GC Determination of Synthetic Hydrocarbon-Based Thermal Heating Fluid in Vegetable Oils

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ABSTRACT: A combination of alumina column chromatography and GC procedures was developed for the determination of synthetic hydrocarbon-based thermal heating fluid (trademarked as Therminol 55™) in vegetable oils. In each run, 3 g of sample solution was loaded onto the alumina (50 g) column and was eluted with 200 mL hexane. The eluate was then concentrated to 1 mL with the aid of a nitrogen stream prior to GC analysis. The GC chromatogram of the thermal heating fluid was characterized by the presence of a bell-shaped hump that could not be resolved into individual peaks. The lowest detection limit based on various spiked palm olein samples was 20 µg/g. The CV obtained were 6.5–8.9% for the intra-day study and 8.1–9.7% for the inter-day study. Overall recoveries of these samples ranged from 68.0 to 85.7%, and the method was found to be good enough for quality control purposes.

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KEY WORDS: Gas chromatography, thermal heating fluid, Therminol 55™.

Thermal heating fluids are still commonly used as a heating medium in many of the older edible oil refinery plants. A survey carried out by Tang *et al*. (1) showed that thermal heating oils used in the vegetable oil processing industries can be categorized into three main types: biphenyl-diphenyl oxide, partially hydrogenated terphenyls, and synthetic hydrocarbons. Since all thermal heating fluids are derived from petroleum sources, there are concerns about their contamination of vegetable oils, which may result from pinhole leaks or faulty joints in the heating systems (2,3).

Several GC methods have been reported for the determination of biphenyl-diphenyl oxide type of thermal heating fluid in vegetable oils after TLC cleanup or a distillation step (4–6), whereas the American Oil Chemists' Society (AOCS, Method Cd 25-96) employed a solvent extraction step (7). As biphenyl and diphenyl oxide exhibit strong fluorescence, a direct HPLC with fluorescence detection method was reported by Moh *et al*. (8,9). The main advantage of the HPLC method is that no tedious sample pretreatment step is required. The HPLC method has also been accepted by AOCS as Recommended Practices Method Cd 25a-00 (7).

Recently, Moh *et al*. (10) reported another HPLC procedure for the determination of hydrogenated terphenyl-based thermal heating fluid in vegetable oils and oleochemicals. This class of thermal heating fluid is a complex mixture of terphenyls (3–8%), partially hydrogenated terphenyls (74–87%), quaterphenyls, higher polyphenyls, and their hydrogenated products (18%). Because of its strong fluorescence property, the quantitative analysis of the fluid was once again achieved using fluorescence detection.

Various analytical methods have been employed to detect hydrocarbons or mineral oils in vegetable oils (11–15). The IUPAC Method 2.611 has employed a TLC procedure for extracting mineral oils in edible oils and fats (16). Although the limit of detection reported was 100 µg/g, the contamination is considered positive only if more than 500 µg/g of mineral oils are found. Nonetheless, there are no reports on methods that detect contamination with thermal heating fluids. In this study, we propose a combination of alumina column chromatography and GC for the determination of synthetic hydrocarbon-based thermal heating fluid in vegetable oils.

MATERIALS AND METHODS

Reagents. The acetonitrile, dichloromethane, and hexane used were of HPLC grade. Eicosane standard and alumina (Type WN-3: Neutral) were purchased from Sigma (St. Louis, MO). Thermal heating fluid (Therminol 55™) was obtained from Solutia (St. Louis, MO).

Preparation of glassware. All washed glassware was rinsed with distilled water and then dried in an oven at 150°C. Prior to analysis, all the glassware was rinsed with acetonitrile followed by dichloromethane and hexane.

Glass column chromatography. The glass column (250 × 20 mm i.d., with sintered glass disc and fitted with Teflon stopcock) was pre-filled with about 50 mL of hexane before 50 g alumina was gradually added. Then the column was washed with an additional 100 mL of hexane, and the level of the solvent was allowed to fall to about 2–3 mm above the surface of the alumina.

Recovery studies. A 1000-µg/mL standard solution was prepared by dissolving 0.1 g of eicosane in a 100-mL volumetric flask with hexane. Appropriate aliquots of the stock solution were diluted to produce working standard solutions of 500, 100, 10, and 1 µg/mL. Subsequently, 1 µL of each working solution was analyzed with GC, and the calibration

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graph was obtained by plotting the peak areas against the concentrations of the working solutions.

