

CASE REPORT

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Chemical Analysis of Vegetable Oils Following Spontaneous Ignition

REFERENCE: Coulombe R. Chemical analysis of vegetable oils following spontaneous ignition. *J Forensic Sci* 2002;47(1):195–201.

ABSTRACT: Two cases of spontaneous ignition of vegetable oil in fabrics after being washed and dried are reported. In both cases, the analysis revealed the consumption of unsaturated fatty material and the recovery of higher proportions of saturated fatty material along with saturated fatty diacids. The investigators reported that in the first case the origin of the fire was in a plastic container filled with cotton towels and in the second case, a garbage bag. In both cases, the fabrics had been washed and were freshly dried. In the second case, the recovery of the nonpolar volatile fraction disclosed the presence of 1-phenylalkanes along with oxygenated species.

KEYWORDS: forensic science, fire origin and causes, vegetable oils, spontaneous ignition, fatty acid methyl ester, clothes washing and drying, diacids, dimethyl azelate, 1-phenylalkanes

Spontaneous ignition by vegetable oils is a well known and documented phenomenon in the field of fire cause determination. Recently Dixon published an article that included a case study on this topic (1). Another published study reported that ignition of linseed oil on cotton cloth revealed that there was no nonreacted linseed oil in the burnt cloth after ignition (2). This paper reports the findings of chemical analyses of partially burnt residues of clothes and towels suspected of containing frying oils after having been washed and dried.

Frying oils are composed of triglycerides of fatty acids. These acids are mainly unsaturated C18, such as oleic and linoleic acids. There are also some saturated acids, mainly C16 (palmitic) and C18 (stearic), that occur in lower proportions than the unsaturated acids. If the reactions of oxygenation or polymerization occur, as a result, the proportion of unsaturated glycerides should be significantly lower than in the original oil. Therefore, the ratio of saturated to unsaturated glycerides increases the more the oils react. The results of this reaction should be chemically observable by analyzing the fatty acid distribution in the burnt substrate, if there is any left. However, the reaction products, according to their nature, might not be readily detected and identified. For example, the polymerized residues could be difficult to isolate and dissolve. More volatile products might evaporate and burn. There may, however, be certain chemical compounds not previously present.

The mechanism by which vegetable oils can lead to spontaneous

ignition is directly related to their unsaturated fatty components (3). Heating slowly decomposes the frying oils to volatile species (4). However, heating also promotes polymerization of the oil. In some instances, polymerization and reaction with atmospheric oxygen can lead to fires through spontaneous ignition, usually when absorbed in clothes or towels. This process, as expected, requires some form of initial heat. It is a complex chemical process involving the formation of peroxides at the carbon chain unsaturation. The oxygenation of the oil, therefore, begins in the drier and continues in the insulated stacked laundry. The quantity of material involved may not be elevated. It is a sneaky cause of fire because one would expect the laundry to be well cleaned and not to be dangerous. But improper cleaning is the starting point. The time frame may also vary according to different factors.

This paper describes how to test for these telltale compounds whose presence demonstrates the preexistence of conditions proper to spontaneous ignition. One way is to test for a glyceride fraction that can be extracted and analyzed through saponification and derivatization to Fatty Acid Methyl Esters. Second, there is a less polar fraction that is volatile and that can be analyzed in the same manner as petroleum residues.

Case 1

Fire Investigation

In the present case, evidence was collected by a police officer investigating a fire in a golf club house. Laundry had been washed, dried, and put randomly in a large plastic container. Investigation of the fire scene by this officer led to the conclusion that the origin of the fire was in the plastic container close to a table near the industrial gas drier. The drying temperature was not known. The investigation revealed these facts:

- Two washes had been done with only dirty towels, mainly from the kitchen.
- The laundry was dried for an hour and put in a plastic container while still hot.
- The drier stopped at 1400 h and the towels were dropped in the container at 1430 h.
- A fire-like odor was noticed at 1600 h by the same clerk who had done the laundry. He cleaned the dust under the drier, thinking it was the source of the odor.
- At 1800 h, the manager inspected the area and nothing unusual was noted.
- The clerk says he is a nonsmoker and so is the manager.

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Received 22 Sept. 2000; and in revised form 22 Jan. 2001, 30 May 2001; accepted 1 June 2001.

- The container was very full, containing a minimum of 50 towels.

The fire department was called at 2230 h.

