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Comparative Analysis of Lubricants Used for Weapons

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ABSTRACT: A method for analysis and comparison of mineral oil-based greases thickened with a metal soap is presented. The greases are first analyzed with Fourier-transform infrared spectroscopy (FT-IR). This analysis differentiates between greases with different main constituents. When two samples can not be differentiated with IR, a more thorough analysis has to be performed. The base oil and the soap are separated. The soap is derivatized and the two components are each analyzed with gas chromatography. The metal ions of the soap are analyzed with scanning electron microscopy with an energy dispersive X-ray detector (SEM-EDX). By the method presented, grease from a weapon may be differentiated or proven to be identical to grease collected from a suspect. As the results indicate that the grease does not change with respect to composition when the weapon is fired, the method may be used in many cases. The application of the method to an authentic case is reported.

KEYWORDS: forensic science, criminalistics, grease, lubricant, weapon, gas chromatography, metal soap thickener, Fourier-transform infrared spectrophotometry, scanning electron microscope, energy dispersive X-ray detector

Since grease is found everywhere in the industrialized society, it is quite plausible also to be found at crime scenes. Due to its versatility, grease may be interesting in many different forensic investigations. Grease from a gun or from a rape scene could be identified as grease from the clothes of a suspect or as grease in a container in the home of a suspect. The ability to identify or differentiate between manufacturers, or even between batches, can be crucial for investigations. The aim of the present study was to obtain a strategy for analysis of mineral oil-based grease thickened with a metal soap.

Background

Lubricants are composed of a base fluid, a thickening agent, and additives.

The base fluid is either a mineral oil or a synthetic fluid. The petroleum-based mineral oils are undefined mixtures of, i.e., alkanes, alkenes, alicyclic, and aromatic hydrocarbons (1). Synthetic

fluids are composed of a variety of complex mixtures, commonly synthetic hydrocarbons as polyalphaolefins (PAO), organic esters, polyglycols, and silicones (2). The thickening agent can be a metal soap, graphite, clay, polyurea, or other (3). The additives are present to give the grease improved performance for different applications. The desired properties may include resistance to oxidation, rust inhibition, improved durability, or improved performance under high pressure or high temperature (4).

There are several reports on how to chemically analyze and compare lubricants. Many methods require sample amounts not normally available in forensic science investigations (5). Infrared and ultraviolet spectroscopy were used early for grease analysis (6–8). In more recent reports, different chromatographic and mass spectrometric methods have proven to be useful (3,4,9). There are only a few reports dealing with exclusively forensic applications of grease analysis. Siegel et al. (10,11) developed methods for three-dimensional (3-D) fluorescence analysis, which they showed beneficial.

In this study, a method is presented by which greases thickened with a metallic soap can be analytically compared. Initially, the base oils and thickening agents of the greases are analyzed using Fourier-transform infrared spectroscopy (FT-IR) after which they are separated. The base oils and the soaps, converted into fatty acid methyl esters, are analyzed by using gas chromatography with a flame ionization detector (GC-FID) and gas chromatography with mass spectrometric detector (GC-MS). The metal ions in the soaps are determined by using scanning electron microscopy with an energy dispersive X-ray detector (SEM-EDX). The full method is recommended for cases where a large amount of the sample is available. However, with only a small amount available, the analyses may be performed without the separation of the base fluid and thickening agent.

Experimental

Materials—Heptane, dichloromethane, toluene, methanol, and sulfuric acid were obtained from Merck, Darmstadt, Germany. All solvents were of analytical grade.

The two most common weapon greases in Sweden today, both consisting of a mineral base oil and an aluminum soap thickener, were examined. Vapenfett 101 (Weapon grease 101) was obtained from Åkers krutbruk protection AB, Åkers Styckebruk, Sweden. Jaktia Vapenfett (Jaktia weapon grease) was obtained from Järnia AB, Ulricehamn, Sweden.

FT-IR—Jaktia Vapenfett was enclosed in a spray can. Prior to analysis some of the grease was transferred to a glass beaker and placed in a heating cabinet (40°C) for three days in order to remove

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the propellant gas. Jaktia Vapenfett and Vapenfett 101 were applied between KBr-disks with a film thickness of 0.025 mm. Infrared spectra (4000 to 400 cm^{-1}) were acquired at a resolution of 4 cm^{-1} on a Perkin-Elmer system 2000 FT-IR spectrometer equipped with a KBr beamsplitter and a TGS detector. Ten scans were averaged.

