Electronic Supplementary Material (ESI) for Analytical Methods.

INFRARED AND RAMAN SPECTROSCOPY OF AUTOMOTIVE PAINTS FOR FORENSIC IDENTIFICATION OF NATURAL WEATHERING

Andrey Giovanni Gomes de Oliveira[1*], Ewelina Wiercigroch[2], Juliano de Andrade Gomes[3], Kamilla Malek[2*]

[1]Fundação de Peritos em Criminalística Ilaraine Acácio Arce, Rua das Figueiras, Lote 07, 71.906-750 Brasília, Brazil

[2]Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Krakow, Poland

[3]Instituto de Criminalística, Polícia Civil do Distrito Federal, Setor de Áreas Isoladas, bloco C, 70.610-907 Brasília, Brazil

This supplementary information contains a figure illustrating the natural environment where the impounded vehicles were weathered and the collection of the paint samples took place. It also shows a comparison of optical microphotograph cross sections of samples R1 and W1 depicting original and post-manufacture coatings. Tables describing the assignment of bands of chemical components in automotive paint by using Infrared and Raman spectroscopies. Furthermore, NIR Raman imaging and average spectra recorded on the surface of W1 LD sample as well as a comparison between Vis Raman spectra collected from the R2 LD basecoat and primer surfacer are exhibited.

TABLE S1. Absorption bands in IR spectra characteristic for automotive binder components.

Band position (cm^{-1})	Mode Assignment	Binder Component
700	=C-H deformation of the aromatic ring	Styrene [33]
760	Out-of-plane deformation of the CH	Styrene [33]
815	Out-of-plane deformation of the triazine ring	Melamine [33]
848	Unknown	
991	Unknown	
1090–1050	C-C stretching	Urethane
1170, 1160, 1150	C-O stretching of the ester groups	Acrylic [3, 13, 33]
1218	Amide III – NH and CN vibrations	Urethane [36]
1236	Amide III – NH and CH vibrations	Urethane [36]
1455, 1375	CH bending of the CH_2 and CH_3 groups	Acrylic [3, 26]
1460	Isocyanurate ring stretching	Urethane [33]
1495	Aromatic ring stretching vibrations	Styrene [26]
1525, 1520	Amide II – NH bending and CN stretching	Urethane [22, 26]
1550	In-plane deformation of the triazine ring	Melamine [33]
1605	Amide I – band of primary urethane	Urethane [26]
1690, 1685	Carbonyl C=O stretching	Urethane [21]
1730, 1725	Ester carbonyl C=O stretching	Acrylic [4]
1730	C=O Stretching of the urethane linkage	Urethane [22]
3000–2800	Aliphatic CH stretching	Acrylic/ Urethane [4, 26]
3380	OH and NH stretching	Acrylic/ Urethane [20]

TABLE S2. Changes in the IR profile of the clearcoats of the weathering vehicle MD samples in comparison to the LD samples; ↑: intensity increase, ↓: intensity decrease, –: no change.

Band position (cm^{-1})	Binder Component	W2	R2	S1	S2
700	Styrene	↑	↓	↑	↓
760	Styrene	↑	↓	↑	↓
850	unknown		↓		
990	unknown			↓	
1030	unknown				↓
1090–1050	Polyurethane	↑	↓	↓	
1170–1100	Acrylic	↓	↑	↓	↓
1220	Urethane	↓			
1240	Urethane			↓	
1380	Acrylic	↓	↓	↓	↓
1460–1450	Acrylic, Urethane	↓	↓	–	↓
1525	Urethane	↓	↑	↓	
1575–1545	unknown				↑
1605	Urethane		↓		
1640	Urethane	↓	↓	↓	↑
1690	Urethane	↓		↓	
1725	Acrylic	↓	–	↓	↓
2855	Acrylic/ Urethane	↑	↓	↑	↑
2930–2920	Acrylic/ Urethane	↑	↓	↑	↓
2950	Acrylic/ Urethane				↓
3380	Acrylic/ Urethane	↑	↓	–	red-shift by ca. 100 cm^{-1}

TABLE S3. Raman bands characteristic for automotive binder and pigment components.