Evidence Submitted

The police officer gathered a few burnt towels still present near the origin of the fire. He also took a sample of the vegetable oil used in the kitchen. He did not identify the precise nature of the oil but it was thought to be commercial frying oil. The object of the request was to confirm the presence of vegetable oil in the towels that had supposedly been washed and dried. He noticed no odor of accelerant and his investigation did not lead him to request that type of analysis. When the towels were first examined at the lab, the odor of vegetable oil was still noticeable.

Experimental

In the first step, pieces of burnt towels were extracted with ethyl ether to collect what was left of the vegetable oil. The ether was filtered and evaporated. In the second step, the residue was submitted to saponification with a 5% solution of potassium hydroxide in methanol with gentle warming. The solution was then extracted with ethyl ether as a clean-up to discard extraneous and nonreacted material. The saponified residue was then acidified with hydrochloric acid and reextracted with fresh ethyl ether. In the third step, the ether fraction was evaporated and treated with BF_3 in MeOH to achieve esterification to FAME (Fatty Acid Methyl Esters) (5). The FAME were extracted with isooctane for gas chromatography along with mass spectrometry. The vegetable oil was saponified and derivatized in the same manner.

Instrumental Analysis

Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph with a split/splitless injection port operating with a 100:1 ratio and a flame ionization detector (FID).

Injection port and detector were at 310°C.

The capillary column was a 30 m by 0.25 mm fused silica DB-5 (5% phenyl methyl silicone) (J & W Scientific, Folsom, California). The oven was initially held at 100°C for 4 min, then heated to 260°C at 5°C/min. The carrier gas was nitrogen at 18 psi.

The GC/MS system was a Varian Saturn II with a Varian 3400 gas chromatograph (Varian Corp., Palo Alto, California). Mass acquisition was every two seconds. The injection port was set at 280°C. The system uses the same type of capillary column as in the GC. The carrier gas was helium at 5 psi.

To determine the presence of petroleum residues, which was done only in Case 2, the oven was initially held at 50°C for 2 min and then heated to 225°C at 8.7°C/min.

Results and Discussion

In comparing the FAME of the reference vegetable oil and of the towel residue, it is important to look for similarities and differences. Similarities show the presence of oil in the towel, although it has been washed, and possibly common features and origin with the reference oil. Differences may indicate an event such as spontaneous ignition.

Figure 1 shows the FAME of the reference unidentified vegetable frying oil. It has two features of compounds commonly found in vegetable oils. First, the proportion of methyl palmitate (hexadecanoate or C16) at RT 24.90 min is greater than the proportion of methyl stearate (octadecanoate or C18) at RT 28.92 min.

Secondly, the predominant peaks found at RT 28.46 and 28.59 min, although not positively identified here, are shown to be unsaturated C18 methyl esters by their mass spectra. These proportions can vary substantially for different types of oils such as sunflower oil and palm oil (6). Figure 1 features also a peak at RT 16.24 min identified as dimethyl azelate (nonanedioate or C9 diester). This is peculiar because it shows that the oil could have had some rancidity prior to laundering. Pure vegetable oils do not contain diacids or their glycerides but rather aldehydic acids (6).

Since the sample is a real case, these towels could contain other sources of fatty material, which could explain some of the differences between Figs. 1 and 2. Figure 2 shows the FAME of the towel residue which was isolated in minute quantity. First of all, the identification of methyl palmitate and methyl stearate at RT 24.88 and 28.90 min, respectively, shows the presence of vegetable oil. Also, methyl arachidate (eicosanoate or C20) and methyl behenate (docosanoate or C22), although in trace amounts, have been detected by mass spectrometry in both samples, showing there is some common origin possible between the two samples. Secondly, the most striking feature of Fig. 2 is the near elimination of the C18 unsaturated esters. One of these peaks is at RT 28.54 min and the other is not even recorded due to its low intensity. Such an important change may have been the result of an event such as spontaneous ignition.

Case 2

Fire Investigation

This fire occurred in an apartment building. The occupant worked in a restaurant and was exposed to frying oils. The fire occurred after the washing and drying of her clothes, aprons, and towels. The origin of the fire was reported to be a plastic bag. When received, the clothes had the characteristic odor of vegetable oil. The chronology of the event was not reported.

Evidence Submitted

The investigator gathered a partially burnt apron and cloth and a partially burnt plastic bag.