Palm olein (10 g) was accurately weighed into each of four 100-mL volumetric flasks. Then 10 mL of each working solution (500, 100, 10, and 1 µg/mL) was added to the palm olein and diluted to 100 mL with hexane to provide spiked solutions containing 500, 100, 10, and 1 µg/g eicosane. The sample solution (30 mL) was then pipetted into the alumina column, which had been pre-conditioned as mentioned earlier. Once the sample solution had fallen to about 2–3 mm above the surface of the alumina, 200 mL of hexane was introduced. The eluant was collected and then evaporated in a water bath (90°C) to 1 mL under a gentle flow of nitrogen stream. Concentrate (1 µL) was then injected into the gas chromatograph for analysis.

Spiked oil samples with thermal heating fluid. A 1000 µg/mL solution was prepared by dissolving 0.1 g thermal heating fluid in a 100-mL volumetric flask with hexane. The aliquot was further diluted to obtain solutions containing 100, 50, 30, 20, and 10 µg/mL thermal heating fluid. Then 10 mL of each aliquot was pipetted into a 100-mL volumetric flask containing a 10 g oil sample and diluted to 100 mL with hexane. This provided spiked solutions containing 100, 50, 30, 20, and 10 µg/g of thermal heating fluid. A 30-mL aliquot of each of these spiked solutions was then chromatographed on the alumina column according to the procedure described earlier.

Quantitative GC–FID. The system used was an Agilent 6890 (Agilent Technologies Inc, Wilmington, DE) GC equipped with an Agilent 7683 auto-injector. The capillary column used was an HP-5 cross-linked with 5% phenyl

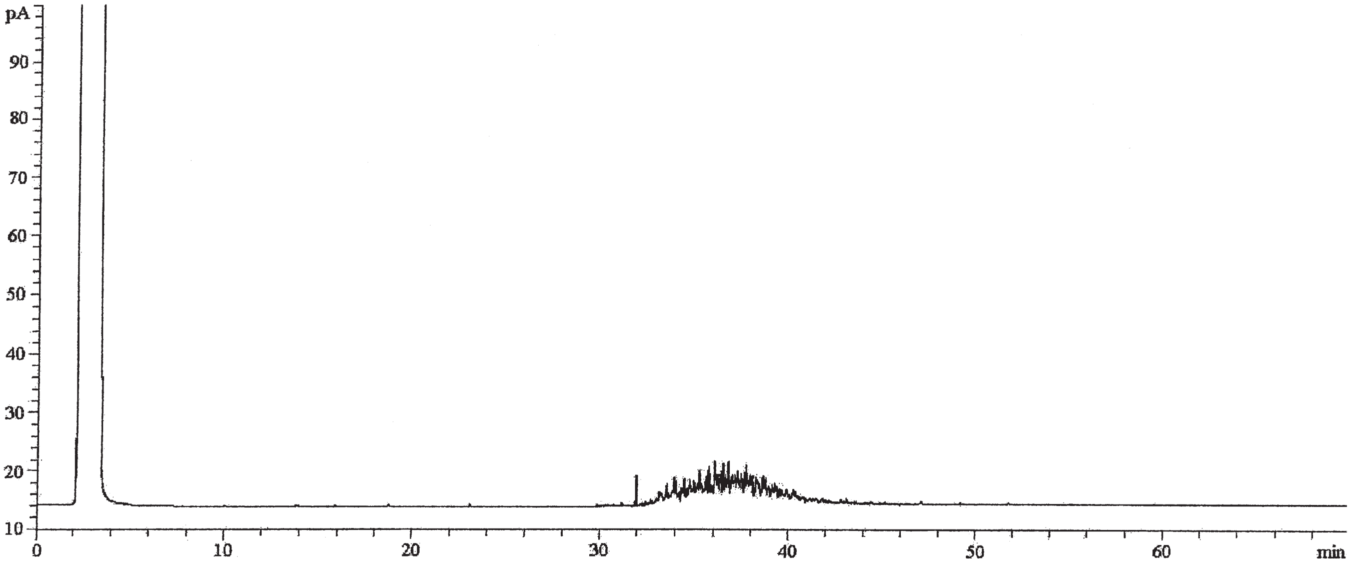

FIG. 1. Gas chromatogram of Therminol 55™ (1000 µg/mL; Solutia, St. Louis, MO). GC conditions: Oven temperatures were set at 70°C for the first 5 min, then programmed to 280°C at 5°C/min, and finally held at 280°C for an additional 23 min. The injector temperature was 280°C, and the detector was 290°C.

