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TECHNICAL NOTE

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Analytical Methods Used for the Discrimination of Substances Suspected to be Bar Soap: A Preliminary Study*

ABSTRACT: The submission to forensic laboratories of unknown specimens suspected of being biological or chemical warfare agents has increased tremendously with the threat of terrorism. Oftentimes, a threatening correspondence that contains hoax materials is intended to make the recipient(s) believe they have been exposed to a toxin. In some cases, the perpetrator can use standard household products, such as detergents and soaps. Once these materials are received, they become forensic evidence and may be analyzed for identification and/or comparison with known seized material from a suspect(s). Two separate studies were conducted using different analytical protocols for bar soaps. In the first set, the forensic laboratory at the United States Secret Service conducted tests on 68 bars of soap using solid-phase microextraction and gas chromatography coupled with mass spectrometry. The 68 different soaps displayed unique total ion chromatogram profiles. Energy-dispersive X-ray analysis in conjunction with scanning electron microscopy was also used to characterize 46 of the 68 soaps as a preliminary study. In a second set of studies, as part of a homicide investigation, the laboratory at the California Department of Justice, Riverside, conducted examinations on 13 bars of soap by utilizing Fourier transform-infrared spectroscopy. The case study demonstrated that it is possible to distinguish some bar soaps using infrared analysis. Furthermore, the bar soaps could be distinguished from typical laundry detergents using this technique.

KEYWORDS: forensic science, trace evidence, bar soap, soap, unknown substances, surfactants, SPME, SEM, GC/MS, FT-IR

After reviewing the forensic literature, limited information was found that specifically addressed the forensic examination of bar soaps. This paper will review the findings of independent studies conducted at the United States Secret Service (USSS) and the California Department of Justice (DOJ) using a variety of analytical approaches. The cases that were originally submitted to the respective agencies involve different circumstances. This investigation will focus on the discrimination of various bar soap samples rather than the overall chemical characterization of the many constituents that can be found in soap products. It is the authors' hope that this paper will serve to stimulate further research studies that address the issue of the chemical characterization of soaps utilizing some or all of the discussed techniques.

USSS Case Scenario

Since the anthrax poisonings that took place in October 2001 and the release of news reports pertaining to chemical and biological threats, law enforcement agencies have received numerous hoax letters and/or packages involving unidentified material(s). Materials of unknown origin are often submitted for forensic examination and can be characterized using a variety of analytical techniques. Recent evidentiary submissions at the USSS have included unidentified substances suspected of being chunks of bar soap. The perpetrator(s) of these crimes was apparently attempting to instill fear by making the recipients believe they had been exposed to a chemical or biological agent. Investigators requested that the unknown substance(s) be conclusively identified and/or compared with known materials that were seized from the suspect(s).

In one adjudicated case investigated at the USSS forensic laboratory, numerous small soap pieces, each *c.* 3 mm in length, were found in three separate alleged "bomb" packages that were thought to be linked. Known soap materials, including numerous bars of commercially available soap, were also seized from the suspect's residence. The request was to determine whether the suspect material was consistent in composition with any of the soap bars of known origin. Therefore, to test the hypothesis that bar soaps have distinctive chemical profiles and can be chemically differentiated, 68 commercial bar soaps were obtained and analyzed using standard instrumentation found in many forensic laboratories. After conducting preliminary examinations using optical and spectral techniques, solid-phase microextraction

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(SPME) with gas chromatography/mass spectrometry (GC/MS), Fourier transform-infrared spectrophotometry (FT-IR), and scanning electron microscopy-energy-dispersive X-ray analysis (SEM-EDXA), the SPME-GC/MS technique was found to be the most discriminating and efficient. The results indicated that significant differences between the soap specimens could be classified using a flow chart/database, potentially identifying the brand and manufacturer of the soaps. Through a literature search, it was determined that there were no known databases that identified soap(s) based on their volatile organic compounds (VOC) content. Therefore, the focus of the USSS study was to identify the discriminating VOC components present in bar soaps. Forty-six commercial soaps were simultaneously examined using SEM-EDXA to ascertain the feasibility of using this technique for further discrimination. The qualitative results for these 46 soaps are also reported and discussed.

In the aforementioned USSS case, the suspect material was found to be a heterogeneous mixture of "soap-like" flakes, based on their color and texture. Before instrumental analysis, the mixed soap pieces were physically separated into homogeneous populations. Optical examinations using an ultraviolet (UV) lamp, alternate light source (ALS), and/or the Foster and Freeman Video Spectral Comparator® (VSC) (Evesham, Worcestershire, U.K.) were useful for distinguishing between like-colored soaps. In addition to capabilities such as viewing with coaxial and transmitted light sources, and multiple imaging capabilities, the VSC can be used to view materials in the visible and near-IR (NIR) regions to measure variations in their absorption and reflectance properties.

The soap pieces were examined using SPME coupled with GC/MS, a widely utilized technique to detect volatile and semivolatile compounds. Numerous articles have been published describing the use of SPME in various forensic disciplines such as fire debris analysis (1), the detection of volatile compounds from spent cartridges (2), the characterization of currency inks (3), and the analysis of VOC associated with methamphetamine (4). A series of manufacturer (Supelco™) (Bellefonte, PA) publications describes a variety of SPME applications (5,6). The sampling device used for SPME consists of a needle-like apparatus that contains a specialized silica-coated micro-fiber that is designed to adsorb organic compounds when exposed to their vapors. The SPME apparatus allows the probe (needle) to be inserted through the septum of a capped vial. After insertion, the retracted fiber is then pushed out of the needle and exposed for a fixed time. The emitted volatiles and semivolatiles are adsorbed onto the fiber. The device is then removed and inserted into a GC injection port where the fiber is exposed at a fixed temperature and desorption of the VOC occurs. The desorbed compounds are then separated by GC where their individual constituents can be further analyzed by MS.

Finally, a blind study was conducted in the forensic laboratory at the USSS. SPME-GC/MS analysis was performed on 10 randomly chosen homogeneous soap samples to determine whether they could be accurately "matched" with their original chromatographic profiles.