Band position (cm^{-1})	Band assignment	Binder/ Pigment Component
609, 446, 238	Ti-O vibrations	Rutile - PW6 [5, 40, 41]
824, 340	Vibrations of CrO_4^- and MoO_4^- anions	Lead chromate molybdate - PR104 [42]
830–720	Ring deformation of benzene	Styrene [5]
900–850	Symmetric C–N–C stretching from secondary amines	Urethane [5]
975	Triazine ring breathing	Melamine [5]
1001	Trigonal ring breathing	Styrene [5]
1031	In-plane aromatic CH deformation	Styrene [5]
1190	C_6H_5–C stretching	Styrene [5]
1305	CH_2 in-phase twisting	Acrylic
1310–1175	CH_2 twisting and rocking vibrations	Acrylic [5]
1449	CH_3 and CH_2 deformations	Acrylic
1602	Ring stretching	Styrene [5]
1603, 1549, 1488, 1361, 1243	C=C, C=N stretching and deformations	Monoazo-PR170 [42]
1730, 1725	Carbonyl C=O stretching	Acrylic [5]
2960–2940	C-H stretching	Acrylic/Urethane [20]
3060	Aromatic CH stretching	Styrene/Urethane [5]

FIGURE S1. Outdoor area where the Civil Police of the Federal District (PCDF) keeps impounded vehicles in Brasília, Brazil.

FIGURE S2. Studied vehicles under natural weathering conditions at the Civil Police of the Brazilian Federal District: A) W1 right door, LD, a) W1 roof, MD, B) W2 left fender, LD, b) W2 front bumper, MD, C) R1 front bumper, LD, c) R1 back bumper, MD, D) R2 front bumper, LD, d) R2 back bumper, MD, E) S1 back bumper, LD, e) S1 hood, MD, F) S2 back bumper, LD, f) S2 right fender, MD. Red arrows indicate a site on the panels from where the paint chips were extracted. W (white), R (red), S (silver) denote colors of the vehicles while LD and MD indicate the degree of damage (less- and more-degraded vehicle paints, respectively).