Separation of oil and soap components—0.1 g of grease was shaken in a test tube with 3 mL of heptane, whereby the base oil and the thickener were separated. The tube was then centrifuged and the heptane layer removed. The precipitated soap was washed twice with 1.5 mL of heptane.

Analysis of oil component—The base oil was further examined according to the Nordtest method Chem 001 edition 2 (12). This is a comparative method for mineral oils, where the oils are initially analyzed using GC-FID and thereafter analyzed and compared in more detail using GC-MS.

Analysis of soap component—Excess heptane from the separation procedure was evaporated, and the soap was dissolved in 1.3 mL of toluene. The toluene solution was heated to 60°C for 25 min with 1.3 mL of methanol and one drop of concentrated sulfuric acid in order to transform the soaps into their corresponding methyl esters. The solution was left for 1 h at room temperature and then shaken with distilled water. After centrifuging, the toluene phase was analyzed with GC-MS.

When only small amounts of the sample are available, consider excluding the separation step and dissolve the entire sample in toluene, i.e., to esterify the soap component with the base oil present. This strategy of analysis was also evaluated. The resulting solutions were analyzed with GC-MS.

GC-MS—The GC-MS analysis was performed using a HP 5890 gas chromatograph with a HP 5972A mass selective detector. 0.5

μL was injected with a HP 7673 autosampler. Injections were in the splitless (2 min) mode for the analysis of base oil and in the split mode for the fatty acid methyl esters. The injection port temperature was 300°C . The chromatographic separation was achieved with an HP Ultra 1 column (25 m by 0.2 mm), coated with cross-linked methyl silicone ($0.33\text{ }\mu\text{m}$ film thickness). Temperature program: 60°C for 4.5 min, then raised $6^\circ\text{C}/\text{min}$ to 300°C and kept there for 20 min. The MS transfer line temperature was held at 300°C . The mass spectrometer was operated in the electron ionization mode (scanning range: m/z 35 to 630).

SEM-EDX—For SEM-EDX analysis, the soap was separated from the base oil as described above. The soap was analyzed using an acceleration voltage of 20 kV and a probe current of 300 pA for 100 s by a scanning electron microscope Leo 435 VP (variable pressure) with a Link Pentafet model 7059 energy dispersive detector.

Study of possible modification of the grease upon firing the weapon—Two firearms were washed with light petroleum and thereafter greased with Vapenfett 101. The weapons were fired ten times and the grease sampled from the breech face and the firing pin by using glass wool. The breech face was exposed to heat, and the mechanical movement during shooting affected the firing pin. The glass-wool was extracted with toluene. The toluene solutions were analyzed using gas chromatography.

Results

FT-IR—Differences between the two samples were observed as shown in Fig. 1. Jaktia Vapenfett (Fig. 1a) displayed a triplet (1569, 1587, and 1606 cm^{-1}) due to an aluminum complex soap (7). The definition of complex soaps is somewhat controversial, but

