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A Review of the Analysis of Vegetable Oil Residues from Fire Debris Samples: Analytical Scheme, Interpretation of the Results, and Future Needs

ABSTRACT: This paper reviews the literature on the analysis of vegetable (and animal) oil residues from fire debris samples. The examination sequence starts with the solvent extraction of the residues from the substrate. The extract is then prepared for instrumental analysis by derivatizing fatty acids (FAs) into fatty acid methyl esters. The analysis is then carried out by gas chromatography or gas chromatography-mass spectrometry. The interpretation of the results is a difficult operation seriously limited by a lack of research on the subject. The present data analysis scheme utilizes FA ratios to determine the presence of vegetable oils and their propensity to self-heat and possibly, to spontaneously ignite. Preliminary work has demonstrated that it is possible to detect chemical compounds specific to an oil that underwent spontaneous ignition. Guidelines to conduct future research in the analysis of vegetable oil residues from fire debris samples are also presented.

KEYWORDS: forensic science, fire debris analysis, vegetable oil, fatty acids, spontaneous ignition, self-heating, fire investigation, gas chromatography, mass spectrometry

The examination of fire debris samples for vegetable oil residues (VOR) consists of four steps:

A. Extraction–isolation of VOR,
B. Preparation of the extract,
C. Analysis of the extract,
D. Interpretation of the results.

The first three steps have already been well researched and developed in the chemical and food industries. As seen below, the same procedures and techniques can be used or adapted for fire debris analysis. A problem arises with the fourth step, where very little formal research has ever been conducted to provide a proper interpretation of the results.

Extraction–Isolation of VOR

Similar to regular fire debris analysis for ignitable liquids residues (ILR), the first step in VOR analysis is to extract or isolate the residues from the sample. These residues are adsorbed onto a substrate and therefore, a suitable extraction procedure must be used. Well-established ASTM standards provide the criminalist some help for ILR (1–5); however, this is not the case for VOR.

The choice of an extraction technique is dictated by the nature of the substance to be extracted, the substrate onto which it is adsorbed, and the analyses subsequently performed. The cost and labor involved can also be of concern. As seen in the previous article, vegetable oils are composed of lipids, which are, for the most part, nonvolatile compounds (6). Cruwys et al. (7) have successfully used a headspace technique to recover fatty acids (FAs) ranging from C_2 to C_5. However, in the fire investigation application, the carbon range pertinent to the analysis of VOR is usually from C_{10} to C_{22}. Furthermore, the compounds of interest are found in the form of triacylglycerides (TAG). Hence, the most volatile compound of interest to the fire debris analyst presents a boiling point well above 300°C. Therefore, a headspace technique is not appropriate to recover VOR. Jungen demonstrated that the application of passive headspace concentration on activated charcoal using ASTM Standard Practice E1412 does not recover any FAs or TAG from sunflower oil (8).

The only other choice left for the analyst is a solvent extraction. Vegetable oils being constituted of lipids, are soluble in nonpolar organic solvents. There are many solvent extraction techniques that have been developed to extract and concentrate vegetable oils from different substrates and that have been used in the food industry for many years (9–11). It is also important to note that some extraction techniques include the acidic hydrolysis of the TAG into free fatty acids (FFAs), which is not necessarily pertinent to the fire debris application. Nevertheless, some extraction techniques have also been developed with an *in situ* transesterification.

Folch et al. (12) were the first to propose an extraction technique for lipids. They recommend the use of a solution of chloroform:methanol (2:1). This technique is also recommended by Christie (10). Hara and Radin (13) reported the use of hexane:2-propanol (3:2), thus eliminating the danger of the chloroform solution. Barthet et al. (14) demonstrated that an exhaustive extraction with petroleum ether yielded the greatest recovery of TAG from flaxseed and canola oil. A longer extraction technique involves the use of heptane:0.17 M NaCl in methanol (66.6:33.3) for 2 h at 80°C (15). The utilization of a microwave oven in conjunction with the use of water and methanol has been reported by Ganzler et al. (16) to accelerate the extraction. Carrapiso and Garcia (17) recently reviewed the literature related to new extraction techniques and more particularly procedures involving the use of microwave or supercritical fluid (CO_2). They also placed some emphasis on the extraction techniques providing an *in situ* transesterification.

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In more particular forensic applications, Ehara et al. (18) used ether to extract vegetable oil stains in their laboratory experiments. Coulombe (19) used ethyl ether to extract VOR from a burned towel. Johansson et al. (20) used heptane to precipitate soap containing FAs from weapon lubricants. When only small amounts were available, they advised to dissolve the lubricant in toluene. Jackowski (21) recommended the use of cyclohexane. Nic Daéid et al. (22) used methanol to extract samples of FAs from cotton. Keto reported the successful use of pentane to extract VOR from wood debris (R. Keto, personal communication, October 2003). This author successfully extracted VOR from charred fire debris samples using nonpolar solvents such as pentane, hexane, or heptane.

Once extracted, if the volume of solvent is too large, reconcentration is readily feasible, particularly with light solvents such as pentane or hexane. Although the FAs or triglycerides have elevated boiling points, the solvent can be slowly evaporated at room temperature, but should not be heated as it may further degrade the sample. Keto also used a stream of nitrogen at room temperature to reconcentrate his extracts (R. Keto, personal communication, October 2003).

Preparation of the Extract

The preparation of the extract depends on the analytical technique used. As presented in "Analysis of the Extract," different techniques can be used. For infrared spectroscopy, the sample preparation is minimal, if nonexistent. However, it is not the case for other techniques such as the ones involving gas chromatographic (GC) separation. There are two main strategies used for the analysis of VOR by GC: Analyzing the FFAs or analyzing the derivates of FAs. The latter requires an extra derivatization step. It is also possible to analyze TAGs directly, but this requires a high-temperature column and a mass spectrometer capable of handling the molecular weights of such compounds that are in the range of several hundred atomic mass units (amus) (23). Nevertheless, in this particular forensic application, this leads to results that cannot be reasonably interpreted, as the proportions of saturated and unsaturated FAs cannot be easily determined.

FFAs

Although it is possible to analyze FFAs directly by gas chromatography, it is not an easy process. FFAs are not volatile and are very reactive. This requires a particular chromatographic column and injection set-up, which have been specifically deactivated to handle acidic compounds (24). FFAs represent only a small proportion (usually 1–8%) of the total content of vegetable oils and most of the components of interest are in the form of lipids or TAG. Unless the analyst wishes to analyze only the FFA content, the sample needs to be prepared by hydrolyzing the lipids into FFAs. Presently, the analysis of FFAs is not recommended in fire debris analysis as its significance has not yet been evaluated.

Derivatization of FAs

Derivatization of FAs yields to two main advantages: a decrease in reactivity and an increase in volatility. Additionally, the breaking apart of TAGs into single FAs, followed by their derivatization, allows for the analysis and easy quantification of the FA content of a lipid (25). There are many available techniques of derivatization that use different derivatizing agents. The most widespread derivates are the fatty acid methyl esters (FAMEs), but other derivates, such as ethyl esters, are also available. FAMEs are the simplest esters that can be prepared. They offer a low molecular weight and therefore, elute from the chromatographic column at relatively low temperatures.

There are several good derivatization techniques that might be applied to VOR. Each technique might be more suitable to a particular oil and situation. The analyst can improve the derivatization by choosing the most appropriate technique. Christie states that "*. . . methods suitable for gram amounts may be less suitable for microgram quantities . . .*" (26). Thus, the quantity of VOR recovered might be a parameter to take into account when choosing a derivatization technique. No literature dealing with the optimization of the derivatization procedures for residues from fire debris samples has been published. Also, as the criminalist usually does not know what kind of and how much oil is expected in the debris, it would be very difficult to optimize an extraction technique. In the absence of such information, the different preparation techniques can only be presented with their advantages and drawbacks. Although the ultimate choice of the best technique is left to the criminalist, recommendations will be given to the reader.

Preparation of FAMEs

Preparation of methyl esters can be performed either by esterification of FFAs or by transesterification of triglycerides. This is illustrated in Fig. 1.

Derivatization techniques are classified as either one-step or two-step procedure. The one-step derivatization is a transesterification of the triglycerides into FAMEs. While this type of technique is usually much faster and less cumbersome than the two-step alternative, it will not include the FFA content of the sample, except with acid-catalyzed derivatization procedures, which simultaneously esterify FFAs. Unless new developments prove otherwise, this is presently not a very important issue in this forensic application, because the FFA content of an oil is usually only a couple of percent. The two-step procedure usually consists of the hydrolysis of TAGs into FFAs followed by the esterification of FFAs into FAMEs. Hence, such a procedure includes the original

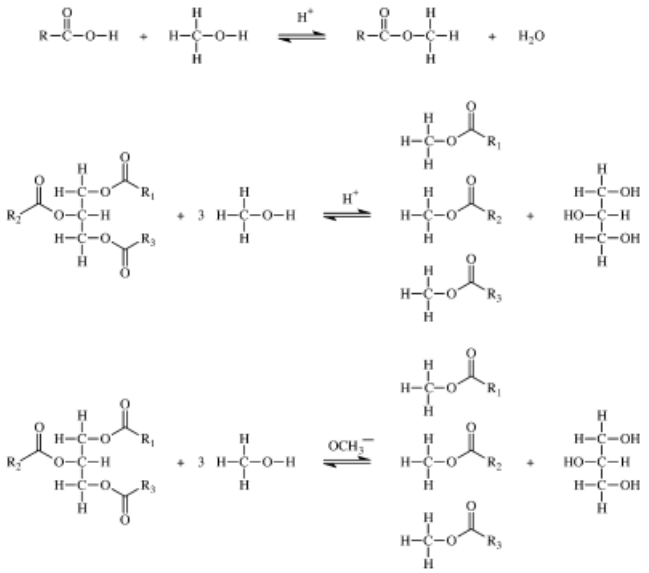

FIG. 1—*Illustration of the esterification of a free fatty acid (top) and transesterification of a triglyceride by either acid-catalyst or base-catalyst process (middle+bottom).*

