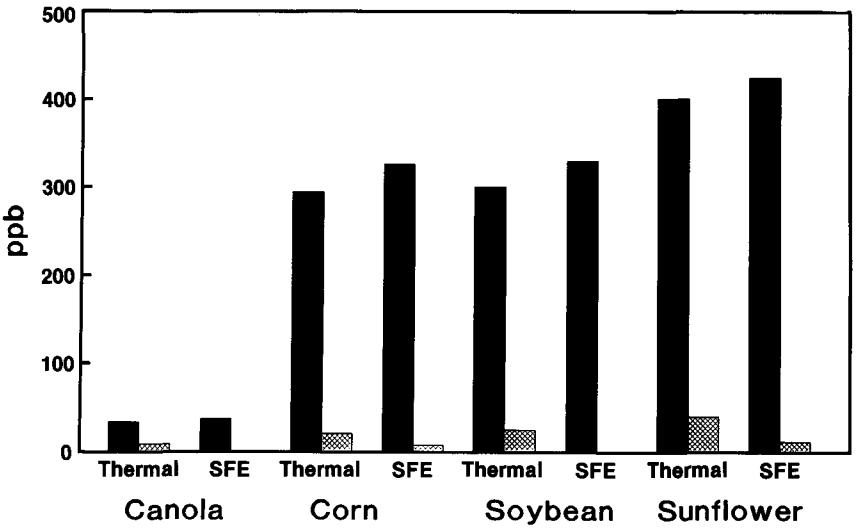

FIG. 4. Hexanal concentrations from the first and second desorption of each oil for both thermal and SFE desorption methods. See Figure 2 for abbreviation. Solid bar = first desorption; hatched bar = second desorption.

desorption process. However, SFE is definitely more suitable for the desorption and analysis of high-molecular weight compounds.

REFERENCES

1. Mordet, F., O. Morin and J.-L. Coustille, *Rev. Fr. Corps Gras 32*:193 (1985).
2. Snyder, J.M., E.N. Frankel, E. Selke and K. Warner, *J. Am. Oil Chem. Soc. 65*:1617 (1988).
3. Snyder, J.M., and T.L. Mounts, *Ibid. 67*:800 (1990).
4. Wyatt, D.M., *J. Chromatogr. Sci. 25*:257 (1987).
5. Selke, E., and E.N. Frankel, *J. Am. Oil Chem. Soc. 64*:749 (1987).
6. Westendorf, R.G., in ACS Symposium Series 289, *Characterization and Measurement of Flavor Compounds*, edited by D.D. Bills, and C.J. Mussinan, American Chemical Society, Washington, D.C., 1985, pp. 138-153.
7. Selke, E., H.A. Moser and W.K. Rohwedder, *J. Am. Oil Chem. Soc. 47*:393 (1970).
8. Frankel, E.N., W.E. Neff and E. Selke, *Lipids 16*:279 (1981).
9. Hawthorne, S.B., M.S. Krieger and D.J. Miller, *Anal. Chem. 60*:472 (1988).
10. Hawthorne, S.B., D.J. Miller and M.S. Krieger, *J. Chromatogr. Sci. 27*:347 (1989).
11. Raymer, J.H., E.D. Pellizzari and S.D. Cooper, *Anal. Chem. 59*:2069 (1987).
12. Thomas, P., *LC-GC 10*:832 (1992).
13. King, J.W., R.L. Eissler and J.P. Friedrich, in ACS Symposium Series No. 366, *Supercritical Fluid Extraction and Chromatography: Techniques and Applications*, edited by B.A. Charpentier, and M.R. Sevenants, American Chemical Society, Washington, D.C., 1988 pp. 63-88.
14. Friedrich, J.P., and E.H. Pryde, *J. Am. Oil Chem. Soc. 61*:223 (1984).
15. King, J.W., J.H. Johnson and J.P. Friedrich, *J. Agric. Food Chem. 37*:951 (1989).

[Received September 28, 1993; accepted December 16, 1993]