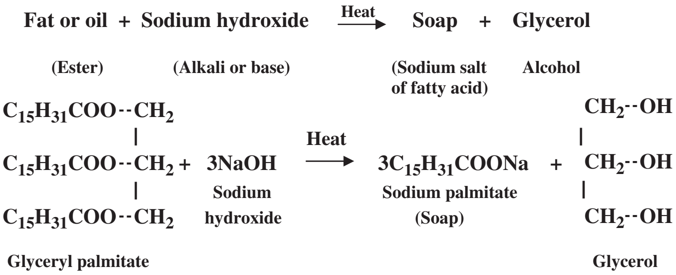
California DOJ Case Scenario

A forensic study of bar soap specimens was conducted by the California DOJ as a result of a homicide investigation that took place 10 years after the death of a female victim. The woman's death was initially considered to be the result of asphyxiation after the aspiration of gastric contents. The victim was found to have a 1 kg mass of soap in her stomach. Ten years later, newly developed information, including an autopsy on the exhumed body, suggested that the victim may have been forced to eat bar soap over a long period of time, and may have been beaten, tortured, and strangled by her husband. Evidence of torture, including the possible forced consumption of soap, was sought.

In the course of the homicide investigation, small soap-like particles were found on a belt that could have been used to strangle the victim, along with blood stains that were consistent in DNA type with the victim. The California DOJ conducted an FT-IR analysis of these particles to ascertain whether they were consistent with bar soap. Subsequent FT-IR examination of 13 commonly used bar soaps and at least three common laundry detergents was also performed to determine whether there were any differences in the FT-IR spectra that could be used to identify the brand of bar soap, and whether typical laundry detergents could be distinguished from bar soaps using FT-IR.

Chemistry of Soap

Soaps are anionic surfactants, or surface-active agents, that assist in the cleaning process by reducing the surface tension of wet surfaces and by emulsifying (i.e., dispersing) soil in suspension until it can be rinsed away (7–11). The surfactants are water-soluble sodium or potassium salts of fatty acids that are derived from fats or oils, or their fatty acids, by chemically treating them with a strong alkali.



$$\underset{\text{(Ester)}}{\text{Fat or oil}} + \underset{\text{(Alkali or base)}}{\text{Sodium hydroxide}} \xrightarrow{\text{Heat}} \underset{\text{(Sodium salt of fatty acid)}}{\text{Soap}} + \underset{\text{Alcohol}}{\text{Glycerol}}$$

$$\begin{array}{lcccc} C_{15}H_{31}COO\text{--}CH_2 & & & & CH_2\text{--}OH \\ \qquad\qquad\quad | & & & & | \\ C_{15}H_{31}COO\text{--}CH_2 + & 3NaOH & \xrightarrow{\text{Heat}} & 3C_{15}H_{31}COONa \ + & CH_2\text{--}OH \\ \qquad\qquad\quad | & \text{Sodium} & & \text{Sodium palmitate} & | \\ C_{15}H_{31}COO\text{--}CH_2 & \text{hydroxide} & & \text{(Soap)} & CH_2\text{--}OH \\ \text{Glyceryl palmitate} & & & & \text{Glycerol} \end{array}$$

The fats (or oils) used in soapmaking consist of distinctive mixtures of different triglycerides, in which three fatty acid molecules are attached to one molecule of glycerol (glycerin)—the process known as saponification. Soap is the sodium (or potassium) salt of the original fatty acid. The addition of sodium chloride (NaCl) acts to precipitate the soap out of solution, causing it to float on the surface. The soap flakes are then removed and pressed into molds after perfumes and colorants have been added. Soap can be made from many natural products, including vegetable oil, olive oil, and animal fats.

The cleansing action of potassium and sodium soaps is associated with the "micelle" structure of the soap molecule, which consists of a long hydrocarbon chain and a polar ($-COO^-M^+$) end in a ring-shaped complex [$M^+ = K^+$ or Na^+].

The nonpolar (hydrophobic) ends of the molecule are attracted to the fat, grime, or dirt (lipophilic) material, which is also nonpolar. The polar, or ionic, ends of the molecule attract the water molecules. A closed, spherical structure is formed, with the polar portions on the surface and the nonpolar portions in the center of the molecule; this arrangement is due to the mutual repulsion of the positively charged heads. The barrier between dirt and water is broken, and the resulting surfactant properties of the soap facilitate the removal of dirt from clothing or other soiled surfaces.

In contrast to soluble potassium and sodium salts of fatty acids, magnesium (Mg) and calcium (Ca) salts are insoluble, and form a cloudy scum or curds at the surface. To achieve the same washing or cleaning action, more soap must be added.

$(C_{17}H_{35}COO^{--})_2\ Mg^{++}$ $(C_{17}H_{35}COO^{--})_2\ Ca^{++}$

Magnesium stearate **Calcium stearate**

In water that contains calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, known as "hard water," the cleaning action of soaps is disrupted due to the precipitation of these insoluble complexes as a sticky scum. To overcome this problem, synthetic detergents were developed, which have replaced soap for many household cleaning jobs.

Synthetic detergents also contain long-chain molecules, such as sodium *n*-docecyl benzene sulfonate and sodium *n*-dodecyl sulfate, as shown below:

$CH_3(CH_2)_{11}(C_6H_4){-}{-}SO_3^{--}Na^+$ $CH_3(CH_2)_{10}CH_2){-}{-}SO_4^{--}Na^+$

Sodium n-dodecyl benzene sulphonate **Sodium n-dodecyl sulphate**

Like soaps, synthetic detergents contain a long hydrocarbon tail and a short ionic head, which are water repellent and water attracting, respectively. The cleansing action of a synthetic detergent molecule is very similar to that of soap. Their development was beneficial for users who had relatively hard tap water in their homes.

Washing powders are a combination of soaps, detergents, and other chemicals, which generally contain *c*. 15–30% of synthetic detergents, by weight. Washing powders can also include additional additives that perform various functions, including sodium sulfate and sodium silicate (dessicants), sodium triphosphate or sodium carbonate (alkalinity control, softener), carboxy methyl cellulose (emulsifier), and sodium perborate (bleaching).

The Consumer Product Safety Commission (CPSC) regulates "true soaps" and defines them as substances composed of "fats and an alkaline constituent." Most body-cleansing bar soaps, however, contain additional ingredients such as antibacterial, antiperspirant, or hypoallergenic agents, and are regulated by the Food and Drug Administration (FDA). These products can be sold to consumers as "soap," but they must have labels that list all of the active ingredients.

Materials and Methods

USSS Analytical Study

Sixty-eight bar soaps were collected from various sources, including retail stores and hotels. The soaps were selected from different brands, as well as from different types of soap from the same manufacturer. A complete list of the soap brands and their physical descriptions is presented in Table 1.

Each bar of soap was weighed and photographed. A small portion of material was cut off from each bar and placed in a small glass jar for storage; the samples were each assigned a number from 1 to 68. A small amount of finely cut up soap was placed in a GC vial (12 mm × 32 mm; 2 mL) and capped with a rubber snap top.