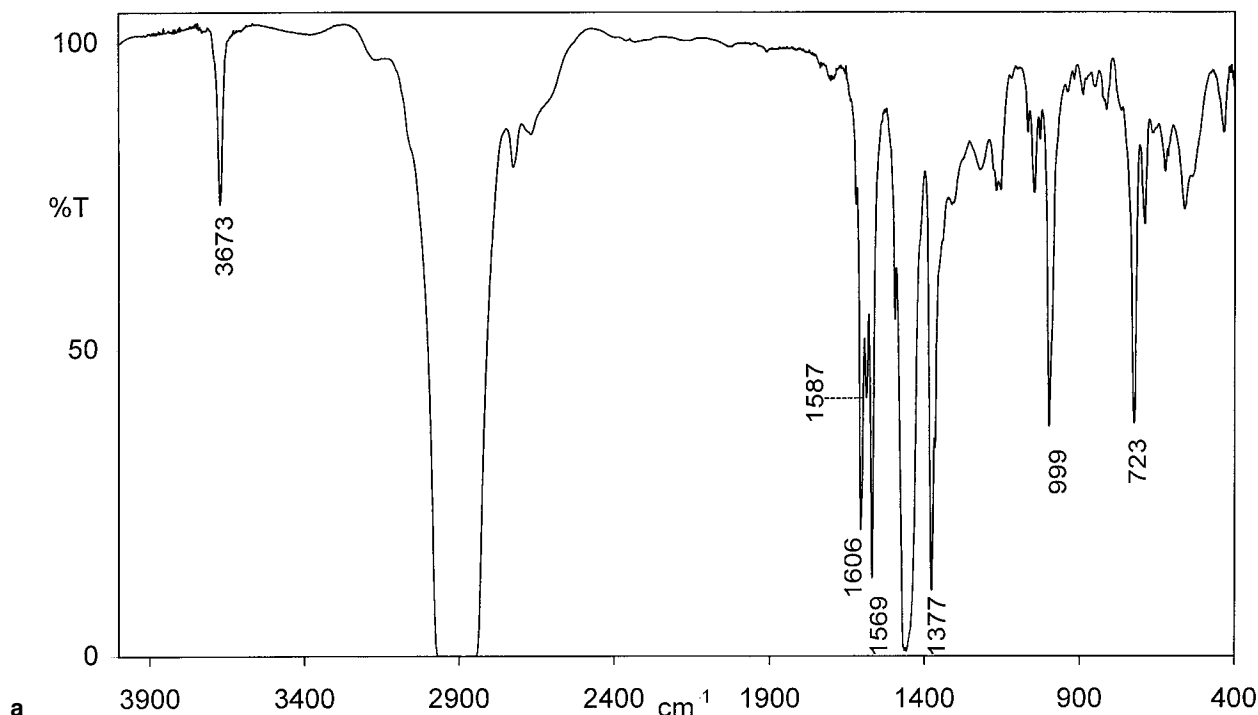


FIG. 1—(a) IR spectrum of Jaktia Vapenfett. Assignments: 999 cm^{-1} Al-O bond; 1569, 1587, and 1606 cm^{-1} carbonyl stretching absorption of an aluminum complex soap; 3673 cm^{-1} phenolic antioxidants. (b) IR spectrum of Vapenfett 101. Assignments: 988 cm^{-1} Al-O bond; 1590 cm^{-1} carbonyl stretching absorption of an aluminum soap; 1737 cm^{-1} lanolin; 3693 cm^{-1} phenolic antioxidants.

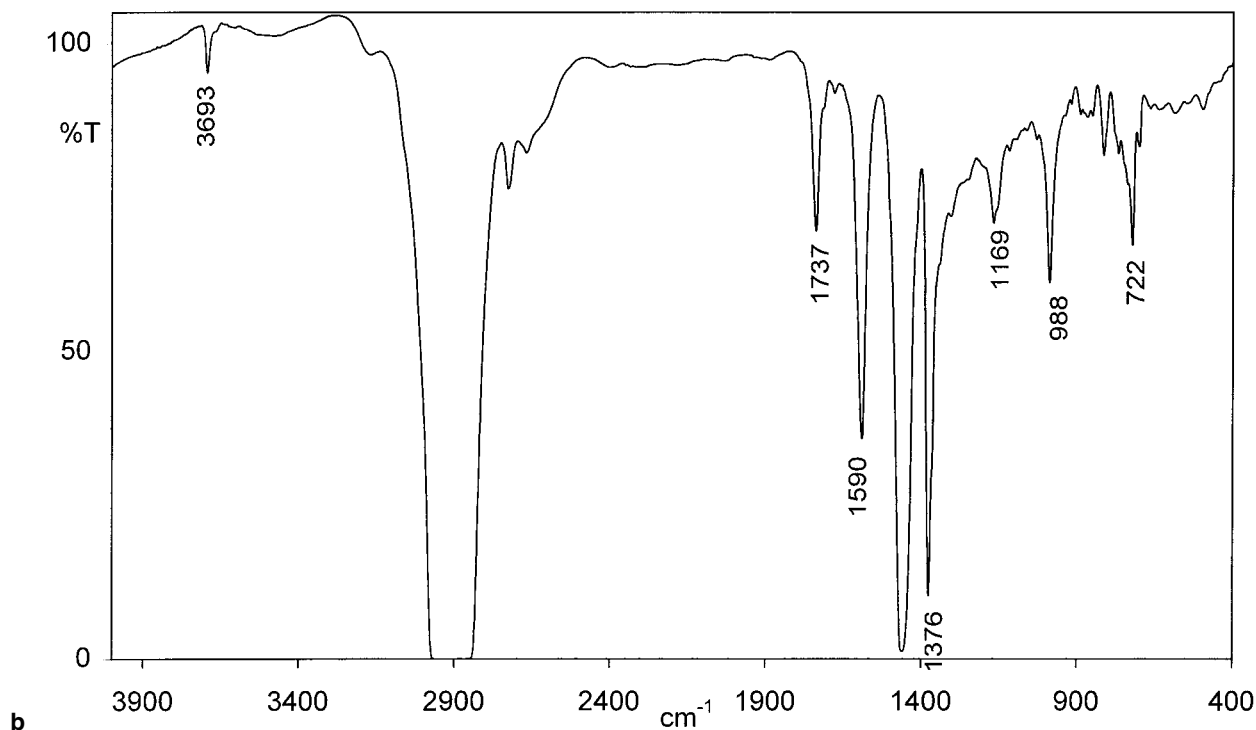


FIG. 1 (continued)

