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Sara C. McNorton,[1,†] *M.S.; Guy W. Nutter,*[2] *B.S.; and Jay A. Siegel,*[3] *Ph.D.*

The Characterization of Automobile Body Fillers*

ABSTRACT: Body fillers are sometimes encountered with paint evidence from hit-and-run accidents. Little forensic research has been conducted and published on the subject since 1986. The objective of this study was to determine if chemical and physical differences in body fillers from various manufacturers existed and could be identified. Thirty-three samples of light-weight automobile body fillers and spot putties were obtained. The fillers and putties were compared using light microscopy, infrared spectroscopy, scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX), and pyrolysis gas chromatography (pyGC). Results from fourier transform infrared spectroscopy analysis placed the samples into five groups and differentiated six samples. Light microscopy placed the samples into one of five color groups. PyGC placed the samples into three groups and differentiated one sample. SEM-EDX placed the samples into four groups and differentiated 13 samples. Using these analysis methods, 19 of the 33 samples could be discriminated. The best discriminatory tool was found to be SEM-EDX.

KEYWORDS: forensic science, criminalistics, trace evidence, automobile body filler, body filler analysis, spot putty analysis, infrared spectroscopy, gas chromatography, scanning electron microscopy

Automobile body fillers are used in repair shops to aid in fixing minor body damage. Because the bond between the filler and the body of the car is relatively weak, pieces of filler are usually transferred along with adhering paint chips in traffic accidents (1).

The majority of body fillers that were used in this study were comprised of five main components: polyester resin, talc, styrene, titanium dioxide, and glass/silica bubbles. The polyester resin is a proprietary formulation determined specifically by the manufacturer; it comprises the majority of the filler. Talc is added to aid in the sanding process. Styrene cross-links with the polyester resin when the hardener (comprised mainly of benzoyl peroxide) is added, producing a 3-dimensional polymer. Titanium dioxide increases the opacity of the hardener and gives a visual indication of the uniformity achieved when the hardener and filler are being mixed (1). Finally, "lighteners" may be added which decrease the density of the final product; examples of these low weight, high volume lighteners are quartz, silica, and glass bubbles (3).

The spot putties that were examined were comprised of a wider variety of ingredients. The two components that were seen in all of the spot putties were talc and xylene. The talc, as mentioned above, aids the sanding. Xylene is used as a solvent to keep the spot putty in a liquid form until it is used.

The light-weight brands of body fillers are used most commonly because of their use in repairing damage to the metal in automobiles. Heavier degrees of fillers are commercially available, but are mostly used to repair damaged plastic parts; therefore, they were not used in this study. When mixing the body fillers with hardeners, most body shop personnel make no precise measurements of the proportions used. The body filler is laid out and a strip of hardener is mixed into it. The hardeners add color to the finished body filler, and are a potential source of variation in the final color of the cured body filler. Although some body shops contacted for this study are now replacing entire damaged vehicle parts, a substantial amount of fillers and putties are still used to repair automotive body damage (FinishMaster and Collex, personal communication).

The purpose of this project was to propose an analysis scheme for unknown body filler or spot putty samples and to determine if variations in body filler ingredients from different manufacturers could be detected. The goal of this study was to classify the fillers and putties into the smallest number of groups as possible with an analysis scheme comprising multiple analysis tools. In the past 15 years with advances in technology, product compositions have potentially changed. No studies have been done in the United States on attempting to characterize body fillers and spot putties and the authors wanted to start a new study which incorporated as many different body fillers and spot putties as could be found commercially (see Table 1). The information from this study will fill a void in the literature on automotive body fillers and spot putties.

A literature search for papers relating to vehicle body fillers found only three articles. Cleverley (2) in New Zealand determined that the brand of the filler could be determined by examining the color and infrared spectrum of 12 body fillers. In 1980, Home et al. studied the automobile body fillers from Britain by comparing the results obtained through color, pyrolysis gas chromatography (pyGC), and X-ray fluorescence analysis to provide a scheme for their analysis (1). Most recently in 1986, Walsh et al. looked at 37 different formulations of body filler available in New Zealand from 12 different manufacturers and surveyed them using scanning electron microscopy–energy

[1]School of Criminal Justice, Michigan State University, East Lansing, MI 48824.
[2]Trace Evidence Unit, Michigan State Police Crime Laboratory, Northville, MI 48167.
[3]Forensic & Investigative Sciences Program, IUPUI, Indianapolis, IN 46202.
[†]Present address: 3544 Innerkip Cres., Windsor, ON, Canada N8W 5V1.