TABLE 1—*Listing of the brand names and colors of the 68 soaps used in the United States secret service study.*

	Brand	Color
1	Bath & Body Works Cool Citrus Basil Moisture-Rich Cleansing Bar	Green (Light)
2	Bath & Body Works Cucumber Melon Glycerin Soap	Green
3	Bath & Body Works Plumeria Glycerin Soap	Red
4	Caress Moisturizing Body Bar	Peach
5	Coast Max	Blue (Aqua w/ White Streaks)
6	Dial Antibacterial (Packaged in a Box)	White (w/ Green Specks)
7	Dial Antibacterial (Packaged in Paper)	Blue-Green
8	Dial Antibacterial (Packaged in Paper)	Orange
9	Dove Sensitive Skin Hypoallergenic Fragrance Free	White
10	Fels-Naptha Laundry Bar Soap	Yellow
11	Frangipani Soap w/aloe	Pink (Salmon)
12	Gilchrist and Soames Cleaning Bar Moisture Balance with Aloe Vera	Cream
13	Irish Spring Deodorant Icy Blast	Blue w/ White Streaks
14	Irish Spring Deodorant Soap Aloe	White (w/ Green Streaks)
15	Irish Spring Deodorant Soap Original	Green
16	Ivory Pure	White
17	Ivory Soap	Cream
18	Jergens	Cream
19	Jergens Deodorant Soap	White
20	Jergens French Milled Deodorant Soap	Cream
21	Jergens Mild Moisturizing Facial Soap	White
22	Lever 2000 Antibacterial Fresh Scent Mild Formula	White
23	Lever 2000 with Aloe Vera	Green (Light)
24	Marriott Residence Inn Bath Bar	White
25	Marriott Residence Inn Facial Bar	White
26	Neutrogena French Milled Soap	Cream
27	Olay	White
28	Old Spice High Endurance Refreshing Deodorant	Green (Lime)
29	Palmolive Classic Scent (Mild All Family Soap)	Green (Lime)
30	Palmolive Gold Deodorant Soap	Gold
31	Portico Verbena Milled Soap	Beige
32	Pure and Natural Complexion Soap	White
33	Tone with Moisturizing Cocoa Butter Original Scent	Tan
34	Unknown	Red
35	With Compliments	White
36	Zest	Green (Light)
37	Zest	Blue
38	Golden Door (Leaf Shape)	Green
39	Cambria & Taylor Deodorant Soap	Cream
40	Cambria & Taylor Facial Soap	White
41	Ambi Complexion-Cleansing Bar	Green
42	Dove Pink	Pink
43	Dove Unscented	White
44	Dove White	White
45	Caress Moisturizing Body Bar (Berry Fusion)	Pink
46	Caress Shimming Body Bar	Purple
47	Neutrogena French Milled Soap	White
48	ProTerra Milk and Honey Bar	White
49	Bath & Body Works Cucumber Melon Cleansing Bar	Green
50	International Camay Classic	Pink
51	CVS Antibacterial Deodorant Soap	Orange
52	CVS Spring Fresh Deodorant Soap	Green
53	Golden Door Facial Soap	Green
54	Raspberry Fragranced Soap	Pink
55	Marine Fragranced Soap	Blue
56	Savon De ∼ luxe French Milled Soaps (Moisturizing and Exfoliating)	Gray
57	Clinique Extra Strength Soap	Orange
58	Soap from Bangkok, Thailand	Cream
59	ASiRA Body Care (Fragrance Free Hand and Face)	Cream
60	ASiRA Body Care (Exfoliating Oatmeal–Almond)	Gray
61	The Marx	White
62	Garden Botanika	White
63	Adam's Mark	Cream
64	Clinique Mild Soap	Cream
65	Clinique Extra-Mild Soap	White
66	Sheraton Moisturizing Bar	White
67	Marriott Philadelphia	White
68	Marriott Boston	White

Optical Examinations

Soaps can be subjected to preliminary screening using optical techniques. Before instrumental examination, 254 and 366 nm wavelength UV sources were used to determine whether the submission is homogeneous, especially when soaps are close in color. The Foster and Freeman® Video Spectral Comparator 2000 High

Resolution (VSC 2000 HR) was also used to document, observe, and record IR reflectance and IR luminescence properties of the soaps. These individual soap properties were measured against a standard white chip that was provided with the VSC to provide a consistent baseline for IR measurements.

SPME-GC/MS

A Supelco™ StableFlex SPME fiber, 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane coating (Supelco™ part number 57328-U), was used in this study.

This fiber best adsorbs volatiles and semivolatiles with molecular weights in the range of 40–275 amu. A description of SPME methodologies can be found in the 2003/2004 Supelco™ catalogue (12). The SPME device was inserted into the rubber-capped vial where adsorption was allowed to proceed for 30 min at room temperature.

The soaps were analyzed using an Agilent® (Palo Alto, CA) 6890N Series gas chromatograph and a 5973 Network mass selective detector. The injection port temperature was set at 250°C and a flow rate of 12.5 mL/min was used in the splitless mode. The GC temperature was programmed to begin at 70°C for 1 min and increased at a rate of 8.0°C/min to 225°C. The mass spectrometer detector was set in the full scan mode and programmed to scan compounds ranging from 28 to 500 amu.

SEM-EDXA

The soap samples were analyzed by SEM-EDXA to determine their elemental compositions. A Hitachi S3500N variable pressure SEM (VPSEM) with an EDAX® (Mahwah, NJ) Detector Unit (− 750 V DC bias) was used. EDXA spectra were collected from pressed smears of the individual soaps under variable pressure in the backscattered electron (BE) mode using an accelerating voltage of 20 kV at 0° tilt and a working distance of 10 mm for 200 sec (live time).

USSS "Semiblind" Study

Approximately 0.5–1.0 g portions were removed from 10 randomly chosen bars of soap and placed in separate vials labeled Q1–Q10. Because the soaps were not previously mixed together, no ALS was needed to help distinguish between like colors. The 10 unknown samples were analyzed using the SPME-GC/MS technique described in "Materials and Methods." The 10 samples used are identified as numbers 14, 17, 23, 26, 32, 35, 41, 43, 49, and 53 in Table 1.

California DOJ: FT-IR Examination

Thin smears of small soap-like particles from the belt were placed on barium fluoride polished disks and analyzed for 128 scans using a Nicolet 5DXC IR spectrometer (Waltham, MA) with a Spectra-Tech IR-plan microscope (Waltham, MA) attachment. IR spectra were obtained between 4000 and 700 cm using a resolution of 4 cm^{-1}. Additionally, 13 bar soaps and three different common laundry detergents were obtained from various sources, including retail stores and hotels. A Digilab model FTS-7 FT-IR spectrometer with a diamond anvil cell was used for the analysis of the known bar soaps and detergents. Samples were scanned for up to 1000 scans at a resolution of 4 cm^{-1}.

