

TECHNICAL NOTE

Lisa M. Schwenk,^{1,†} M.S.F.S. and Michelle R. Reardon,² M.S.F.S.

Practical Aspects of Analyzing Vegetable Oils in Fire Debris*

ABSTRACT: Vegetable oils undergo burning, self-heating, and spontaneous ignition, resulting in their presence in fire debris. As these processes can affect the fatty acid content of vegetable oils, it is important that debris be properly handled in order to obtain reliable and informative data. This research investigated changes in vegetable oil content as a result of storage conditions and different types of burning. Material spiked with vegetable oils and burned was stored under various long-term conditions, and debris was tested by heating overnight using passive headspace concentration. Results indicated that refrigeration is ideal for fire debris samples suspected of containing vegetable oils and that including passive headspace concentration in the analytical scheme would not affect oils. Spontaneous ignition experiments were conducted to compare the effects of various burning processes on vegetable oil content. Vegetable oils that experienced nonpiloted ignition, self-heating, and spontaneous ignition produced noticeably different chromatograms from those that underwent piloted ignition.

KEYWORDS: forensic science, autoignition, fatty acid methyl ester, fire debris, self-heating, spontaneous ignition, vegetable oils

Vegetable oils may be found in fire debris for any number of reasons. An arsonist could have selected a vegetable oil as an “accelerant,” cleaning rags with vegetable oils may have spontaneously ignited, or the oils could have been incidental to the scene of the fire and ignited with the structure. Whatever the reason, valuable information can be obtained by analyzing vegetable oils in fire debris. Vegetable oils contain fatty acids (FAs) and can be analyzed for their presence. The FA composition is characteristic for an individual vegetable oil (1). It has been noted that the FA composition can change through the process of oxidation, which is why it is essential to understand the factors affecting this reaction, such as storage conditions and the ignition process (2). This information can then be used in fire debris analyses to identify oils present or possibly the ignition source of the fire.

Oilseeds and plants are the most common source of vegetable oils. These sources are crushed, and the essential oils are extracted with solvent by direct compression and then filtration (3). The extracted essential oils are then subjected to a refining process which not only removes undesired natural compounds, but may also add materials to alter the oil’s physical characteristics, resulting in a product with more desirable properties.

The primary components of vegetable oils are lipids in the form of triglycerides (1,4,5). Triglycerides have an esterified glycerol backbone with three FAs. While any combination is possible, the FAs are generally straight chains of mainly 16 to 18 carbons (3). FAs can be considered saturated or unsaturated. Saturated FAs have straight chains of only single carbon-to-carbon bonds, while

unsaturated FAs can have one or more double bonds present in the hydrocarbon chain (1,3). The degree of unsaturation increases with the number of double bonds and affects their physical state at room temperature. While saturated FAs will generally be solids at room temperature, the double bonds in unsaturated FAs create bends in the carbon chains preventing crystallization to a solid, and thus, are usually liquids (1,3).

Common and International Union of Pure and Applied Chemistry (IUPAC) names of FAs exist, but a shorthand nomenclature takes into account the hydrocarbon chain length as well as the number of double bonds. This designation is in the form of C_x:y where “x” represents the total number of carbons in the hydrocarbon backbone and “y” represents the number of double bonds present in the chain. As an example, C₁₈:1(n-9) indicates that there are 18 carbons and one double bond located at position 9. C₁₈:1(n-9) is commonly known as oleic acid or by its IUPAC name of *cis*-9-octadecenoic acid, and has a chemical formula of C₁₇H₃₃COOH. The number of double bonds present in the FA structure is significant, as the more unsaturated an oil is, the greater the propensity for autooxidation to occur and degradation of the oil to begin (3).

Before oxygen can react with the vegetable oil, it must first deplete the oxidative inhibitors present in vegetable oils. These inhibitors are natural plant products that do not generate free radicals upon reaction with oxygen (6). The autooxidation of vegetable oils is an exothermic reaction that follows the induction period, which is the time during which the oxidative inhibitors are consumed (6,7). Following consumption of the inhibitors, the oil can then be oxidized, releasing heat and thus increasing the temperature of the oil and consequently, the rate of the autooxidation reaction. This temperature increase resulting from the autooxidation process is referred to as self-heating (8). If the oil is present in an environment where the heat generated by self-heating will not be dispersed to its surroundings, and there is sufficient oxygen for the oxidation reaction to progress, the temperature could rise to the point of ignition (1,6). Self-heating of a material to the point of ignition is referred to as spontaneous ignition, which is ignition due to a

¹Virginia Commonwealth University, Richmond, VA.

²Bureau of Alcohol, Tobacco, Firearms and Explosives, Forensic Science Laboratory, 6000 Ammendale Road, Beltsville, MD 20705.

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[†]Present address: Lisa M. Schwenk, Missouri State Highway Patrol Crime Laboratory, 1510 East Elm Street, Jefferson City, MO 65102.

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chemical or biological process, without an external ignition source (9). For spontaneous ignition to occur, the oil must be appropriately dispersed on a substrate to increase its surface area and access to oxygen without significant loss of heat to its surrounding environment (10). Ignition of a material in the presence of an external ignition source, such as a spark or flame, is referred to as piloted ignition. Autoignition differs from spontaneous ignition, as autoignition occurs when a material is ignited by an increase in surrounding temperatures without the presence of an external ignition source (9). In autoignition, the material's temperature increases to the point of ignition because of its surrounding environment, not as the result of a chemical or biological process creating heat within the mass.