they are believed to be double salts formed from two acids, differing significantly in molecular weight, and a polyvalent metal ion (8). Vapenfett 101 (Fig. 1b), having a single peak at 1590 cm^{-1} , did not contain a complex soap. The peak at 1737 cm^{-1} originated from lanolin (hydrous wool fat), which acts as a rust inhibitor in Vapenfett 101. Both samples exhibited sharp peaks in the region of 3670 to 3700 cm^{-1} . These peaks are most likely due to sterically hindered phenols used as anti-oxidant additives.

Separation of oil and soap components—It was established that the base oils of both samples dissolved fully in heptane by comparing the chromatograms obtained from the GC-MS analysis of the heptane-dissolved oils to chromatograms of the non-separated samples in toluene. The heptane solutions of both base oils were also analyzed with FT-IR. No peaks related to the soaps could be observed. It was thus concluded that the separation was complete for both samples.

GC-MS—The base oils differed significantly as can be seen from the TIC chromatograms in Fig. 2. Vapenfett 101 (Fig. 2b) contained a broad hump with fewer specific peaks than Jaktia Vapenfett (Fig. 2a). These differences gave enough information to conclude that the oils were nonidentical. If the samples can not be differentiated by comparison of the TIC (or FID) chromatograms, the oils should be further analyzed using SIM (selected ion monitoring) as described in the Nordtest method (12).

The fatty acid composition of the soap components of the two samples differed as shown in Fig. 3. The soap in Vapenfett 101 (Fig. 3b) almost entirely consisted of palmitic and stearic acids. The soap in Jaktia Vapenfett (Fig. 3a) was also dominated by palmitic and stearic acid, but there were also considerable amounts of benzoic, arachidic, and behenic acids present. The theory of a complex soap, as indicated by the infrared spectroscopy, was hereby confirmed. When there is only a small

amount of sample available, it is recommended to analyze the oil and the thickener without separation. Figure 4 shows the base oils and the methylated fatty acids for Jaktia Vapenfett (Fig. 4a) and Vapenfett 101 (Fig. 4b). The fatty acid distributions of the soaps are similar to Fig. 3, although the quantitative relations between the peaks are more difficult to evaluate when the acids are not separated from the oil. In addition, the Nordtest method can be used for the base oils with the fatty acid methyl esters present.

SEM-EDX—The metal ions in the soaps were determined using SEM-EDX. This analysis was performed using the separated soap, as the base oil would partly evaporate and clog the vacuum chamber. Both soaps exhibited a dominant Al peak. This peak originated from the metal ion of the fatty acid soaps. In Jaktia Vapenfett no other metal ion was detected. In Vapenfett 101 a small Na-peak was present.

Impact on grease during shooting—No change in Vapenfett 101 was observed after firing a greased gun ten times. This indicated that grease can be collected anywhere on the surface of the fire arm. If possible, avoid collecting grease from the interior of the gun since residues of earlier used oil or grease could contaminate the sample.

Discussion

A strategy for analysis and comparison of mineral oil-based greases thickened with a metal soap is presented. The greases examined were used for maintenance of weapons, but the method allows any mineral-based grease thickened with a metal soap to be analyzed. The greases can be differentiated in each of several analytical steps. This gives the forensic analyst a high degree of confidence.

