

The interpretation of paint evidence through the use of population studies: two case examples

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ABSTRACT

In a burglary case, some paint traces were observed on a crowbar seized from the suspect. Comparative analyses did not distinguish these traces from the reference paint originating on the forced door. In another case involving a hit-and-run, a red trace was recovered on a vehicle's rear bumper. The suspect, who owned of a red car, denied the event and thus a comparative analysis of the two samples was performed. The red trace and the red reference paint coming from the suspect's car were indistinguishable.

In both cases, the resulting questions were identical: what should the forensic scientist conclude when a trace evidence is indistinguishable from its putative source? What is the evidential value of such an association? In an attempt to answer these questions, information on the rarity of the physical and chemical features of paint such as color, binder type, pigments, and extenders, was sought. Indeed, two population studies on architectural and automotive paints were carried out to obtain useful data for the interpretation of paint evidence. Population studies involve the observation of the variations of different characteristics (polymorphism) in a representative sample set belonging to a reference population.

Concerning architectural paint, 131 samples were collected at burglary scenes by police officers. The color distribution was observed, but more importantly, further subclasses were obtained using FTIR and Raman spectroscopic data. For automotive paint, the population study consisted of 154 foreign traces recovered on damaged cars that were randomly collected in several automotive body shops. These samples were used to evaluate the occurrence of each paint type. The methodology consisted of submitting all samples to the same analytical scheme as the one used for the regular comparative analysis of paint samples.

The benefit of obtaining data regarding the rarity of different characteristics of paint traces is discussed. In addition, thoughts and questions that could arise during the interpretation of mass-produced items like paint are also presented.

In both aforementioned cases, the physical and chemical profiles observed during the trace-putative source comparative analyses were not present within the samples of the relevant population study used. This demonstrated that the observed characteristics have a rare occurrence in the population.

INTRODUCTION

For the interpretation of transfer evidence like paint, the forensic scientist is very frequently confronted with the fact that a given trace of discovered evidence and its putative source cannot be differentiated: they are analytically indistinguishable. In order to formulate an opinion according to a common origin, knowledge about the ubiquity or the rarity of the observed properties is required. This aspect is ideal when dealing with mass produced items like paint.

Several studies have been carried out to obtain useful data for the interpretation of paint evidence (Willis *et al.*, 2001).

In this project the interpretation of paint evidence is suggested through the use of population studies which involve the observation of the variations of different characteristics (polymorphism) in a randomly selected set of samples belonging to a reference population.

Two population studies were carried out: the first concerning architectural paint and the second concerning automotive paints. In order to evaluate the rarity of paint samples within a population, their characteristics like color and spectroscopic infrared and Raman profiles were studied. The contribution of such analytical methods revealed variations subclasses. Indeed, FTIR spectroscopy was applied in order to determine the binder type and some extenders. On the other hand, Raman spectroscopy was used for the detection of organic and inorganic pigments.

The aim was to submit paint samples belonging to the known population to the same analytical sequence as the one used for the questioned paint traces.

The usefulness of the collected data is shown through two typical caseworks examples.

Case 1 – Paint traces recovered on a crowbar

A burglary was committed in a factory where a tool was used to force a blue and pink two-layer door. A suspect was found by the police and a crowbar was recovered in the trunk of his car. Some blue and pink traces were observed on the crowbar and thus comparative analyses were requested between such evidence and the reference paint coming from the forced door.

Case 2 – Hit-and-run accident between two vehicles

A driver was traveling in a city street when a car collided from the rear: this second car did not stop. The driver was able to note the plate number and called the police. The suspect, owner of a red car, denied the event. A red trace was recovered from the rear bumper of the damaged vehicle. A comparative analysis between the red trace and the reference paint coming from the suspect's vehicle was carried out.

In both cases the comparative analyses did not distinguish between the evidential material and its reference material.