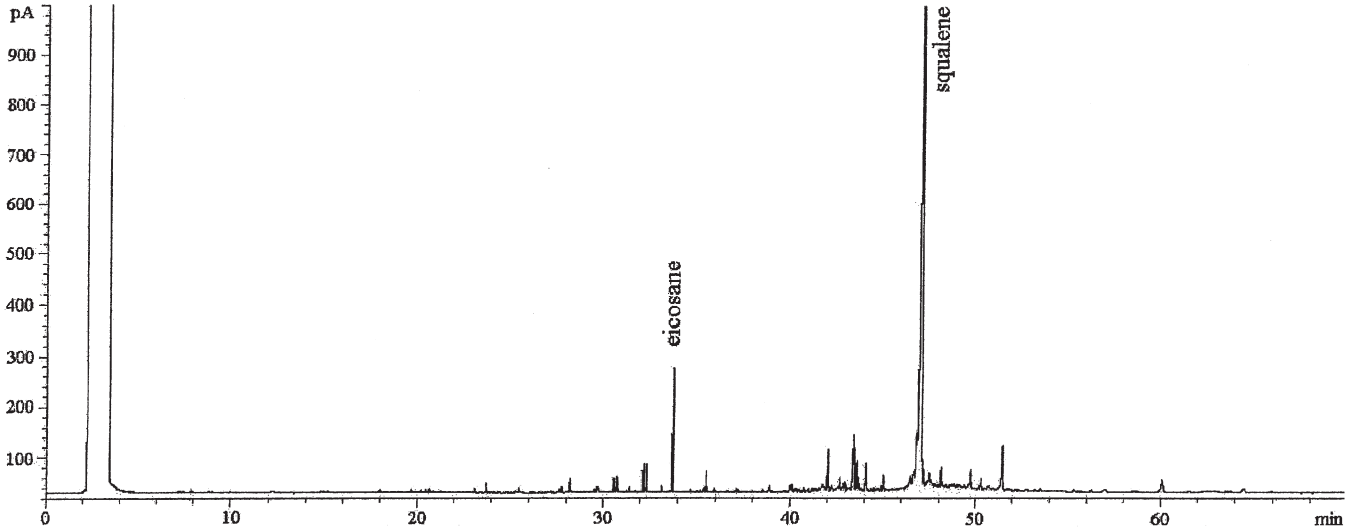

FIG. 2. Gas chromatogram of palm olein extract spiked with 10 µg/g eicosane. For gas chromatograph conditions see Figure 1.

methylsiloxane capillary column (30 m × 0.32 mm i.d., Hewlett-Packard, Palo Alto, CA). The oven temperatures were initially set at 70°C for the first 5 min, then programmed to 280°C at the rate of 5°C/min, and finally held at 280°C for an additional 23 min. The injector temperature was set at 280°C while the detector was set at 290°C. The carrier gas was He at a flow of 0.8 mL/min, and all analyses were performed on splitless mode.

RESULTS AND DISCUSSION

Thermal heating fluid. Therminol 55 is a complex mixture of synthetic hydrocarbons (17). This clear, pale yellow fluid is odorless and has an operational range of −25 to 290°C. Preliminary analysis of the fluid showed weak UV absorption as well as fluorescence. Thus, the analytical method based on UV or fluorescence detection is not quite suitable for the analysis of Therminol 55.

Figure 1 illustrates the gas chromatogram of Therminol 55. Unlike diesel or mineral oil profiles that contain distinct *n*-alkane peaks (18), Therminol 55 is characterized by the presence of a broad bell-shaped hump (32 to 44 min) that cannot be resolved by GC into individual peaks. Therefore, in the case of contamination, the presence of Therminol 55 can easily be recognized. Based on the analysis of a series of Therminol 55 solutions (10–1000 µg/mL), the sensitivity of the GC instrument was found to be able to detect Therminol 55 to as low as 20 pg. The quantitation of Therminol 55 was based on the peak area counts in the region of 32–41 min.

Recovery studies. The efficiency of the alumina column was examined by the analysis of the blank and spiked palm olein samples with eicosane at various concentrations (1, 10, 100, and 500 µg/g). Eicosane was chosen for the recovery study because it eluted closed to Therminol 55. With hexane as mobile phase, eicosane was eluted in the 50–140 mL fraction together with squalene and other nonpolar minor components present naturally in palm olein. The typical GC trace of the hydrocarbon standard (10 µg/g) extracted from spiked palm olein is shown in Figure 2.

The influence of oil loading in the alumina column was also assessed. The study found that at least 15 g of alumina was required to retain 1 g of vegetable oil. In addition, a faster flow rate reduced the capacity of the alumina to retain the oil. The optimal flow rate in this study was about 25 mL/min.