Experimental

Two different analyses were performed on these clothes because the circumstances surrounding this fire were not as clear as in Case 1. The presence of accelerant had to be verified. Therefore, a different protocol consisting of two different and consecutive analyses was set. The initial analysis was for the presence of petroleum residues. This analysis requires heating the sample to 90°C with a DFLEX® (Albrayco Laboratories, Cromwell, CT) carbon strip which is desorbed with CS_2 . The second analysis was the FAME and performed subsequently on the same sample. This analysis, as described in Case 1, includes the following steps: extraction of the clothes with ether, filtration, and evaporation of the ether, saponification of the residue with KOH in MeOH, extraction with ether as a clean-up and discarding the ether, acidification with HCl and reextraction with fresh ether, evaporation, and finally derivatization with BF_3 in MeOH and extraction of the FAME with isooctane. The reference oil was not available.

The reader will note some minor differences in the retention times between chromatograms of the same compounds in Case 1 versus Case 2. The main difference is in the initial gap for the occurrence of the solvent peak. The reasons for this are that although the same type of columns have been used, they have been changed periodically because of deterioration and slight pressure changes. Another reason for the slight variations may be that all injections are done manually.

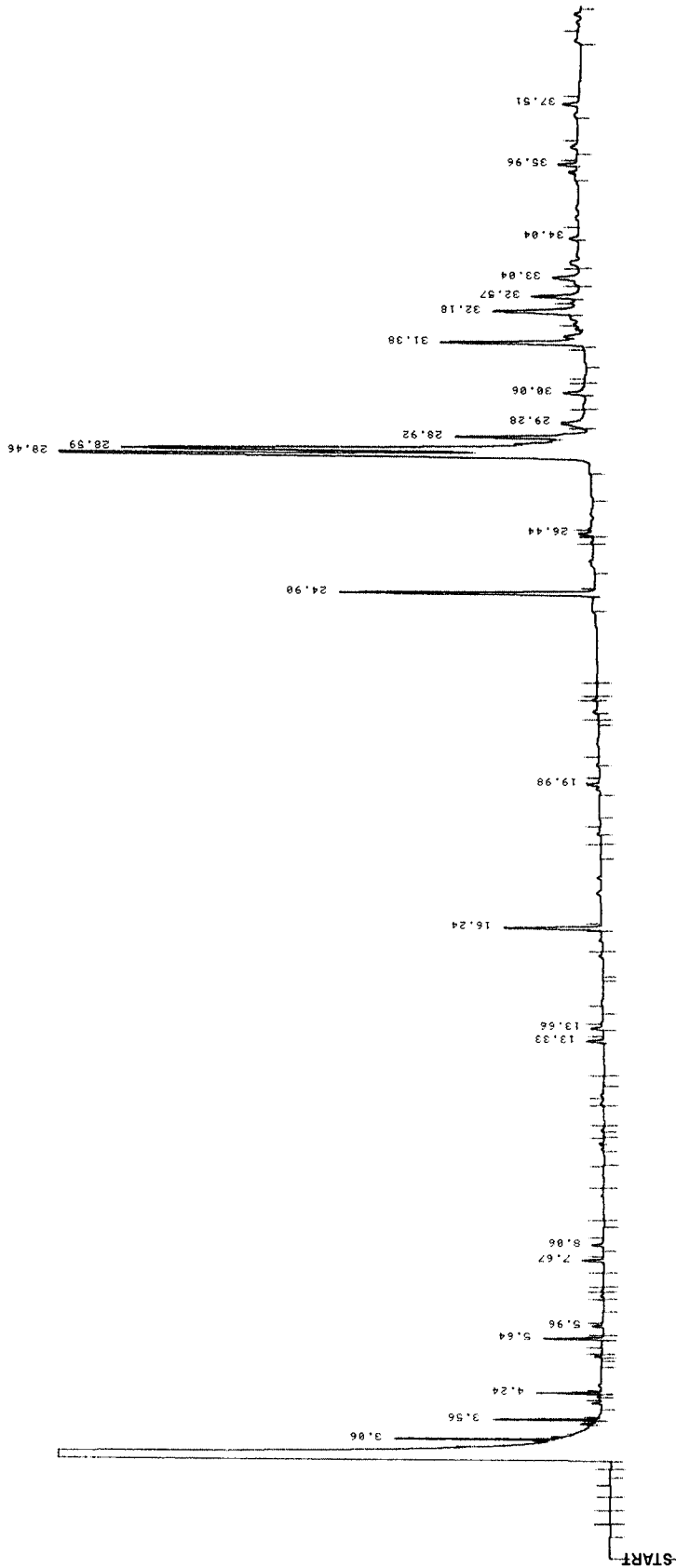


FIG. 1—FAME of vegetable oil, Case 1.