MATERIALS AND METHODS

Analytical sequence and procedure

The analytical sequence undertaken for both cases started with the *in situ* observation of the evidence by stereo microscope. Then, Fourier transform infrared spectroscopy and Raman spectroscopy were carried out.

Fourier Transform infrared spectroscopy (FTIR)

Infrared analysis was performed on a Digilab Excalibur FTS 3000 FTIR spectrometer coupled to a UMA 600 microscope (15x reflecting objective). The instrument is equipped with a mercury cadmium telluride (MCT): a 4 cm^{-1} spectral resolution was used and the spectral range was comprised between 4000 and 650 cm^{-1} . The Digilab Resolutions Pro 4.0 software was used for the display and management of data. The samples were analyzed in transmission mode: they were collected and supported on a KBr pellet.

Raman spectroscopy

A Renishaw System RM 1000 spectrometer fitted with a Leica DM L research microscope was used. Four excitation sources were available: argon ion laser at 514.5 nm , helium-neon laser at 632.8 nm and two near infrared (NIR) semiconductor lasers at 785 nm and 830 nm . For focusing on the samples, the 50x and 100x objectives were used allowing a 1-3 microns laser spot size. A Peltier-cooled charge coupled device (CCD) camera was used as the detector. The spectrometer worked with a 1200 lines/mm grating as the dispersive element. Measurement times were generally 10 seconds and the spectra were collected in the spectral region of 2000 - 200 cm^{-1} . GRAMS/32 (Galactic Industries Corporation) software was used for the display and management of data.

Population studies

Two population studies were carried out on architectural and automotive paints. Concerning the methodology, the color (being the most important feature for paint) was noted first. The population was then divided into several classes. Within a sample class of

a given color, further subclasses were obtained according to the distribution of the chemical features of such samples. The main subclasses were again subdivided according to the distribution of the binder type (and some extenders) for infrared spectroscopy and on the distribution of the types of pigments for Raman spectroscopy. The presence of additional bands (not belonging to the main constituents) within the collected spectra permitted the further subdivision of the observed subclasses.

For the architectural paint, 131 paint samples were collected by Swiss police officers at burglary scenes. The reference population consisted to a set of forced painted surfaces (doors, windows, etc.) during a burglary. Every time police officers observed a forced entry, they proceeded to collect fragments of the damaged painted surface. The color distribution was first observed and all the samples were analyzed with FTIR spectroscopy. Raman spectroscopy was only applied for those samples with the same color as the evidential material encountered in casework.

For the automotive paint population, a study on the foreign traces recovered on damaged cars was conducted. One hundred and fifty-four samples were collected in car body shops. When a damaged car went to a car body shop for repair, the part of its body carrying traces was cut off and transmitted to our laboratory. The criterion of selection of such traces was random. The color distribution was observed and the paint samples of the same color as the evidential material encountered in casework were analyzed with FTIR and Raman spectroscopy.

RESULTS

Given that in both cases the quality of the evidence was in the form of an abrasion smear (vs. fragments) and the quantity of the recovered material was poor, the spectroscopic techniques were the most informative. The chemical profiles based on the binder type, extender and pigment compositions were obtained. The Raman analyses of these two cases (among other examples) are detailed in Buzzini *et al.* (2006).

Case 1

Blue, pink and white traces were observed on the blade of the crowbar. Given that the forced door was a two-layer blue and pink one, comparative analyses focused on these two colors. Infrared spectroscopy allowed observing an alkyd orthophthalic binder type as well as magnesium silicate (talc) and titanium dioxide (rutile form) as extenders, for both blue and pink paints. Raman spectroscopy permitted the detection of the blue phthalocyanine pigment C.I. PB 15 and the titanium dioxide extender. The Raman analysis of pink samples did not allow obtaining informative spectra because of fluorescence. Infrared and Raman spectra are shown in Figure 1.