Results and Discussion

Optical Examinations

Figure 1 shows a composite plot of the reflectance of green soaps over the visible through NIR range of 400–1000 nm. An attached camera in the VSC, equipped with longpass and variable bandpass filters, was also used to image the specimens. Figure 2 shows different soaps as viewed under light sources from different regions of the electromagnetic spectrum. The four white soaps viewed under visible light (Fig. 2*a*) appear similar in color and

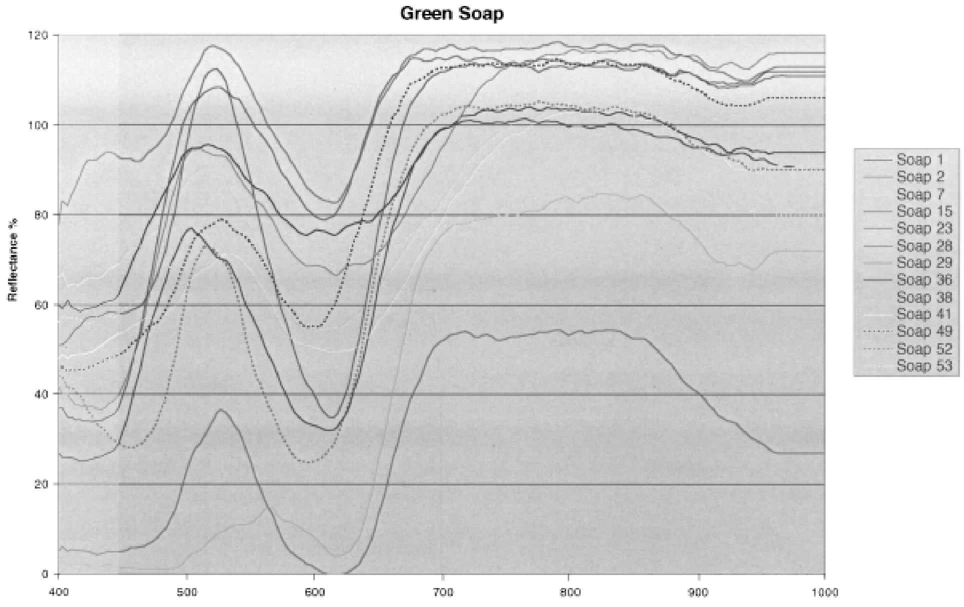
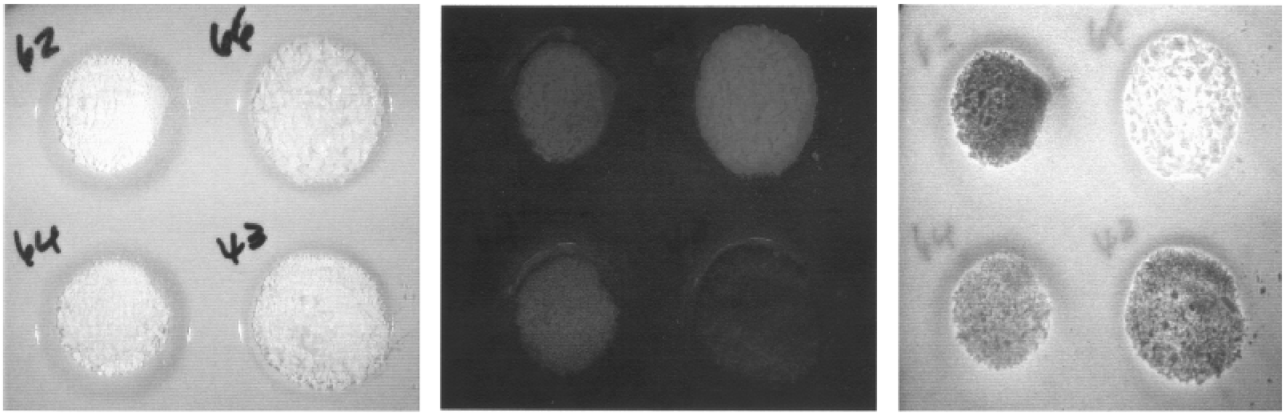


FIG. 1—*A high-resolution video spectral comparator was used to measure the reflectance percentage of the each soap. The soaps were plotted on a separate graph based on their color. The purpose is to distinguish similar colors of soap from each other based on their varying reflectance over the light spectrum of 400–1000 nm. The graph shows absorbance versus wavelength for the green soaps.*



(a) visible light (b) ultraviolet light (c) infrared luminescence

FIG. 2—*The use of the Video Spectral Comparator® aids the examiner in differentiating between like colors. The first is a photo taken from visible light, the second is with ultraviolet light, and the last is soap under an illumination of 400–540 nm, (a) visible light, (b) ultraviolet light, (c) infrared luminescence.*

would be difficult to separate. Using an UV source (Fig. 2*b*), the soaps can be partially distinguished based on their respective fluorescence properties. Another way to view the soaps is under light of specific wavelengths. Using the VSC, a bandpass filter of 400–540 nm illuminated the sample and a longpass filter allowed only excited light greater than 590 nm to enter the camera lens (Fig. 2*c*). Using these types of illumination and filters, the soaps are distinguishable based on their luminescence at specific wavelengths.

SPME-GC/MS

The total ion chromatograms (TIC) of the soaps were obtained and compared. All 68 soaps displayed distinguishable profiles that separated them from one another. For each chromatogram, the peaks mark the respective retention times and associated VOC that collectively represent the profile for a particular soap. Using the chromatograms obtained from the direct sampling of the soaps, a database was created using the five strongest peaks from each soap. Representative TICs from two of the soaps (designated numbers 16 and 17) are shown in Fig. 3. A library search using the NIST MS Search® 2.0 program was used to indicate the probable chemical structure of each peak (note that standards of known compounds were not simultaneously analyzed to verify the structural identity of any of the listed components found in the soaps).

The chromatograms from these two soaps are different, indicating that the SPME method was effective in separating them, even though they were produced by the same manufacturer. Based on the library search, although both soaps contained many common components, the main peaks were diagnostic.