Peak Identification	Retention Time, min.
Dimethyl suberate (octanedioate or C8)	13.66
Dimethyl azelate (nonanedioate or C9)	16.24
Methyl palmitate (saturated C16)	24.90
Unsaturated C18 methyl esters	28.46 and 28.59
Methyl stearate (saturated C18)	28.92
Methyl arachidate (saturated C20)	32.57
Methyl behenate (saturated C22)	35.96

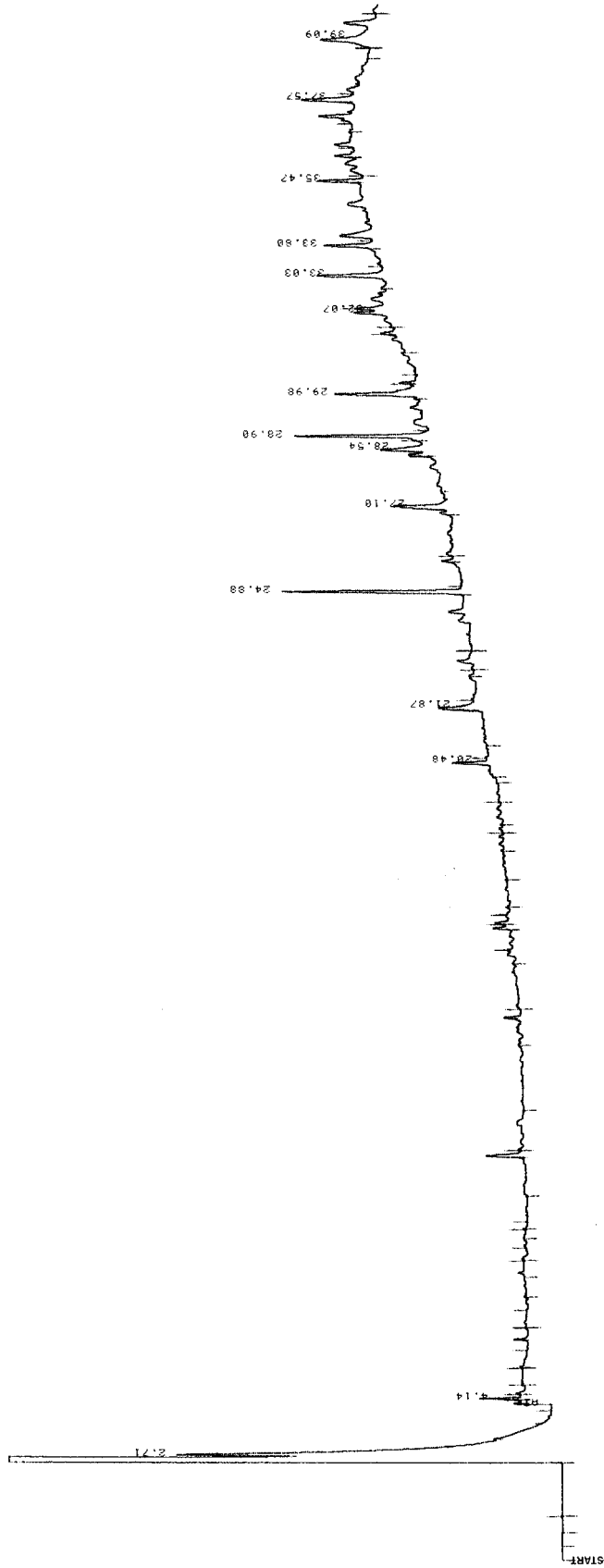


FIG. 2—FAME of towel residue, Case 1.

