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APPLICATION OF MICRO-RAMAN AND FT-IR SPECTROSCOPY IN FORENSIC ANALYSIS OF AUTOMOTIVE TOPCOATS IN THE REPUBLIC OF MACEDONIA

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Raman and infrared spectroscopy are two complementary spectroscopic techniques that can produce fast, efficient and accurate detection of the pigments and/or binders used in automotive topcoats. Micro-Raman spectroscopy, due to its non-destructiveness, has been extensively used for identification of pigments and dyes in forensic investigation of hit-and-run accidents. This technique provides very useful and significant information from very small samples of evidence without any previous preparation of the sample. The recorded Raman spectra of the unknown/suspected samples can be compared with a spectrum of the referent sample, which can coincide with the one already existing in the Raman database of pigments.

In order to form our own spectral database of automotive paints for forensic investigations in hit-and-run offences in Republic of Macedonia, an investigation of automotive topcoats of different origins was carried out. In our previous study, pigments in some automotive topcoats, produced by *Mobihel*, have been identified using micro-Raman and FT-IR spectroscopy. In the present study, we report micro-Raman and FT-IR spectra of ten base coat automotive topcoats, as well as some of their mixtures, produced by *Glasürit*. In order to demonstrate the availability and/or the advantages of the micro-Raman spectroscopic technique in forensic investigation in road accidents, four successfully solved cases from the police investigation in hit-and-run accidents are presented in this work.

Key words: micro-Raman and FT-IR spectroscopy; automotive paints; pigment identification; forensic investigations; criminalistics

ПРИМЕНА НА МИКРО-РАМАНСКА И ФТ ИНФРАЦРВЕНА СПЕКТРОСКОПИЈА ВО ФОРЕНЗИЧКАТА АНАЛИЗА НА АВТОМОБИЛСКИТЕ БОИ ВО РЕПУБЛИКА МАКЕДОНИЈА

Раманската и инфрацрвената спектроскопија се две комплементарни спектроскопски техники кои можат да дадат брзо, ефикасно и точно определување на пигментите и/или сврзувачите користени во автомобилските бои. Поради недеструктивниот карактер, микро-раманската спектроскопија сѐ почесто се користи за идентификацијата на пигментите и боите во полициската истрага на сообраќајните незгоди. Анализите добиени со микро-раманската спектроскопија даваат корисни и значајни информации од многу мали примероци, без нивна претходна посебна подготовка. Снимените рамански спектри на непознат/сомнителен примерок се споредуваат со соодветните спектри на референтниот примерок, а потоа пигментите се определуваат преку базата на податоци за раманските спектри на пигменти.

За да се образува сопствена база на податоци на пигментите од автомобилските бои за полициската истрага при сообраќајните незгоди во Република Македонија, направени се испитувања на автомобилските бои од различно потекло. Во нашите претходни испитувања, со помош на инфрацрвена и раманска спектроскопија, определени се пигментите во десет автомобилски бои произведени од фирмата *Mobihel.* Во овој труд, со помош на инфрацрвена и раманска спектроскопија, определени се пигментите, како и некои нивни смеси, на десет основни бои произведени од фирмата *Glasürit*. Можностите, како и предностите на микро-раманската техника во полициската истрага на сообраќајните незгоди се поткрепени со презентирање на некои успешно решени случаи од полициската практика.

Клучни зборови: микро-раманска и инфрацрвена спектроскопија; автомобилски бои; идентификација на пигменти; полициска истрага; криминалистика

INTRODUCTION

Conventional automotive paints and coatings are usually comprised of four main components: a polymer, which acts as a binder; a pigment for obtaining the color; a liquid carrier – generally a solvent and various additives. The first two are permanent constituents; the binder is providing the adhesion and cohesion, keeping the pigment within the coating and ensuring that the paint remains attached to the substrate while the pigments are mainly responsible for decorative quality of paint coat, like its color, shade and opacity. The pigments used in automotive industry can generally be arranged in four categories: inorganic, organic, metallic and pearlescent. Their main purpose is to provide opacity, protection and beautiful look on the metal and plastic bodies of the car. The ability of the pigments to achieve those performances depends mainly on their particle size. The size of the pigment particles are generally of the order of a fraction of micrometer [1].