As stated above, a greater number of carbon-to-carbon double bonds indicates the vegetable oil is more likely to experience self-heating and possibly spontaneous ignition. The double bond reduces the strength of the neighboring carbon's bond to hydrogen, requiring less energy for oxidation, or removal of the hydrogen, to occur (1). The study of this process is significant as varying decomposition products have been obtained from materials subjected to different forms of heating and fire (3).

Due to the large molecular weights and high boiling points of triglycerides, they are unsuitable compounds for separation by gas chromatography (GC). Triglycerides are thus broken to create single FAs; however, as FAs are not volatile, the existing fire debris methods of dynamic and passive headspace concentration (11,12) are not appropriate. To analyze FAs by GC, they must be derivatized into fatty acid methyl esters (FAMES), which are more stable and volatile because they are relatively low molecular weight compounds (13). FAMES are named in the same manner as their corresponding FAs, as seen in Table 1 (3).

This research utilized the derivatization of FAs to FAMES to allow for the examination of factors causing degradation of vegetable oils. Various storage conditions were examined to determine the ideal environment. Piloted ignition, nonpiloted ignition, self-heating, and spontaneous ignition were also initiated to reveal the effect of these processes on the composition of the vegetable oil residues. The analytical scheme consisted of solvent extraction, base-catalyzed transesterification for the derivatization of the triglycerides to FAMES and analysis by gas chromatography–mass spectrometry (GC–MS).

TABLE 1—Designations of fatty acid methyl esters (FAMES).

Designation	Common Name	IUPAC Name	Formula
C6:0	Methyl caproate	Methyl hexanoate	C ₅ H ₁₁ COOCH ₃
C7:0	Methyl enanthate	Methyl heptanoate	C ₆ H ₁₃ COOCH ₃
C8:0	Methyl octanoate	Methyl octanoate	C ₇ H ₁₅ COOCH ₃
C9:0	Methyl nonylate	Methyl nonanoate	C ₈ H ₁₇ COOCH ₃
C10:0	Methyl decanoate	Methyl decanoate	C ₉ H ₁₉ COOCH ₃
C12:0	Methyl laurate	Methyl dodecanoate	C ₁₁ H ₂₃ COOCH ₃
C14:0	Methyl myristate	Methyl tetradecanoate	C ₁₃ H ₂₇ COOCH ₃
C16:0	Methyl palmitate	Methyl hexadecanoate	C ₁₅ H ₃₁ COOCH ₃
C16:1	Methyl palmitoleate	Methyl hexadecenoate	C ₁₅ H ₂₉ COOCH ₃
C17:0	Methyl heptadecanoate	Methyl heptadecanoate	C ₁₆ H ₃₃ COOCH ₃
C18:0	Methyl stearate	Methyl octadecanoate	C ₁₇ H ₃₅ COOCH ₃
C18:1	Methyl oleate	Methyl octadecenoate	C ₁₇ H ₃₃ COOCH ₃
C18:2	Methyl linoleate	Methyl octadecadienoate	C ₁₇ H ₃₁ COOCH ₃
C18:3	Methyl linolenate	Methyl octadecatrienoate	C ₁₇ H ₂₉ COOCH ₃
C20:0	Methyl arachidate	Methyl eicosanoate	C ₁₉ H ₃₉ COOCH ₃
C22:0	Methyl behenate	Methyl docosanoate	C ₂₁ H ₄₃ COOCH ₃
C22:1	Methyl erucate	Methyl docosenoate	C ₂₁ H ₄₁ COOCH ₃
C24:0	Methyl lignocerate	Methyl tetrasanoate	C ₂₃ H ₄₇ COOCH ₃

Materials and Methods

Sample Preparation

Details on the sample preparation for each experiment will be discussed under the appropriate section.

Storage Conditions

Individual pieces of wood (6.4 × 6.4 × 2.0 cm) were spiked with 1 mL of either raw linseed oil (E.E. Zimmerman Co., Pittsburgh, PA) or extra virgin olive oil (Pompeian, Baltimore, MD). Samples were allowed to sit for 1 h to let the oil soak into the wood. Samples were burned through piloted ignition with a propane blow torch until thoroughly charred, and then the flames were extinguished with a small amount of tap water. Samples were stored in quart cans in a refrigerator at 4°C, a hood in the laboratory, an outdoor structure (bunker) of uncontrolled temperature and humidity, and in a box exposed to the outside elements. Oil samples with sealed and unsealed lids were prepared in triplicate for each environment. Comparison samples were also prepared in triplicate for each storage condition. Only samples in sealed cans were prepared for refrigeration, since other chemicals and samples were being stored in the refrigerator. For the bunker and outdoor samples, all cans were placed in boxes with the flaps folded down. Following a time period of 2 months, samples were then analyzed using the procedures discussed in the Extraction and Derivatization sections.