TABLE 1—*Physical and chemical characteristics of FAMEs.*

FA Designation	FAME Name	Formula	MW (amu)	BP (°C)
C2:0	Methyl acetate	CH_3COOCH_3	74	
C4:0	Methyl butyrate	$C_3H_7COOCH_3$	102	103
C5:0	Methyl pentanoate	$C_4H_9COOCH_3$	116	
C6:0	Methyl hexanoate	$C_5H_{11}COOCH_3$	130	151
C8:0	Methyl octanoate	$C_7H_{15}COOCH_3$	158	192.9
C10:0	Methyl decanoate	$C_9H_{19}COOCH_3$	186	223
C12:0	Methyl dodecanoate	$C_{11}H_{23}COOCH_3$	214	
C14:0	Methyl tetradecanoate	$C_{13}H_{27}COOCH_3$	242	323
C16:0	Methyl hexadecanoate	$C_{15}H_{31}COOCH_3$	270	
C16:1(n-7)	Methyl hexadecenoate	$C_{15}H_{29}COOCH_3$	268	
C18:0	Methyl octadecanoate	$C_{17}H_{35}COOCH_3$	298	215*
C18:1(n-7)	Methyl octadecenoate	$C_{17}H_{33}COOCH_3$	296	
C18:1(n-9)	Methyl octadecenoate	$C_{17}H_{33}COOCH_3$	296	
C18:1(n-12)	Methyl octadecenaote	$C_{17}H_{33}COOCH_3$	296	
C18:2(n-6)	Methyl octadecadienoate	$C_{17}H_{31}COOCH_3$	294	
C18:3(n-3)	Methyl octadecatrienoate	$C_{17}H_{29}COOCH_3$	292	
C18:3(n-6)	Methyl octadecatrienoate	$C_{17}H_{29}COOCH_3$	292	
C20:0	Methyl eicosanoate	$C_{19}H_{39}COOCH_3$	326	
C20:4(n-6)	Methyl eicostetraenoate	$C_{19}H_{31}COOCH_3$	318	
C20:5(n-3)	Methyl eicosapentaenoate	$C_{19}H_{29}COOCH_3$	316	
C22:0	Methyl docosanoate	$C_{21}H_{43}COOCH_3$	344	
C22:1(n-9)	Methyl docosenoate	$C_{21}H_{41}COOCH_3$	342	
C22:6(n-3)	Methyl docosahexaenoate	$C_{21}H_{31}COOCH_3$	332	
C24:0	Methyl tetracosanoate	$C_{23}H_{47}COOCH_3$	372	
C24:1(n-9)	Methyl tetracosenoate	$C_{23}H_{45}COOCH_3$	370	
C26:0	Methyl hexacosanoate	$C_{25}H_{51}COOCH_3$	390	

*15 mmHg.
FAME, fatty acid methyl ester.

TAG and FFA contents. Table 1 summarizes some chemical and physical properties of FAMEs.

Using FAMEs allows for a serious reduction of the size of the TAG. One molecule, which usually contains several tens of carbon atoms, is split in three molecules of a maximum of two dozen carbon atoms. The molecular weight is thus reduced from several hundred to a couple of hundred amus. Also, when the boiling points of FAMEs are compared with the boiling point of their corresponding FA (as shown in Table 2 of the previous article), the average drop is at least 40°C (6).

Table 2 presents an overview of the most important derivatization techniques, along with their use, advantages, and disadvantages (26–37). All the acid-catalyzed techniques will both act on TAGs and FFAs. However, in some instances, the triglycerides do not dissolve very well in the reagents and might take a significant time to transesterify. In such instances, it is advised to add a solvent to the reaction such as toluene or tetrahydrofuran (THF) to accelerate the reaction (26). Also, all acid-catalyzed techniques can introduce some artifacts, particularly when the solvent evaporates. Base-catalyzed techniques only transesterify TAGs. Hence, the FFA content of a sample is not esterified and not detected. In general, base-catalyzed techniques are much simpler, faster, and safer than the acid ones.

In a more particular forensic application, Coulombe (19) first esterifies his samples using a 5% solution of KOH in methanol, extracts this solution with ethyl ether, acidifies it with HCl, reextracts with ethyl ether, and finally derivatizes it using the BF_3 technique. In another experiment with Gélin, he adds an extra drying step with magnesium sulfate before the derivatization with boron trifluoride (38). Keto uses the regular BF_3 technique, without adding calcium sulfate to absorb residual water in the organic phase (R. Keto, personal communication, October 2003) (28). This last step is not performed because it has jeopardized the cleanliness of the GC injector in prior experiments (R. Keto, personal communication, August 2004). Ehara et al. (18) use tetramethylammonium hydroxide (TMAH) to proceed to the transesterification to FAMEs. Pitts and Thomson (39) use TMAH in their experiment on the classification of vegetable oils. Johansson et al. (20) heats the soap containing the FAs in toluene:methanol (1:1) with a drop of concentrated sulfuric acid for 25 min at 60°C. The solution is then left at room temperature for 1 h, shaken with distilled water, and centrifuged. The FAMEs are collected in the toluene phase. Finally, the author of this article had great success using the KOH in methanol procedure with both pure (used) oil samples and fire debris extracts.

Other Esters

FAMEs are not the most suitable esters for the separation of the different isomers. For instance, it has been demonstrated that propan-2-ol esters resulted in a better separation of the *trans* isomers of linolenic acid than methyl esters (40). Other possible esters are butyl esters, pentafluorobenzyl esters, or picolinyl esters (40). Each ester type offers its own advantages and disadvantages, such as a more specific mass spectral identification or a higher boiling point. It is possible that future research will show some pertinence in the use of some of these esters in the particular application of VOR analysis. At present time, the author recommends the use of FAMEs with either the BF_3 or KOH techniques for the derivatization of VOR.

Analysis

Several analytical techniques have been described in the literature. They include gas chromatography, high-performance liquid chromatography, supercritical fluid chromatography, thin-layer chromatography (TLC), Fourier transform infrared spectrometry, nuclear magnetic resonance, UV-visible spectrometry, and X-ray scattering (11,41–48). Not all of these techniques are pertinent or applicable to VOR extracted from fire debris samples. Hence, the review will confine itself to the infrared spectrometry, thin-layer, and gas chromatographic techniques.

Fourier Transform Infrared Spectrometry

Reese et al. (49) mentioned the use of infrared spectroscopy for the analysis of extracts of vegetable oils or animal fats from fire debris; however, they do not provide any further indications or references.

The use of attenuated total reflectance (ATR) infrared spectroscopy has been developed for the analysis of vegetable oils (50). Using this technique, the presence of FFAs and unsaturated FAs can be observed. FFAs show a slightly different absorption between 1725 and 1700 cm^{-1}, whereas unsaturated FAs show a slightly different absorption around 700 and 3000 cm^{-1}. The advantage of using such a technique lies in the relative ease of sample preparation. However, the main drawback is that while it reveals the presence of a vegetable oil and might reveal the presence of some unsaturation, it does not allow the analyst to estimate the exact nature and amount of unsaturated FAs.

The problem with the use of an infrared spectroscopic technique is twofold. First, it requires a pure sample, which is not readily available in the context of fire debris analysis. When dealing with extracts from fire debris, other contaminants are likely to be present, which will strongly interfere in the spectrum. Second, it is not reasonably possible to determine with enough satisfaction the nature and amounts of the different FAs present, which is necessary to estimate the oil's propensity to self-heat: a crucial piece of information for the fire investigator. Therefore, the use of

TABLE 2—*Different derivatization techniques for FAMEs.*

Derivatization Technique	Use	Advantages	Disadvantages
Acid-catalyzed methods			
HCl in MeOH (25,27)	The sample is placed in 5% (w/v) solution of HCl in methanol. The mixture is heated and cooled down.	Premade reagents are readily available in the commerce Better for bulk preparation	Very time consuming (>1 h) Preparation of reagents can be cumbersome Artifacts might occur
H_2SO_4 in MeOH (25,28)	The sample is placed in a nonpolar organic solvent and a 10% solution of H_2SO_4 in methanol. The mixture is heated, cooled down, and a saturated $NaHCO_3$ solution in water is added with more solvent. The mixture is vortexed, and the nonpolar organic solvent layer is removed. It contains the FAMEs.	Premade reagents are readily available in the commerce	Can be time consuming PUFAs might decompose if solvent evaporates
BF_3 in MeOH (25, 29–34)	The sample is placed in a nonpolar organic solvent and a 10% solution of BF_3 in methanol. The mixture is boiled and a saturated NaCl solution in water is added. The mixture is vortexed and the nonpolar organic solvent layer is removed. It contains the FAMEs.	Premade solutions of BF_3/MeOH can be purchased	May bring extra peaks in the chromatogram The BF_3/MeOH technique reacts with BHT Reagent needs to be fresh Reagent needs to be well-prepared Not very safe
BCl_3 in MeOH (25,35)	The sample is placed in a nonpolar organic solvent and a 10% solution of BCl_3 in methanol. The mixture is boiled and a saturated NaCl solution in water is added. The mixture is vortexed and the nonpolar organic solvent layer is removed. It contains the FAMEs.	As efficient as BF_3/MeOH Safer than BF_3/MeOH and does not bring extra peaks in the chromatogram	Almost never used
Base-catalyzed methods			
$NaOCH_3$ in MeOH (26,36)	The sample is placed in a nonpolar organic solvent (but not chloroform) and a 0.5 M solution of $NaOCH_3$ in methanol. The mixture is heated and cooled down. Water and hexane or heptane are added. The nonpolar organic solvent layer is removed. It contains the FAMEs	Simple Rapid	
$KOCH_3$ in MeOH (26)	The sample is placed in a nonpolar organic solvent (but not chloroform) and a 0.5 M solution of $KOCH_3$ in methanol. The mixture is heated and cooled down. Water and hexane or heptane are added. The nonpolar organic solvent layer is removed. It contains the FAMEs.	Better catalyst than sodium	Can react vigorously with methanol and be dangerous
KOH in MeOH (31)	The sample is placed in a nonpolar organic solvent and a 2 M solution of KOH in methanol. The mixture is vortexed and centrifuged. The upper layer contains the FAMEs.	Extremely simple Extremely rapid Long shelf life	KOH needs to be free of water Not very efficient with oil with acid value >2

FAME, fatty acid methyl ester; BHT, butylated hydroxytoluene.

IR techniques, unless preceded by a separation technique, such as gas chromatography, is not recommended when performing VOR analysis from fire debris samples.

Thin-Layer Chromatography

TLC is a fast, simple, and inexpensive technique used to separate the main classes of lipids, FFAs, and hydrocarbons (45). In one dimension of separation, it is possible to separate hydrocarbons, cholesterol esters, TAG, FFAs, diacylglycerides, and monoacylglycerides. Then, it is possible to perform further analysis on each fraction.

Several different procedures exist for the TLC of lipids, each adapted for a specific application. For general application, Christie (51) recommends the use of silica gel G plates without fluorescent indicator. He furthers described the following procedure (51):

- A "blank" migration of the plate is performed in chloroform:methanol (1:1).
- After drying, the lipids are applied and the plate is eluted in hexane:diethyl ether:acetic acid (70:30:1).
- After drying again, the plate is sprayed with a primuline solution (5 mg in 100 mL of acetone:water [80:20]) and observed under a UV light.

As there has been very little literature about the significance and changes of the chemical composition of oils in regard to the phenomenon of spontaneous ignition, it is not yet known if TLC is a valuable technique for this purpose. It is possible that the analysis of TAGs only, provides a pattern independent of the one exhibited by FFAs. In such a case, the characterization of an oil could be improved. If further research demonstrates that separate analyses of these different classes are pertinent, TLC offers a rapid means of preparing the extract for such analyses.