Besides the industrial importance, the analysis of automotive topcoats is of great significance for forensic science, especially for the investigation of hit-and-run accidents [2]. Paint samples for forensic analysis received from automotive topcoats are usually very small chips and/or smears, which are sometimes mixed with the support or other materials. Therefore, the analytical methods/techniques should be capable of producing significant and valuable information from the microsamples. The analytical challenges for forensic analysis are further complicated by the need to retain a portion of the sample for examination by other scientific experts. Because the analyzed samples are often well below a square millimeter in size, it is desirable to use non-destructive or micro-destructive tests that will consume the smallest amount of sample. In the case of analysis of paint evidence, the choice of applied analytical micro-technique should be directed towards the ability to examine all major components, but also to discriminate between similar paints [2]. Finally, the comprehensive forensic examination should employ tests to examine both the binder and the pigment fraction of the coating [3].

In the last ten years, spectroscopic methods, in particular, laser assisted micro-Raman spectroscopy, has proved to be a powerful tool for forensic investigation of paint traces. In this work, micro-Raman and Fourier transformed infrared spectroscopy (FT-IR) were used in the analysis of automotive topcoats. For the purpose of database formation of pigments used in automotive topcoats, in our previous study [4], we recorded the micro-Raman and FT-IR spectra (in the region of 2000 to 400 cm^{-1}) of ten automotive topcoats and their corresponding spectra of the basic polymer, produced by "Mobihel".

In this paper, we report the IR and micro-Raman spectra of ten basic paints of automotive topcoats and their corresponding spectra of the basic polymer, produced by "Glasürit" [5]. The infrared spectra of these automotive topcoats are similar and most of the IR bands can be assigned to the vibrations of the molecules from the binding media. On the contrary, the corresponding Raman spectra are characteristic and are very different from each other. On the basis of the recorded Raman spectra and the literature data, the pigments used in the studied automotive topcoats were identified.

In order to examine the possibility of micro-Raman and FT-IR techniques for detecting particular pigments used in the mixtures of automotive paints, few mixtures of referent automotive paints were prepared and their Raman and FT-IR spectra were analyzed.

Finally, the accessibility of the micro-Raman spectroscopic technique was demonstrated by four examples of solved cases from hit-and-run accidents, already analyzed in the Laboratory for Analysis of Micro-traces at the Department of Criminality Technique, Ministry of Internal Affairs of the Republic of Macedonia [6].

EXPERIMENTAL

Instrumentation

Micro-Raman spectrometer

Micro-Raman analyses were performed using Raman spectrometer, FORAM 685-2, with He-Ne (685 nm) laser as an excitation line and a maximum output power of 5 mW on the sample. The microscope was equipped with interchangeable objective lenses with magnifications of ×5, ×10 and ×20, but the ×20 objective was preferred. The Raman spectra were recorded in the region 400–2000 cm^{-1} with the integration time varying between 5–30 seconds, with 5–20 scans and a spectral resolution of around 7 cm^{-1}. All spectra were baseline corrected. GRAMS/32 software was used for spectra acquisition. The automotive paints were coated on a microscopic slide and the Raman spectra were obtained directly under the microscope.

FT-IR spectrometer

Infrared analyses were performed using a Fourier-transform infrared (FT-IR) spectrometer (Perkin-Elmer 2000) by the method of KBr pellets. The spectra were recorded in the region 400 – 4000 cm^{-1}, but for the purpose of this work only spectra from 400 to 2000 cm^{-1} are presented. All the spectra were baseline corrected. GRAMS/32 software was used for spectra acquisition. The spectral resolution was 4 cm^{-1}. The FT-IR spectra of the automotive paints were recorded by scratching paint from the microscope slides and mixing it with 250 mg of KBr.

Materials/samples

Referent automotive topcoats

Ten basic paints of automotive topcoats used for creating the database of pigments were obtained by the courtesy of *Skenderovski Garage* in Skopje, Republic of Macedonia. The ten basecoat/clear coat automotive paints, used for creating a database, taken from the *Glasürit* catalogue [5] for the year 2006 are: 25 (white), 146 (yellow), 257 (orange), 306 (brick), 324 (red), 427 (maroon), 430 (green), 555 (dark blue), 640 (violet) and 929 (black). Besides these, two and three component mixtures of automotive paints were made from some of the above mentioned automotive topcoats. The mixtures were made according to the procedure given from the *Glasürit* catalogue [5].

Samples for the case studies

Case studies samples were taken from the documentation of the hit-and-run accidents from the Department of Criminality Technique, Ministry of Internal Affairs of the Republic of Macedonia, which were previously analyzed in the Laboratory for analysis of micro-traces [6].