Passive Headspace Concentration

Three vegetable oils were used to study the effects of overnight heating from passive headspace concentration on the FA content. Wood (6.4 × 6.4 × 2.0 cm in size) and carpet were combined and used as the substrate. Each material was spiked with 0.5 mL of raw linseed oil, canola oil (Super G, Landover, MD), or extra virgin olive oil, for a total of 1 mL per sample and was allowed to soak into the material for 1 h. A comparison sample of carpet and wood without oil was also included. Samples were burned with a propane torch until the wood was thoroughly charred and the carpet was partially melted. A small amount of tap water was used to extinguish any flames. Once cooled, samples were extracted with two 1.0 × 1.3-cm strips of activated charcoal (Albrayco Laboratories Inc., Cromwell, CT) suspended from the lid of the sealed quart can by a paperclip and magnet. Triplicate samples were extracted overnight for *c.* 16 h either in an oven at 65°C (149°F) or at room temperature. The comparison sample was also extracted overnight at 65°C. Following the designated time period, samples were removed from the oven and allowed to cool. Both heated and room temperature fire debris samples were extracted in pentane, derivatized and analyzed using GC–MS. (Refer to the Extraction and Derivatization sections for details.) The charcoal strips were removed from the samples heated overnight in the oven, extracted with 400 μL of carbon disulfide (Fisher Scientific, Fair Lawn, NJ) and analyzed by GC–MS.

Spontaneous Ignition

Part I (indoors)—Three cardboard boxes, 30 × 30 × 46 cm in size, were filled with cotton wiping cloths (Ansley Inc., Shelby, NC) and spiked with 500 mL of boiled linseed oil (Crown, Pearland, TX) that was poured into the middle of the cloths. Three thermocouples were included at the top, middle, and bottom of each box. Three 1-gallon cans containing cloths spiked with boiled

linseed oil were also included. Can A-1 contained an oil-soaked cloth wrapped in a second cloth. Can B-1 was filled with loosely packed cloths and one oil-soaked cloth included in the middle. Can C-1 had loosely packed cloths that were all soaked, but not dripping, with oil. Boxes and cans were set up indoors under normal room temperature conditions of *c.* 24°C (75°F). After a time period of 6 h for the boxes and 2 h for the cans, no significant temperature change had occurred. At this point, it was decided that spontaneous ignition would not occur within a reasonable time. The exterior surface of the cans was heated for at least 2 min from the outside with a propane torch in an attempt to cause nonpiloted ignition. Boxes were then set on fire through piloted ignition with a propane torch. After 45 min, all boxes and cans were extinguished with just enough water to prevent any further burning. Fire debris was collected in gallon cans and the vegetable oil residues were analyzed following the methods described in the Extraction and Derivatization sections. Neat samples of each oil used were also analyzed for comparison.

Part II (outdoors)—Arbitrarily labeled cardboard boxes, 15 × 25 × 36 cm in size, and gallon cans were prepared using two brands of boiled linseed oil (Crown, Pearland, TX; E.E. Zimmerman Co.) or timber oil (Samuel Cabot Inc., Newburyport, MA). The timber oil used in this study contained primarily linseed oil and tung oil. The containers were filled to two-thirds of their capacity with cotton cloths that were soaked in oil with any excess being squeezed out. Refer to Table 2 for box and can content identifications. It was necessary to use two types of linseed oil because of the limited supply available. Testing confirmed that both brands contained the same composition of FAMES. All containers were placed outdoors in the sun on a 30°C (86°F) day. One thermocouple was included in the middle of each box. Due to the limited quantity of oil available, one box (Box 4) and two cans (Cans C and D) were prepared using timber oil and three boxes (Boxes 1, 2, and 3) and two cans (Cans A and B) were prepared using linseed oil. All boxes and cans were extinguished with the smallest amount of water necessary to prevent complete charring and destruction of the samples. Fire debris from box samples were collected and stored in gallon cans, and can samples were sealed in their original container. Any areas of discolored oil were extracted and derivatized according to the procedures discussed in the following sections. Where charred material was present, this portion was analyzed separately (see Fig. 1 for the distinction between color-changed and charred). Neat oil samples of boiled linseed and timber oil were also analyzed for comparison.

TABLE 2—Spontaneous ignition (Part II) box/can content.

	Content
Box	
1	Boiled linseed oil
2	Boiled linseed oil
3	Boiled linseed oil
4	Timber oil (mixture of linseed oil and tung oil)
Can	
A	Boiled linseed oil
B	Boiled linseed oil
C	Timber oil
D	Timber oil (mixture of linseed oil and tung oil)

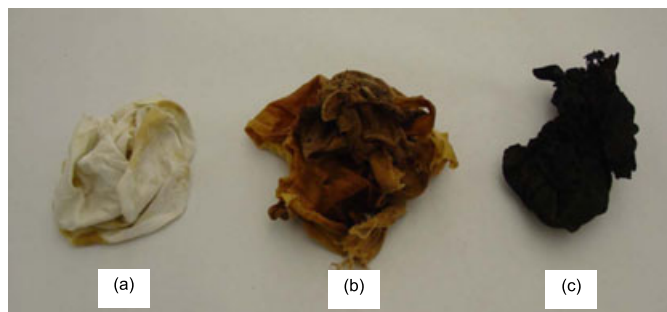


FIG. 1—(a) Oil stained rags. (b) Discolored, oil-stained rags. (c) Charred, oil-stained rags.

