HPLC Method for the Determination of Synthetic Thermal Heating Fluid (Therminol 55^{TM}) in Basic Oleochemicals

M.H. Moh[a],*, T.S. Tang[b], and G.H. Tan[c]

[a]Advanced Oleochemical Technology Division and [b]Technical Advisory Services Unit, Malaysian Palm Oil Board, 43650 Kajang, Selangor, Malaysia, and [c]Department of Chemistry, University of Malaya, Lembah Pantai 50603 Kuala Lumpur, Malaysia

ABSTRACT: A combination of alumina column chromatography and HPLC procedures was developed for the determination of synthetic hydrocarbon-based thermal heating fluid (trademarked as Therminol 55™) in basic oleochemicals. In each run, 3 g of sample solution was loaded onto the alumina (50 g) column and was eluted with 200 mL of hexane. The eluate was then concentrated to 1 mL with the aid of a nitrogen stream prior to HPLC analysis. The HPLC chromatogram of Therminol 55 was characterized by a humped shape that could not be resolved into individual peaks. The lowest limit of quantification obtained from various spiked samples was 30 μg/g. The recovery results obtained from the method were good, ranging from 70 to 80%, whereas the overall CV were all below 10%. The method is simple and thus is ideal for quality assurance purposes.

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KEY WORDS: Basic oleochemicals, HPLC-fluorescence detection, synthetic 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 and oleochemical distillation and fractionation plants. An early survey carried out by Tang *et al*. (1) showed that thermal heating fluids used in these 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, which may result from pinhole leaks or faulty joints in the heating system (2,3).

Several GC methods have been reported for the determination of the biphenyl-diphenyl oxide type of thermal heating fluid in vegetable oils after TLC cleanup or a distillation step (4–6), whereas AOCS Method Cd 25-96 uses a solvent extraction step (7). As biphenyl and diphenyl oxides exhibit strong fluorescence, a direct HPLC method with fluorescence detection was developed by Moh *et al*. (8,9). This HPLC method does not require a tedious sample pretreatment step and has been accepted by AOCS as Recommended Practices Method Cd 25a-00 (7).

Moh *et al*. (10,11) have also reported an 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 used to detect hydrocarbons or mineral oils in vegetable oils (12–16). IUPAC Method 2.611 uses a TLC procedure for extracting mineral oils from edible oils and fats (17). Although the limit of detection reported is 100 μg/g, the contamination is considered positive only if more than 500 μg/g of mineral oil is found. Nonetheless, there are no reports on methods that detect contamination of oleochemicals with thermal heating fluid. In this study, we propose a combination of alumina column chromatography and HPLC for the determination of synthetic hydrocarbon-based thermal heating fluid in oleochemicals.

MATERIALS AND METHODS

Chemical and reference standards. Palm-based glycerin (99.5%) and FA (>99%) were all supplied by the local oleochemical industries. Alumina (Type WN-3: neutral, activity Grade 1) for column chromatography was purchased from Sigma (St. Louis, MO). The thermal heating fluid (Therminol 55^{TM}) was a gift from Solutia Inc. (St. Louis, MO). All the solvents used were of HPLC grade, and deionized distilled water was used throughout the experiment.

Preparation of glassware. All washed glassware was rinsed with deionized distilled water and then dried in an oven at 220°C. After cooling, and just prior to use, the glassware was rinsed with acetonitrile followed by dichloromethane and hexane.

Glass column chromatography. The glass column (250 × 20 mm i.d., with a sintered glass disc and fitted with a Teflon stopcock) was prefilled with about 50 mL of hexane before 50 g of alumina was gradually added. The column was then 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.

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*To whom correspondence should be addressed at Advanced Oleochemical Technology Division, Malaysian Palm Oil Board, No. 6 Persiaran Institusi, Bandar Baru Bangi, 43650 Kajang, Selangor, Malaysia.
E-mail: felixmoh@yahoo.com

Spectrofluorometry. Fluorescence excitation and emission spectra were recorded with a PerkinElmer Model LS 50B spectrofluorometer (PerkinElmer Corp., Norwalk, CT) using the FL Winlab software (PerkinElmer). The slit-width of the instrument was set at 3.0 nm with a scanning speed of 1000 nm/min ranging from 200 to 600 nm.