In order to assess the evidential value for the two undifferentiated items, the following question arose: what is the occurrence of blue and pink traces with the observed chemical profile within a population of architectural paints? And, what is the chance of randomly observing such characteristics? The rarity of such characteristics was searched in the chosen population. The color distribution was first considered and is shown in Figure 2. Among the 131 reference samples, the blue color was observed for seven samples (about 5%). The color pink was not observed in the reference population.

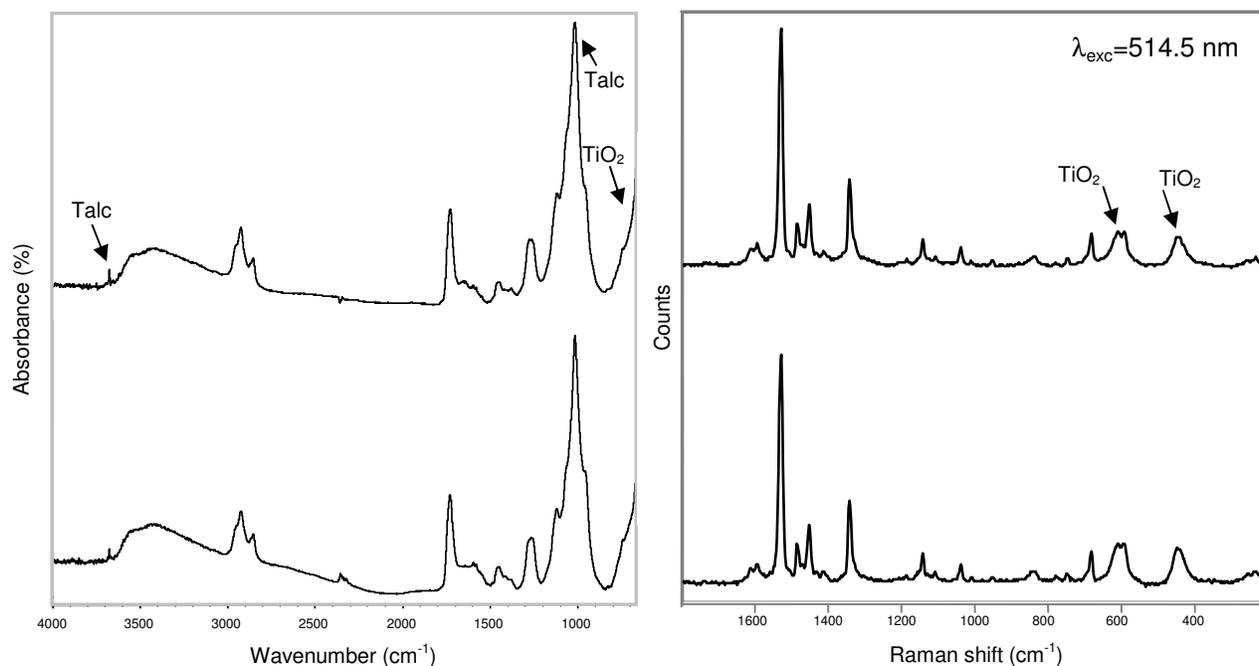


Figure 1 – Infrared (left) and Raman (right) spectra of the blue trace recovered on the crowbar (top) and the blue reference paint coming from the forced door (bottom).

The infrared and Raman spectra observed for the blue traces were compared to those obtained for the seven blue population samples (Figure 3). Of the seven, only one sample (FR05) presents an infrared spectrum with the same absorption bands as the ones of the evidence, but the relative intensity of such bands is discordant. The sample FR05 presents a different Raman spectrum than the one obtained for the blue trace. It can also be noted that one blue sample (FR15) supplies a Raman spectrum presenting the same general shape as the one obtained for the trace. However, an additional band (indicated with an arrow) permits differentiating between them.