Gas Chromatography and Gas Chromatography-Mass Spectrometry—Gas chromatography (GC) is the most suitable analytical technique to separate and detect the different FAs constituting a vegetable oil. It provides the user with qualitative and (semi) quantitative data with regard to the acids present in a mixture. A gas chromatograph equipped with a flame ionization detector (GC-FID) is enough to perform this kind of analysis, if suited with the proper column. A gas chromatograph equipped with a mass spectrometer (GC-MS) provides an extra level of information, which is necessary when the GC is not equipped with the optimal column.

The Association of Official Analytical Chemists (now AOAC International) official method 963.22 recommends the use of a polar liquid stationary phase such as diethylene glycol in order to provide the required resolution (52). Such columns are sold under

TABLE 3A—*Instrumental and analytical conditions used with a column Supelco® SP-2380. Courtesy of Ray Keto (retired), Bureau of Alcohol, Tobacco, Firearms & Explosives, Ammendale, MD.*

Column	Type	Supelco® SP-2380 (95% Cyanopropyl 5% Phenyl Polysiloxane)
	Dimensions	30 m × 0.25 mm × 0.20 μm
Mobile phase	Carrier gas	Helium
	Flow rate	0.5 mL/min (flow electronically controlled)
Injection	Type	Liquid/autosampler Split 50:1
	Volume injected	1 μL
Temperatures	Injector	250°C
	Column	120°C for 0 min 4°C/min to 200°C for 0 min 10°C/min to 265°C for 0 min Total run 26.5 min
	Transfer line	265°C
	Quadropole	150°C
	Source	230°C
Mass Spectrometry	Scanning range	33–433 amu
	Solvent delay	3.00 min
	A/D samples	8

TABLE 3B—*Instrumental and analytical conditions used with a column HP-5.*

Column	Type	Hewlett-Packard HP-5 (5% Diphenyl Methyl Siloxane)
	Dimensions	30 m × 0.25 mm × 1.00 μm
Mobile phase	Carrier gas	Helium
	Flow rate	1 mL/min (flow electronically controlled)
Injection	Type	Liquid/autosampler Split 20:1
	Volume injected	1 μL
Temperatures	Injector	250°C
	Column	220°C for 5 min 0.5°C/min to 225°C for 0 min 4°C/min to 245°C for 15 min Total run 35 min
	Transfer line	280°C
	Quadropole	150°C
	Source	230°C
Mass spectrometry	Scanning range	33–400 amu
	Solvent delay	2.00 min
	Sampling	3.92 scans/sec

the names of DB-WAX, HP-WAX, or Supelcowax™ (Supelco, Bellefonte, PA). In the same method, it is also stated that "Nonpolar phase can be used for certain separations." In a study comparing four capillary columns, it was shown that polyalkylene glycol phases produced an elution order that corresponded to the carbon chain length (53). It was also demonstrated that high-polarity columns containing a high proportion of cyanopropyl in the phase would separate *cis* and *trans* isomers, but would exhibit a significant carbon chain overlap in the elution order (53). On a more recent note, David et al. (54) compared three different chromatographic columns for the separation of FAMEs. They concluded that the DB-WAX column (polyethylene gycol) is useful for the separation of classical edible oils and fats, however it does not separate *cis* and *trans* isomers (54). The DB-23 column (50% cyanopropyl methylpolysiloxane) provides excellent separation of more complex FA mixtures such as in fish oils as well as partial separation of *cis* and *trans* isomers (54). Finally, the column HP-88 (90% bis-(cyanopropyl) polysiloxane) offers a complete *cis* and *trans* isomer separation (54).

The separation of *cis* and *trans* isomers is neither necessary nor desired in the fire debris application. Thus, a polyalkylene glycol phase is the most suitable phase for the analysis of VOR. It is the author's recommendation that a GC-FID only be used with the proper polar column. A GC-MS is necessary when a regular nonpolar column such as a DB-1 (polydimethylsiloxane) or DB-5 (5% diphenyl/95% dimethylsiloxane) is used. The reason is that the nonpolar column does not allow for baseline resolution between methyl octadecenoate (C18:1), methyl octadecadienoate (C18:2), and methyl octadecatrienoate (C18:3), which cannot be identified based on their retention times only. Hence, the extra spectral information provided by the mass spectrometer allows for the proper identification. The use of a proper polar column allows excellent resolution between C18:1, C18:2, and C18:3 as well.

Coulombe (19) reported the use of a GC-FID equipped with a DB-5 column. With Gélin, he also used a GC-MS for the peak identification (38). Ehara et al. (18) used a GC-MS equipped with a purge-and-trap system and an HP Innowax column. Pitts and Thomson (39) used a GC-MS equipped with a DB-WAX column and obtained excellent separation. Johansson et al. (20) used an HP-1 column, but their samples do not exhibit any unsaturated FAs. Duchesne (55) used both a DB-WAX on some samples, which offered excellent resolution and an HP-50+, with which he could not resolve C18:0 and C18:1 as they were coeluting and not completely resolved from C18:2. Keto used a Supelco SP-2380 (95% cyanopropyl 5% phenylpolysiloxane) column to attain baseline resolution of FAMEs from C12:0 to C18:3(n-3) (R. Keto, personal communication, October 2003). The instrumental and analytical conditions used with this column are presented in Table 3A. The author of this article always successfully discriminated between C18:0, C18:1, C18:2, and C18:3 using an HP-5 column on a GC-MS and the instrumental and analytical conditions presented in Table 3B. These conditions even allow for the separation of some isomers as shown in the figures hereafter. Although the temperature program and some other parameters of the GC-MS have been optimized for VOR analysis, the instrument is the same as that used for regular ILR analysis.

Chromatograms of the FAMEs obtained from boiled linseed oil from two different systems are presented in Figs. 2*a* and *b*. Linseed oil is very often encountered in fires caused by spontaneous ignition, as it is widely used as a drying oil in paint and stain products. According to Ettling and Adams (56), historically, linseed oil was boiled in order to rearrange the positions of the double bonds into a conjugated configuration, making the oil much more reactive and prone to autooxidation. Dixon (57) also demonstrated that boiled linseed oil has a higher propensity toward spontaneous ignition than linseed oil. Today, the term "boiled" does not imply that the oil has been boiled. Some linseed oils are still heated, however, for most of them, the term "boiled" signifies that metallic catalysts have been added to accelerate the drying process (58). Such catalysts contain zirconium, cobalt, or manganese. ASTM standard D260-86 "Standard Specification for Boiled Linseed Oil" does not specify its preparation nor its metallic content (59).

The first system uses the SP-2380 column with the parameters presented in Table 3A and the derivatization procedure is BF_3/methanol as reported by Keto (R. Keto, personal communication, October 2003). The second system uses the HP-5 column with the parameters presented in Table 3B and the KOH/methanol derivatization procedure. Both systems use a mass spectrometer as detector.

Upon observation of these two chromatograms, it is obvious that the separation offered by the more polar column (Fig. 2*a*) resolves

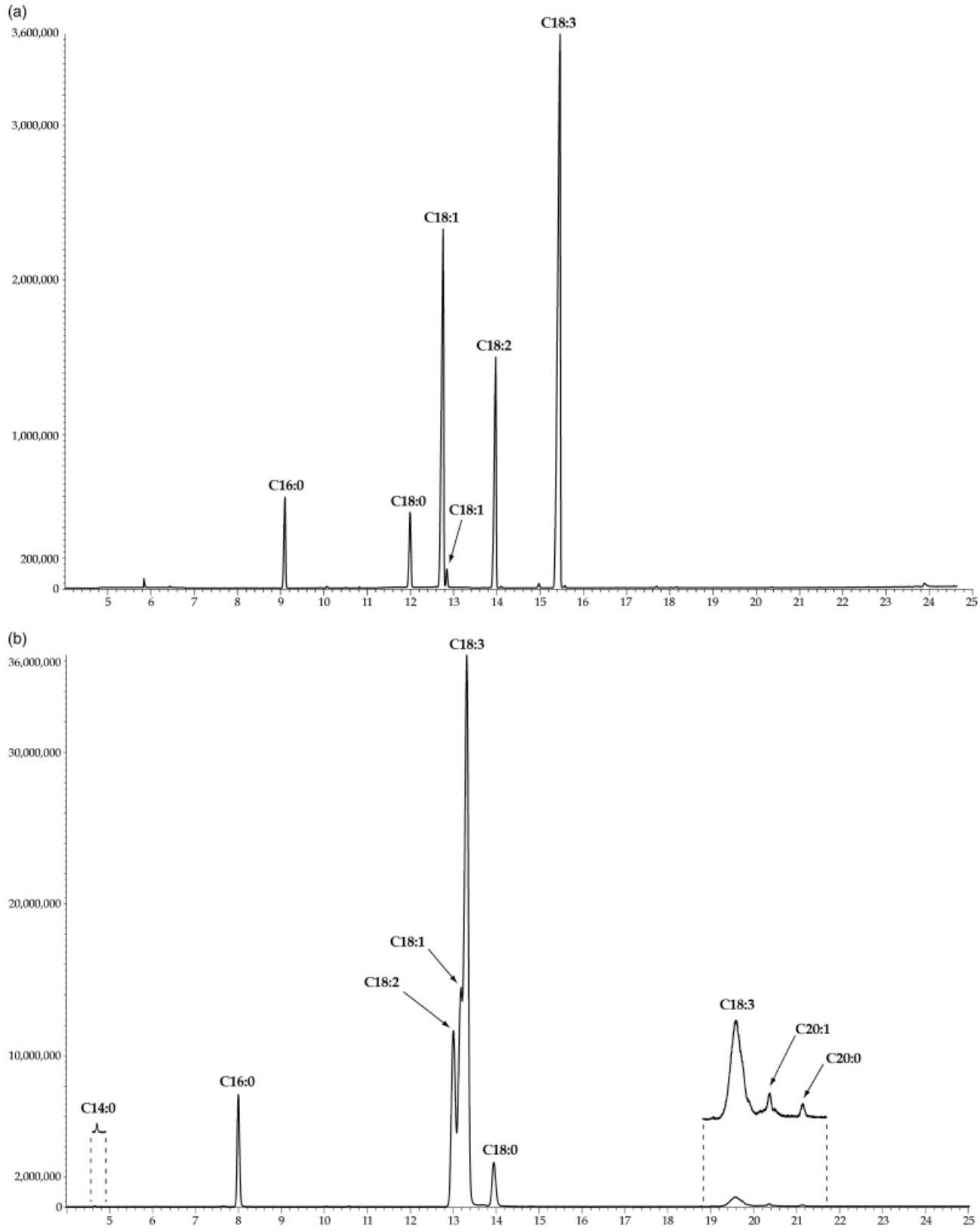

FIG. 2—*(a) Chromatogram of fatty acid methyl esters (FAMEs) obtained from linseed oil (range from 4 to 25 min) using a Supelco® SP-2380 column with the conditions described in Table 3A. Data courtesy of Ray Keto (retired), Bureau of Alcohol, Tobacco, Firearms & Explosives, Ammendale, MD. (b) Chromatogram of FAMEs obtained from linseed oil (range from 4 to 25 min) using an HP-5 column with the conditions described in Table 3B.*

all the peaks of interest. Furthermore, the elution order follows the degree of unsaturation for each compound. Conversely, the separation offered by the typical column used for fire debris analysis (Fig. 2*b*) leads to coeluting peaks (C18:1, C18:2, and C18:3), which are the most pertinent compounds of interest in VOR analysis. This renders the exact quantification of the results