Extraction

All extractions were performed in clean disposable beakers. Piloted ignition samples of wood and carpet were washed for *c.* 2 min with 40 mL of pentane (Fisher Scientific, Fair Lawn, NJ). Two milliliter aliquots of the extract were removed and placed into glass vials for future derivatization, filtration, and analysis by GC-MS. The remaining extracts were stored in separate glass vials. If the original extract was found to be too dilute, this stored portion was concentrated through evaporation with nitrogen gas, and then derivatized, filtered, and analyzed by GC-MS. If samples contained water, pentane was used to extract the sample by agitation. The aqueous and organic layers were allowed to separate and the top, organic layer was decanted off into a new, clean disposable beaker. The pentane was then dried with anhydrous sodium sulfate (Fisher Scientific, Fair Lawn, NJ). The 2 mL aliquot of extract was then removed, and the remaining extracts were stored in glass vials.

Self-heated, auto- and spontaneous ignition samples of rags were extracted with 100 mL of pentane. The debris was removed from the beaker with the excess pentane being manually squeezed out. If water was present, anhydrous sodium sulfate was used for drying, and then the 2 mL aliquot was removed with the remainder being stored.

Derivatization

A 2.0 N solution of potassium hydroxide (KOH; Fisher Scientific) in methanol (Burdick & Jackson, Muskegon, MI) solution was prepared for use in this procedure. 0.5 mL of the KOH solution was added to a vial containing 2 mL of fire debris extract. For neat oil samples, 1 drop of oil was added to a glass vial with 10 mL of pentane and 0.5 mL KOH solution. Vials were capped and manually shaken for 10–15 sec. Layers were allowed to separate, and the top layer was removed and filtered through a Whatman AUTOVIAL® 5 (Whatman, Sanford, ME) syringeless filter device into a vial for GC-MS analysis. Filter devices used polytetrafluoroethylene (PTFE) filters in polypropylene housing with a pore size of 0.45 µm. A plasticizer in this device inconsistently appeared in chromatograms as a peak at *c.* 8.4 min.

GC-MS

Fire debris extractions and neat oil samples were analyzed on a Hewlett-Packard (Agilent, Palo Alto, CA) HP 6890 GC with an HP 5973 MS. The GC was equipped with a Supelco (Bellafonte, PA) SP2380 capillary column. Refer to Table 3 for operating conditions. The FAME reference standard (GLC 17AA' (prime) from Nu-Chek Prep Inc., Elysian, MN) was prepared in methanol. The

TABLE 3—GC-MS conditions for fire debris solvent extracts and neat oil samples (Agilent HP 6890/HP 5973 GC-MS).

GC Parameters	
Column	Supelco SP-2380 (95% Cyanopropyl 5% Phenyl Polysiloxane) 25 m × 0.22 mm × 0.1 μm
Temperature Program	105°C for 0 min 4°C/min to 200°C for 0 min 20°C/min to 260°C for 0 min
Injector	250°C Split 20:1 Injection volume 1 μL
Carrier gas	Helium Flow 1.0 mL/min
MS Parameters	
Analyzer	Quadrupole 150°C
Ionization mode	EI
Full scan	50–550 m/z
Scan rate	2.94 scans/sec
Solvent delay	1.90 min
Source	230°C
Transfer line	265°C

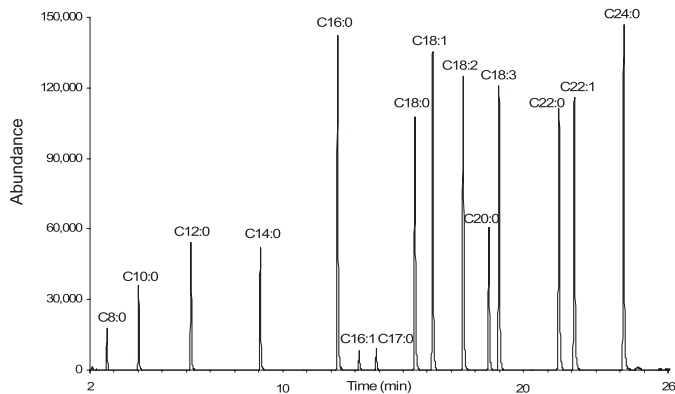


FIG. 2—Total ion chromatogram of fatty acid methyl ester (FAME) standard.

contents of the ampoule (100 mg) were added to 200 mL of methanol and heated until dissolved. The standard contained C8:0, C10:0, C12:0, C14:0, C16:0, C16:1, C17:0, C18:0, C18:1, C18:2, C18:3, C20:0, C22:0, C22:1, and C24:0 (Fig. 2). FAMES in vegetable oil and debris extracts were identified based on comparisons of retention time to the standard and examination of mass spectral data. Chromatograms of reference oils used can be seen in Figs. 3–6. Charcoal strip extractions from passive headspace concentrations were analyzed on an Agilent 6890N GC with an Agilent 5973 MS. Refer to Table 4 for operating conditions.