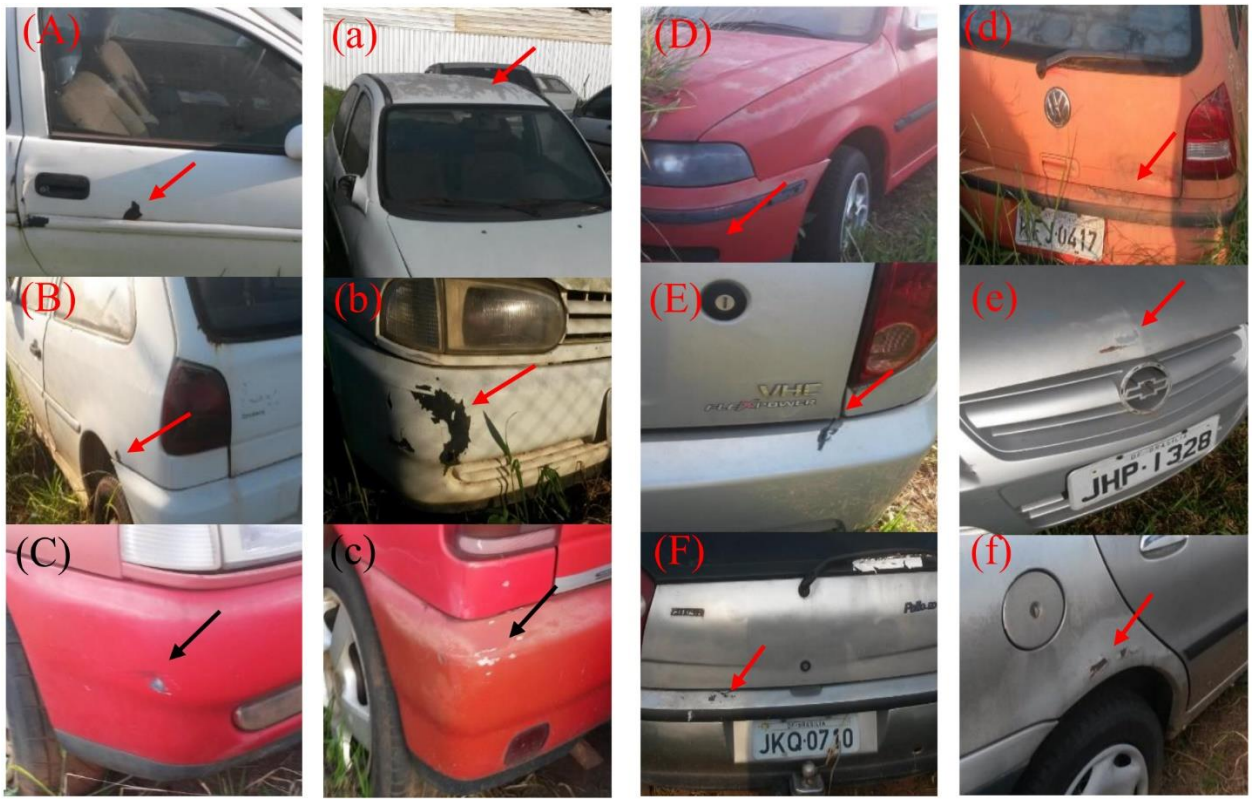

FIGURE S3. Microphotography of cross-sections of the samples R1 and W1: (a) R1 back bumper, MD, (b) R1 front bumper, LD (c) W1 right door, LD, (d) W1 roof, MD. Left (a and c) and right (b and d) panels show original- and post- manufacture coating, respectively.

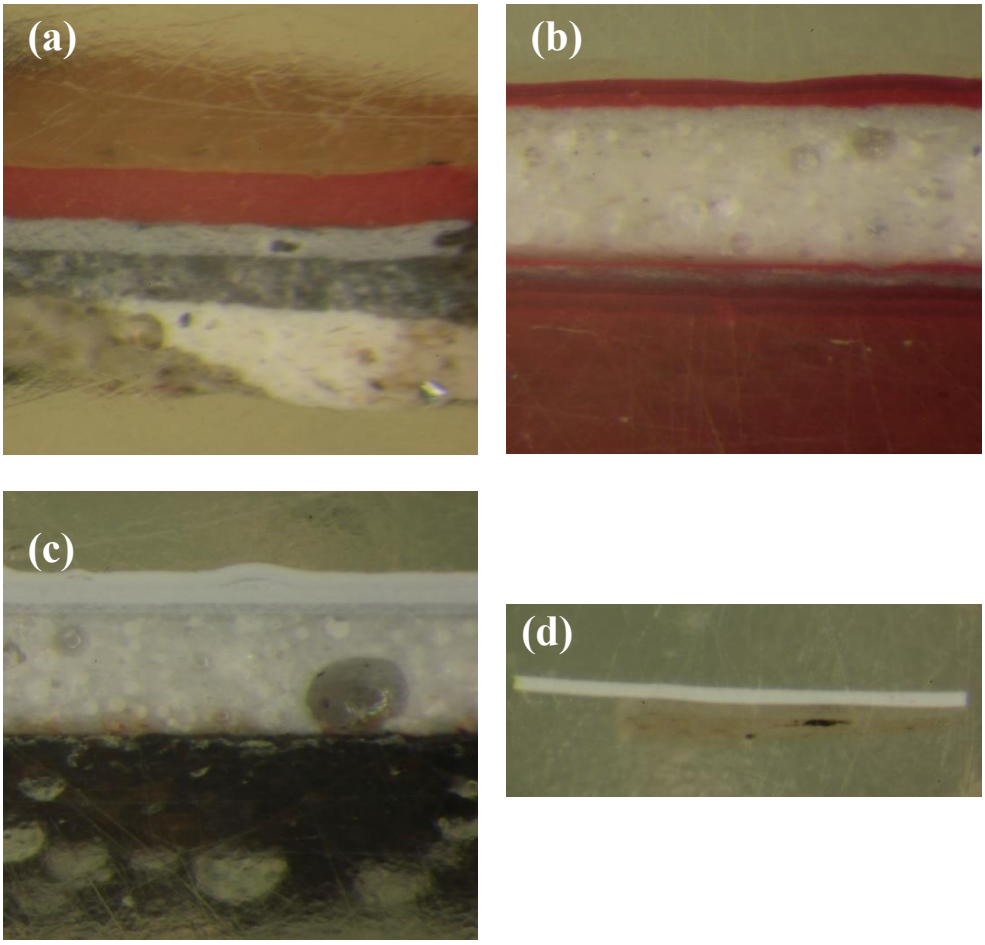

FIGURE S4. (a) Visual image of the surface of the sample W1 LD with labelled Raman mapping area (6.56 mm^2), (b) UHCA false-color cluster map, (c) average NIR Raman spectra extracted from the cluster map in (b), the colors of spectra correspond to the colors of clusters in (b).