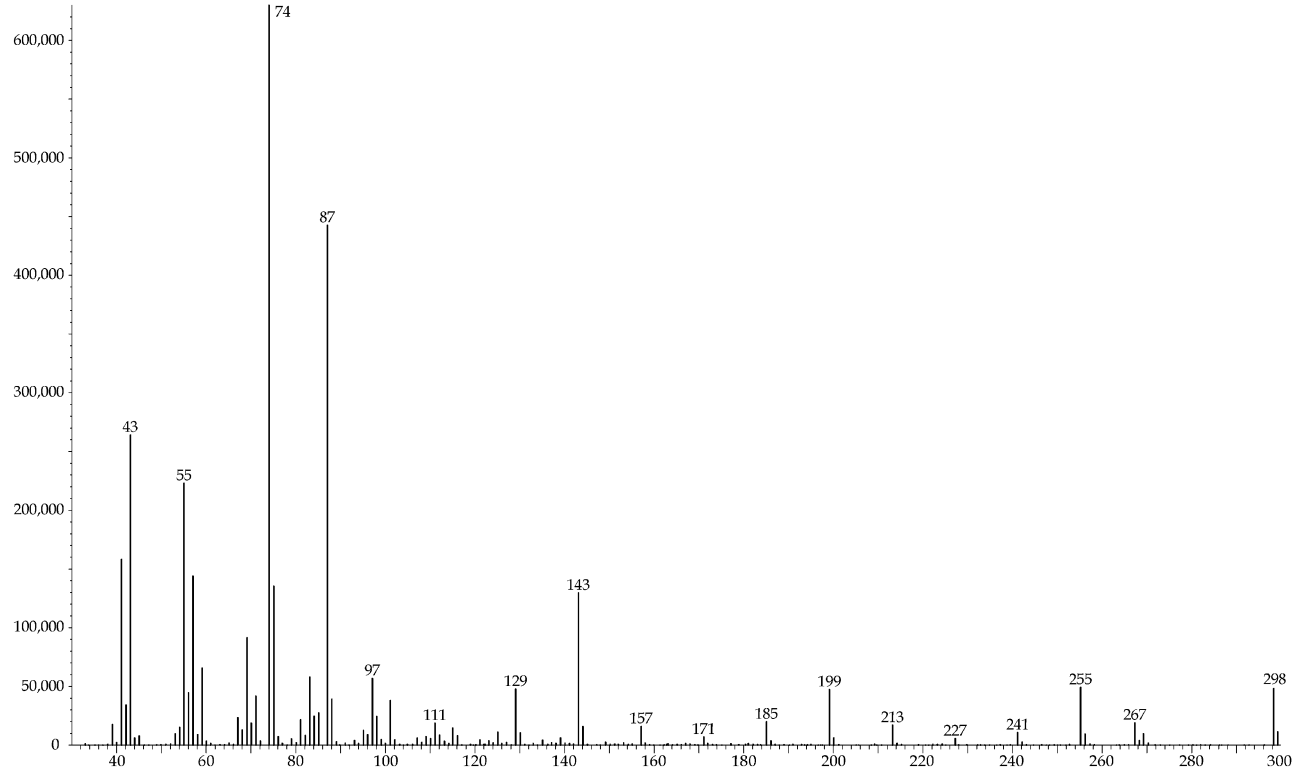

FIG. 3—*Mass spectrum of methyl octadecanoate (C18:0).*

extremely difficult. Additionally, it is very delicate to quantify each component based on molecular ion peaks, as the peak's intensity relative to the overall mass spectrum varies from one ester to another. However, this is not a detrimental issue as the exact quantification of the different FAMEs is not pertinent in this particular forensic application. The composition of a given oil can substantially vary depending on its origin and manufacturing process. Furthermore, as explained in "Interpretation of the Results," the different FAs of an oil degrade at different rates outside the control of the analyst. Thus, VOR analysis is not about iden-

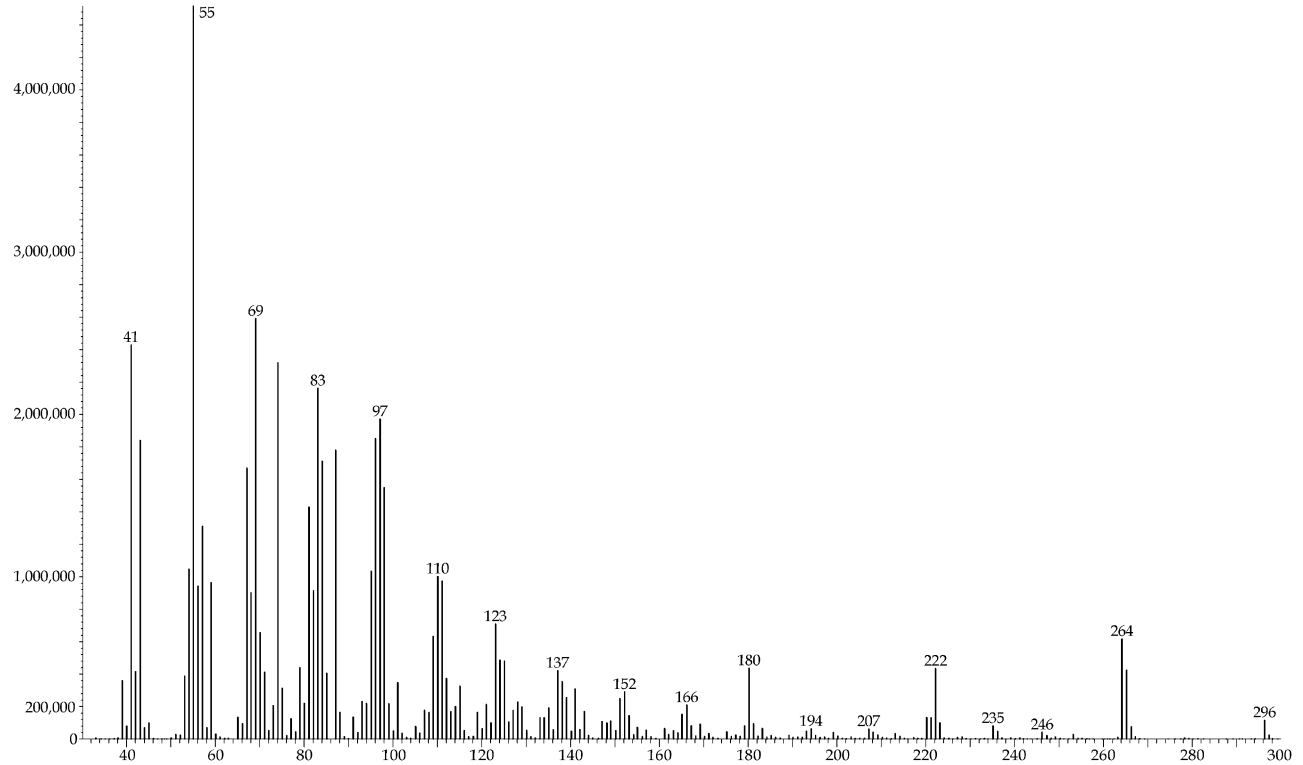

FIG. 4—*Mass spectrum of methyl octadecenoate (C18:1).*

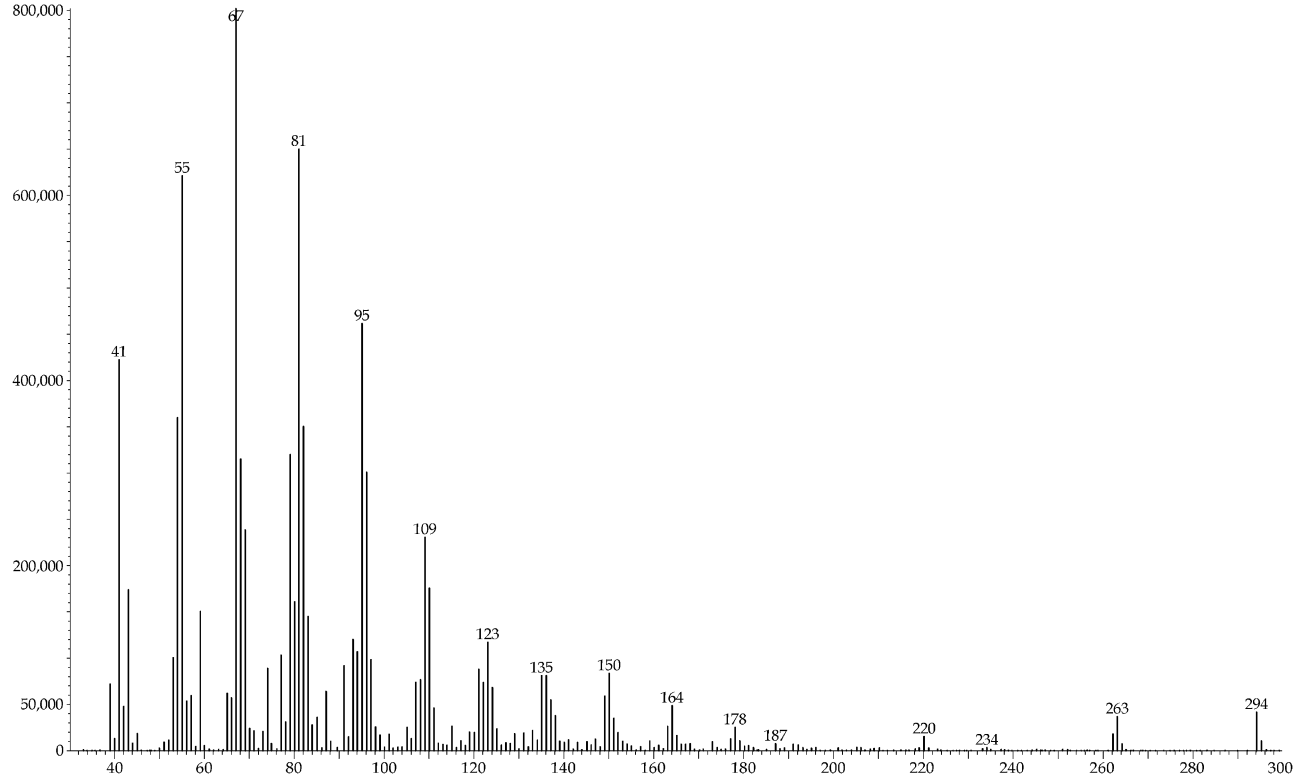

FIG. 5—*Mass spectrum of methyl octadecadienoate (C18:2).*

tifying the exact type of oil present, but rather about identifying the presence of substances that can or have undergone spontaneous ignition.