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TABLE 1—*The body fillers and spot putties used for the analysis.*

#	Manufacturer	Product Name
Body Filler		
1	U.S.C.	Quality Light-Weight Feather-Rite
2	U.S.C.	Premiere Light-Weight
3	U.S.C.	Basecoat/Clearcoat Extra
4	U.S.C.	Lightweight Kromate Light
5	3M	Light-Weight
6	Marson	Body Light
7	Bondo	Body Filler
8	Marson	White Fill
9	Marson	Platinum Premium Light-Weight
10	Marson	Golden Extra
11	Evercoat	Rage Gold
12	Evercoat	Light-Weight
13	Evercoat	Chrome-A-Lite
14	Evercoat	Rage
15	Evercoat	Z-Grip
16	Evercoat	Tack Free
23	Dupont	Final Fil
24	Dynatron	Ultimate Premium Light-Weight
25	Dynatron	Ultragrip
26	U.S.C.	Easywhite Lite
27	U.S.C.	Blue Ice
28	3M	Premium Body Filler Gold QBA
32	3M	Zebra Tack Free Light-Weight
33	3M	Premium Light-Weight
Spot Putty		
17	PPG	Red Oxide
18	Evercoat	Ever-Glaze and Spot Putty
19	Bondo	Glazing & Spot Putty
20	Nitrostan	Red Spot & Glayze Putty
21	Dynatron	Glazing & Spot Putty
22	3M	Acryl Green Spot Putty
29	Marson	Spot & Glazing Putty
30	Nitrostan	Green Spot Putty
31	Nitrostan	Grey Spot Putty

dispersive X-ray spectrometry (SEM–EDX), visible microspectrophotometry, infrared spectrometry (IR), and density. Nearly all of the samples of the different formulations could be discriminated using this analysis scheme (3).

Four different analysis techniques were chosen based on their likelihood of utility for analyzing body filler and spot putty samples; these techniques are also commonly found in forensic laboratories. Stereomicroscopy was employed to examine the color and texture of the samples. Fourier transform infrared spectroscopy (FTIR) and pyGC were used to provide a comparison of chemical composition. Finally, SEM-EDX was used to compare elemental composition of the samples.

Methods

Sample Preparation

The manufacturer's instructions were followed in preparation for each of the 24 body filler samples; the instructions called for 2% hardener by weight added to each sample of body filler.

Approximately 1.00 g of body filler was weighed out along with *c*. 0.02 g of hardener. The filler and hardener were mixed together and spread onto a microscope slide. The slide was placed in a fume hood and allowed to dry for at least 30 min.

For the nine spot putty samples, a small amount of the spot putty was placed on a wooden stick and spread onto a microscope slide. The prepared slide was then placed in a fume hood and allowed to dry for at least 30 min at room temperature.

Fourier Transform Infrared Spectroscopy

The Perkin-Elmer Spectrum One FTIR Spectrometer with Spectrum Spotlight FTIR Imaging System (Perkin-Elmer Life and Analytical Sciences, Inc., Wellesley, MA) was used for preliminary studies and to compare the chemical compositions of the body fillers and spot putties.

Aging Study—FTIR Microscope—The purpose of this portion of the study was to determine if the chemical composition of the body fillers and spot putties changed over time. To reduce the number of variables, one brand of body filler was chosen: Bondo. The sample was prepared according to manufacturer's directions. At specific time increments, a small amount of the body filler was scraped off the slide, flattened, and placed onto an FTIR salt plate for analysis. Samples were collected at the following intervals: 30 min (estimated drying time as suggested by the manufacturer), 60 min, 24 h, and 5 weeks.

The spectra were analyzed to compare peaks and to determine if any of the spectra changed over time. The sample of Bondo was stored at room temperature, between the time intervals. It was determined that there was no continuous trend of change as the samples aged at room temperature.

Hardener Study—FTIR Microscope—The purpose of this portion of the study was to determine if chemical differences existed between the different colors and manufacturers of the various hardeners used in body filler preparation. Each of the 19 hardeners was prepared by spreading a thin layer onto a microscope slide with a wooden stick. The hardeners were allowed to dry by placing them in the fume hood at room temperature for 24 h. To prepare the hardener for analysis, a small amount was scraped off the slide, flattened, and placed on an FTIR salt plate. Three different locations were scanned on each hardener sample and the spectra obtained were compared.

By comparing the spectra, the hardeners could be separated into seven groups. Next, one hardener from each group was mixed with Bondo body filler, and allowed to dry in the fume hood. Once dry, a small amount was scraped off, flattened, placed on the salt plate, and analyzed with the FTIR microscope.

Results indicated that there was no change in chemical composition found when Bondo was mixed with any of the hardeners.

Sample Analysis—FTIR Bench—Each of the 33 body filler and spot putty samples was made into KBr pellets and run on the FTIR bench. The samples were prepared for analysis as follows: a 0.5×0.5 cm^2 of the sample was removed from the microscope slide and placed into a mortar. Approximately 1.0 g of KBr was added and ground in with the sample using a pestle. A small amount was placed into a press and a pellet was made. The pellet was placed into the FTIR holder and placed into the instrument. Sixteen co-added scans of each sample were collected from 4000 cm^{-1} to 450 cm^{-1} with a resolution of 4 cm^{-1}.

The spectra from the 33 samples analyzed on the FTIR bench were collected, compiled, and entered into a database. Future samples could then be run and compared against these standards.