Peak Identification	Retention Time, min.
Methyl palmitate (C16)	24.88
Unsaturated C18 methyl esters	28.54
Methyl stearate (C18)	28.90

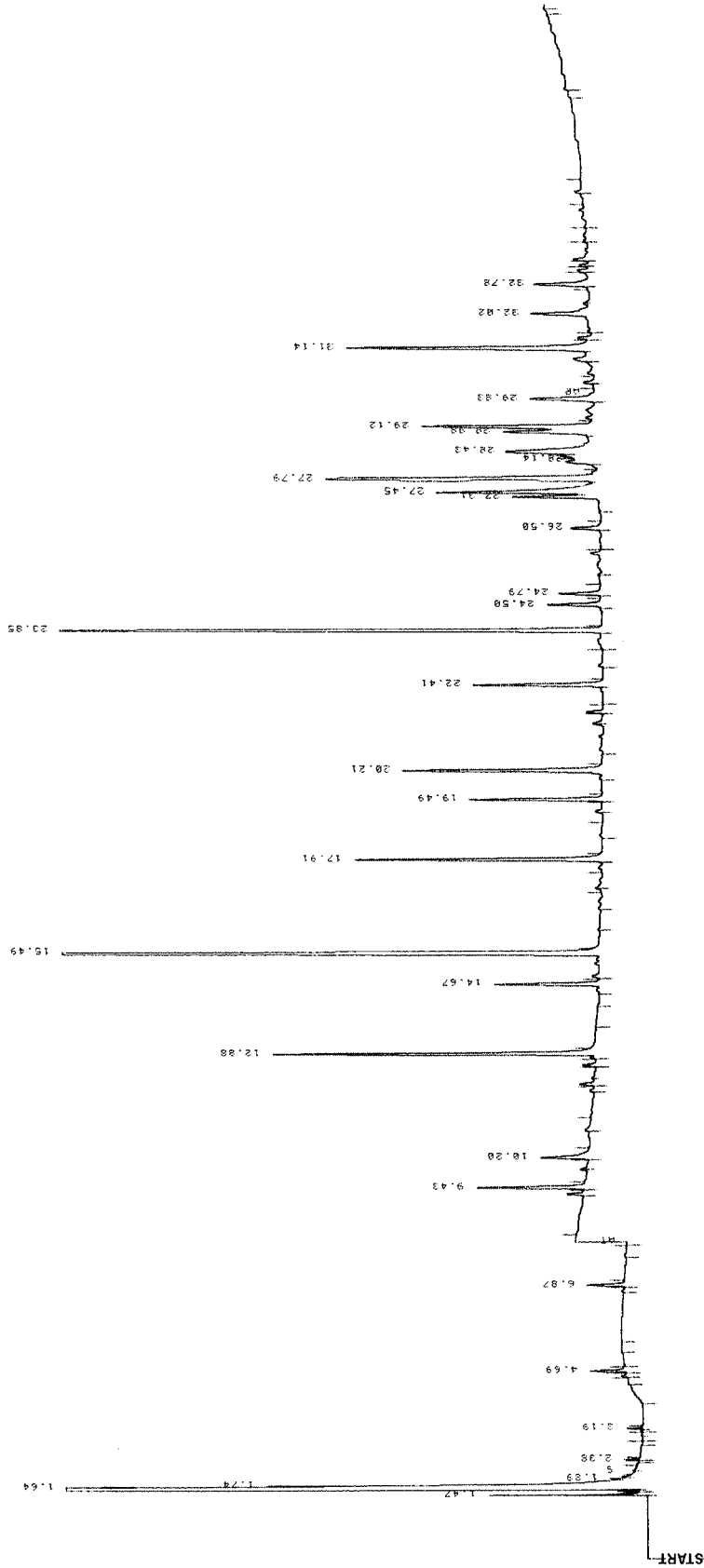


FIG. 3—FAME of residue, Case 2.

Peak Identification	Retention Time, min.
Dimethyl pimelate (heptanedioate or C7)	10.20
Dimethyl suberate (octanedioate or C8)	12.88
Methyl laurate (saturated C12)	14.67
Dimethyl azelate (nonanedioate or C9)	15.49
Dimethyl sebacate (decanedioate or C10)	17.91
Methyl myristate (saturated C14)	19.49
Dimethyl undecanedioate (C11)	20.21
Dimethyl dodecanedioate (C12)	22.41
Methyl palmitate (saturated C16)	23.85
Unsaturated C18	27.31
Unsaturated C18	27.45
Methyl stearate (saturated C18)	27.79