RESULTS AND DISCUSSION

Infrared spectra of the ten clear coat automotive paints produced by "Glasürit" and their corresponding Raman spectra in the 400–2000 cm^{-1} region are shown in Figs. 1a and 1b. The bottom trace in Figs. 1a and 1b corresponds to the spectrum of the binder (basic polymer).

The infrared spectra of all ten automotive topcoats are rather similar, although some differences are observed, particularly in the spectral region below 1000 cm^{-1} (Fig 1a). Nevertheless, the spectra indicate that most of the IR spectra are mainly dominated by the bands due to the basic polymer (bottom spectrum). According to the literature data, the infrared spectrum of the basic polymer of these clear coat automotive paints could probably be identified as poly(methyl)methacrylate resin [7–9]. Its monomer unit consists of C=O, C−O, CH_2 and CH_3 functional groups. Indication for the presence of these groups is supported by its infrared spectrum (Fig. 1a); the strong absorption band due to ν(C=O) vibration is at 1730 cm^{-1}; the CH in-plane deformational vibration appear between 1450 and 1380 cm^{-1}; the ν(C−O) vibration appears as a broad and strong band at around 1150 cm^{-1} followed by two less intense bands at around 1235 and 1270 cm^{-1} and the weak band at around 700 cm^{-1} could be assigned to the CH_2 rocking vibrations. The vibrational bands in the Raman spectrum of the basic polymer (Fig. 1b, bottom spectrum), although less pronounced and fewer in number, support the assignment based on the infrared spectrum. The Raman peaks at 1740 cm^{-1}, 1450 cm^{-1}, and the bands between 1270 – 990 cm^{-1} and between 850 – 800 cm^{-1} can be assigned to C=O stretching, C–H bending, C−O stretching, and CH_3 rocking vibrations respectively.

The Raman spectra of ten automotive topcoats shown on Fig. 1b, are significantly different between each other, but also differ from the corresponding spectrum of the basic polymer (bottom spectrum on Fig. 1b). The pigments used in those automotive topcoats have been identified by their Raman spectra [10–13] (Table 1 and Fig. 1-b). Some of them are inorganic and some organic.