Visible Microscopy (Stereoscope)

Each sample was selected and examined on the microscope slide on which it had been prepared using a Leica MZ7[5]

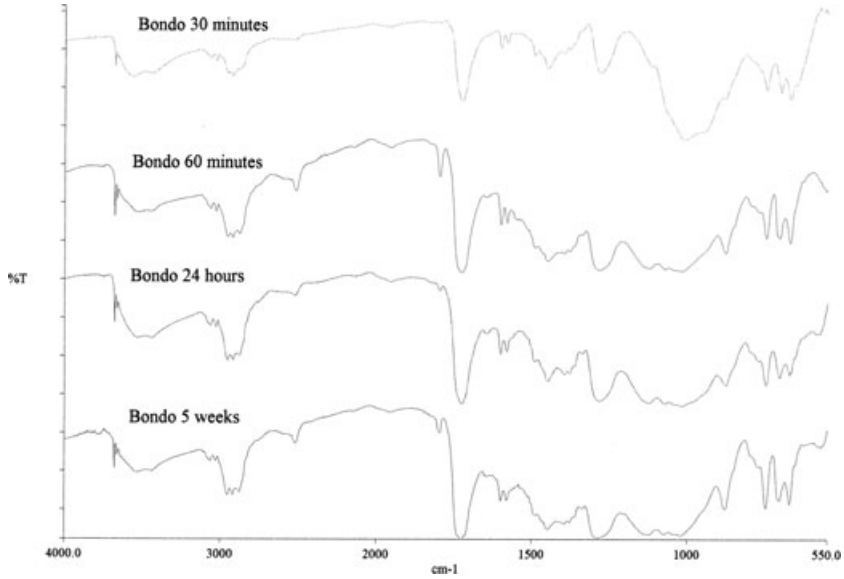

FIG. 1—*Fourier transform infrared spectroscopy (FTIR) spectra result from aging study, showing Bondo at four different drying time intervals.*

stereoscope (Leica Microsystems Inc., Bannockburn, IL) under 20× magnification. The color of all of the samples was inter-compared and each was placed into a general color category.

Pyrolysis Gas Chromatography

A pyrolysis apparatus (Chemical Data Systems, Brockville, ON) with an Agilent 5971 Gas Chromatograph (Agilent Technologies, Foster City, CA) was used for comparing the organic components of each of the 33 body filler and spot putty samples. The following method was employed: pyrolysis at 800°C for 20 sec, followed by 65°C for 2 min then 15°C per minute to 280°C, then hold for 4 min. Interface temperature was kept at 250°C. Each of the samples was run twice through this method. To guard against contamination, blank runs were performed after every eight samples, and the method was designed to have long holds at the final temperature before the next sample was analyzed. The spectra were compared by checking for reproducibility and similarities and/or differences amongst the samples.

SEM-EDX

A Zeiss DSM 960A SEM with an Oxford ISIS EDX (Carl Zeiss SMT Inc., Thornwood, NY and Oxford last, Concord, MA) was employed to analyze the elemental composition of the body fillers and spot putties. An accelerating voltage of 25 kV and working distance of 10 mm was used with a 100-sec acquisition time. Thin peels were taken from each sample and mounted on carbon tape on aluminum SEM mounts. In addition to each of these samples, the samples used in the hardener FTIR study were also mounted and analyzed to determine if different colored hardeners would have different elemental compositions in the final product.

Spectra were collected from large areas of each thin peel to obtain an accurate average composition. The results of large area scans were used to categorize samples based on their elemental composition.

Results

Fourier Transform Infrared Spectroscopy

Aging Study—No changes in chemical composition were detected by the FTIR as the samples aged at room temperature. The spectra for all of the samples did not differ significantly from each other (see Fig. 1). This suggests that drying time past 30 min does not affect IR spectra.

Hardener Study—The 19 hardeners in this study were arbitrarily numbered and could be classified by color (pink, blue, and red). All of the pink hardeners could be considered one group, with similar spectra. The blue hardeners were further subdivided into four groups and the red hardeners into two groups. This resulted in the discrimination of seven different groups of hardeners from the 19 original samples based on their FTIR spectra (see Table 2).

TABLE 2—*The hardeners tested in the hardener study, showing their groupings.*

Hardener Number	Hardener Color	Group
6	Pink	1
15	Pink	1
17	Pink	1
1	Blue	2a
13	Blue	2a
7	Blue	2b
3	Blue	2c
12	Blue	2c
11	Blue	2d
2	Red	3a
5	Red	3a
8	Red	3a
9	Red	3a
10	Red	3a
16	Red	3a
18	Red	3a
19	Red	3a
4	Red	3b
14	Red	3b