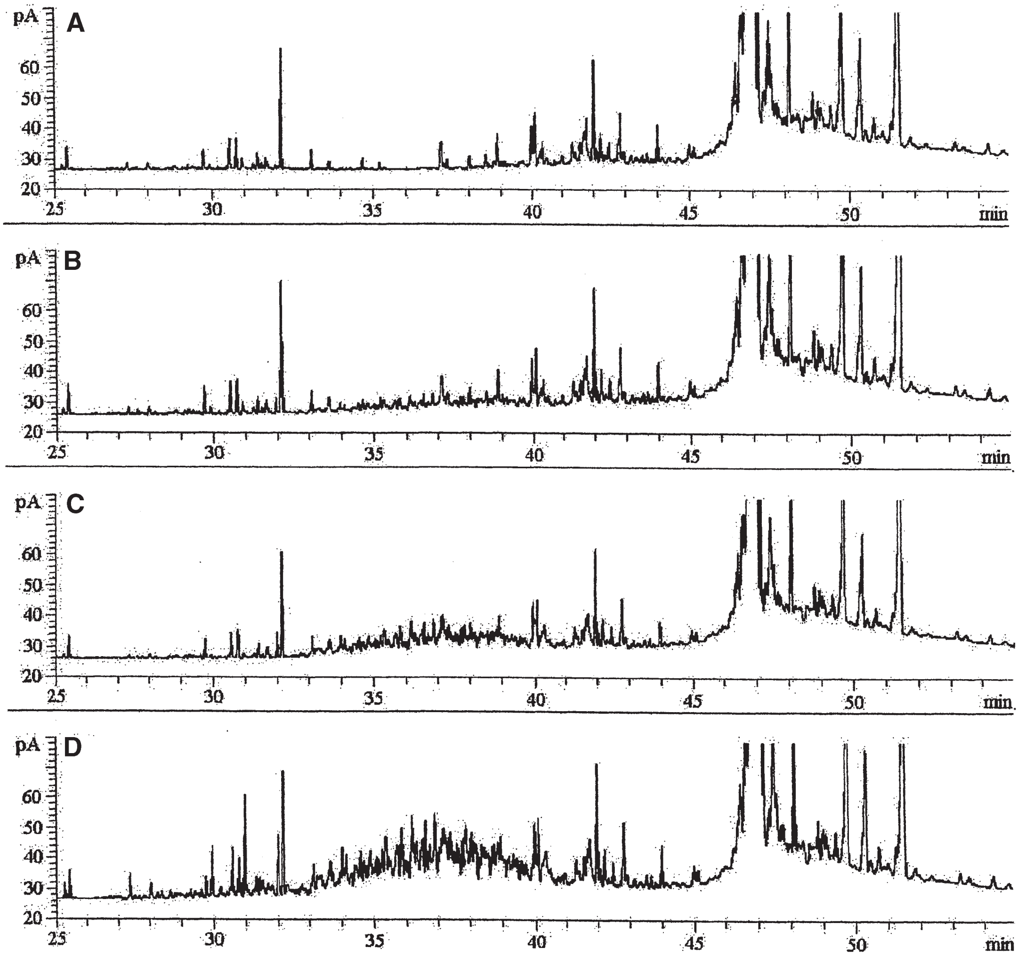

FIG. 3. Gas chromatograms of (A) blank and (B–D) palm oleins spiked with 20, 50, and 100 µg/g Therminol 55, respectively.