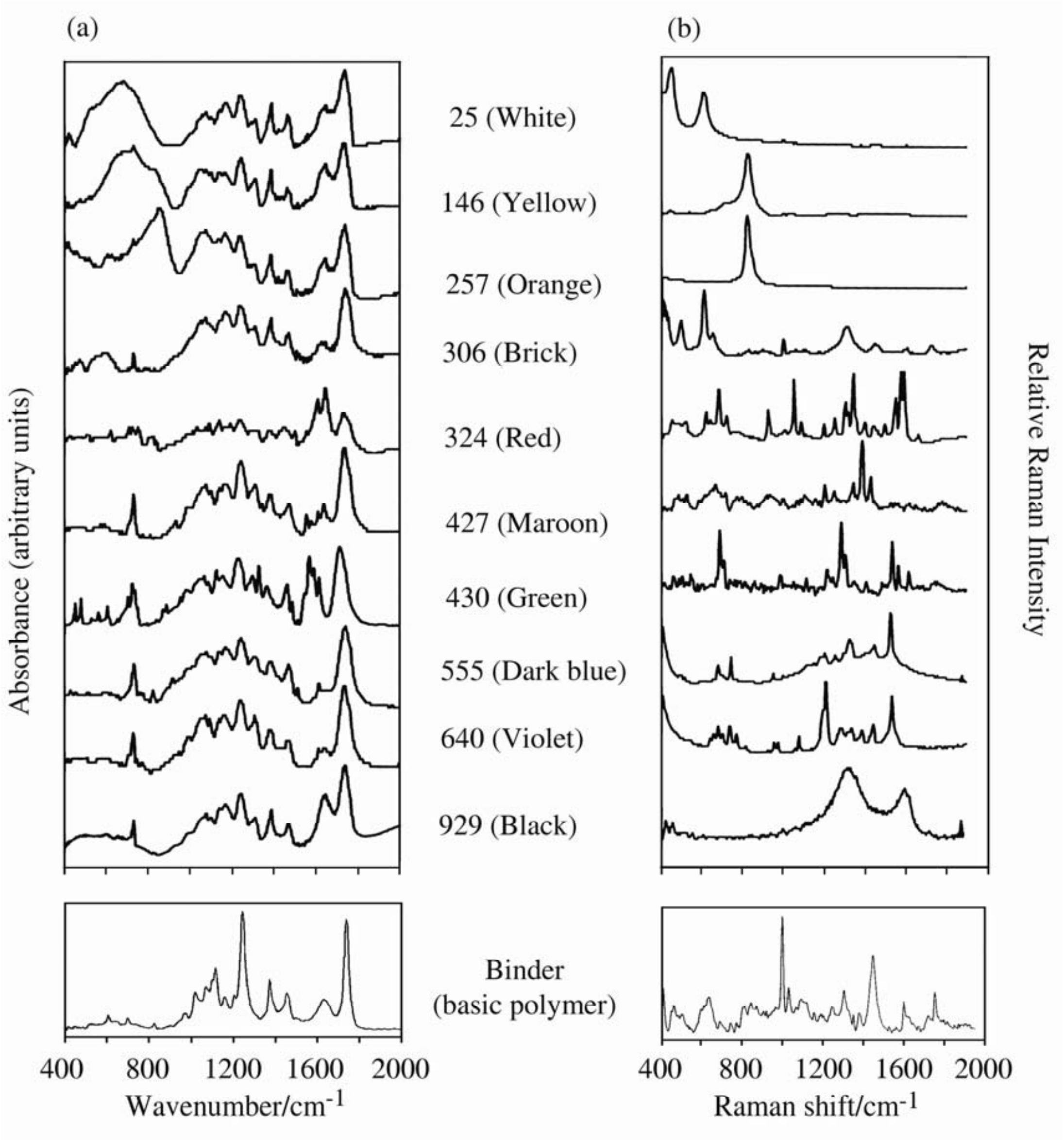

Fig. 1. Infrared (a) and Raman (b) spectra of ten analyzed automotive topcoats (*Glasürit*)

The Raman spectra of the inorganic pigments have few bands, while the organic pigments have spectra rich with sharp bands. Thus, the Raman spectra of the white, yellow and orange topcoats (Fig. 1b) can be identified as rutile (TiO_2), chrome yellow ($PbCrO_4$) and chrome yellow orange ($PbCrO_4 \cdot PbO$), the pigment used for the green and dark blue automotive topcoats, for instance, has been identified as polychloro copper phthalocyanine and copper phthalocyanine respectively, while the black automotive topcoats contain carbon. All pigments present in the clear coat automotive topcoats were identified according to the literature data [9–13] and are listed in Table 1.

Table 1

Identified pigments used in ten analyzed automotive topcoats (Glasürite)

Color	Catalogue number (*Glasürite*)	Pigment
White	25	Rutile
Yellow	146	Lead chromate
Orange	257	Lead chromate/Lead molybdate
Brick	306	Rutile + Cadmium sulfide
Red	324	Diketo pyrido pyrrol
Maroon	427	Quinacridone
Green	430	Polychloro copper phthalocyanine
Dark blue	555	Copper phthalocyanin
Violet	640	Dioxazine
Black	929	Carbon black

In order to examine the capability of the two complementary spectroscopic techniques of identifying pigments in mixtures of automotive paints, mixtures of two and three component clear coat automotive topcoats were prepared. Their IR and the corresponding Raman spectra are shown in Figs. 2 and 3. The characteristic Raman bands of the pigments present in these mixtures can be unambiguously identified (Figs. 2b and 3b). On the contrary, on the basis of their infrared spectra, a clear difference between the infrared bands originating from a particular pigment and the ones from the basic polymer can not be distinguished (Figs. 2a and 3a). These infrared spectra are mainly dominated by the absorption bands from the binder (basic polymer).