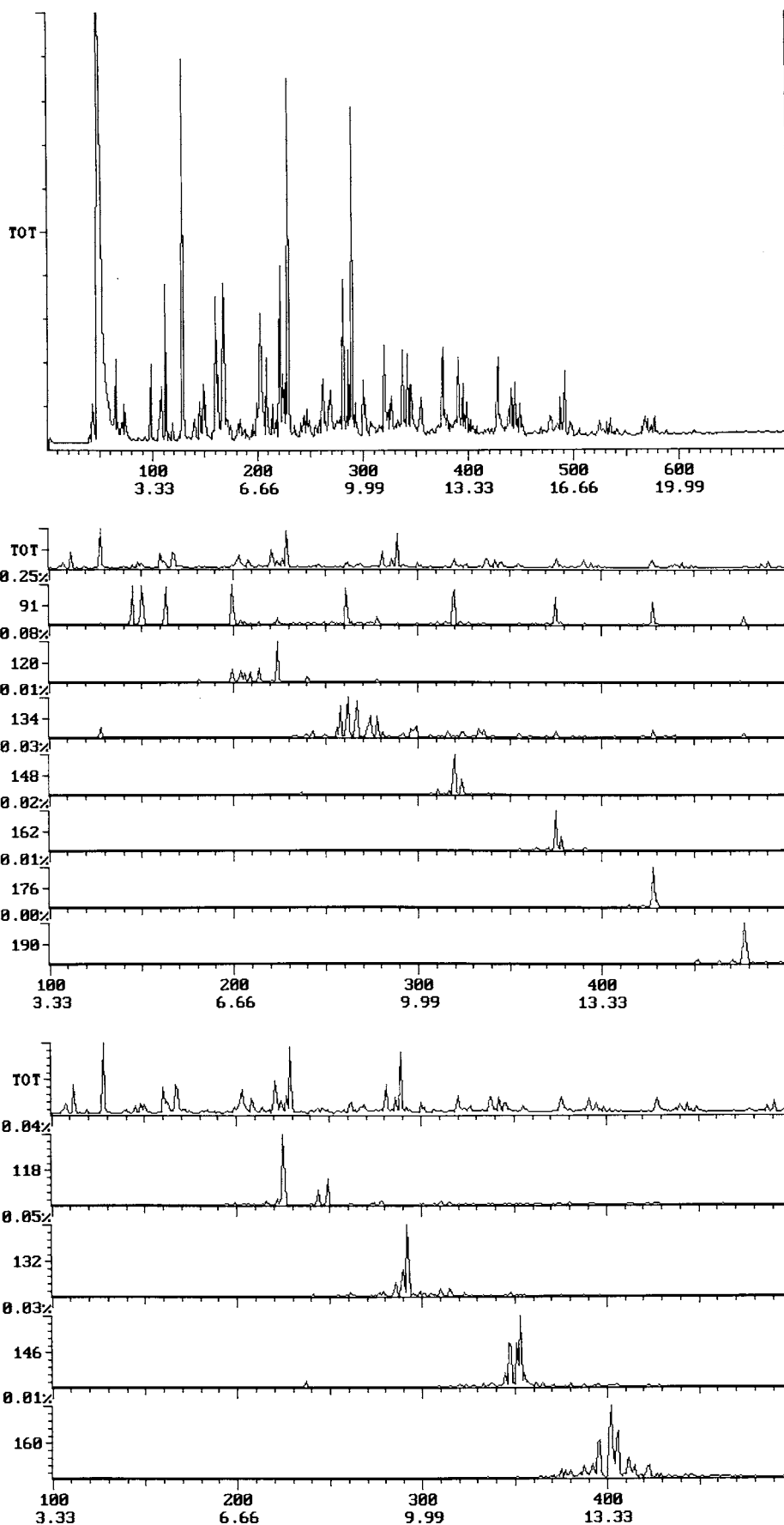


FIG. 4—Volatile residue, Case 2. Top: Total ion chromatogram, Middle: M/z 91 and aromatic homologues, Bottom: Benzofurans and homologues.

Furthermore, the chromatographic column used is not adequate for perfect separation of all fatty ester components since it is intended for petroleum analysis. The process is, however, capable of adequately separating many components.

Results and Discussion

Figure 3 is the chromatogram of the FAME derivatization of the sample. More peaks are present than in Fig. 2. The fact that more material was isolated in Case 2 may explain partly that result.