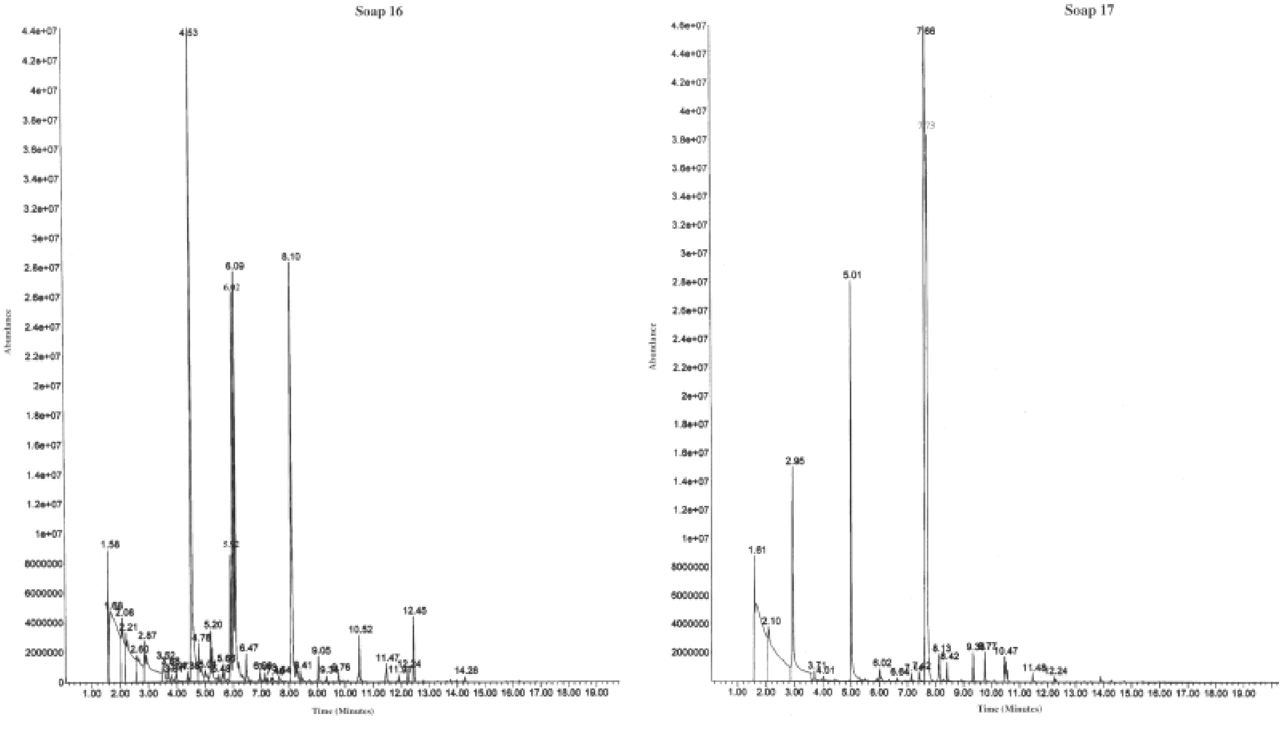


FIG. 3—*Chromatograph results for soaps 16 and 17. Although they are from the same manufacturer, they are distinguishable based on their solid-phase microextraction gas chromatography coupled with mass spectrometry profile.*

Generally, when comparing the chromatographic profiles of fresh soaps, it was relatively unproblematic to interpret the results. In most cases, a dominant peak from the TIC was initially identified and compared with other chromatograms that contained the same peak with a similar retention time. The list of possible matches was then reduced, and further comparisons could be made by identifying the remainder of the more prominent peaks in the TIC.

There were, however, concerns about the reproducibility of the results, i.e., how the VOC profiles would change over time if a piece of soap was left exposed to the environment, and whether a VOC analysis of soaps was feasible when multiple samples were submitted as a mixture. The authors did address these concerns. Random samples of the fresh soaps were analyzed multiple times using the SPME-GC/MS method and the results were found to be reproducible. After leaving samples of soap exposed to the ambient environment, subsequent TIC profiles indicated diminished intensities of some of the peaks. To overcome this effect, small pieces of the soaps were crushed, placed in a capped GC vial, and allowed to stand for an extended time (*c.* 30 min). The crushing and containment of the soaps did facilitate the release of volatile and semivolatile components, and hence, a chromatographic profile with more intense peaks. In choosing a storage method, it is important to understand that volatiles are constantly escaping from the soaps; the appropriate storage step should serve to minimize this loss. All samples in this study were stored in sealed glass containers, which led to simple and reliable handling.

Two observations were made after leaving some of the soaps exposed to the environment. First, soaps that were translucent generally indicated a greater relative decrease in their VOC constituents compared with some of the other colored soaps. The general consistency of the translucent soaps in this study was similar, allowing the authors to speculate that the volatiles in these soaps escape more readily. Second, fragrant soaps presented a different dilemma. These soaps are generally sold for the purpose of providing a pleasant odor, releasing an "aroma-type" scent, which results in a strong VOC profile. As expected, samples from a fresh bar of soap with a strong odor had significantly different GC profiles when compared with corresponding samples that had been exposed and emitted a diminished odor. Fortuitously, the strong fragrant soaps in this study usually possessed a "rare" or unique constituent (relative to the other products), which proved to be a diagnostic indicator component when comparing the soaps.

It was observed that the chromatographic profiles of an individual soap may become altered if that soap is analyzed as part of a mixture of two or more soaps. This behavior was observed in several instances (upon comparison of the individual profiles with those of known standards), although many of the principal components from the individual soaps were still present and identifiable. As a result, it was determined that performing qualitative assessments of both prominent and "rare" components is a reliable method for identifying an unknown material that is suspected to have originated from a bar of soap. Although not utilized in this study, perhaps a principle components analysis (PCA) could be used to classify the compounds found in the various soaps. PCA, a multivariate statistical technique, has proved to be useful by some researchers when making comparisons of clusters of data (13,14).

SEM/EDX Analysis

The SEM/EDXA results for the soaps are summarized in Table 2. For the 46 soaps examined, the elemental compositions generally fell into three broad groups. Soaps in Group "A" (consisting of 32 soaps) all contained carbon (C) as the predominant element (100% full scale by relative peak height) with lesser quantities of sodium (Na) [45–75%] and oxygen (O) [25–47%], all relative percentages to the predominant peak. Traces of aluminum (Al) [0–13%], chloride (Cl) [0–10%], and titanium (Ti) [0–5%] were also observed.