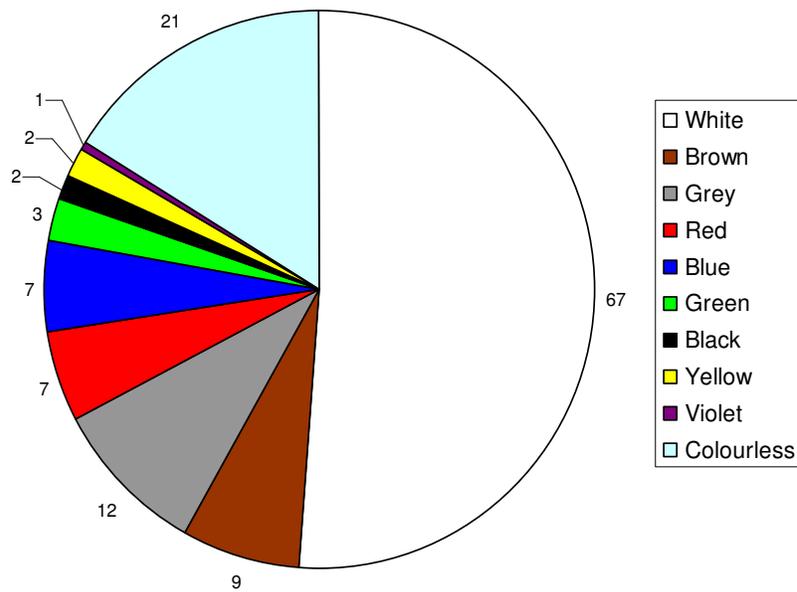


Figure 2 – Color distribution of the population of architectural paint collected on burglary scenes (N=131).

Case 2

The trace and the reference paint coming from the suspect vehicle was both a non-metallic red color and results were undistinguishable after the analytical sequence. Indeed, FTIR spectroscopy detected an orthophthalic binder type and absorption bands attributed to the red pigment diketo pyrrolo pyrrol (C.I. PR 254) (Figure 4). Raman spectroscopy permitted the unequivocal detection of PR 254.

For the interpretation of this case, the arising question was the following: what is the chance of observing red traces with the chemical profile within a population of foreign traces recovered on damaged vehicles?

The occurrence of red color within the considered population is about 22% (Figure 5), meaning 34 samples, but this subclass can be further reduced considering only red non metallic samples, which are 11 (about 7%).

In terms of occurrence, the configuration of infrared absorption bands observed in the FTIR spectra of the red trace and its reference paint was not found in the mentioned subclass.