Data Analysis

Data obtained from all studies were analyzed and compared in the same manner. Chromatographic peak areas of the predominant fatty acids found in vegetable oils (C16:0, C18:0, C18:1, C18:2, and C18:3) were normalized to the sum of the areas of these peaks of interest. All points were plotted and the overall percentage of each peak was examined. Changes in FAME content, indicated by percentage changes when compared to neat reference oils, were considered indications of changes in vegetable oil content, as were the appearance of new FAME peaks. No percentage changes of FAME peaks or no appearance of new peaks indicated the absence of degradation in the vegetable oil.

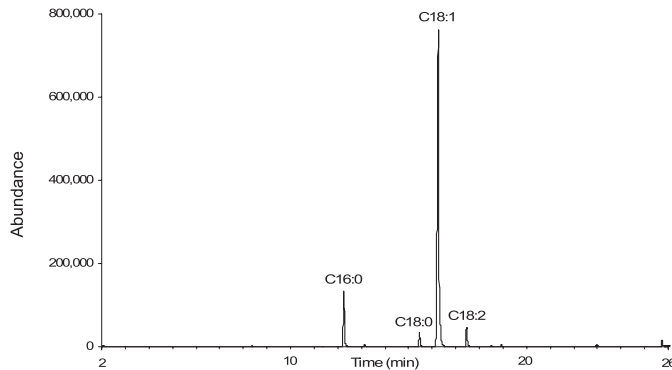


FIG. 3—Total ion chromatogram of extra virgin olive oil.

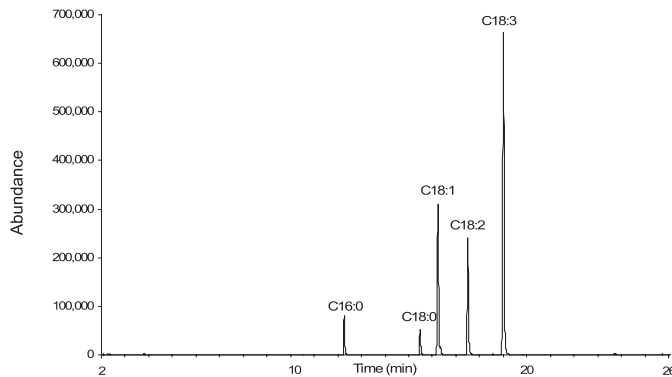


FIG. 4—Total ion chromatogram of raw linseed oil.

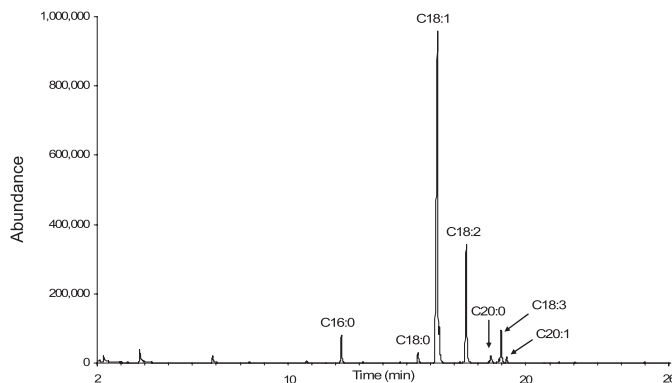


FIG. 5—Total ion chromatogram of canola oil.

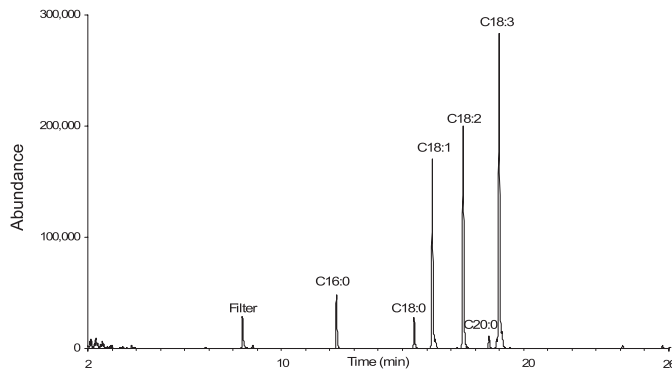


FIG. 6—Total ion chromatogram of timber oil.

TABLE 4—GC-MS conditions for charcoal strip extractions (Agilent 6890N/5973 GC-MS).

GC Parameters	
Column	Agilent DB-1MS (dimethylpolysiloxane) 30 m x 0.25 mm x 0.25 μm
Temperature Program	40°C for 2 min 5°C/min to 120°C for 0 min 12°C/min to 300°C for 5 min
Injector	250°C Split 20:1 Injection volume 1 μL
Carrier gas	Helium Flow 1.2 mL/min
MS Parameters	
Analyzer	Quadrupole 150°C
Ionization mode	EI
Full scan	33–300 m/z
Scan rate	2.80 scans/sec
Solvent delay	1.85 min
Source	230°C
Transfer line	280°C

Results and Discussion

Storage Conditions

The effect of storage conditions of vegetable oils was investigated to compare the “worst case scenario,” such as outside in the summer heat, with the ideal circumstance, which would be refrigeration. Four different environments were chosen which included storage in a refrigerator, laboratory hood, bunker, and outdoors. This was done to identify a suggested method of storing collected fire debris samples suspected of containing vegetable oils and to determine potentially detrimental effects when stored under less than ideal conditions. The two oils chosen represented oils with a relatively low (olive oil) and a slightly greater (raw linseed oil) propensity for self-heating. Raw linseed oil, unlike boiled linseed oil, does not contain catalysts to accelerate the drying time, and thus, may not spontaneously ignite as easily. However, the FAME content for both the raw and boiled linseed oil exemplars was indistinguishable, with the major component being C18:3, which is a primary indicator of an oil’s ability to self-heat.