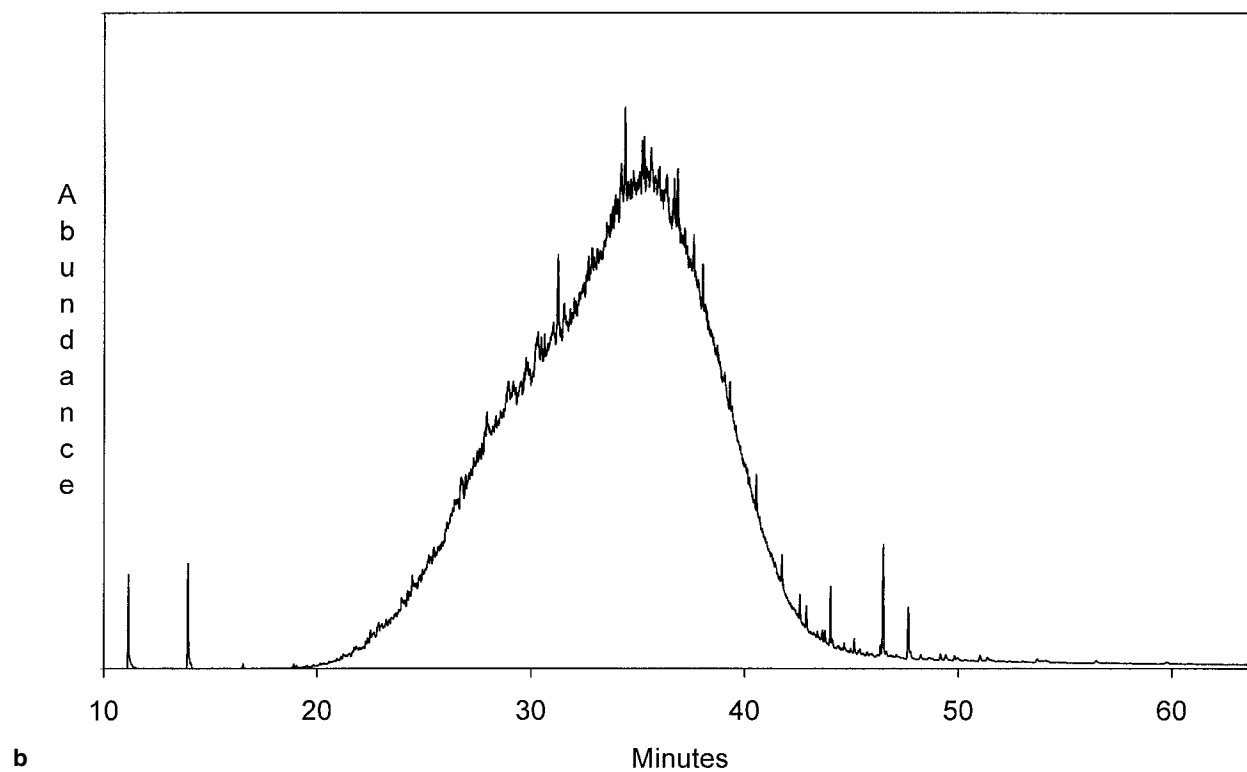
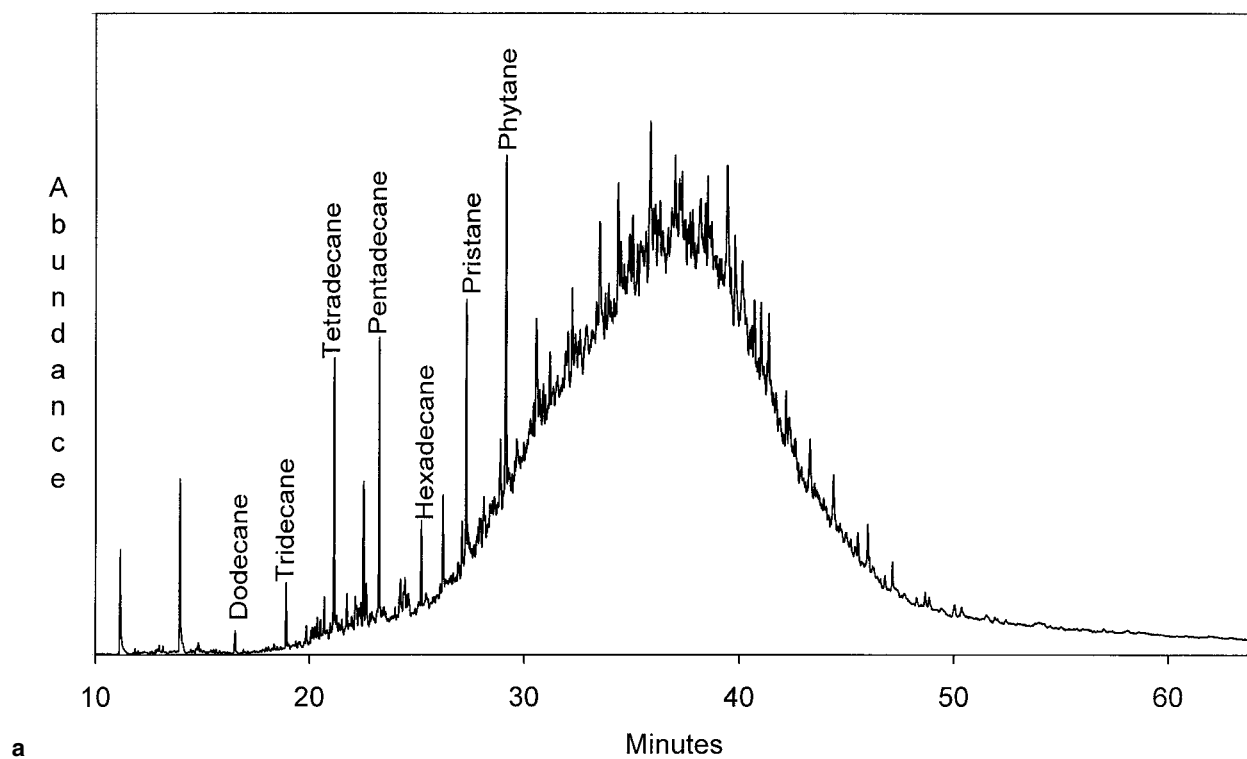