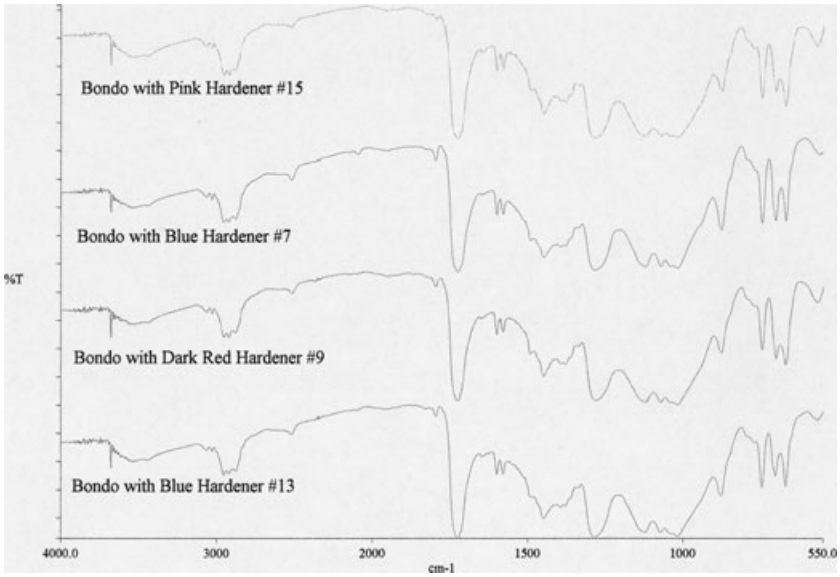

FIG. 2—*Fourier transform infrared spectroscopy (FTIR) representative spectra of Bondo with four hardeners, showing members from hardener groups 1, 2b, 3a, and 2a, respectively.*

No change was found in the chemical composition observed when the Bondo was mixed with any of the seven different hardeners (see Fig. 2). Therefore, one hardener (red) was used to prepare all of the body filler samples for analysis.

Sample Analysis—The results from the FTIR bench analysis of the body fillers and spot putties resulted in the 24 body fillers being categorized into two groups with an additional three samples giving individual spectra and the nine spot putties into three groups with an additional three samples giving individual spectra. This gave a total of five groups comprised of two to 14 members (see Figs. 3 and 4) and six individual spectra. Each sample was classified by peak shapes and locations found in the fingerprint region of the FTIR spectra. More specifically, the most pronounced differences were observed from 1700 to 1200 cm^{-1}, with smaller, but still significant differences from 750 to 500 cm^{-1}. These differences can be attributed to the concentration of calcium carbonate ($CaCO_3$) (high, low, or absent) and the presence or absence of styrene and talc for the body fillers. For the spot putties, these differences can be attributed to the presence or absence of $CaCO_3$ and nitrocellulose as well as the presence or absence of barium sulfate ($BaSO_4$) and talc. This method provided straightforward criteria for classifying the samples.

Visible Microscopy

A stereoscopic examination was done to see if the body filler and spot putty samples could be distinguished by their color alone.

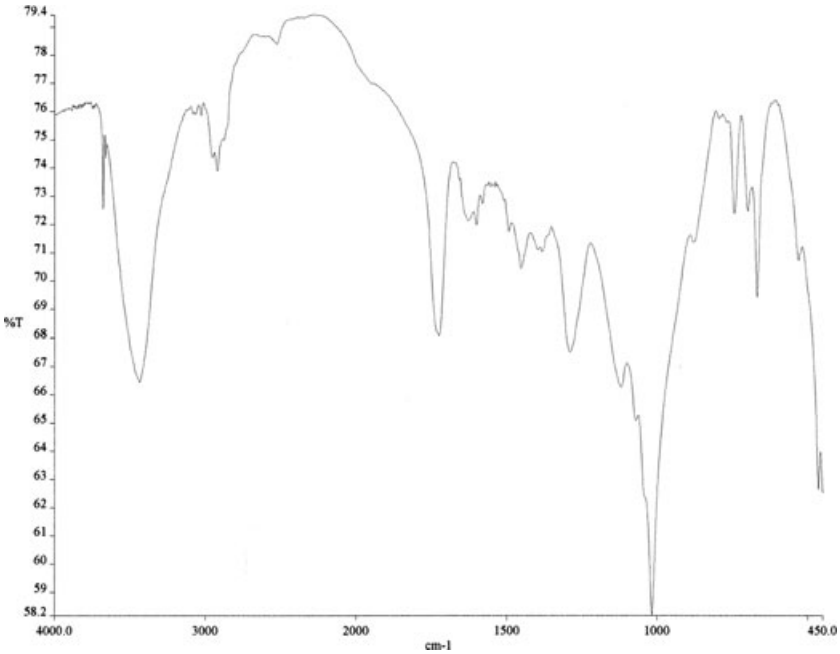

FIG. 3—*Fourier transform infrared spectroscopy (FTIR) representative spectra from group 1.*