TABLE 2—*Forty-six of the soaps that were analyzed by SEM/EDXA for differing elemental composition.*

Soap #	C	O	Na	Al	Cl	Ti	S	Mg	Si
Group A									
1	100	40	67	tr	tr	tr			
5	100	35	53	tr	tr	0			
6	100	35	60	8	6	tr			
7	100	47	60	10	7	0			
8	100	35	50	tr	tr	0			
10	100	36	56	7	6	0			
11	100	35	70	tr	6	0			
12	100	31	63	0	tr	0			
13	100	30	60	6	7	0			
14	100	25	45	tr	tr	tr			
15	100	35	68	10	10	0			
16	100	30	70	8	0	0			
17	100	40	67	tr	8	0			
18	100	33	63	tr	tr	tr			
19	100	30	55	tr	tr	tr			
20	100	35	58	tr	tr	tr			
21	100	35	70	tr	tr	tr			
24	100	35	65	0	tr	tr			
25	100	37	70	tr	tr	tr			
26	100	35	60	tr	tr	0			
28	100	27	61	tr	tr	0			
29	100	26	55	0	tr	0			
30	100	30	67	0	7	0			
31	100	45	70	13	tr	tr			tr
32	100	30	70	10	6	tr			
33	100	28	63	tr	tr	0			
34	100	40	60	tr	0	0			
35	100	25	75	7	5	0			
38	100	39	73	0	0	0			
39	100	30	62	tr	10	tr			
40	100	42	63	tr	tr	tr			
41	100	33	65	0	tr	0			
Group B									
2	100	85	56	tr	tr	0	22		
3	100	85	54	tr	tr	0	25		
4	100	88	83	0	0	0	78		
9	85	100	90	10	tr	0	87		
22	67	83	100	0	tr	0	55		
23	92	65	100	tr	tr	tr	38		
42	100	74	60	tr	tr	0	50		
43	100	97	89	0	tr	tr	93		
44	79	70	79	22	8	tr	100		tr
45	98	93	92	tr	0	0	100		
46	86	100	73	28	tr	tr	85		27
Group C									
27	60	75	60	tr	tr	tr	100	28	35
36	100	45	85	tr	22	tr	33	32	30
37	100	45	87	tr	19	tr	33	25	23

Approximate relative percentages were assigned to each element. The soaps were grouped into three categories, each dependent upon their elemental composition.

tr, ⩽5%.

SEM/EDXA, scanning electron microscopy-energy-dispersive X-ray analysis; C, Carbon; O, oxygen; Na, sodium; Al, aluminum; Cl, chlorine; Ti, titanium; S, sulfur; Mg, magnesium; Si, silicon.

Soaps in Group "B" (11 soaps) contained significant amounts of C [67–100%], O [70–100%], Na [54–100%], and sulfur (S) [22–100%], with varying (lesser) amounts of Al [0–28%], Cl [0–8%], and Ti [0–5%]. It is noted that one soap (soap 46) also contained 27% silicon (Si). The three soaps comprising Group "C" (soaps 27, 36, and 37) contained significant quantities of C [60–100%], S [33–100%], Na [60–87%], and O [45–75%]. In addition to these elements, moderate levels of Magnesium (Mg) [25–32%] and Si [23–35%] were also detected, as well as traces of Al and Ti.

The sources of the inorganic constituents detected can be attributed to a number of commercial additives in the soap-making process (15–17). Sodium can originate, for example, from "soda" soaps (Na^+ cation of the carboxylate moiety), sodium carbonates/sulfates (softeners), and sodium lauryl sulfate (wetting agent/detergent), among other materials. Aluminum "zeolites" (softeners) and kaolin (aluminosilicate fillers), titanium dioxide (pigment, opacifier, filler), NaCl (precipitating agent), sulfur (sulfate softeners, antibacterials), Mg (hardeners), sand and pumice (exfoliants), and various silicates (water retention, fillers) are also among common soap additives.

It is noted that the EDXA data for the soaps represent semiquantitative comparisons based on the relative peak heights of their elemental constituents. The spectra were collected under identical instrumental conditions as described above. The qualitative and relative ratios of the (nonvolatile) constituents would be expected to remain reliable indicators of the elemental profiles for these and other commercial soap products.

"Semiblind" Study

Most, if not all, of the "unknown" soaps can be readily identified based on the correlation of their respective GC/MS profiles (i.e., the retention times of the five strongest peaks and their characteristic mass spectra) with corresponding "original" profiles (from standards) stored in the database. Additional "rare" constituent peaks were also matched, which served to eliminate chromatograms with "similar" patterns, but lacked the unique diagnostic component. All 10 of the randomly chosen samples were correctly identified in this manner. The soaps that were chosen were immediately stored in sealed vials after sampling and are considered relatively fresh, as the emitting vapors were contained.

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The IR spectra of the thirteen bar soaps consistently contained peaks at or near 1561 cm^{-1} and triplet peaks between 1469 and 1420 cm^{-1} (Fig. 4). These peaks represent carboxyl groups, generally sodium carboxylate moieties, with long hydrocarbon chains, and are indicative of bar soaps (Bartolo R, Procter and Gamble®, Cincinnati, OH). By comparison, the IR spectra of some popular synthetic laundry detergents (ionic sulfonates/sulfates) do not contain these peaks (Fig. 5). The presence of the ionized carboxyl groups in laundry detergents would render the detergents less soluble in hard (Ca^{2+}-, Mg^{2+}-containing) water, thereby diminishing their cleaning power.

Some of the bar soaps exhibit relatively simple IR spectra below 1420 cm^{-1} (Fig. 6). However, other soaps (Fig. 7) have more complicated spectra in this region and their spectra are different, indicating that some bar soaps can be distinguished by FT-IR analysis. The differences may be attributable to the various constituents found in certain soaps, including oleate salts (hardeners/softeners), antibacterials, emollients (e.g., shea, cocoa butter), sequestrants (chelating molecules), and particular formulations of natural fats or glycerides selected for different commercial brands. Numerous "specialty" soap types (e.g., toilet, marine, curd, mottled, yellow, settled, medicated, etc.) can introduce even more unique additives into the basic soap composition.

The IR spectrum of an unknown particle from the belt in the homicide case contained a peak at 1559 cm^{-1} and triple peaks between 1420 and 1469 cm^{-1}, indicating that it was from a bar soap (Fig. 8). However, except for these peaks, the unknown spectrum did not contain any other peaks that were similar to those in any of the spectra from the 13 known bar soaps.