Although the separation between C18:1, C18:2, and C18:3 does not exhibit baseline resolution with a nonpolar column such as the HP-5, these different compounds can be easily identified through the mass spectral data (60,61). Figures 3–6 present the mass spectra obtained for C18:0, C18:1, C18:2, and C18:3, respectively. The molecular ion peak is different for each of the four spectra, as it starts at *m/z* 298 for the saturated methyl octade-

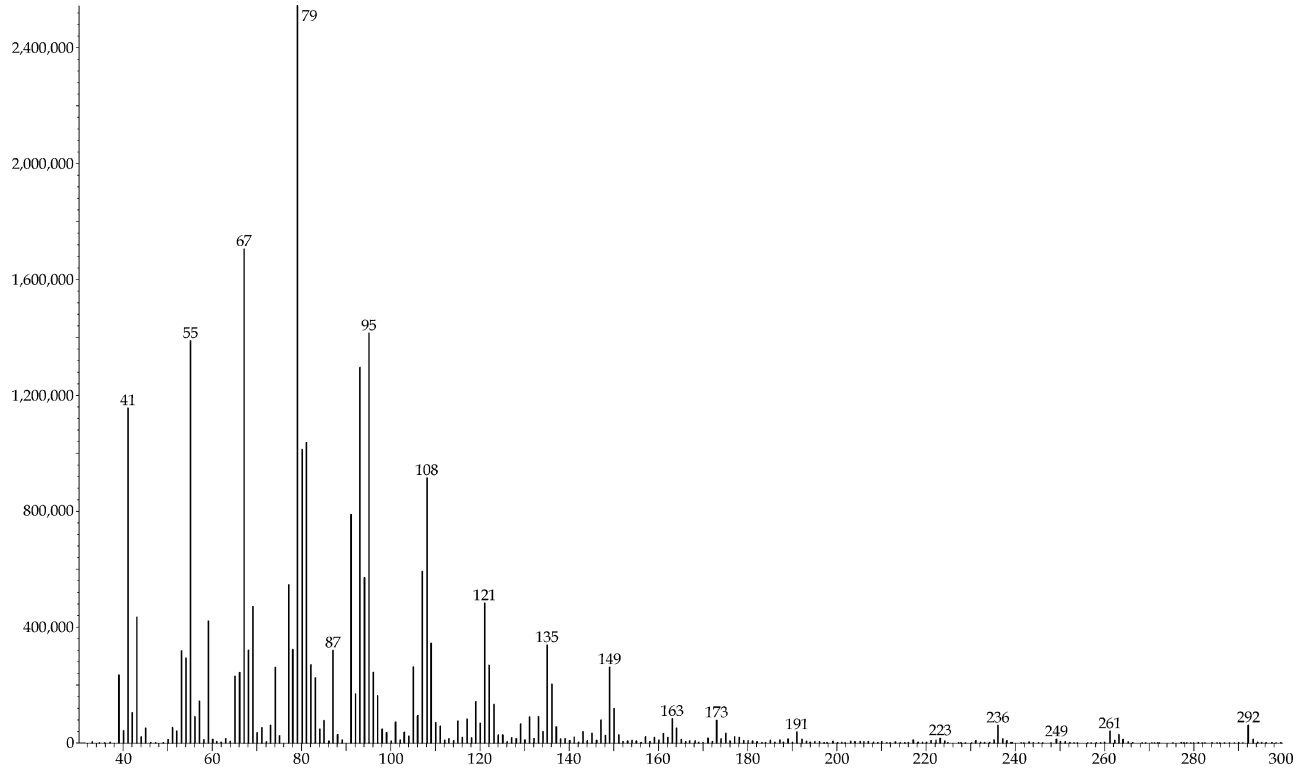

FIG. 6—*Mass spectrum of methyl octadecatrienoate (C18:3).*

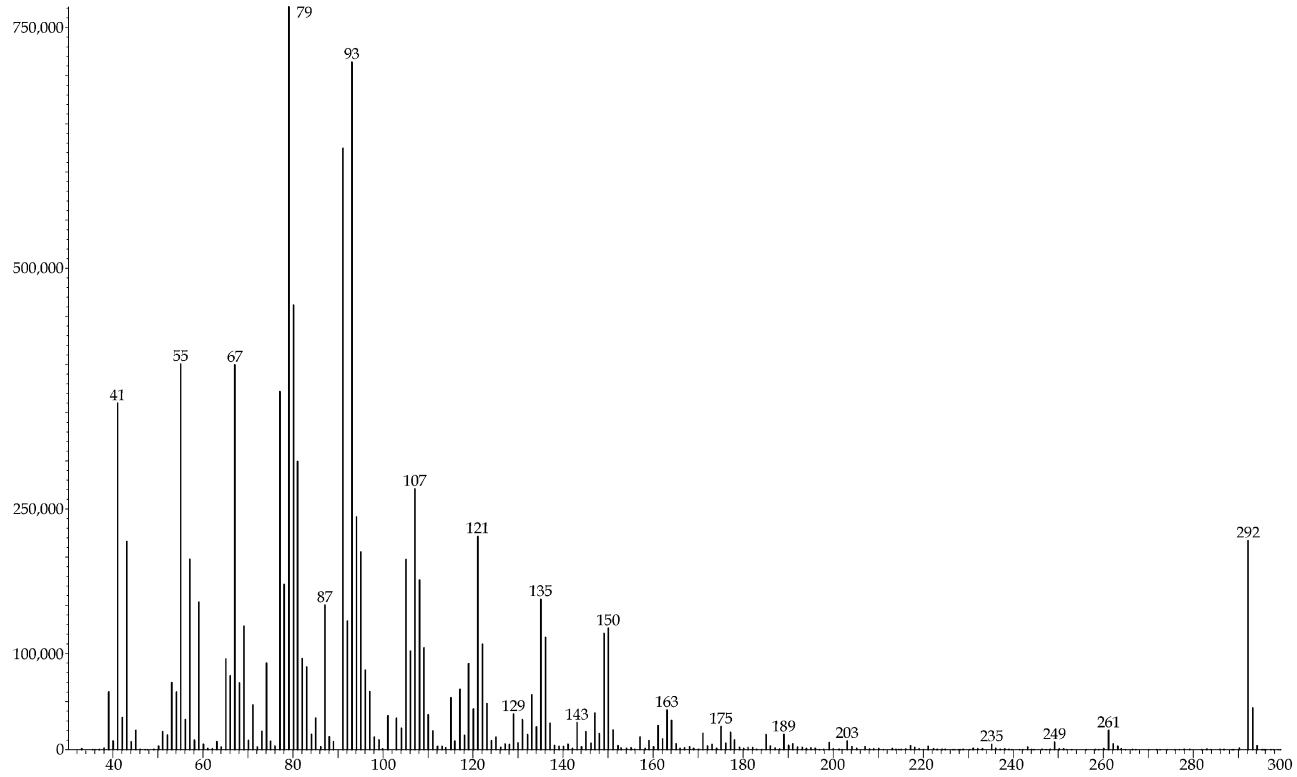

FIG. 7—*Mass spectrum of methyl α-eleostearate (C18:3).*

canoate, and decreases by two units for each additional double bond.

Figure 7 shows the mass spectrum obtained for an isomer of C18:3 (eleostearic acid) present in tung oil. The molecular ion peak is much more prominent in this spectrum. When comparing Figs. 6 and 7, it is possible to see that the first part of the mass spectrum, until about *m/z* 79, is similar, but the remainder presents significant differences in the produced ions.

Although the molecular ion peaks are not dominant in the mass spectra of FAMEs, they are sufficient to obtain useful extracted ion profiles (EIP). Figures 8*a* and *b* illustrate the use of EIP with the chromatograms presented in Figs. 2*a* and *b*.

In this fashion, the analyst can use the molecular weight information listed in Table 1 to create EIP for each FAME. Therefore, with the additional information provided by the mass spectrometer, the use of a GC-MS conditioned to perform regular ILR analysis is suitable to perform VOR analysis and obtain useful results. It is possible to easily differentiate C18:0, C18:1, C18:2, and C18:3 and estimate approximate ratios.

The followed figures should make the reader more familiar with the chromatographic patterns exhibited by VOR. They are also the first part of the approach to the interpretation of the chromatographic results. These chromatograms were obtained by derivatization into FAMEs using the KOH/methanol technique and were run with the system described in Table 3B.

Figure 9 is a chromatogram obtained from FAMEs of olive oil. The dominant peak is constituted of *cis*-methyl octadecenoate (C18:1). In this sample, the proportion of C18:2 is extremely low. C16:1 is in very low proportion compared with C16:0. A visual estimate would suggest the presence of C18:2 at less than 10%. No C18:3 was detected. This corresponds well to the ratios presented in Table 3 of the previous article (6). It is possible to distinguish a C18:1 isomer, probably the *trans*-C18:1 at the end of the main C18:1 peak between 13 and 14 min. Although olive oil typically exhibits a low tendency toward self-heating and spontaneous ignition, Coulombe and Gélin (38) reported a case where olive oil underwent spontaneous ignition in towels after washing and drying.

Figure 10 is a chromatogram obtained from Crisco® oil (Smucker, Orrville, OH), which is a blend of natural vegetable oils. This chromatogram shows a dominant pattern of C18:1, but with a more pronounced presence of C18:2 and C18:3. A rough estimate of the relative amounts of C18:2 and C18:3 is about 20% and 10%, respectively.

When observing the chromatogram in Fig. 2*b* (boiled linseed oil), the reader quickly sees the dominant pattern of C18:3. The presence of some isomers of C18:3 is shown between 19 and 20 min, at the left of C20:1. This chromatogram presents roughly 50% of C18:3, which corresponds to the value found in Table 3 of the previous article (6).

Figure 11*a* shows a chromatogram with an even more pronounced pattern of unsaturated FAs. It is a chromatogram obtained from FAMEs of tung oil. As in Fig. 2*b*, a dominant pattern of C18:3 is present, but with a stronger presence of isomers. It is possible to count at least four of them on this chromatogram. The peak at approximately 18 min is very likely eleostearic acid ([9,11,13]-*cis*, *trans*, *trans* octadecatrienoic acid) methyl ester. This acid is found in great proportion in tung oil. The conjugated double bonds cause its very high propensity to autooxidation, and therefore, self-heating.

When using the EIP on this chromatogram, it is possible to readily pinpoint the presence of the different isomers and to identify the different saturated and unsaturated FAs. This is shown as an example in Fig. 11*b*.