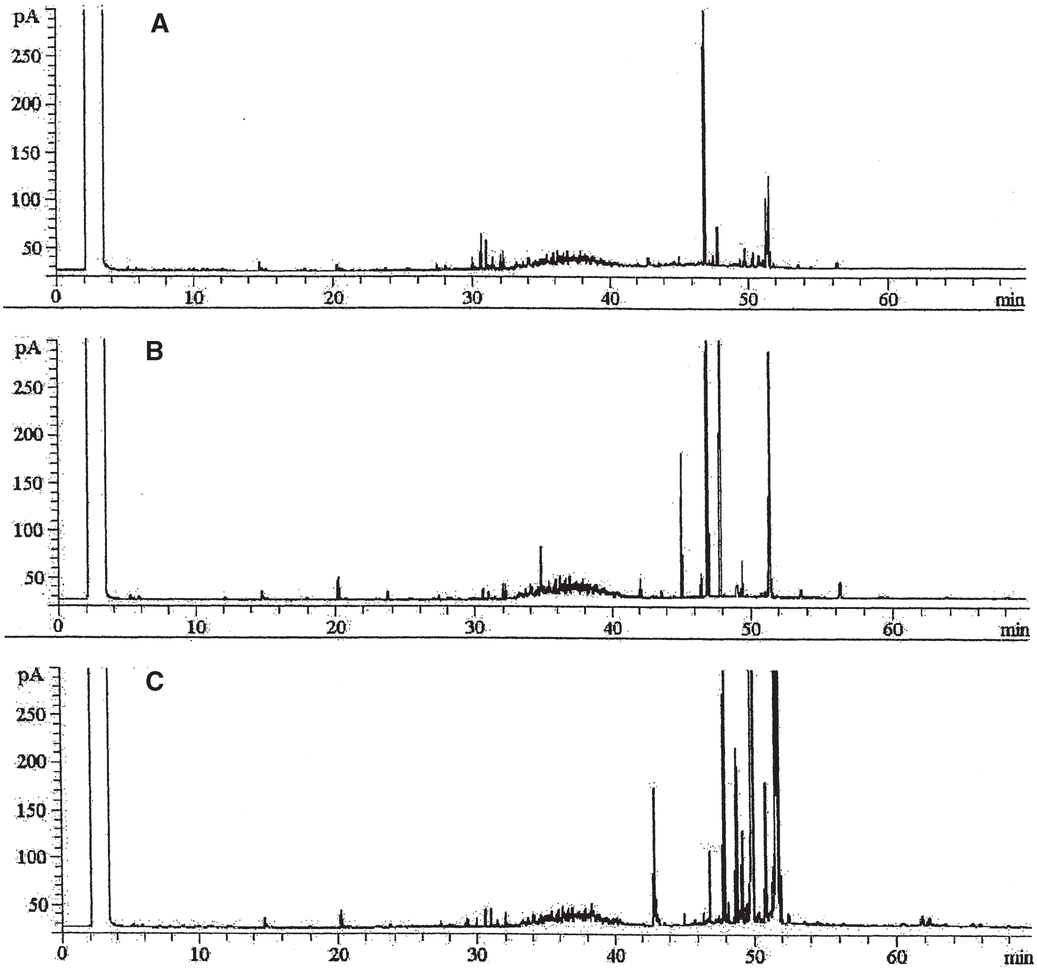

FIG. 4. Gas chromatograms of (A) soybean oil, (B) sunflower oil, and (C) canola oil spiked with 100 µg/g Therminol 55.

A typical calibration curve over the range of 1–1000 µg/mL of eicosane analyzed in triplicate produced a regression of $y = 17.83x + 77.9$ with a correlation coefficient of 0.9999 (where y is the peak area count and x is the concentration of eicosane). The mean recoveries of eicosane obtained from various spiked palm oleins were generally good, ranging from 73.5 to 88.0%. The overall CV were 6.11–9.06%, within the acceptable limit of 20%. The lowest limit of quantitation for eicosane was down to 1 µg/g.

Analysis of spiked vegetable oils. The GC chromatogram of the extracts from blank palm olein is given in Figure 3A. A closer look at the GC trace of a blank palm olein sample (25–55 min) showed that the extract contained many other minor peaks. They were mainly hydrocarbons and esters of the nonpolar materials that originated from the oil itself (19,20).

The chromatograms of spiked palm olein samples are illustrated in Figures 3B–D, and the lowest detectable limit was 20 µg/g. The accuracy and precision of the results obtained from three spiked concentrations are summarized in Table 1. The intra-day precision was 6.5–8.9%, whereas the overall analytical variability tested on inter-day precision was 8.1–9.7%.

Figures 4A–C illustrate the GC chromatograms of spiked soybean oil, sunflower oil, and canola oil with 100 µg/g of Therminol 55, respectively. The details of the recovery studies obtained from two different concentrations are also given in Table 2. The limits of detection were similar to that of palm olein.

The procedure described in this paper is more sensitive than that of IUPAC. It is also generally good for quality control purposes.

TABLE 1
Reproducibility of GC Analysis of Therminol 55™ in Spiked Palm Olein

	Mean calculated[a] (µg/g)	CV (%)	Recovery (%)
Intra-day study[b]			
30	13.6	6.54	68.0
50	43.0	7.21	86.0
100	79.7	8.98	79.9
Inter-day study[b]			
30	15.2	9.75	76.2
50	42.8	8.76	85.7
100	80.5	8.15	80.5

[a] Mean of three readings.
[b] Examined at three different concentrations (µg/g).

TABLE 2
Recovery of Therminol 55™ of Various Spiked Oils (*n* = 3)

	Spiked at 30 μg/g		Spiked at 100 μg/g	
Sample	Recovery (%)	CV (%)	Recovery (%)	CV (%)
Soybean oil	72.5	13.5	81.2	9.1
Sunflower oil	76.3	8.5	79.6	10.9
Canola oil	76.2	12.9	77.3	6.5

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