Following an examination, it may be determined that an unknown substance possesses physical and chemical properties that are consistent with bar soap. Indeed, forensic examiners should be aware of the chemical differences between soap and synthetic detergent products, as discussed, if an opinion is to be rendered in a written report, keeping in mind the differences in the legal def-

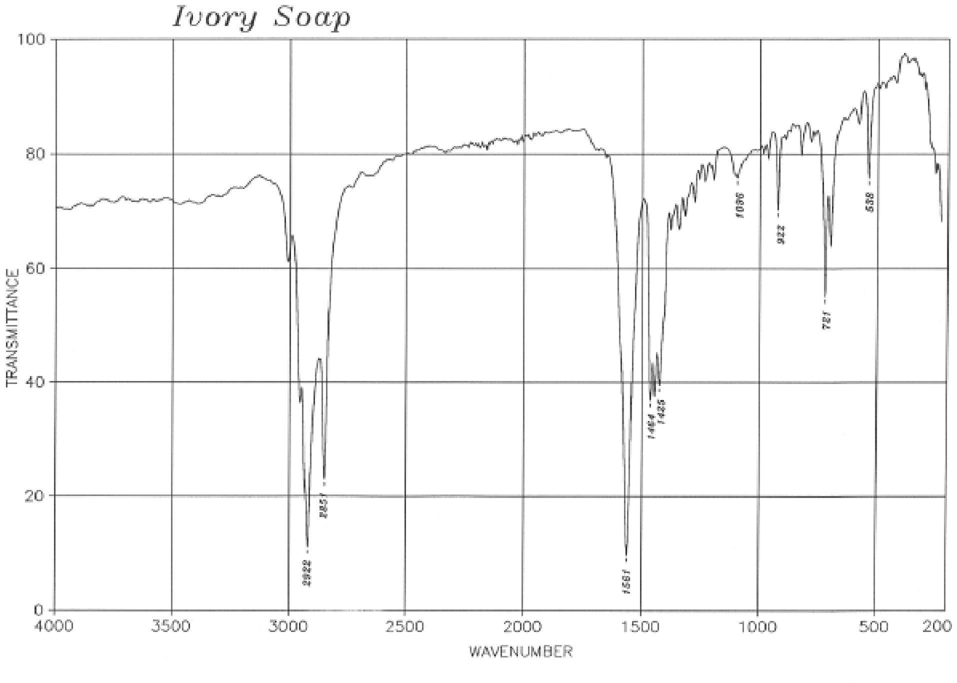

FIG. 4—*Example of an Fourier transform-infrared spectrum characteristic of bar soap, containing a peak at 1561 cm^{-1} and a triplet peak between 1469 and 1420 cm^{-1}.*

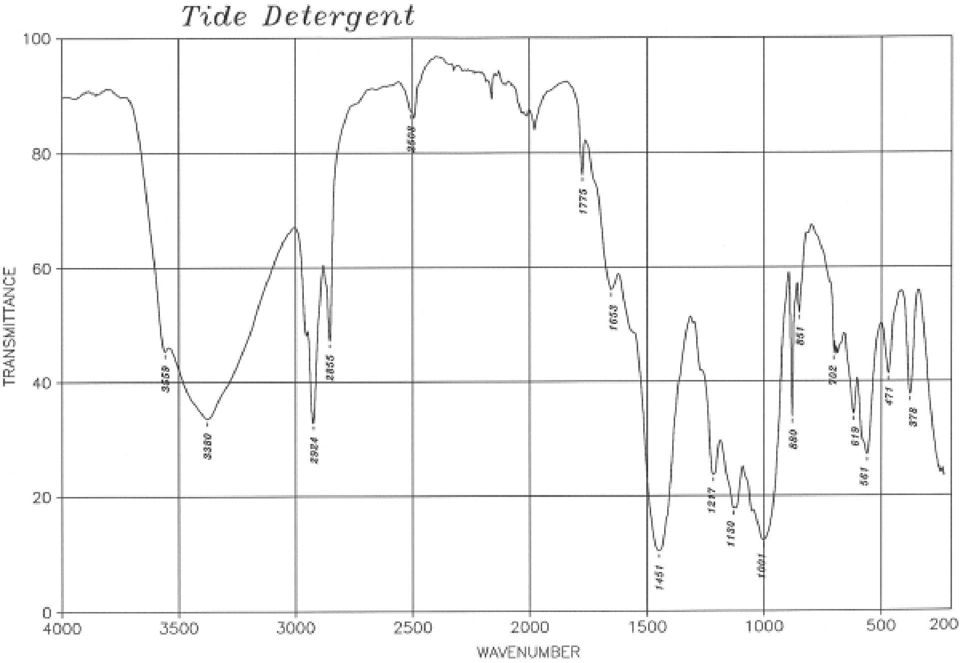

FIG. 5—*Example of an Fourier transform-infrared spectrum characteristic of laundry detergent, lacking the peaks commonly found in bar soap.*

initions of soaps by the different regulatory agencies (the CPSC and the FDA).

Conclusions

Two separate studies were conducted using various analytical protocols to characterize a variety of commercial bar soaps. The TIC of 68 soaps were different enough to distinguish the specimens from one another. Sampling soaps directly from the bar yielded the greatest number of diagnostic peaks. In cases where the soap samples had been previously cut into pieces and subsequently exposed to an open environment, the resulting chromatographic profiles of the VOC were significantly diminished, i.e., smaller peak areas. It was found that crushing the soap pieces and placing them into sealed vials had yielded increased peak intensities (likely due to the exposure of large surface areas with subsequent release of more volatiles). When comparing the chromatographic profiles of questioned and known soaps, it is more important to rely on qualitative similarities and differences rather than relative peak heights, especially if the questioned soap(s) has been exposed to an open environment. In some cases, physical and optical examinations can be extremely