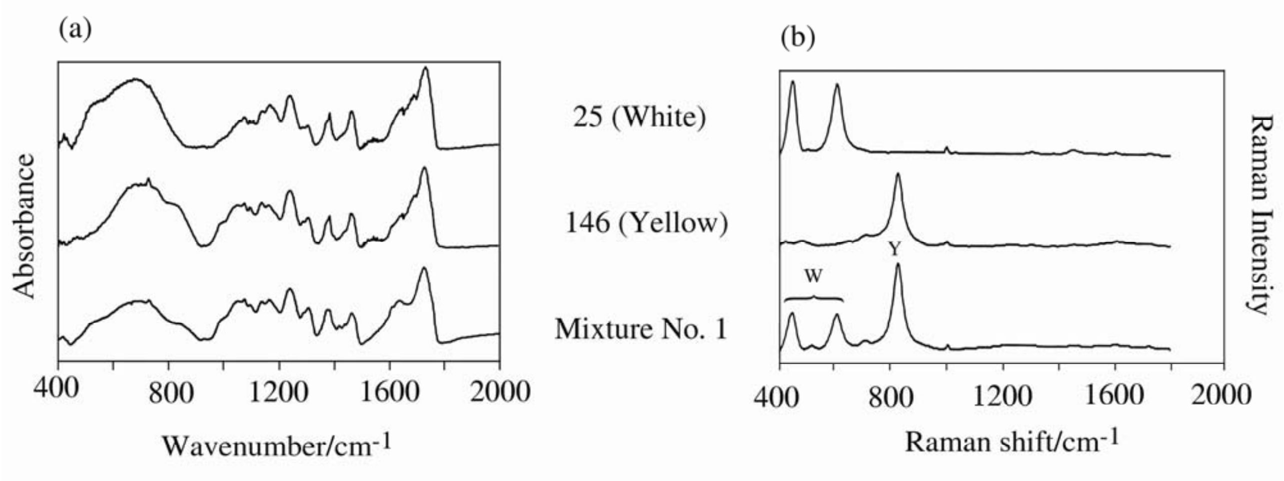

Fig. 2. Infrared (a) and Raman (b) spectra of mixture No. 1 consisting of white and yellow automotive topcoats (*Glasürit*). W – white; Y – yellow

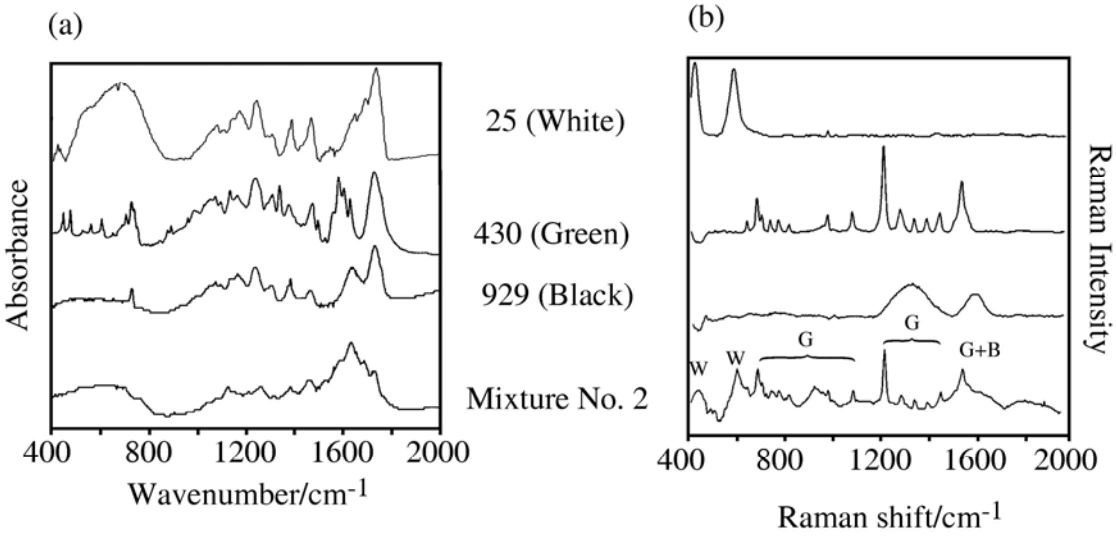

Fig. 3. Infrared (a) and Raman (b) spectra of the mixture No. 2 consisting of white, green and black automotive topcoats (*Glasürit*). W – white; G – green; B – black

CASE STUDIES

During the police investigation of road accidents, such as hit-and-run accidents, fast and correct identification of the traces of samples of evidence taken from the place of the accident are required. In the last decade, micro-Raman and FT-IR spectroscopic techniques provide useful and complementary information for characterization of traces of automotive paints. Four cases/examples from the police investigation in hit-and-run accidents performed and already analyzed in the Laboratory for Analysis of Micro-traces at the Department of Criminality Technique, Ministry of Internal Affairs of the Republic of Macedonia, have been presented below.