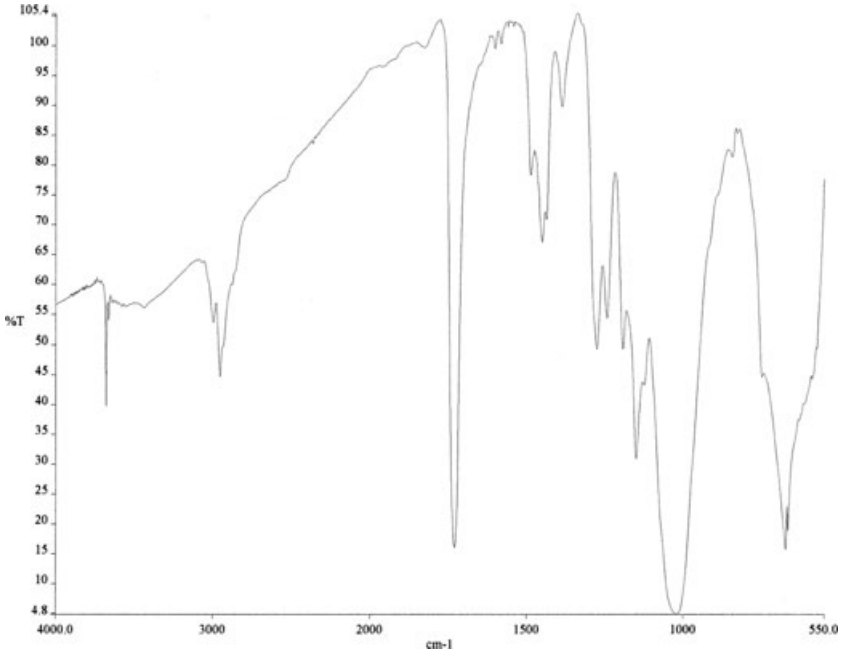

FIG. 4—*Fourier transform infrared spectroscopy (FTIR) individual spectra of 3M acryl green spot putty.*

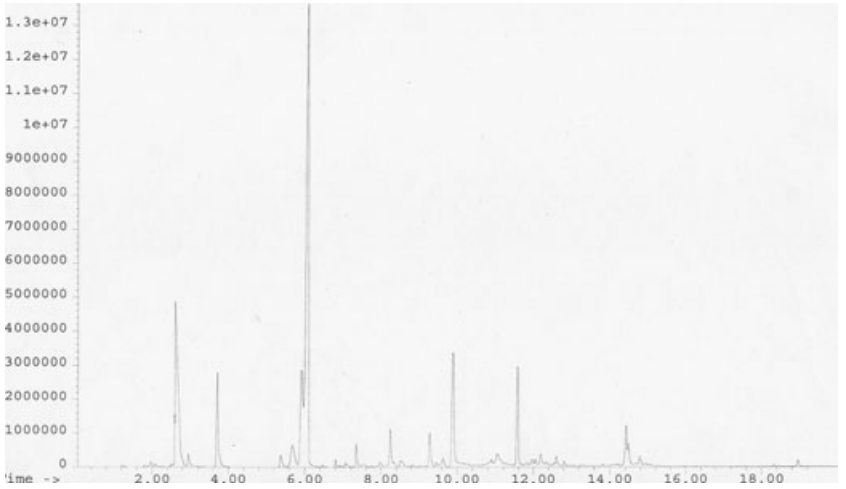

FIG. 5—*Pyrolysis gas chromatography (pyGC) representative chromatograph from group 1B.*

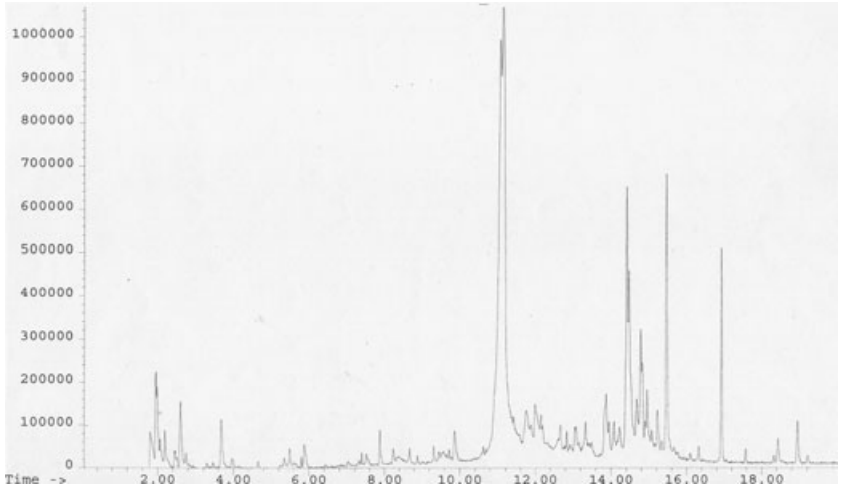

FIG. 6—*Pyrolysis gas chromatography (pyGC) representative chromatograph from group 3.*

TABLE 3—*The composition of the body fillers and spot putties to determine where the inorganic elements could have originated.*

Body Filler Composition	# of Fillers in Which This is Contained (out of 24)
Polyester resin	20
Styrene	23
Talc/nonasbestiform	20
Glass beads/bubbles/microspheres	16
Calcium carbonate	13
Titanium dioxide (TiO_2)	13
Silica	8
Magnesite	3
Zinc phosphate/acrylate/silicon dioxide	2 each
Spot Putty Composition	**# of Putties in Which This is Contained (out of 9)**
Talc	7
Xylene	6
$BaSO_4$/Silica/TiO_2/toluene/alkyd resin/acrylic resin/iron oxide/ nitrocellulose/several alcohols	Various samples

Please note that some fillers/spot putties did not list ingredients.