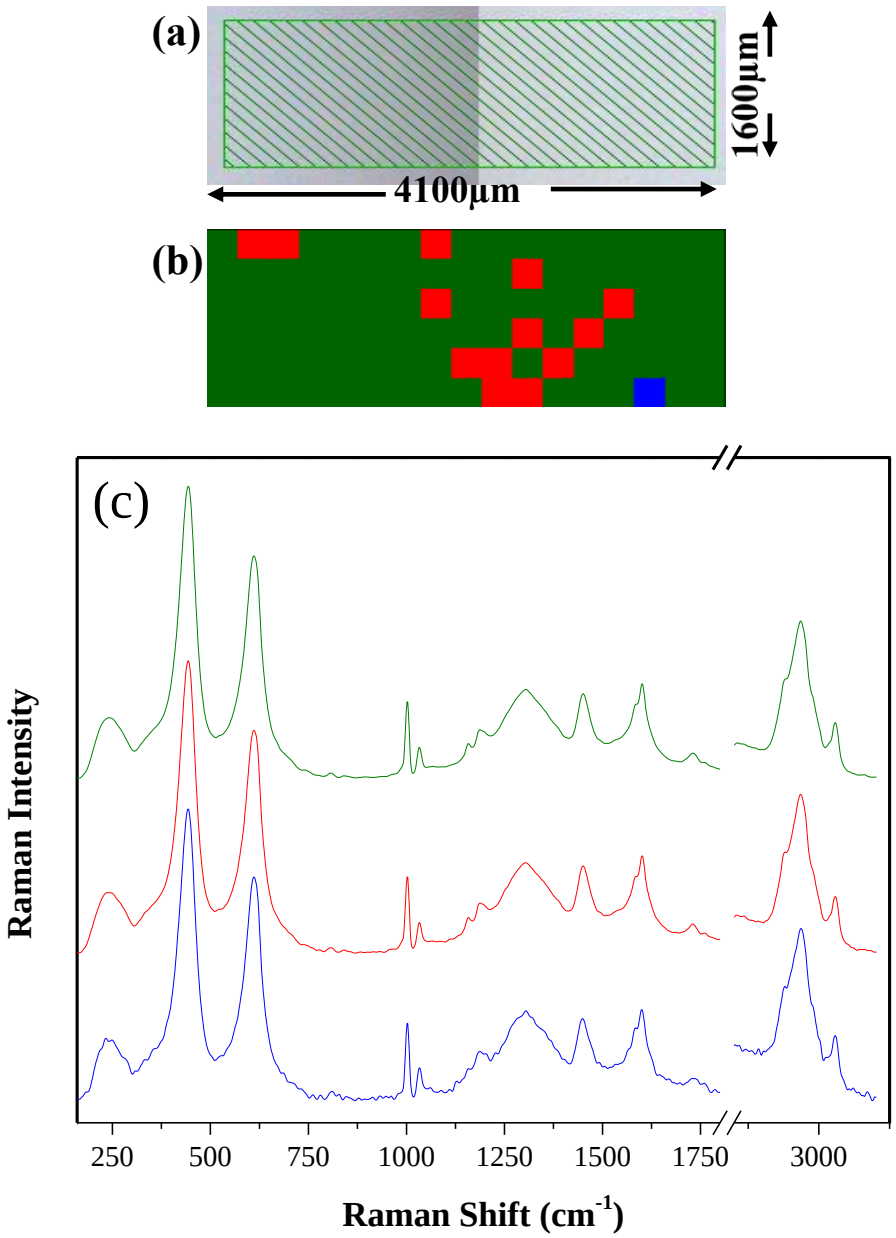

FIGURE S5. Single point Vis Raman spectra collected from the cross-section layers of R2 LD: (a) the basecoat (red layer). b, c) the primer surfacer (white layer).