Case 1 – collision with a parked car

A car was parked when another car hit it from the back. The driver of the second car did not stop and left the place of the accident. A man saw the collision and noted the plate number of the car. He found the owner of the damaged car and they called the police. The driver of the suspected car denied that a collision has occurred between the two vehicles. The police searched for transferred traces on the vehicles. Yellow traces were observed on the right back side of the damaged car which were collected by adhesive tape (Fig. 4a). Reference paints were also collected from the suspected (non-metallic yellow) car (Fig. 4b).

The traces collected from the damaged car were in form of abrasive smears which means that the quality of the traces was not excellent and there was a risk of getting a mixture of the support if collected for classical FT–IR spectroscopic analysis. The advantage of Raman microscopy allowed easy visualization of the trace directly on its support and an analysis was carried out directly on the yellow traces. Chrome-yellow pigment was identified in the traces collected from the damaged car as in the reference paint chips taken from the suspected car, which indicated that they most likely had common origin (Fig. 4c).

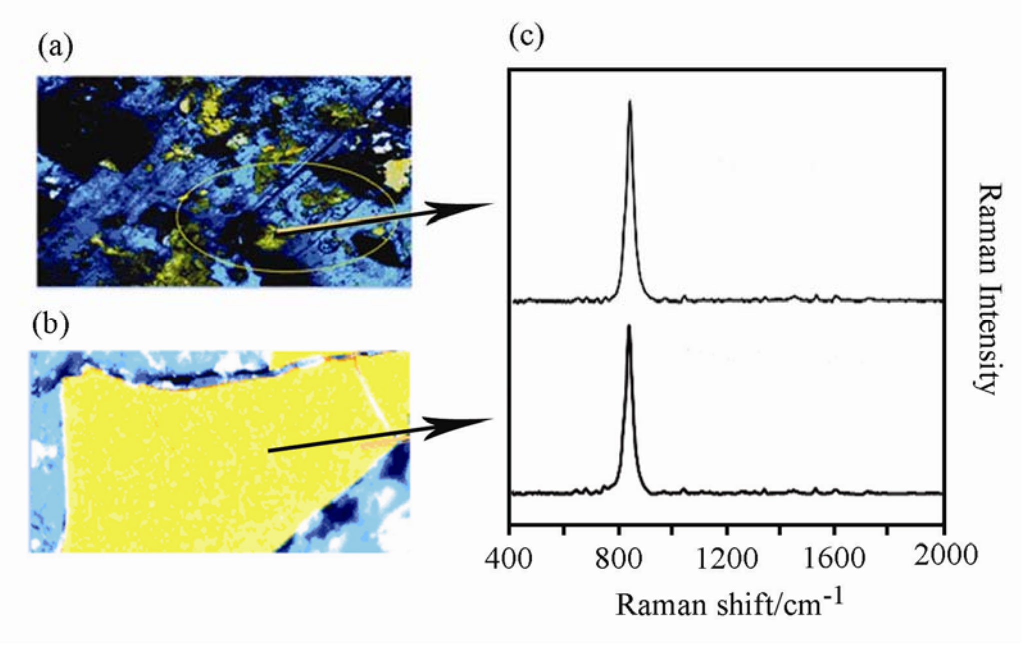

Fig. 4. Case 1: (a) Yellow paint traces observed on the damaged car –×20 lens objective; (b) Reference yellow paint chip taken from the suspected car – ×20 lens objective; (c) Comparison of the Raman spectra obtained from the traces collected from the damaged car and reference paint chips taken from the suspected car

Case 2 – collision of two cars

During one night, two cars driving in different direction on the motorway had a collision. The vehicle 1 (red "Zastava") was damaged on the right side (Figure 5a), while the vehicle 2 (silver "Ford") was damaged on the left side but also on the front (Figure 5b). The drivers and passengers were asked about the dynamics of the accident and each one supplied different information.

The two damaged cars were fully inspected in order to search information on the points of accident and to collect transferred paint traces. Transferred paint traces were collected from the right side of "Zastava" and left side of "Ford" in order to supply useful information about the accident and the points of contact. Reference paints were also collected from both cars.