Body fillers and spot putties look very different from each other: texture and luster make it easy to separate the body fillers from the spot putties. After examining each of the samples under the stereoscope, the body fillers were placed into one of two groups (red-yellow or yellow) and the spot putties were placed into one of three groups (red, green, or grey).

Pyrolysis Gas Chromatography

Pyrolysis gas chromatography placed the body filler and spot putty samples into three groups with one additional sample having a unique chromatogram. Using pyGC, the first group of samples had to be further divided into two subgroups because of subtle differences in the chromatograms. The samples were separated into different groups based on the presence/absence of a peak at 2 min and the sizes and shapes of peaks present at and around 6 min. Although many other peaks were present, these peaks were chosen because they represented the most significant differences between the pyrolysis groups as seen on the chromatograms. Group 1A had similar chromatograms to group 1B except for the presence of a tall peak at 2 min (around 1,500,000 abundance), whereas group

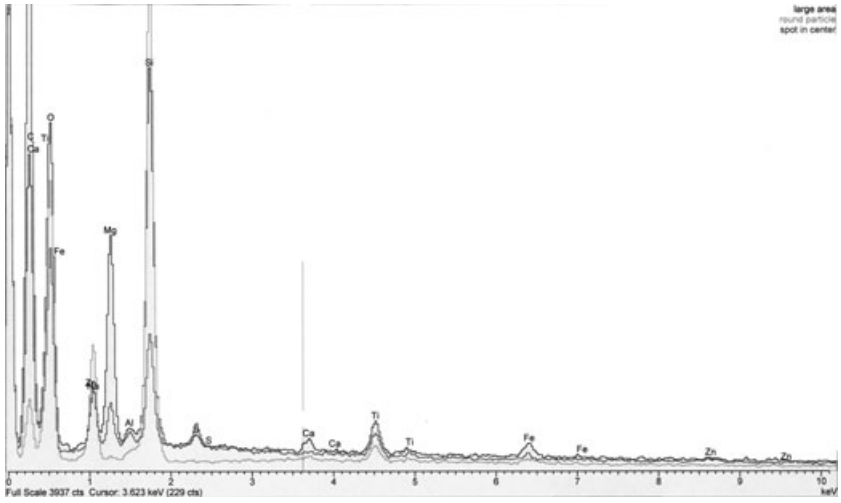

FIG. 7—*Scanning electron microscopy (SEM) representative spectra from group A.*

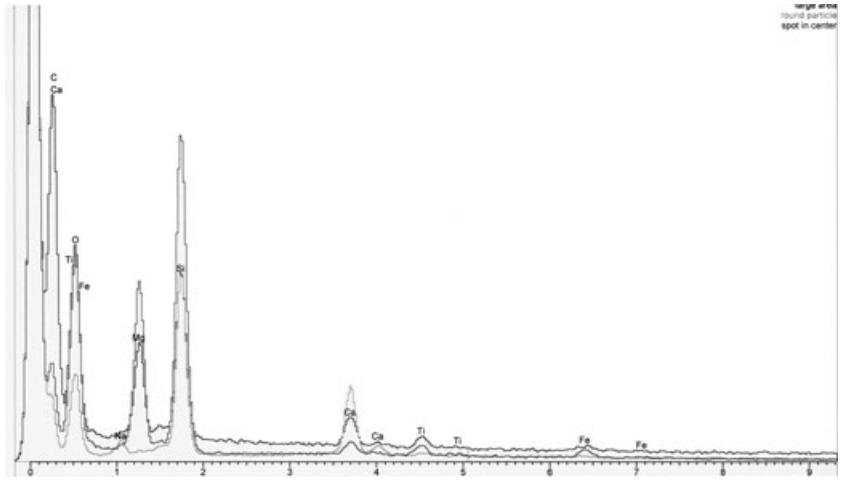

FIG. 8—*Scanning electron microscopy (SEM) representative spectra from group B.*

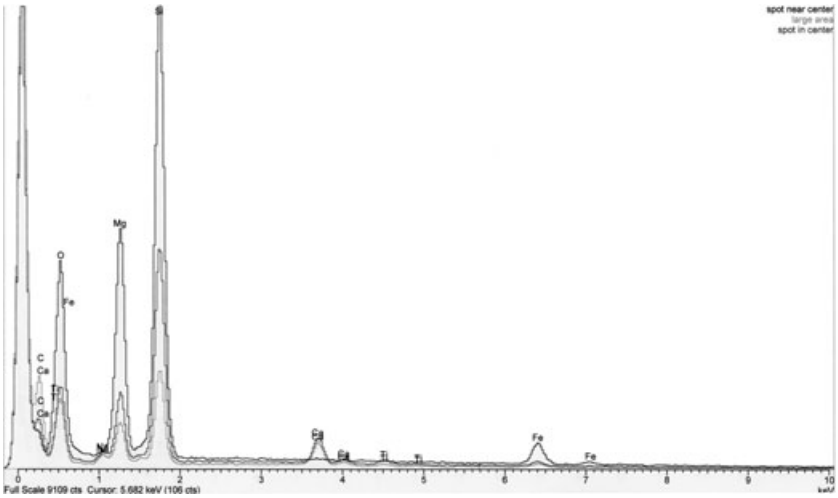

FIG. 9—*Scanning electron microscopy (SEM) representative spectra from group C.*

1B had virtually no or a small peak (<500,000) for the same time interval. The sample that gave the unique chromatogram stood out because of the absence of any significant peak at 2 or 6 min. Group 2 was characterized by the presence of a doublet peak between 6 and 8 min and a small peak at 2 min, whereas group 3 showed multiple peaks at 2 min and a small, single peak around 6 min (see Figs. 5 and 6).