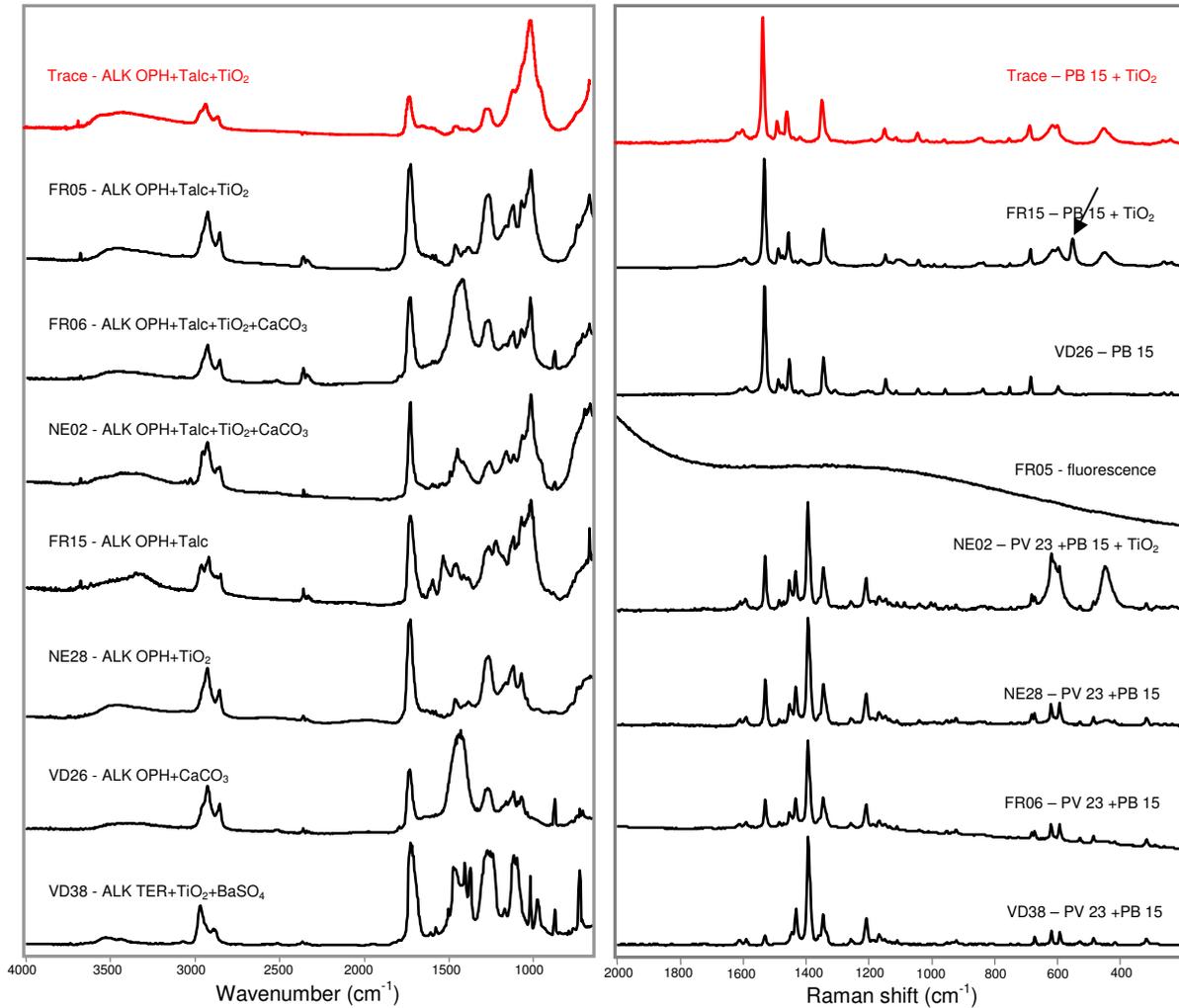


Figure 3 – Infrared (left) and Raman (right) spectra distribution of the seven blue samples of the considered population compared to those of the blue traces. The arrow in Raman spectra indicates an additional band not present in the spectrum of the trace.

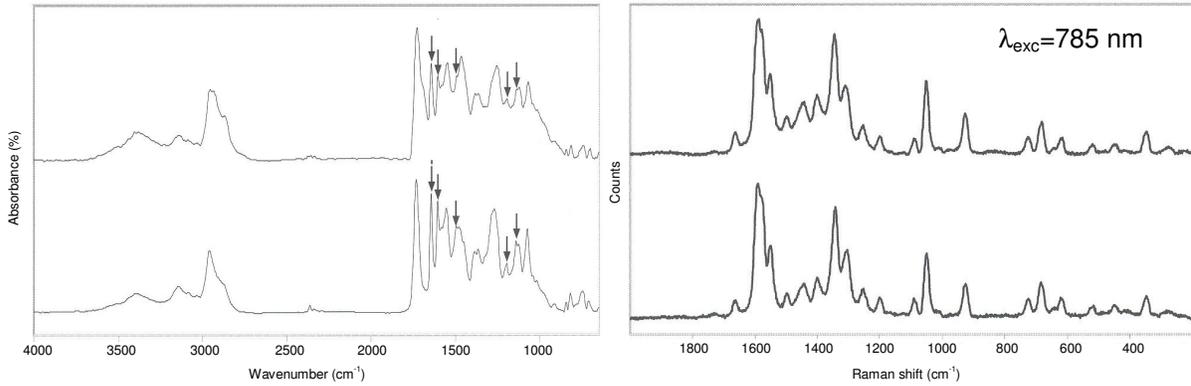


Figure 4 – Infrared (left) and Raman (right) spectra of the red trace recovered on the damaged car bumper (top) and the red reference paint coming from the suspected vehicle (bottom). Arrows in IR spectra indicate the absorption bands of the red pigment PR 254.