FIG. 2—GC-MS TIC chromatograms of the base oil of (a) Jaktia Vapenfett and (b) Vapenfett 101. The eluting intervals, shapes, and fine structures give sufficient information to differentiate between the two oils.

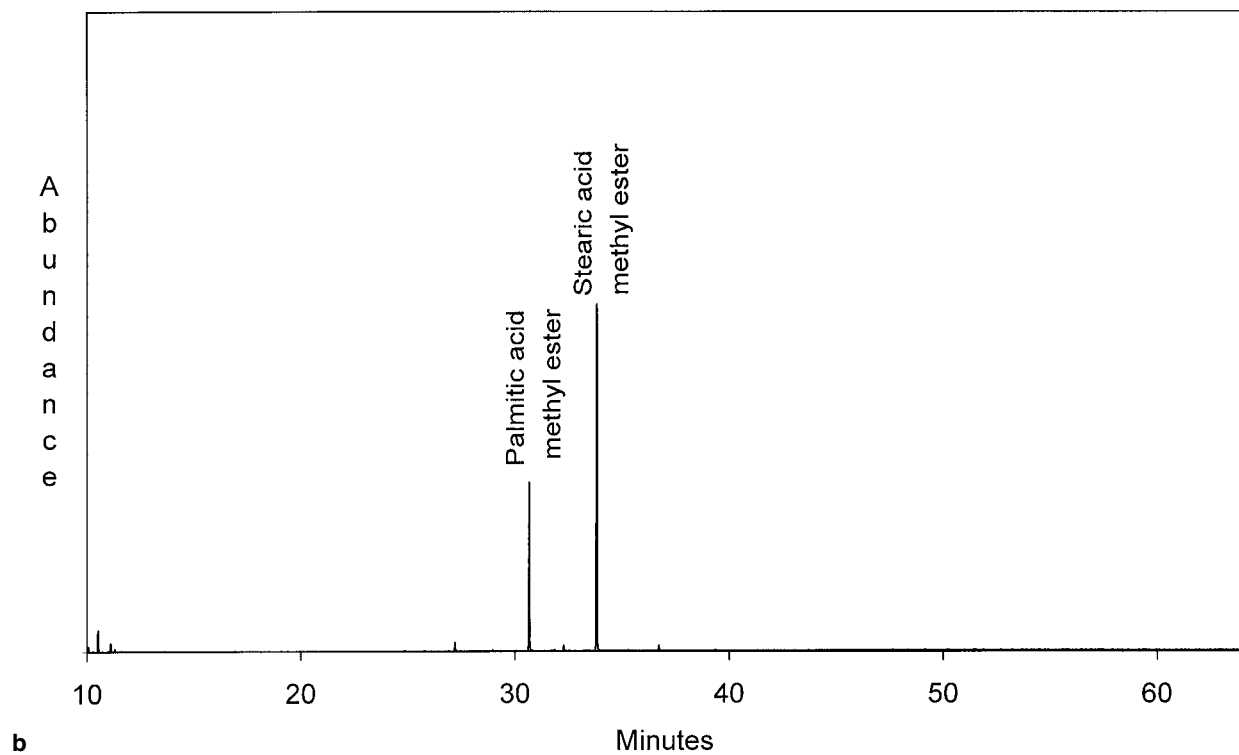
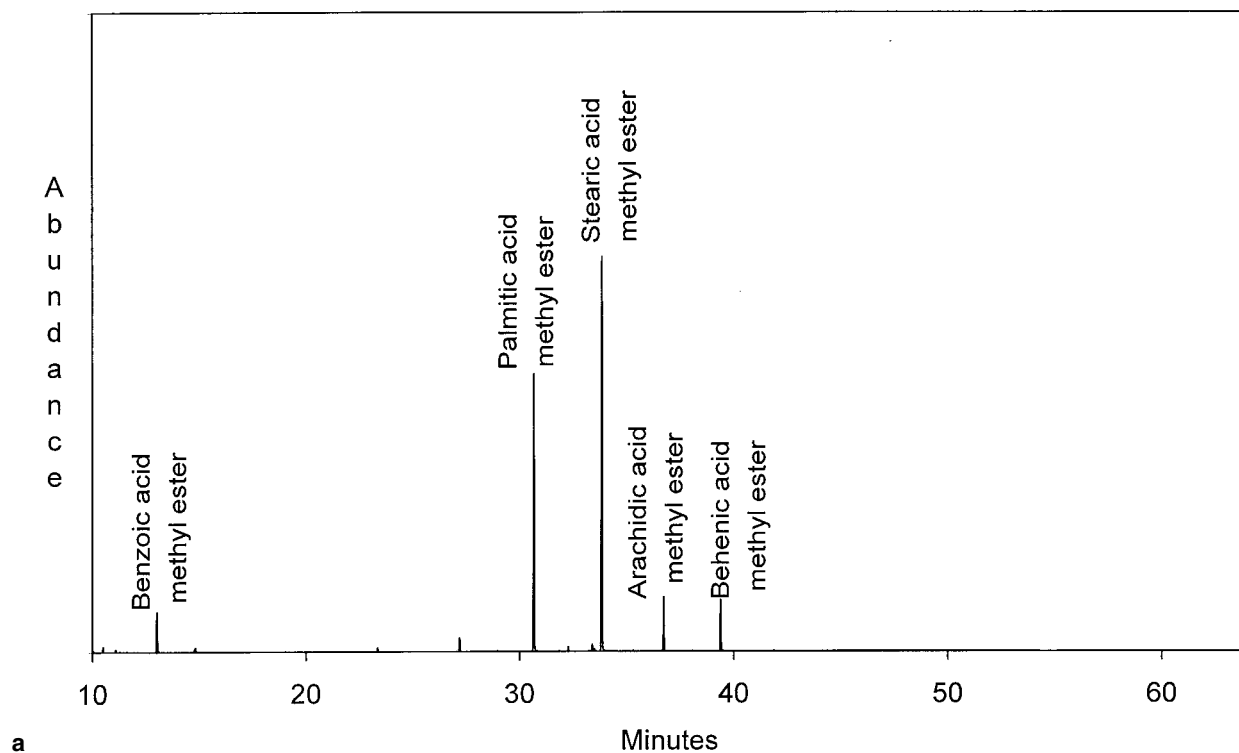


FIG. 3—GC-MS TIC chromatograms of the methylated fatty acids from the soap components in (a) Jaktia Vapenfett and (b) Vapenfett 101. Although palmitic acid and stearic acid are the dominant peaks, some additional carboxylic acids contribute to the complex soap of Jaktia Vapenfett.