Interpretation of the Results

Only unsaturated FAs, and more particularly PUFAs, such as octadecatrienoic acid (C18:3), can undergo significant self-heat-

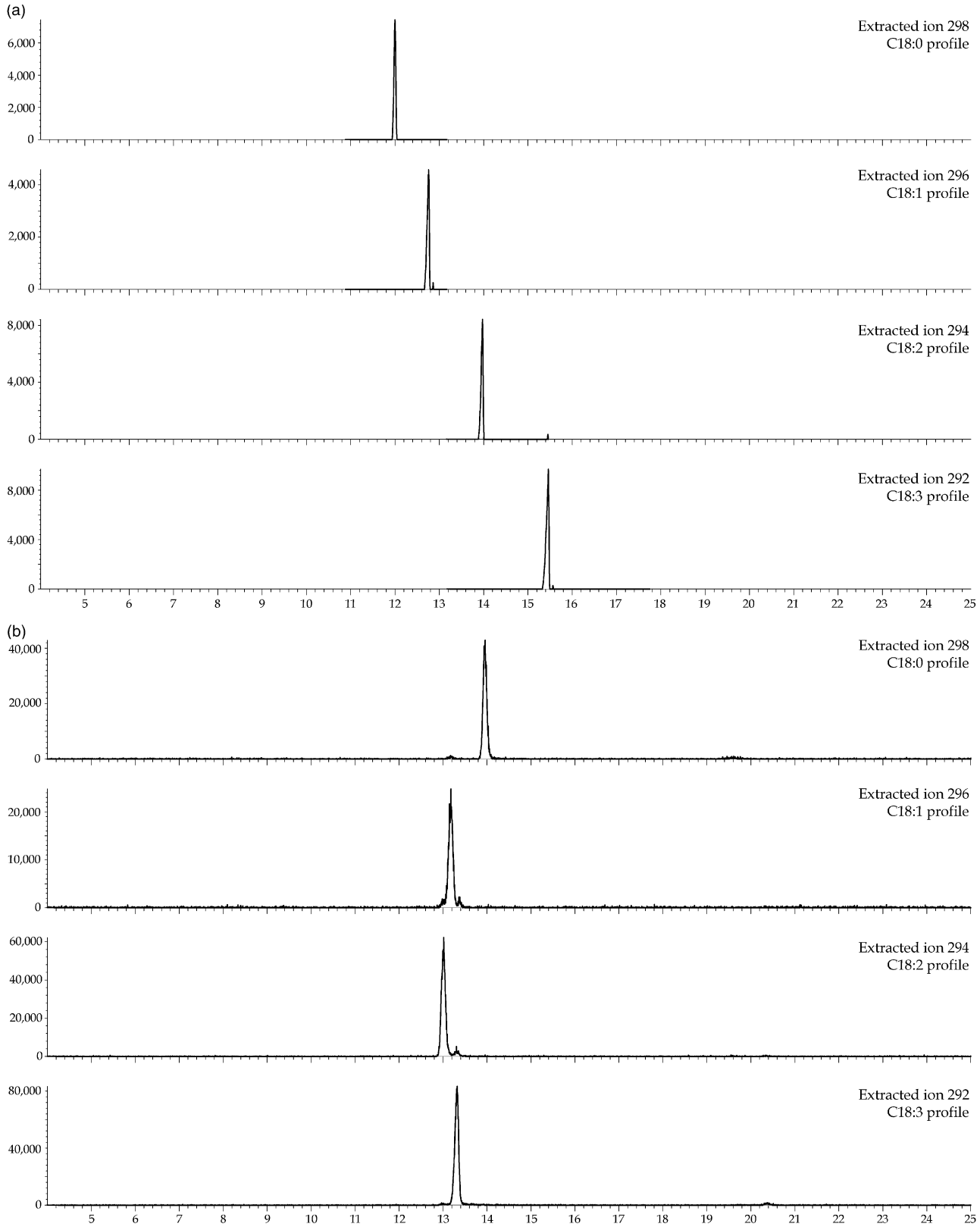

FIG. 8—*(a) Extracted ion profiles of the chromatogram presented in Fig. 2a (linseed oil using a Supelco® SP-2380 column). Data courtesy of Ray Keto (retired), Bureau of Alcohol, Tobacco, Firearms & Explosives, Ammendale, MD. (b) Extracted ion profiles of the chromatogram presented in Fig. 2b (linseed oil using an HP-5 column).*

ing (6). The presence of such compounds in sufficient concentration within the oil is necessary in order for it to be capable, under the right circumstances, of undergoing spontaneous ignition. Different oils present different propensities toward self-heating and spontaneous ignition. Tung oil shows a great propensity toward self-heating due to a large amount of C18:3 (and

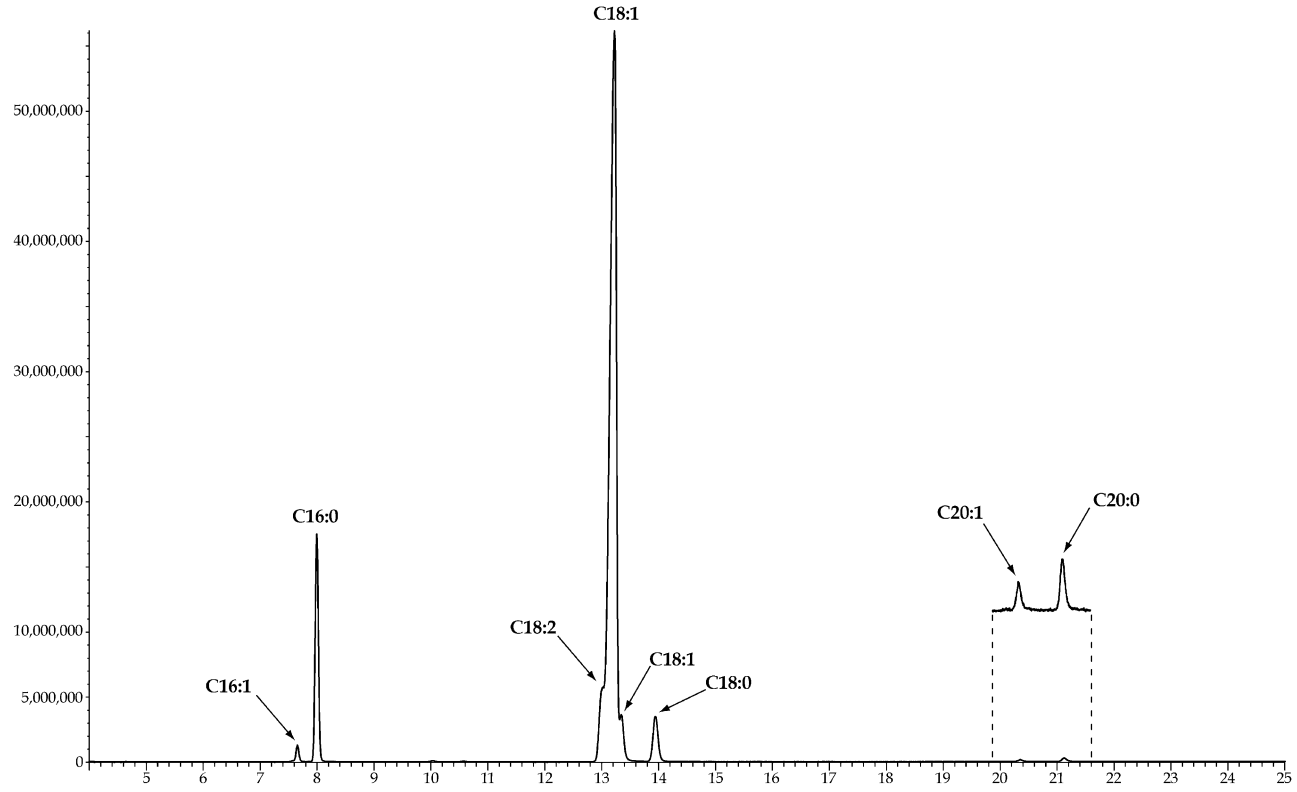

FIG. 9—*Chromatogram of fatty acid methyl esters obtained from olive oil (range from 4 to 25 min).*

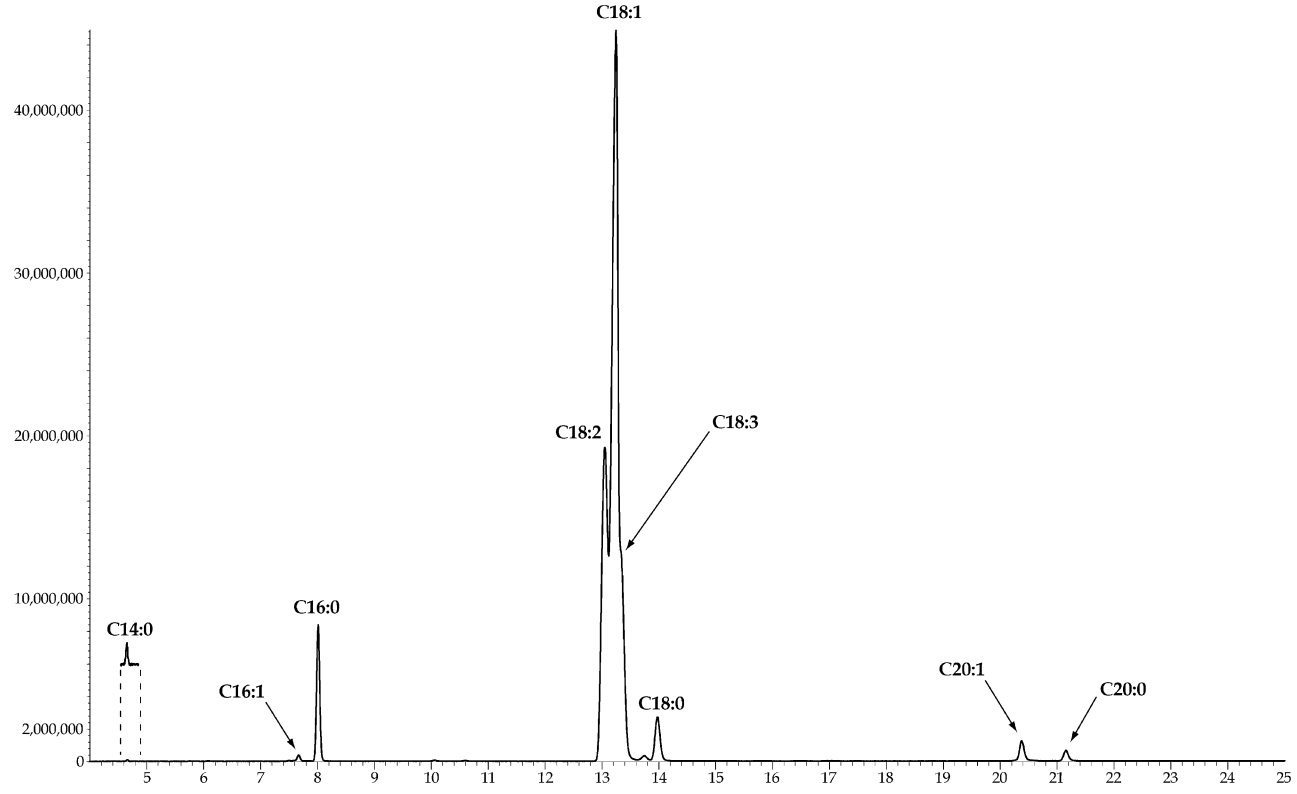

FIG. 10—*Chromatogram of fatty acid methyl esters obtained from Crisco oil (range from 4 to 25 min).*

particularly its isomer with conjugated double bonds), whereas coconut oil has almost no propensity toward self-heating due to a very low concentration of unsaturated FAs. Thus, the mere presence of VOR at the point of origin does not indicate by any means that a spontaneous ignition could have happened or even less, did happen.