Changes were seen with linseed oil samples stored in sealed and unsealed cans. Sealed samples from the refrigerator, hood, and outdoors maintained the same FAME compositions; however, C18:0, C18:1, and C18:3 peak percentages were different from the reference oil (Fig. 7a). The samples stored in the bunker showed even more of a change in these three FAMES. Linseed oil on fire debris in unsealed cans also showed degradation of the vegetable oil (Fig. 7b). As can be seen with the samples stored in the hood and bunker, the percentage of C18:3 decreased with a significant increase of C18:0 and slight increase in C18:1. The mean area percentages of unsealed cans with linseed oil stored in the bunker only included data from two of the three cans as Can 1 was not comparable to the others (Fig. 7c). This was attributed to the white mold that completely covered the debris in Can 1 resulting in more extensive degradation of the vegetable oil. The unsealed linseed oil cans stored outdoors also showed varying data as Can 1 contained c. 1.3 cm of water, Can 2 held less than 0.6 cm of water, and Can 3 only contained trace amounts. As the volume of water, increased, the amount of degradation significantly progressed (Fig. 7d).

All olive oil samples regardless of storage environment showed no significant differences in FAME area percentages and no new FAMES were generated as compared to the olive oil reference

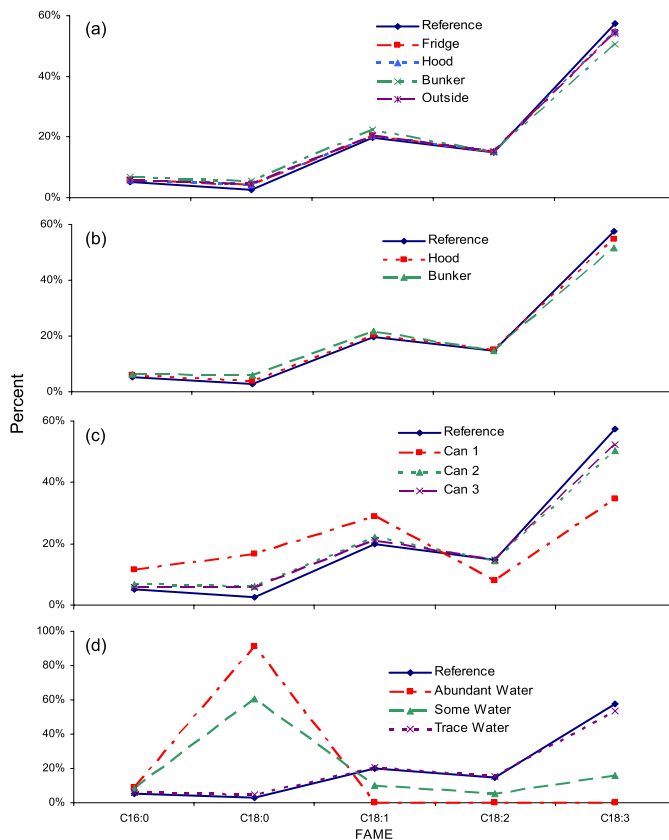


FIG. 7—Linseed oil on fire debris under varying storage conditions: (a) Sealed cans. (b) Unsealed cans. (c) Unsealed cans stored in bunker. (d) Unsealed cans stored outside.

sample. C18:1 remained the most abundant FA in olive oil with C18:3 being the least.

Passive Headspace Concentration and Effects of Overnight Heating

Passive headspace concentration is one of the most common methods for extracting ignitable liquids from fire debris. Samples are placed in a 65°C oven for 16 h with activated charcoal to adsorb ignitable liquid residues. This was performed to confirm that FAs could not be detected, as well as to ensure that vegetable oils would not be degraded or altered in any fashion by being extracted at 65°C overnight. Data obtained from the heated charcoal strip extractions with carbon disulfide for all three oils tested did not show the presence of any FAs. The debris was extracted with pentane and derivatized to look at the FAME content. There were no noticeable differences in the FAME content between the samples initially extracted at room temperature and at 65°C and the reference samples of canola, linseed, and olive oils.

Spontaneous Ignition

Part I (indoors)—Spontaneous ignition was attempted in order to determine if characteristic changes occurred during the process that could be used to distinguish spontaneously ignited oils from those subjected to piloted ignition. Initially, testing was conducted indoors at room temperature; however, these conditions were not ideal. After sufficient time had passed with no noticeable temperature increase or presence of smoke, box samples were subjected to

piloted ignition and the material inside the cans was subjected to autoignition. The single box of cloths with olive oil indicated differences from the neat reference oil. Minimal increases in C18:0 and C18:2 were noted with a more significant increase in the percentage of C16:0 and decrease in C18:1. No new FAMES of shorter hydrocarbon chain length were detected. The three linseed oil boxes all produced similar changes from the reference oil with a significant decrease in C18:3 and increases of C16:0, C18:0, C18:1, and C18:2. A small amount of C8:0 was also detected. Each can produced different results as they were not prepared in the same manner. Can A-1, which smoked the least when heated, resulted in the greatest decrease of C18:3 and greatest increase in C16:0, C18:0, and C18:1 as compared with the reference oil. Each of the cans showed this same degradation pattern with Can B-1 degrading the least. Upon heating, Can B-1 smoked and slightly flamed while Can C-1 produced smoke and even more flame. Smaller chain FAMES were also detected from all of the cans.