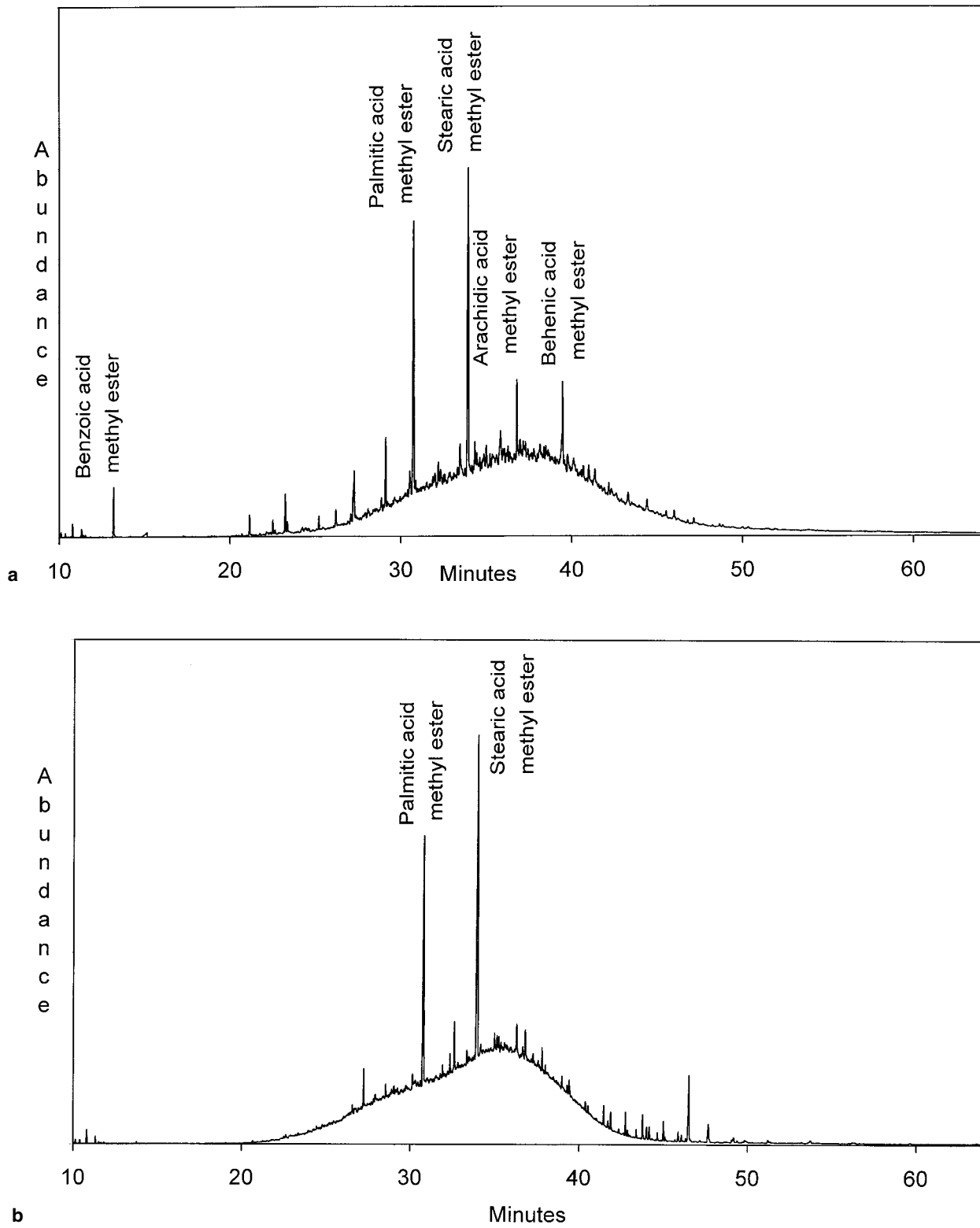


FIG. 4—GC-MS TIC chromatograms of the methylated fatty acids and base oil of (a) Jaktia Vapenfett and (b) Vapenfett 101. The patterns of the fatty acids and the base oils are easily comparable

The greases were first analyzed with FT-IR. This gave an indication of the major constituents. FT-IR is a useful technique for distinguishing greases with differing thickeners or additives. If the greases differ greatly with respect to their major constituents (e.g., different types of thickening agents), FT-IR alone may be sufficient to establish a difference between them. If not, FT-IR should, for forensic purposes, be considered only as a screening method and the results should be confirmed by further analytical techniques. Separation of the thickening agent and the base oil was achieved by using heptane. The base oil was then further examined with GC-FID and GC-MS while the thickener was analyzed with GC-MS and SEM-EDX. If not enough of the sample is available to perform all the analyses, the FT-IR and SEM-EDX steps should be excluded. The chromatographic analysis of the oil and the thickener only requires a small amount of the sample and offers a high degree of certainty. It should therefore be given priority.

This method has already been introduced to our laboratory's casework situations. The first case in which we used this method concerned a greased gun used in a shooting. The grease from the gun was to be compared with a sample from an opened can of grease. The can was found in a store where the suspect was currently employed. The two greases were analyzed with FT-IR and the spectra showed a perfect match. The base oils of both samples were separated from their thickeners as described above. The oils were thereafter analyzed by gas chromatography. The chromatograms revealed that the base oils for the two greases differed. The shape and the span of the oil humps were different. Thereby it was concluded that the samples were nonidentical and no further examinations were performed.

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