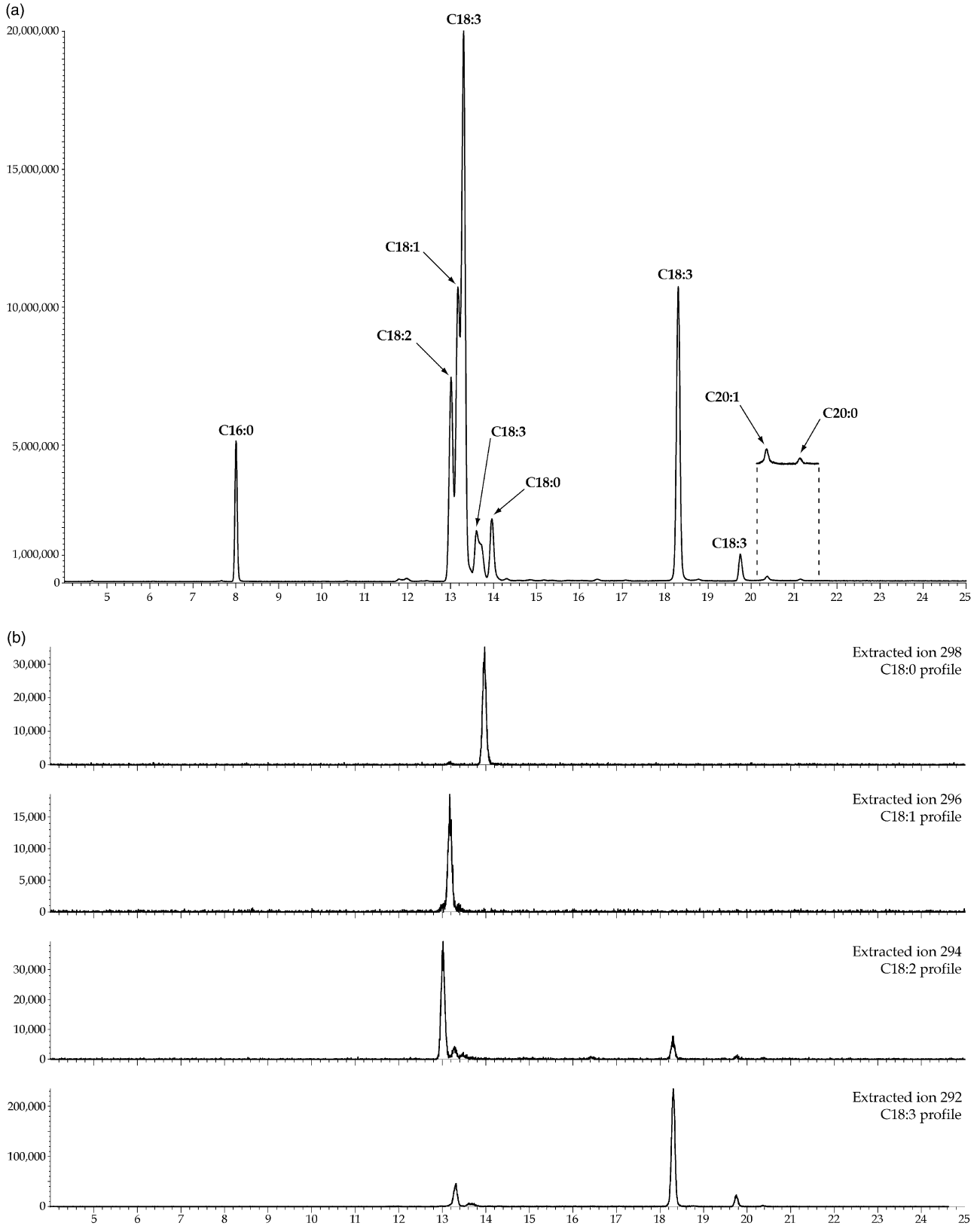

FIG. 11—*(a) Chromatogram of fatty acid methyl esters obtained from tung oil (range from 4 to 25 min). (b) Extracted ion profiles of the chromatogram presented in (a) (tung oil).*

Identification of vegetable oils by their ratios of FAs is routinely performed in food analysis. As shown in Table 3 of the previous article, different oils have different concentrations of FAs, and many configurations are possible (6). Pitts and Thomson (39) demonstrated that the main types of vegetable oil could be discriminated by analysis of pure samples by GC-MS. Thus, the identification of the type of oil (and consequently its propensity to self-heat in most instances) through the relative amounts of FAs is

easily feasible with pure samples. Unfortunately, it is not as straightforward in fire debris analysis. In such instances, the identification of the general type of oil present can be a much more challenging if not an impossible task. There are several reasons for this, as explained below.

The nature and amounts of FAs present in a fire debris sample depend on:

- the nature of the source oil;
- the regular degradation of the oil (mainly due to exposure to oxygen, light, and humidity);
- the thermal degradation of the oil, which could be either due to the self-heating process and/or to an external heat source.

The nature and amounts of FAs recovered from a fire debris sample depend on:

- the nature and amounts of FAs present in the fire debris;
- the nature of the sample on which the VOR are located;
- the extraction process used.

The nature and amounts of FAs analyzed and detected from an extract depend on:

- the nature and amounts of FAs present in the extract;
- the preparation procedure;
- the analytical technique.

The last two parameters are easily controlled by the analyst. Preparation techniques (derivatization) have been well explained and their efficiencies have been measured or can be estimated with the use of internal standards. Indeed, the analytical technique is usually well controlled and the operator is aware of its limits of detection, selectivity, and sensitivity. Therefore, they do not present many problems in the interpretation of the results.

The influence of the nature of the substrate and the extraction process have not been sufficiently evaluated and, therefore, are not well known by the criminalist. Experiments should be designed and executed to better understand their influence.

The nature of the source oil is obviously the unknown parameter of the equation and therefore cannot be controlled. The thermal degradation of vegetable oil under heat and under the self-heating process is also uncontrolled. Very few formal forensic studies have been performed in this regard and, therefore, serious information is either lacking in this sense or has not been compiled yet. Additionally, the regular degradation of an oil due to exposure to light, oxidizers, and humidity can also contribute to the skewing of its original components. Several questions can arise at this point, which can only be partially answered.

Does the Self-Heating Process Degrade the PUFAs at a Faster Rate Than the Monounsaturated or Saturated FAs?

Yes. Such a phenomenon definitely skews the ratios of the FA content and may lead to the misidentification of the type of oil (from a self-heating perspective). Residues from a linseed oil that underwent spontaneous ignition might present a much higher C18:0 to C18:3 ratio, which could get closer to the ratio normally exhibited by an olive oil for example. Such phenomena can be compared with an inverted weathering effect of ignitable liquids such as gasoline, which is well-known by fire debris analysts. Hess and O'Hare (62) demonstrated in their studies that the iodine value of linseed oil dramatically decreases with its autooxidation. They report a change of iodine value from above 180 to below 160 in 4 h at 100°C. This demonstrates the disappearance of double bonds present in the aliphatic chain of FAs. Keto's experiments also showed such a selective degradation of the different components of oils (R. Keto, personal communication, October 2003). Gunstone and Hilditch (63) also reported that C18:3 degrades at a much faster rate than C18:2, which in turn, degrades at a faster rate than C18:1.

Although the unsaturated and PUFAs degrade during the self-heating process, it is not the case for the saturated FAs. They will degrade once there is enough heat to pyrolyze and burn them, but their concentration is not significantly influenced by the self-heating process itself. Coulombe found experimentally that the ratio of C16:0 to C18:0 (from oils from fire debris samples) is often unchanged and corresponds very well to the original ratio of the pure oil (R. Coulombe, personal communication, November 2004). He determined that this ratio is crucial and very helpful in the determination of the type of oil present in the debris. This is definitely an interesting point, which should be explored in greater detail.

Do the Triglycerides Break Down into FFAs at Some Point During the Degradation of Vegetable Oil?

Yes. It is a known phenomenon that has been observed in frying oils (64). This breakdown is known as hydrolysis and occurs at a faster rate when the oil is heated. It would be pertinent to estimate the hydrolysis rate for an oil that is undergoing spontaneous ignition and combustion in order to determine if the amount of FFAs created is important. If so, then the recovery of FFAs might be of importance and their separate analysis might become pertinent. There are many questions of this type that need to be answered before an appropriate interpretation of the results can be performed.

Are There Any Changes in the Chemical Composition of an Oil That Are Specific to the Phenomenon of Spontaneous Ignition?

The answer to this question appears to be yes. Unfortunately, there is only one experiment reported in the literature demonstrating that. Coulombe and Gélin (38) performed some impressive preliminary work studying changes in the composition of canola oil when subjected to piloted ignition in cotton cloth, heated at 320°C for 5 h, heated to autoignition, and left self-heating to spontaneous ignition. Their results are reported in Table 4.

They first realized that some components and ratios do not change when the oil is ignited and allowed to burn. Also, they observed that some changes are specific to the spontaneous ignition process, such as the appearance of methyl tetradecanoate in the chromatograms. These results are promising, but more research needs to be performed with different oils before these trends can be ascertained. For example, methyl tetradecanoate is detected in small amounts in many oils that did not undergo spontaneous ignition, as illustrated in Figs. 2*b* and 10. In addition to these changes, they also observed the presence of 1-phenyl *n*-alkanes when performing a passive headspace concentration extraction on activated charcoal before solvent extraction. These compounds were found in every sample where spontaneous ignition occurred and were not found in any oil samples that did not undergo spontaneous ignition. These compounds have not been reported in other literature as a demonstration of the phenomenon of spontaneous ignition. This is another potential "marker" that definitely requires further investigation.