SEM-EDX

The SEM-EDX results were encouraging because this technique did provide significant discrimination of the samples. The majority of the samples (both body fillers and spot putties) had high concentrations of Mg, Si, Ca, Ti, and Fe. Various other elements in low concentration were observed in some of the samples, which helped

TABLE 4—*The results from all the four analysis techniques, showing the groupings for each sample.*

Group #	Filler #	Manufacturer	Stereoscope	PyGC	FTIR Bench	SEM-EDX
Discriminated	1	U.S.C.	Red-yellow	2	1	C
	2	U.S.C.	Red-yellow	1A	Individual	B
	3	U.S.C.	Yellow	1A	2	C
	7	Bondo	Red-yellow	1B	1	Individual
	9	Marson	Red-yellow	1A	1	Individual
	11	Evercoat	Yellow	1A	2	B
	12	Evercoat	Red-yellow	1B	Individual	B
	13	Evercoat	Yellow	1B	2	B
	15	Evercoat	Red-yellow	1B	2	Individual
	23	Dupont	Red-yellow	1A	Individual	Individual
	26	U.S.C.	Red-yellow	1B	1	Individual
	27	U.S.C.	Red-yellow	1A	2	Individual
	28	3M	Yellow	1A	2	Individual
	32	3M	Red-yellow	1B	2	Individual
I	14	Evercoat	Red-yellow	1A	1	B
	33	3M	Red-yellow	1A	1	B
II	24	Dynatron	Red-yellow	1A	1	A
	25	Dynatron	Red-yellow	1A	1	A
III	4	U.S.C.	Yellow	1B	1	C
	6	Marson	Red-yellow	1B	1	C
	8	Marson	Red-yellow	1B	1	C
	10	Marson	Yellow	1B	1	C
IV	5	3M	Red-yellow	1B	1	B
	16	Evercoat	Red-yellow	1B	1	B
	Spot putty #					
Discriminated	17	PPG	Red	3	Individual	Individual
	20	Nitrostan	Red	3	3	Individual
	22	3M	Green	Individual	Individual	Individual
	30	Nitrostan	Green	2	Individual	Individual
	31	Nitrostan	Grey	3	3	Individual
V	18	Evercoat	Red	3	5	D
	29	Marson	Red	3	5	D
VI	19	Bondo	Red	1B	4	D
	21	Dynatron	Red	1B	4	D

TABLE 5—*The results from all four analysis techniques, showing the manufacturer trends.*