Part II (outdoors)—After determining which conditions needed to be altered in the preparation of spontaneous ignition samples, a second experiment was initiated outdoors on a warm, sunny day. Samples were prepared differently with the vegetable oil spread throughout the rags, rather than being poured into one location. Of the eight samples, only Box 4 (timber oil) contained a thermocouple in a location where the self-heating reaction was occurring. The thermocouple indicated the rags reached a temperature of 265°C (509°F) prior to ignition (Fig. 8a). The other seven thermocouples failed to record a change in temperature.

All four boxes spontaneously ignited within 5 h, but after this same time period only two of the cans (Cans A and B) showed evidence of self-heating. Of the samples containing timber oil, Box 4 ignited, but neither Can C nor Can D smoked. However, these

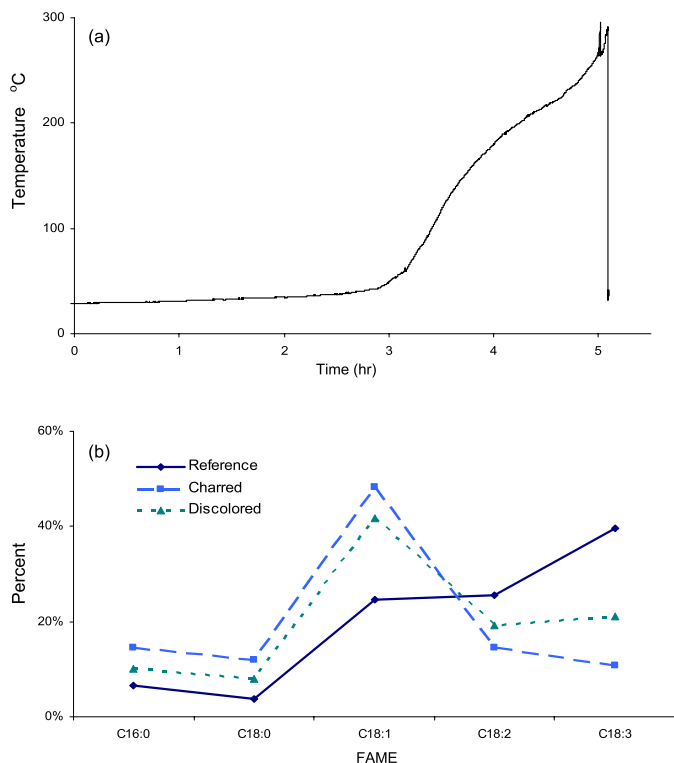


FIG. 8—(a) Temperature rise of self-heated and spontaneously ignited timber oil. (b) Change in fatty acid content of timber oil following spontaneous ignition.

two cans were found to be warm to the touch at the end of the experiment. Both Cans C and D showed changes in FAME composition and the presence of C8:0. The charred debris from Box 4 showed significant changes in FAME composition with the discolored portion exhibiting decreases in the percentages of C18:2 and C18:3, and increases in C16:0, C18:0, and C18:1. This change was intermediate to the FAME composition of the neat reference oil and thoroughly charred portion (Fig. 8b). Chromatograms of both the discolored and charred portions displayed the presence of a low molecular weight FAME, C8:0.

The linseed oil samples showed similar degradation patterns. Cans A and B self-heated, with Can A producing smoke and flame and Can B only smoke. Both exhibited similar changes in FAME content with C18:2 and C18:3 significantly decreasing in percentage and C16:0, C18:0, and C18:1 increasing. Can B showed slightly greater degradation and resulted in the detection of several short chain FAMES such as C6:0, C7:0, C8:0, and C9:0. Boxes 1 and 2 (linseed oil) underwent the same progression of degradation as seen with the timber oil samples. The percentage of C18:3 decreased the most, while C16:0, C18:0, and C18:1 increased. Box 3 (linseed oil) showed degradation; however, the discolored and charred debris showed similar progression. Each of the three boxes produced degradation products of smaller FAs including C8:0 (Fig. 9). The changes in FA composition of linseed oil resulting from spontaneous ignition can be seen in Fig. 10 as compared with the reference oil and the other burning and heating processes tested.