There is also much research published in the food chemistry industry dealing with the degradation of vegetable oils. For ex-

TABLE 4—*Changes observed by Coulombe and Gélin (38) in the chemical composition of canola oil subjected to different heating and burning processes. Courtesy of Dr. Ronald Coulombe, Laboratoire de sciences judiciaires et de médecine légale, Montréal, Québec.*

Artifact	Piloted Ignition in Cotton Cloth	Heated at 320°C for 5 h	Autoignition	Spontaneous Ignition
Destruction of methyl octadecadienoate	No	Very important	Very important	Very important
Cis to *trans* isomerization of methyl octadecenoate	No	Very important	Very important	Significant
Appearance of dimethyl decanedioate	No	Significant	Significant	Significant
Appearance of dimethyl nonanedioate	No	Significant	No	Very important
Appearance of C6–C10 monomethyl esters	No	Significant for C8	Significant for C10	Significant for C8
Appearance of methyl tetradecanoate	No	No	No	Significant

ample, Gardner et al. (65) studied the different compound classes found in unused fyring oils. Kamal-Eldin et al. (66) characterized the aldehydic acids in used and unused frying oils. Sanches-Silva et al. (67) studied the effect of light on FAs in potato chips. Schwab et al. (68) described different thermal degradation mechanisms for soybean oil. Lazzari and Chiantore (69) reported the different oxidative degradation mechanisms for linseed oil. Thus, there is a wealth of information available in the literature either bringing direct answers or leading research in the right direction. Unfortunately, no author has taken the time to compile this information and to determine its value in regard to the issue of VOR analysis.

Answering the Forensic Approach

The forensic approach of the previous part of this paper was asking for the answers to three questions (6):

1. Was there any vegetable oil present at the point of origin before and during the fire? This question is now easily answered with the detection of the presence of TAGs and FAs by extraction, derivatization, and GC or GC-MS analysis.
2. If yes, was that vegetable oil prone to self-heating and spontaneous ignition? The interpretation of the results of VOR analysis is limited to the information available to this date. It is based on the nature and relative amounts of FAs recovered from the sample. One should compare the questioned pattern to patterns of known standards of vegetable oils such as the ones presented in Figs. 2 and 8–11. The conclusion should be limited to one of the four following possibilities:

No FAs Were Detected—The analyst should conclude that no vegetable (or animal) oils, and therefore, no substances known to undergo spontaneous ignition were found. However, this result does not imply that no such substance was present before the fire.

FAs Were Detected, PUFAs Almost Absent (No C18:3 Present)—The analyst should conclude that FAs were detected, which nature and relative amounts are similar to the ones found in a substance typically exhibiting a very slight to low tendency toward self-heating. However, this result does not eliminate the possibility that a substance with higher tendency toward self-heating was present before the fire.

FAs Were Detected, PUFAs Present (More than 20% C18:2, But Less Than 10% C18:3)—The analyst should conclude that FAs were detected, which nature and relative amounts are similar to the ones found in a substance typically exhibiting a moderate tendency toward self-heating, and under the right circumstances, spontaneous ignition. However, this result does not eliminate the possibility that a substance with higher tendency toward self-heating was present before the fire.

FAs Were Detected, with Large Amount of PUFAs (Typically More Than 50% C18:3)—The analyst should conclude that compounds with a high tendency to undergo self-heating and, under the right circumstances spontaneous ignition, were found in the sample. However, this result does not necessarily imply that spontaneous ignition occurred.

3. If yes, did that vegetable oil undergo spontaneous ignition and cause the fire? The only possible answer to this question, from a chemical point of view, would be the detection of compounds specifically produced by the spontaneous ignition process. Coulombe and Gélin (38) have done preliminary work in this regard, however more research needs to be performed before it can be fully validated and used in routine analysis.

It is important to keep in mind that this type of analysis does not pretend to answer the origin and cause determination of a fire scene. It is only one more piece of information that can play an important role in an investigation. Also, while many do not often think to recover such residues from fire debris, practice has shown that it is feasible, as demonstrated by Keto (R. Keto, personal communication, October 2003), Coulombe, and Duchesne (19,55).

Storage

There is no literature dealing with the storage of fire debris samples that may contain VOR. However, the best advice would be to store the debris in a freezer before extraction. Extraction should be performed as soon as possible, as the residues will oxidize over time. The oxidation of the residues occurs at a greater rate at room temperature (or higher), and with exposure to air and/or light. Improper storage procedures could also increase the FFA concentration in the sample (70).

Once the extraction process has been performed, the extracts should not be stored in a "dry" (solventless) state. This would favor the oxidation of the FAs and therefore alter the sample. The samples should be stored in a solvent, away from light and air. They may also be stored in a freezer, and if a long period of storage is required, the freezer should be set at -20°C (11). In addition, the headspace of the container can be purged with nitrogen. Also, a small amount of butylated hydroxytoluene (BHT), an antioxidant, can be added to the sample to prevent any further oxidation. Usually, the BHT is added as a solution of 10 mg/mL in methanol. BHT should not be used if the sample will be derivatized using the BF_3/methanol technique, as it will produce extraneous peaks in the chromatogram. The best course is to extract, derivatize, and analyze the samples as soon as possible, or to

freeze the sample and conduct the entire process in one session at a later date.

Derivatized extracts are much more stable and are not expected to degrade. However, it is always better to be on the safe side, so it is recommended that storage of the derivatized mixtures be away from light and air.

Sequence of Analysis with Other Forensic Examinations

There is almost no literature addressing the integration of VOR analysis in a sequence of other possible forensic examinations. Although the examination of fire debris samples is often limited to ignitable liquid residues analysis, other examinations might be needed in some instances. As the order of examination between regular ILR analysis and VOR analysis, Jackowski (21) recommends to first perform the regular ILR recovery before VOR analysis. This choice appears to be logical with the use of passive or dynamic headspace analysis in conformance with ASTM Standard Practices E1388, E1412, and E1413 (1,4,5). Also, if one wants to look at the volatile fraction in order to detect the presence of the 1-phenyl *n*-alkanes, as reported by Coulombe and Gélin (38), this extraction should be performed first. The drawback lies in the fact that the prolonged heating of the sample may degrade the oil further. However, according to Coulombe, the exposure of VOR to temperature of 90°C for several hours does not affect their composition (R. Coulombe, personal communication, November 2004). If a solvent extraction is performed, it is strongly suggested to use a solvent that is compatible with both ILR and VOR recovery, such as pentane or petroleum ether. The extract is then split in two parts, one for regular ILR and one for VOR analysis.

When other examinations, such as fingerprint, fiber analysis, or elemental analysis are required, the forensic scientist should use common sense and determine a logical sequence based on the destructiveness, compatibility, and pertinence of the examinations.

Future Needs

This review of the available literature directly or indirectly linked to the analysis of VOR from fire debris samples allows for a better understanding of the need for future research in this field. There is a lack of information in regard to many parameters and phenomenon.

Thermal Degradation Products and Content Skewing

The first parameter to study is the thermal degradation of vegetable oils. First of all, skewing of a vegetable oil's composition occurs during the self-heating process, which complicates the interpretation of the results. Experiments should be conducted in which the chemical composition of different vegetable oils is determined at different stages of varying thermal degradations. This should allow for the evaluation of and better understanding of the selective degradation of some components such as PUFAs versus monounsaturated FAs and saturated FAs. Unsaturated and polyunsaturated FAs degrade at different rates during the spontaneous ignition process. The greater the unsaturation, the faster the degradation. As previously stated, it does not appear that the saturated FAs degrade until exposed to sufficient heat or combustion (R. Coulombe, personal communication, November 2004). However, these experiments should not be confined to the monitoring of FAs only, but should include TAG. Also, the same composition monitoring should be performed with the exposure of vegetable oils to external fire or heat source. This should allow the researcher to determine the presence of components or changes specific to a particular type of (thermal) degradation. Second, thermal degradation products should be identified. These products are the results of the pyrolysis and combustion processes. The literature describes different oxidation processes that lead to hydroperoxides, cyclic oxides, aldehydes, and ketones. Some of these compounds might also be specific to a certain type of oil or FA content and might be present in the debris analyzed. If such hypotheses are correct, then researchers should try to isolate, analyze, and record such products. Eventually, this should allow the criminalist to determine if products uniquely specific to the self-heating process that lead to spontaneous ignition exist. If so, the determination of the presence of such products would demonstrate the spontaneous ignition process of the vegetable oil. Research needs to be conducted to identify if this possibility is viable and, if so, analysis can be performed in this direction. Preliminary research demonstrated that it is possible to discriminate between the results of a thermal degradation due to self-heating from a thermal degradation due to exposure to an external source of heat (38). Future research should follow the preliminary work performed by Coulombe and Gélin.

Derivatization Techniques

After a careful study of the influence of the thermal degradation on the FA composition of vegetable oils, a need to concentrate on or eliminate some derivatization techniques might arise. At that point, these techniques should be reviewed, tested, and the optimum ones chosen.

Extraction Techniques

Extraction techniques need to be evaluated and optimized for fire debris samples. Scientific literature contains hundreds of articles dealing with the extraction of lipids from animal and vegetal tissues. Although research has been performed to optimize the extraction from a particular tissue (such as from liver or algae), there is a serious lack of research with regard to the extraction of VOR from fire debris samples. Although fire debris samples can be of very different compositions from one another, they usually have one thing in common: they are charred substrates. This might change the efficiency of some solvents. Experiments should be conducted in which known amounts of vegetable oils are recovered from different substrates with different solvents. The extract is then quantified and the recovery efficiency is determined for a particular oil, substrate, and solvent. Also, this research can only be conducted once research has demonstrated which chemical compounds produced by the oil are the most pertinent to VOR analysis. Until such a research is made available, the analyst has to rely on generic solvents as presented earlier in the text, without really knowing which one would provide the most suitable results.

Storage

Storage conditions for fire debris samples, extracts, and derivatized products should be studied from short to long term. Factors leading to the regular degradation of vegetable oils and more particularly PUFAs have been reported in the literature for many years. Proper storage conditions need to be determined and standardized for fire debris samples and their subsequent extracts.

Integration in the Sequence of Analysis

Finally, a study needs to be conducted to determine how to integrate this kind of analysis in the examination sequence of fire debris, when multiple traces are being sought. It is important to make sure that all variables are taken into account and that deterioration of the sample due to other examinations is evaluated.

Conclusion

Analysis of vegetable (and animal) oil residues from fire debris samples when spontaneous ignition is suspected is possible. The most suitable analytical process consists of the extraction of the residues, their preparation (derivatization into FAMEs) for analysis, their analysis by gas chromatography or gas chromatography-mass spectrometry, and the interpretation of the results. This process allows for the discrimination of saturated FAs from unsaturated and polyunsaturated FAs, which are responsible for the self-heating of the substance. Interpretation of the results is based on the nature and amounts of the FAs present in the sample. Promising preliminary work has demonstrated that self-heating specific products are created within VOR and can be detected. More research is needed in order to optimize the analytical procedure and the interpretation of the results.

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