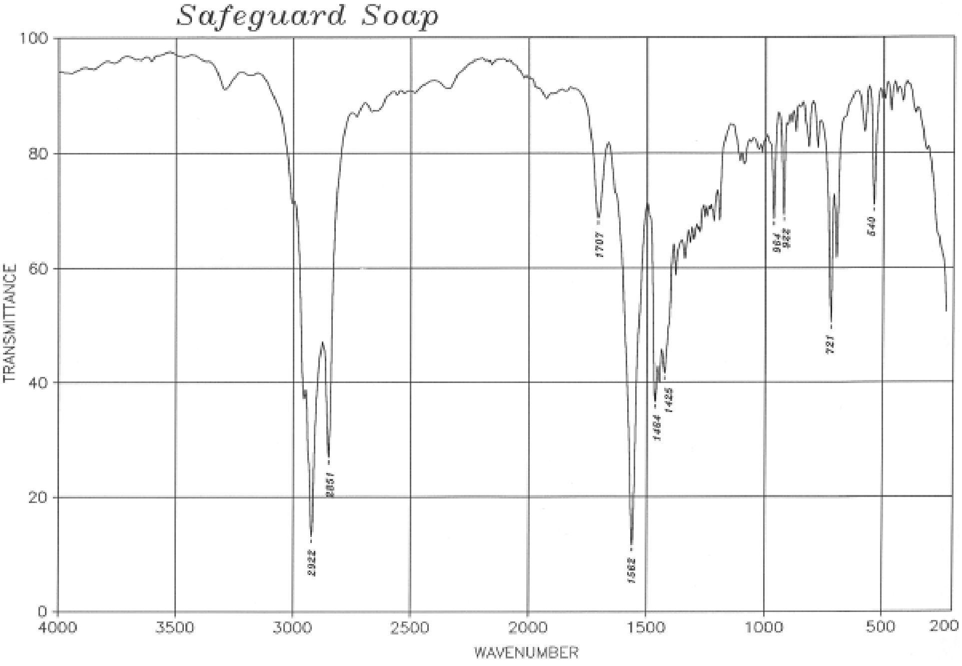

FIG. 6—*Example of an Fourier transform-infrared spectrum of bar soap that has simple spectra below 1420 cm^{-1}.*

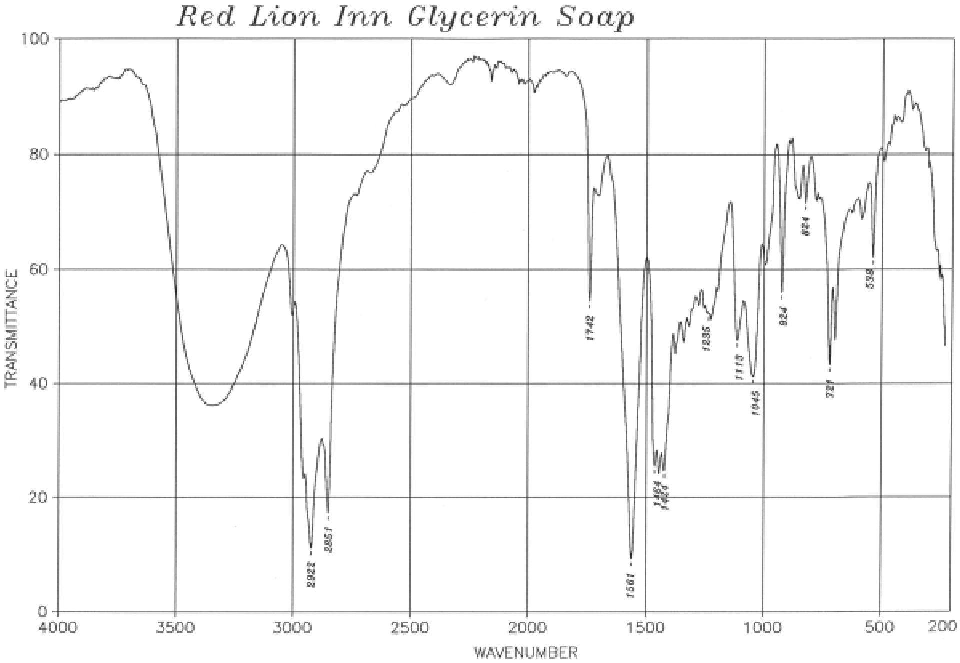

FIG. 7—*Example of an Fourier transform-infrared spectrum of bar soap with more complicated spectra below the 1420 cm^{-1} region.*

beneficial as presumptive screening methods, particularly if the submitted specimen is suspected of being a mixture of different soap particles.

SEM/EDXA also proved to be a useful method for categorizing soaps into three broad groups. One of the groups was comprised of three soaps that contained significant levels of Mg and Si, elements that were not present together in any of the other soaps examined. Further studies utilizing SEM/EDXA, including a more quantitative examination of the inorganic elemental constituents, are warranted. Such studies are expected to yield broader classification schemes for the soaps.

FT-IR spectroscopy can be used to differentiate some brands of commercial bar soaps and it can assist in distinguishing these soaps from typical laundry detergents. In the homicide case discussed in this paper, the FT-IR spectrum of a small particle on the belt contained peaks that were indicative of carboxylate groups, which identified the primary surfactant component of bar soaps. While the particular brand of soap from which this particle likely originated could not be determined, the finding, in conjunction with DNA and blood stain evidence, assisted in the investigation and prosecution of the suspect.

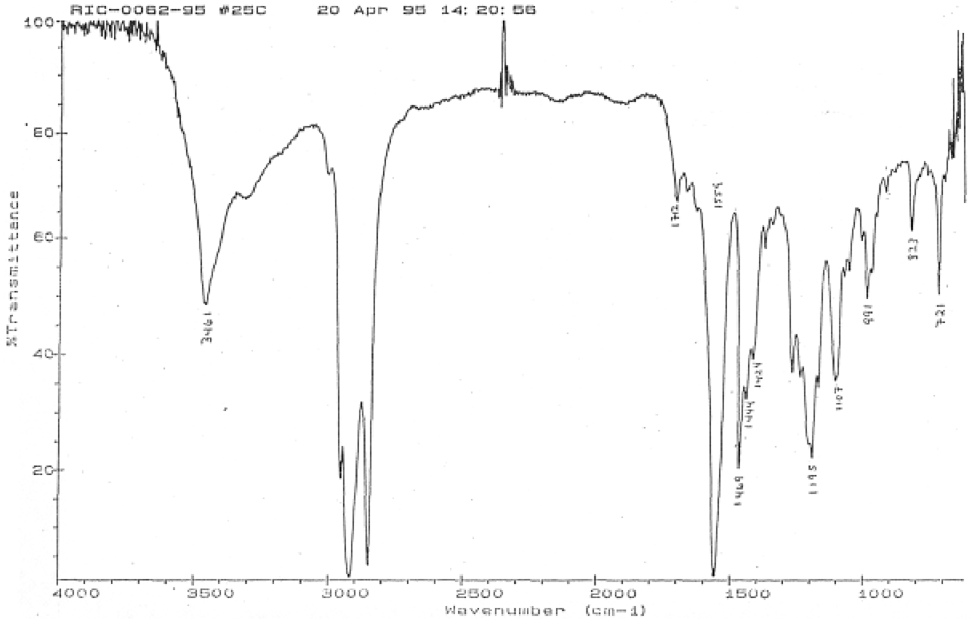

FIG. 8—*Fourier transform-infrared spectrum of an unknown particle from the belt in the California Department of Justice homicide case, containing a peak at 1559 cm^{-1} and triplet peaks between 1420 and 1469 cm^{-1}.*

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