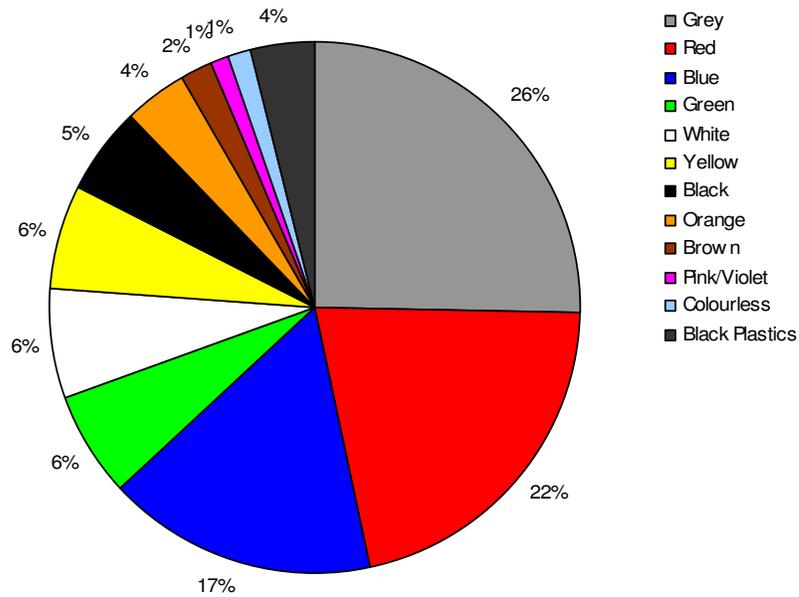


Figure 5 – Color distribution of foreign traces recovered on damaged car bodies (N=154)

DISCUSSION

In an attempt to interpret mass produced items as evidence like paint, it is important to demonstrate that our environment is characterized by a polymorphism and that some features are common and other are rare. For such purpose, and in the specific application of paint analysis, discriminative methods must be combined. Other than color, the main

property of paint, FTIR and Raman spectroscopy techniques were applied. Infrared spectroscopy is a routine and a well established technique for paint analysis (e.g. Beveridge *et al.*, 2001). Raman spectroscopy was chosen because it proved to be an excellent technique for the *in situ* analysis of micro sized abrasion smears as well as for the identification of organic and inorganic pigments.

In order to study the rarity of a given paint sample, the spectroscopic information proved to be suitable. For both techniques, the main detected compounds (a given set of bands) are recurrently observed. In the two proposed cases the alkyd orthophtalic binder type as well as pigments like PR 254 and PB 15 are widely used in industry and therefore are very common. However, an infrared or a Raman spectrum supplies additional bands which cannot be systematically attributed to a given compound, but play a central role in terms of discrimination. That is because they increase the rarity of a given configuration of bands once combined with those attributed to a common compound.

In both cases the infrared and Raman spectra obtained for the evidential material and their respective putative sources were not found in the reference populations. That allowed assessing a high rarity of the exploited characteristics and consequently a high evidential value.

CONCLUSION

The approach based on population studies allowed obtaining objective data for the interpretation of paint evidence. It allowed for knowing which features are commonly observed in our environment and which are rarely encountered.

In both the exposed cases, the physical (based on the color perception) and chemical (based on infrared and Raman information) profiles observed within the trace evidence and their reference materials were considered rare enough to strongly support the opinion of a common origin.

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