HPLC conditions. The HPLC system consisted of a pump (JASCO PU-980; JASCO International Co., Ltd., Tokyo, Japan), a three-line degasser (JASCO DG-980-50), a ternary gradient unit (JASCO LG-980-02S), an autosampler (JASCO 851-AS), and a column oven (JASCO CO-965). A JASCO programmable fluorescence detector (FP-970) that was controlled by Borwin 1.21 (JMBS Developpements, Le Fontanil, France) chromatographic software was optimized at an excitation wavelength of 270 nm and an emission wavelength of 320 nm. A reversed-phase column (5 µm LiChrospher C_{18}, 250 × 4.6 mm i.d.; GL Sciences Inc., Tokyo, Japan) was used with a 50 × 4.6-mm-i.d. guard column packed with the same materials. The system was run isocratically with a mobile phase of ethanol and water (95:5, vol/vol) mixture, and the column was maintained at 40°C.

Quantification. Calibration solutions of Therminol 55 (10 to 1000 µg/mL) were prepared gravimetrically in hexane, and 100 µL of each was injected into the HPLC system in triplicate. Quantification of the thermal heating fluid was based on the peak height counts at 10.9 min, and the baseline was accomplished by drawing a line parallel to the *x*-axis from 0 to 30 min.

The recovery study was carried out on spiked samples since contaminated samples were not available. A 10-g sample was accurately weighed into each of six 100-mL volumetric flasks, then 10 mL of each working solution (500, 100, 50, 30, 20, and 10 µg/mL) was added to the samples and diluted to 100 mL with hexane for FA; to provide spiked sample solutions, glycerin was dissolved in ethanol containing 500–10 µg/g Therminol 55.

A total of 30 mL of the sample solution was pipetted into the preconditioned alumina column. Once the sample solution had fallen to about 2–3 mm above the surface of the alumina, 200 mL of hexane was introduced gradually. The eluate was then collected and evaporated in a waterbath (60°C) to 1 mL under a gentle flow of nitrogen gas. A 100-µL aliquot of the concentrate was then analyzed with HPLC.

RESULTS AND DISCUSSION

Instrumental assessment. Therminol 55 is a synthetic thermal heating fluid used in moderate-temperature applications (ranging from –25 to 290°C). It possesses several important performance attributes: It can be used for a long time, it is more inert to oxidation than mineral oils (10 times better), and it is pumpable even at –25°C (18).

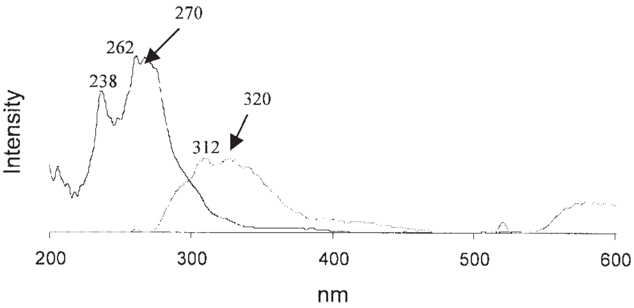

FIG. 1. Fluorescence excitation and emission spectra of Therminol 55 (Solutia Inc., St. Louis, MO).

The fluorescence excitation and emission spectra of the Therminol 55 solution, depicted in Figure 1, shows three distinct excitation bands at 238, 262, and 270 nm, whereas the fluorescence emission spectrum is quite broad and less intense when compared with that of the fluorescence excitation spectrum. The maximum fluorescence emission bands were at 312 and 320 nm.

The reversed-phase HPLC analysis of Therminol 55 is characterized by the presence of a distinct broad peak that cannot be resolved into individual peaks (Fig. 2). The linearity of the fluorescence detectors for the analysis of Therminol 55 based on the peak height counts at 10.9 min showed very good linearity, with correlation coefficients of better than 0.9994 for solutions ranging from 0 to 1000 µg/mL. The detection limit when using fluorescence was at the 3-µg level.