Filler #	Manufacturer	Product name	Stereoscope	PyGC	FTIR bench	SEM-EDX
1	U.S.C.	Quality LW feather-rite	Red-yellow	2	1	C
4	U.S.C.	LW Kromate	Yellow	1B	1	C
3	U.S.C.	Basecoat/clearcoat Extra	Yellow	1A	2	C
27	U.S.C.	Blue Ice	Red-yellow	1A	2	Individual
2	U.S.C.	Premiere LW	Red-yellow	1A	Individual	B
26	U.S.C.	Easywhite Light	Red-yellow	1B	1	Individual
7	Bondo	Body Filler	Red-yellow	1B	1	Individual
19 SP	*Bondo*	*Glazing & SP*	*Red*	*1B*	*4*	*D*
11	Evercoat	Rage Gold	Yellow	1A	2	B
13	Evercoat	Chrome-a-lite	Yellow	1B	2	B
14	Evercoat	Rage	Red-yellow	1A	1	B
16	Evercoat	Tack Free	Red-yellow	1B	1	B
12	Evercoat	Lightweight	Red-yellow	1B	Individual	B
15	Evercoat	Z-grip	Red-yellow	1B	2	Individual
18 SP	*Evercoat*	*Ever-glaze SP*	*Red*	*3*	*5*	*D*
23	Dupont	Final Fil	Red-yellow	1A	Individual	Individual
28	3M	Premium Gold QBA	Yellow	1A	2	Individual
32	3M	Zebra Tack Free LW	Red-yellow	1B	2	Individual
5	3M	LW	Red-yellow	1B	1	B
33	3M	Premium LW	Red-yellow	1A	1	B
22 SP	*3M*	*Acryl Green Spot Putty*	*Green*	*Individual*	*Individual*	*Individual*
24*	Dynatron	Ultimate premium LW	Red-yellow	1A	1	A
25*	Dynatron	Ultragrip	Red-yellow	1A	1	A
21 SP	*Dynatron*	*Glazing & SP*	*Red*	*1B*	*4*	*D*
10	Marson	Golden Extra	Yellow	1B	1	C
6*	Marson	Body Light	Red-yellow	1B	1	C
8*	Marson	White Fill	Red-yellow	1B	1	C
9	Marson	Platinum Premium LW	Red-yellow	1A	1	Individual
29 SP	*Marson*	*Spot & Glazing Putty*	*Red*	*3*	*5*	*D*
17 SP	*PPG*	*Red Oxide*	*Red*	*3*	*Individual*	*Individual*
20 SP	*Nitrostan*	*Red Spot & Glaze Putty*	*Red*	*3*	*3*	*Individual*
31 SP	*Nitrostan*	*Grey SP*	*Grey*	*3*	*3*	*Individual*
30 SP	*Nitrostan*	*Green SP*	*Green*	*2*	*Individual*	*Individual*

SP, spot putty; LW, light weight.
*Indicates samples from the same manufacturer that could not be distinguished from others by that manufacturer.

individualize them (see Table 3). Analysis of the samples from the hardener study showed no consistent variation in composition regardless of the color of the hardener used.

The body filler samples could be put into three groups based on elemental composition (group A consisting of two samples, group B consisting of eight samples, and group C consisting of six samples), and eight samples could be identified. The elements detected in Group A consisted of Ca, Ti, Fe, Zn, Na, Mg, Al, Si, and S. Elemental composition of Group B and C was less complex only containing Ca, Ti, Fe, Mg, and Si with Group C also containing Na (see Figs. 7, 8, and 9). Seven body fillers, that were previously indistinguishable by stereoscopic examination, FTIR, and pyGC, were separated by SEM-EDX.

The spot putty samples were either identified or put into one group. The group consisted of four samples all containing only Ca, Fe, Mg, and Si. The samples that could be separated contained various other elements like Ti, S, Al, and Ba. SEM-EDX did not further discriminate the spot putty samples that had already been identified.

Discussion

The purpose of this research was to characterize different body fillers and spot putties by a battery of analytical methods. The primary goal of this study was to create a scheme by which every sample that may be encountered in a crime laboratory could be differentiated using four different analysis techniques. Upon examining the results, it can be concluded that 19 of the 33 body filler and spot putty samples could be discriminated, whereas the rest of the samples could be put into smaller groups of 2–4.

All of the spot putties could be differentiated from the body fillers based on color. The spot putties have vibrant, unique colors, such as green and red, whereas the body fillers are dull colors of red-yellow and yellow.

Based on the data in Table 4, additional conclusions can be reached about spot putties. Five out of nine spot putties can be discriminated using visible microscopy, pyGC, FTIR, and SEM-EDX together (17, 20, 22, 30, 31). The remaining four can be grouped into two groups: 18 and 29 could not be differentiated from each other and 19 and 21 could not be differentiated from each other.

Additionally, 14 out of 24 body filler samples can be discriminated using the four analysis tools from this study (Table 4: 1, 2, 3, 7, 9, 11, 12, 13, 15, 23, 26, 27, 28, 32). The remaining 10 samples were further divided into four smaller groups: 14 and 33 could not be differentiated from each other; 24 and 25 could not be differentiated from each other; 4, 6, 8, and 10 could not be differentiated from each other; and 5 and 16 could not be differentiated from each other. The combination of four different analysis techniques helped to individualize 19 out of 33 samples, while placing the remainder of the samples into smaller groups.

Further analysis can be considered using Table 5 to determine trends within each manufacturer. However, when examining the table, it is noticed that there are no significant trends. It is important to note that the manufacturer Bondo also produces Dynatron

and Marson (FinishMaster and Collex, personal communication). However, the authors feel that these observations from Table 5 do not indicate any specific manufacturer trend.

In conclusion, if all the four analysis techniques are not available to analyze an unknown body filler or spot putty sample, the authors feel that the best discriminatory technique to employ is SEM-EDX. This instrument classified the samples into four main groups while providing individual spectra for 16 samples. The authors feel that analysis tool is the most logical to use because these samples are comprised of mostly inorganic elements.

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Additional information and reprint requests:
Sara C. McNorton, M.S.
3544 Innerkip Cres.
Windsor, ON
Canada N8W 5V1
E-mail: smcnorto@yahoo.com