The first step is to confirm the presence of vegetable oil by looking for the presence of methyl palmitate and stearate. The chromatogram shows the presence of methyl palmitate at RT 23.85 min and methyl stearate at RT 27.79 min. Methyl palmitate is more abundant than methyl stearate, which is generally observed in vegetable oils, like in Case 1. The second step is to observe the ratio of the C18 unsaturated esters as compared to palmitate and stearate. As in Case 1, a very important reduction from the expected amounts could indicate an event such as spontaneous ignition. The C18 unsaturated peaks are at RT 27.31 and 27.45 min. They are considerably less important than methyl palmitate (RT 23.85 min) and methyl stearate (RT 27.79 min). The proportion of unsaturated C18 has dropped considerably to what would be expected if the oil residue had been unaltered chemically, slightly rancid, or simply used extensively (6).

A most notable feature is the presence of C7 to C12 diesters. These products are not usually present in used frying or vegetable oils (4,6). These products are found, from C7 to C12, at retention times 10.2: 12.88: 15.49: 17.91: 20.21: 22.41 min. The prominent peak at RT 15.49 min has been identified as dimethyl azelate (C9 diester) by mass spectrometry.

If these diesters do arise from chemical oxidation triggered at higher temperatures and represent the degradation of C18 unsaturated glycerides, their distribution tends to show that the unsaturated fat most likely to yield a residue is a fatty acid unsaturated at carbon number 9, which happens to be oleic acid.

The larger amount of residue in Case 2 allowed the disclosing of another clue. If unsaturated glycerides are oxidized to diacids, the end hydrocarbon chain should be oxidized to an acid whose chain length should reflect the position of the unsaturation in the original glycerides, assuming no isomerization has occurred during the fire. Evidence of these acids is present. The peaks at RT 4.69: 6.87: 9.43: 14.67 min have been identified as C8: C9: C10: C12 monoesters respectively. It is possible that animal fats like butter could have been present in the sample and contributed to an unknown extent to these peaks. The distribution of these esters, and typically the relative amount of methyl pelargonate (nonanoate or C9), is somewhat different from what would be observed if there was, for example, some animal fat in the sample (7,8). But, since this finding has not been observed in Case 1, it cannot be ruled out that a contamination by animal fat like butter might have occurred in the tissues of Case 2.

Since the circumstances of the fire were not clear, a petroleum residue analysis of the burnt towels by DFLEX[®] was done and the results are shown in Fig. 4. The total ion chromatogram is shown on top. The major peaks are aliphatic but have not been positively identified. Toluene is at Scan 97. Ion chromatogram of m/z 91 is shown in the middle of Fig. 4 along with other simple aromatic ions. Although xylenes are noted at Scans 143, 150, and 162, this ion 91 chromatogram is clearly not a petroleum derivative chromatogram. Actually, ion m/z 176 at Scan 429 has been identified by the mass spectrometry library as n-heptylbenzene and ion m/z 190 at Scan 478 as n-octylbenzene. The other ions at m/z 120, 134, 148, and 162 are all identified as phenylalkane homologues. These products, although similar in nature to linear alkylbenzenes (LABs), have a lower molec-

ular weight and are predominantly normal phenylalkanes. They do not arise from detergent contamination in the towels (9).

The bottom part of Fig. 4 shows the distribution of ions m/z 118, 132, 146, and 160 that have been identified respectively as benzofuran and its alkylated homologues.

The identification and distribution of all these ions is clear evidence that petroleum derivatives, like gasoline, are not present in this sample. The presence of predominantly normal phenylalkanes (ion chromatogram m/z 91) could be explained by the oxidative decomposition of long chain glycerides. These ion signatures have not been reported in petroleum products or fire debris samples as pyrolysis products and could be evidence of spontaneous heating also.

Conclusion

There is clear chemical evidence of spontaneous ignition of towels containing vegetable oil due to selective reactions of unsaturated fatty components. One key result is the near disappearance of the unsaturated FAME in the treated residue as compared to the saturated FAME. A second key result is the formation, after treatment, of diesters, mainly dimethyl azelate (nonanedioate or C9). A third key result, if a petroleum residue analysis is done, is the detection of linear alkylbenzenes, typically hexyl-, heptyl- and octylbenzene and benzofuran homologues.

Although all appropriated precautions may be taken, the towels may not be cleaned as thoroughly as they should be. Spontaneous ignition has been related to situations such as cotton towels still containing vegetable oil after laundering, dried at high temperatures, and immediately stacked without a chance to cool.

Since this phenomenon seems more common than recognized, further scientific research is warranted per se as well as for the benefit of fire prevention, especially concerning testing different types of oil and whether used or fresh, testing the interaction between different materials like animal and vegetable fats, and studying the time frames and quantities of materials involved.

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