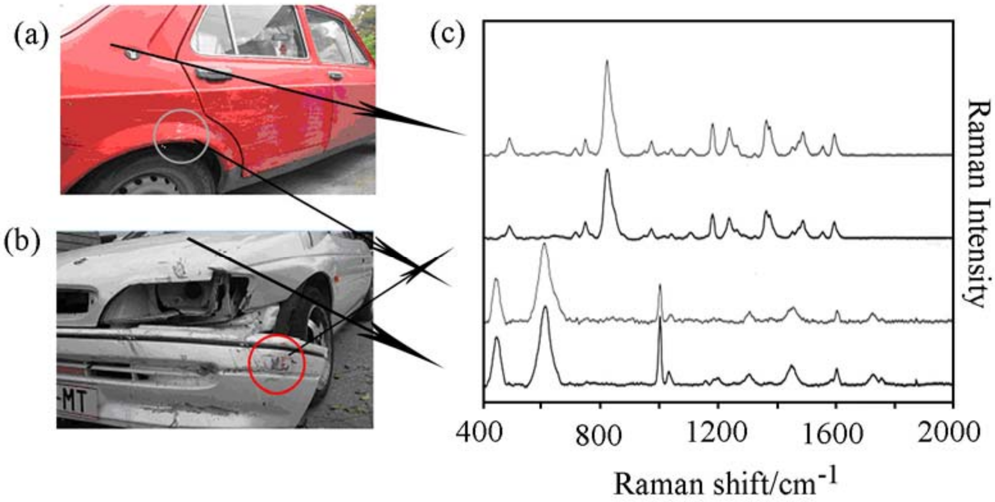

Fig. 5. Case 2: (a) Foreign paint traces observed on the right side of the red "Zastava" – ×20 lens objective; (b) Foreign paint traces observed on the left side of the white metallic "Ford" – ×20 lens objective; (c) Comparison of the Raman spectra obtained from the paint traces with the reference paint chips taken from the two colliding cars

The traces collected from the damaged cars were in the form of abrasive smear and the analyses were carried out directly on the traces. Micro-Raman spectra obtained from the red paint traces collected from the "Ford" and the reference paint from the "Zastava" were compared and are shown in Fig. 5c. The spectra are very similar: lead chromate molybdate pigment was identified in the transferred traces from the silver "Ford", along with some component/s of unknown origin. In the traces collected from both the "Zastava" and in the referent paint chips taken from the "Ford" car, rutile pigment was identified (the two bottom spectra in Fig. 5c). The identification of the pigments in the collected paint smears from both cars indicated that they could have had common origin. However, the foreign paint found in the front of the silver "Ford", also reported as being damaged in the same accident, did not originate from the topcoat of "Zastava", indicating that it did not result from this particular collision between these two vehicles.

Case 3 – man was hit by a blue car

One night a man was walking down the street when a car hit him from the back. The car did not stop. A woman who saw this accident noted the plate number, called the ambulance and the police. The driver of the car denied that he hit the man. The clothes of the victim were inspected in order to search and collect paint traces. Blue paint traces were observed on the pants of the victim (Fig. 6a).

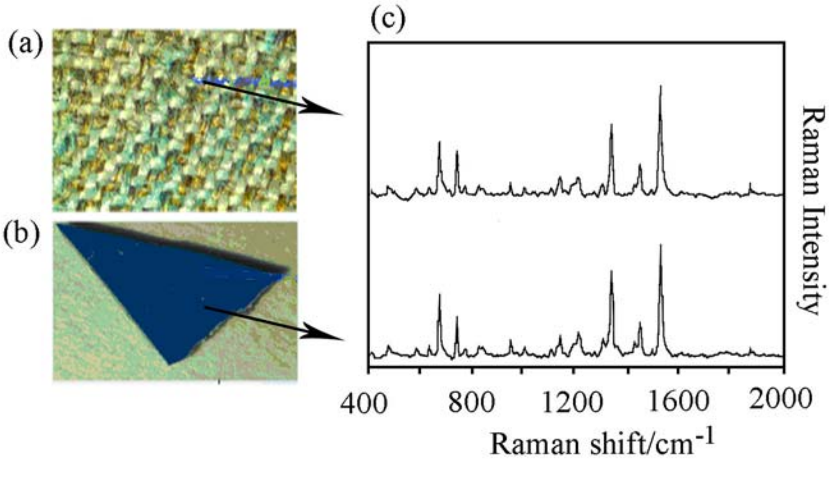

Fig. 6. Case 3: (a) Paint traces observed on the pants of the victim; (b) Reference paint chips taken from the suspected car – ×20 lens objective; (c) Comparison of the Raman spectra obtained from the paint traces observed on the pants of the victim and the reference paint chip taken from the suspected car

The suspected car was blue and reference paint was also collected (Fig. 6b).