Based on the results obtained, once a vegetable oil has experienced self-heating, autoignition, or spontaneous ignition, it can no longer be identified by FAME content. While it is possible to identify vegetable oils following piloted ignition, degradation of the oil occurs during nonpiloted ignition and self-heating processes to a point where the final FAME content is no longer comparable to that of the original vegetable oil. This research demonstrated the possibility of reporting that a process other than piloted ignition occurred in vegetable oils prone to self-heating. A significant increase in C18:1 was repeatedly detected with an accompanying decrease of C18:3, and C8:0 was consistently identified in samples subjected to self-heating, autoignition, and spontaneous ignition. C8:0 is not present in neat or piloted ignition vegetable oil samples

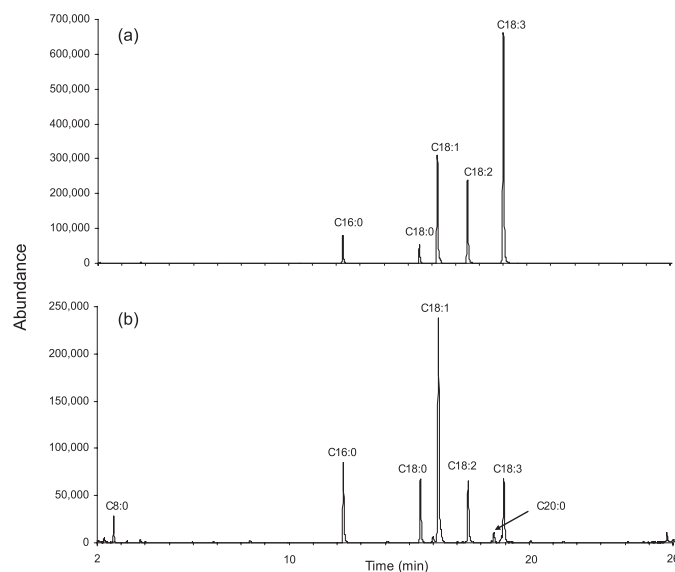


FIG. 9—(a) Total ion chromatogram of boiled linseed oil. (b) Total ion chromatogram of spontaneously ignited boiled linseed oil fire debris.

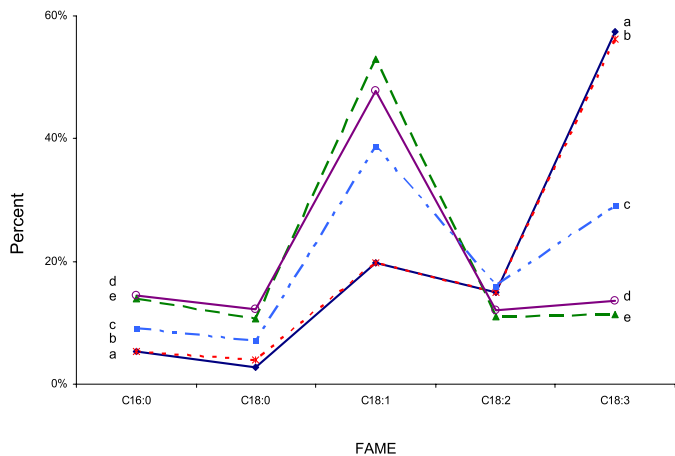


FIG. 10—Heating and ignition processes of linseed oil: (a) Reference oil. (b) Piloted ignition. (c) Autoignition. (d) Spontaneous ignition. (e) Self-heating.

with the exception of linseed oil boxes from Part I of the spontaneous ignition study. This exception can be accounted for because a significant period of time had passed from the start of the test to the point of piloted ignition. Limited self-heating could have taken place resulting in the presence of C8:0. Also, when boxes spontaneously ignited, the entire box rapidly flamed. This was not the case with the piloted ignition samples as the entire box area did not rise in temperature. As boxes were torched, only the immediate area around the flame caught on fire. The time period while the fire was spreading could have allowed for oil near the flames to heat to a point approaching autoignition. This was not seen with olive oil as it is not a vegetable oil with a great abundance of C18:3. A change in the percentage of original FAMES was detected, but as olive oil has a low propensity towards self-heating or autoignition, a longer period of time would be necessary to more thoroughly degrade the oil.

Conclusions

This research has demonstrated that proper storage of fire debris suspected of containing vegetable oils is essential. Debris should be securely sealed in cans with minimal water, if possible, to reduce the potential for degradation and prevent the accumulation of foreign materials. Prompt delivery of collected debris to a laboratory where refrigerated storage is possible would also be beneficial. This will minimize degradation of the oils. When possible, known vegetable oil samples from the fire scene should also be submitted to the laboratory for comparison to the debris. For the fire debris examiner, it is important to note that heating at 65°C for 16 h during passive headspace concentration will not damage vegetable oil content if present. Solvent extraction is still necessary to recover vegetable oils as results verify that FAs cannot be detected through passive headspace concentration.

Spontaneous ignition of vegetable oils can occur and precautions should be taken to prevent autooxidation. If a vegetable oil self-

heats, spontaneously ignites or autoignites, an analyst may be able to distinguish between these processes and piloted ignition by examining the derivatized extracts on GC-MS and comparing the results to a fresh, known sample. While individual vegetable oil type identifications cannot be made, FAME content may indicate that a process other than piloted ignition transpired. To further support this conclusion, additional research will be conducted in the future to examine the FAME content of vegetable oils of varying degrees of saturation following spontaneous ignition, self-heating, and autoignition.

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Additional information—reprints not available from author:

Michelle R. Reardon, M.S.F.S.
Bureau of Alcohol, Tobacco, Firearms and Explosives
Forensic Science Laboratory – Washington
6000 Ammendale Road
Ammendale, 20705-1250 MD
E-mail: michelle.reardon@atf.gov