Nevertheless, such detection limits are not sensitive enough to analyze for Therminol 55 in the case of low levels of contamination without any preconcentration step. Furthermore, the concentration process can only be carried out after the thermal heating fluid has been extracted from the sample matrices. Since Therminol 55 consists of hydrocarbons, solvent–solvent extraction (7) or column chromatography (14–16) can be considered. However, the major drawback in using the solvent–solvent extraction method is that it usually involves a saponification reaction, which can lead to a loss of hydrocarbon content during the saponification and extraction processes, and to solvent evaporation. The concentration process, as well as the distillation procedure, requires a skilled technician. Thus, these two methods were not considered in this study for recovering of Therminol 55 from the sample matrices.

In contrast, column chromatography is more widely used nowadays for the extraction of hydrocarbons from vegetable oil matrices because not only is it more convenient and simpler,

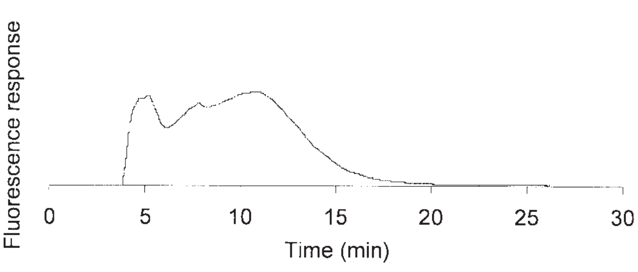

FIG. 2. Typical HPLC chromatogram of Therminol 55 analyzed using fluorescence detection at 270 nm (excitation) and 320 nm (emission).