The traces observed on the pants of the victim were in form of abrasive smears which means that the quality of the traces was poor and there was a risk of getting a mixture of the support when collected for classical FT-IR analysis. Therefore, they were analyzed by micro-Raman spectroscopy directly on its support. Pthalocyanine blue pigment was identified in the traces observed on the pants and in the paint chips taken from the suspected car, which indicates that they could have had common origin (Fig. 6c).

Case 4 – a school girl was hit by an unknown red vehicle

A girl was coming back from school when a car hit her. The car did not stop. A woman, who saw the accident, said that she saw a red car type "Zastava". The clothes of the victim were inspected in order to search and collect paint traces. Red paint traces were observed on the jacket of the victim (Fig. 7a). The police had two suspected cars; they were both red cars, type "Zastava". The reference paint was collected from both cars (Figs. 7b and 7c). The traces observed on the jacket of the victim were analyzed by micro-Raman spectroscopy directly on its support. Lead chromate molybdate pigment was identified in the traces observed on the jacket, mono azoic red pigment was identified in the paint chip of the first suspected car and the pigment present in the paint chip of the second suspected car could not be identified. The result from the micro-Raman analysis (Fig. 7d) indicated that the victim was not hit by any of these two suspected vehicles.

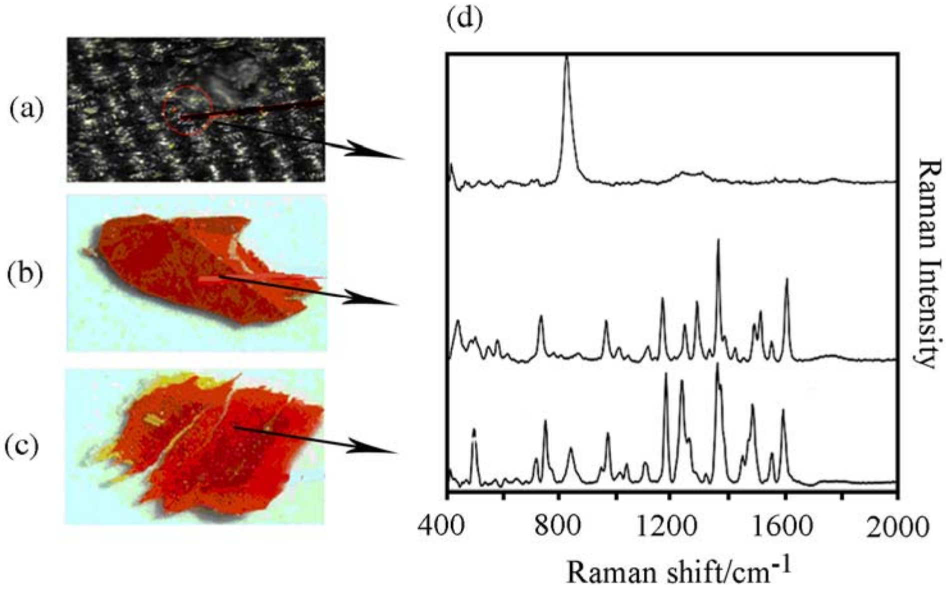

Fig. 7. Case 4: (a) Red paint traces observed on the jacket of the victim – ×20 lens objective; (b) Red paint chips from the first suspected car – ×20 lens objective; (c) Red paint chip taken from the second suspected car – ×20 lens objective; (d) Comparison of the Raman spectra obtained from the paint traces observed on the jacket of the victim and the reference paint chip taken from the two suspected cars

CONCLUSIONS

Micro-Raman spectroscopy is presently being used extensively for forensic investigation of road accidents in the Republic of Macedonia. This technique has proved to be a valuable analytical tool because:

– It is non-destructive; the samples can be analyzed *in situ*, without any previous preparation, placed directly under the microscope.

– The analysis can be performed on practically any kind of support.

– The size of the sample can be as small as tens of micrometers.

– It is fast and reproducible.

– Its biggest disadvantage – fluorescence – can be overcome by using different lasers and/or by its automatic subtraction.

However, if similar pigments were used in the automotive paints, additional investigations, using IR technique must be performed in order to obtain information on the binders. Used together, these complementary spectroscopic techniques can provide valuable information in forensic investigations, not only in hit-and-run accidents, but for many other cases.

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