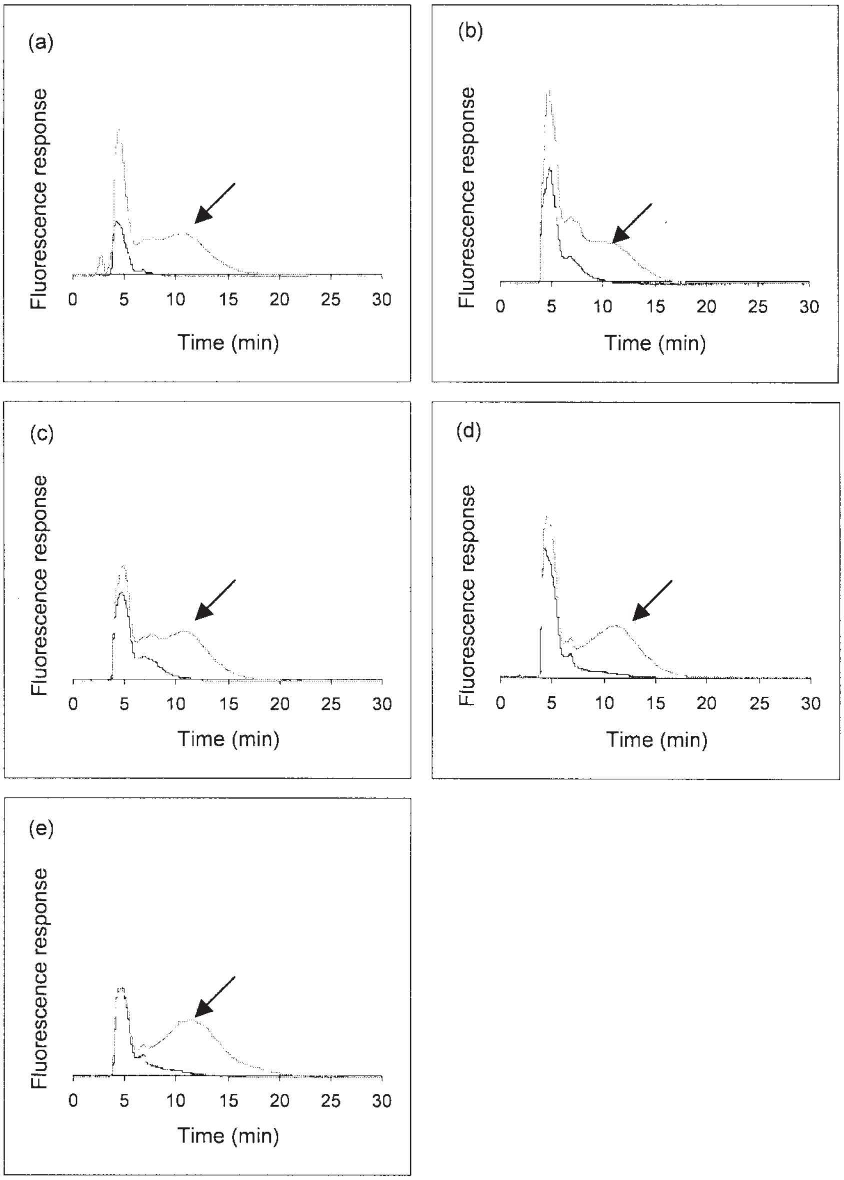

FIG. 3. Typical HPLC-fluorescence chromatograms of a blank and of oleochemicals spiked with 50 µg/g of Therminol 55 (arrow). (a) Glyerin, (b) C12:0, (c) C14:0, (d) C16:0 and (e) C18:0 FA.

but also its flexibility enables scaling up for a larger recovery once the procedure is established. Also, by monitoring the polarity of the mobile phase carefully, compounds of different polarities can be recovered after they have been separated in the column. Moreover, different types of packing materials are readily available for more specific purposes. In view of these advantages, a column chromatographic approach for the extraction of Therminol 55 from the sample matrices was selected in this study.

In a study of the elution behavior of Therminol 55 solutions on an alumina column (19), at least 15 g of alumina was required to retain 1 g of oleochemical. In addition, a faster flow rate reduced the capacity of the alumina to retain the matrix. Thus, the optimal flow rate in this study was about 25 mL/min.

Recovery studies. HPLC chromatograms of blanks and of oleochemicals spiked with 50 µg/g Therminol 55 are presented in Figure 3. A closer look at the HPLC chromatogram of a blank sample (labeled as "a") revealed that a fluorescence peak was present naturally in all sample solutions at about 4–6 min. However, the baseline of the blank chromatogram tended to smooth out after 10 min of elution time. This observation is significant for the quantification of Therminol 55, which starts to elute slightly after 6 min and reaches a maximum at 10.9 min. Therefore, without the presence of any other fluorescence components that co-elute with the Therminol 55, the quantification of the thermal heating fluid is possible based on the maximal fluorescence of the Therminol 55 peak at 10.9 min.

Further recovery studies showed that the limit of detection

TABLE 1
Recovery of Therminol 55^{TM} in Basic Oleochemicals Using HPLC-Fluorescence Detection[a]

Glycerin and FA of different carbon-chain lengths	Concentration (μg/g) 100	50	30
Glycerin	86.5 (6.35)	75.6 (5.69)	79.4 (5.64)
C12:0	84.6 (4.65)	78.7 (5.36)	89.3 (3.56)
C14:0	83.8 (5.22)	73.5 (8.65)	76.3 (7.22)
C16:0	73.6 (4.98)	82.5 (3.56)	74.2 (4.44)
C18:0	86.3 (7.55)	87.7 (5.69)	79.6 (8.88)

[a]The results are reported as percent recovery, with CV (%) in parentheses.

(signal-to-noise ratio = 3) obtained from the spiked samples containing 0 to 500 μg/g Therminol 55 was 20 μg/g, whereas the limit of quantification (signal-to-noise ratio = 10) was 30 μg/g level.

The mean recoveries of Therminol 55 in the oleochemicals ranged from 73–86% at a high concentration level (100 μg/g), 73–87% at a medium concentration level (50 μg/g), and 74–79% at a low concentration level (30 μg/g). The CV of variation were lower than 10% (Table 1).

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