Journal of Molecular Structure 993 (2011) 134–141

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Characterisation of paint samples by infrared and Raman spectroscopy for criminalistic purposes

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ARTICLE INFO

Article history:
Available online 14 December 2010

Keywords:
Paint analysis
Infrared microspectrometry
Raman spectroscopy
Chemical imaging
Forensic science

ABSTRACT

Infrared microspectrometry and Raman microscopy were applied in characterisation of paint coatings, i.e. in identification of pigments and in differentiation between paint samples of similar colour and shade. The use of different excitation lasers enabled us to reduce the fluorescence of the sample and identify the main pigments present in the sample.

It was shown that Raman mapping has great potential for the forensic study of paint samples. It is useful because paints are usually chemically complex and heterogeneous mixtures and spectroscopic images allow an assessment of the chemical heterogeneity of a specimen in terms of the spatial distribution of the molecular constituents.

1. Introduction

Paint samples can provide valuable evidence in a wide variety of forensic casework, such as associating a suspect and a crime scene or tool used in an act as well as establishing a connection between a hit and run victim and a particular vehicle. Paint traces occur in the form of micro-fragments of paint coat, frequently with an area of several mm^2, droplets or smears of paint visible in the form of coloured streaks on the clothing of persons involved in these events. The aim of paint examination is to establish the degree of similarity between the paint trace sample and the sample originating from the suspect, i.e. from his vehicle, clothes or tools used in the act. Identification analysis in order to find the origin and type of the paint trace is also carried out.

Optical microscopy, microinfrared spectroscopy and microspectrophotometry in the visible range are routinely applied in identification and differentiation between paint samples. Infrared spectrometry [1–3] is sensitive to molecular structure and therefore provides much information about the chemical composition of a paint sample, i.e. about its polymer binder and inorganic fillers and pigments. However, the identification of organic pigments present in such a trace is mostly impossible because their content is too low for detection. Raman spectroscopy proved to be a promising technique in the area of forensic examination of paint pigments. The major advantage of Raman spectroscopy is the non-destructive nature of the analytical procedure, which can often be applied regardless of the form of the sample and its preparation for analysis. It is considered as a non-invasive method that can be used *in situ*.

Raman and FTIR spectrometry are the main analytical techniques applied in examination of pigments in works of art such as paintings [4], illuminated manuscripts [5], pottery [6], wall paints [7] and sculptures [8]. They enable analysis of single grains of pigment, which is of great importance when a sample which has undergone conservation treatment is made up of a mix of pigments, each of which is required to be identified [9]. Micro-Raman, micro-FTIR and EDX are considered complementary techniques for the study of cross sections of materials constituting artworks.

Recently, attempts have been made to apply Raman spectroscopy in forensic examinations of traces [10–14]. Raman techniques measure the inelastic scattering of light, depending on the vibrational modes of non-polar bonds of a molecule when excited by an intensive monochromatic source as a laser. These vibrations tend to give a much better signal than those involving polar bonds. However, some difficulties occur concerning strong fluorescence produced by paint components that may overwhelm the weaker Raman scattering peaks. To minimise fluorescence, some of the recent Raman studies of paint have used a Fourier transform Raman instrument, which uses near infrared excitation [15,16]. Other authors propose use of several excitation lasers in measurements of paint samples for the same purpose [17].

Both IR and Raman spectroscopy seem to be good methods for characterisation of multilayered car paint chips enabling identification of inorganic components and organic pigments [18,19].

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doi:10.1016/j.molstruc.2010.12.016

Table 1
Parameters employed for the StreamLine mapping technique.

Parametrs	Turquoise paint (F)	Blue paint (G)	Red paint (H)
Scanned area	115 × 125 μm^2	100 × 125 μm^2	110 × 240 μm^2
Number of spectra	56 048	38 440	23 920
Sampling step (imaging resolution)	0.5 μm (X) 0.5 μm (Y)	0.5 μm (X) 0.5 μm (Y)	1.1 μm (X) 1.1 μm (X)
Spectral window	427 to 831 cm^{-1} (static:centre 630 cm^{-1})	1277 to 1623 cm^{-1} (static:centre 1450 cm^{-1})	500 to 900 cm^{-1} (static:centre 700 cm^{-1})
Exposure time	5s	3s	4s
Total acquisition time	~ 1.5 h	~ 35 min	~ 35 min

Table 2
Examined paint sample.

Sample	Origin	Colour
A	Fiat 126p	Yellow
B	Fiat 125	Yellow
C	Lada	Yellow
D	Opel Astra	Blue
E	Skoda	Blue
F	Citroen	Turquoise
G	Opel Astra	Blue
H	Peugeot	Red
I	Ford Fiesta	Red
J	Skoda Felicia	Red
K	VW Golf	Red
L	Fiat	Red
M	Fiat 126p	Blue
N	Lada	Blue
O	Lada	Green
P	Reno Megane	Green
R	Citroen	Green
S	Fiat 126p	Green
T	Fiat Uno	Blue
U	Fiat Uno	Blue
W	Daewoo	Blue
X	Daewoo	Red
Y	Fiat Uno	Red
Z	Wartburg	Red

The aim of this work was to demonstrate the usefulness of FTIR and the Raman method in identification of pigments and in differentiation between paint samples of similar colour and shade. Raman imaging of the examined samples was applied in order to show the distribution of identified pigments in the examined samples and so, to obtain more information on the sample morphology.

2. Materials and methods

2.1. Infrared measurements

Infrared measurements were performed by means of an FTS 40Pro Fourier-transform infrared spectrometer (BioRad/Digilab, MA) which was equipped with a water-cooled high temperature ceramic source (MIR) and coupled with a UMA 500 microscope equipped with 15× objective and an MCT detector. Each spectrum was obtained by averaging 256 interferograms at 4 cm^{-1} resolution.

Fragments of 24 different car paints were examined. Samples were prepared by cutting each paint chip into 0.02 mm thick slices, perpendicular to the layers. The samples were placed on the microscope stage of the spectrometer, in the infrared beam, the field of view being limited to one layer by means of a variable aperture and IR spectra were measured by the transmission technique.

2.2. Raman measurements

Raman spectra were obtained using a Renishaw inVia spectrometer equipped with a confocal Leica microscope and three types of excitation source: Ar ion (514.5 nm), He–Ne (632.8 nm) and a near infrared semiconductor laser at 785 nm. The laser beam was focused on the samples by a 100× (N.A = 0.9) objective lens, which give a theoretical spot size of approximately 1 μm. The light was dispersed by a diffraction grating with 2400 grooves/mm for the 514.5 nm laser and 1200 grooves/mm for 632.8 and 785 nm. The signal was recorded using a Peltier-cooled charged device (CCD).

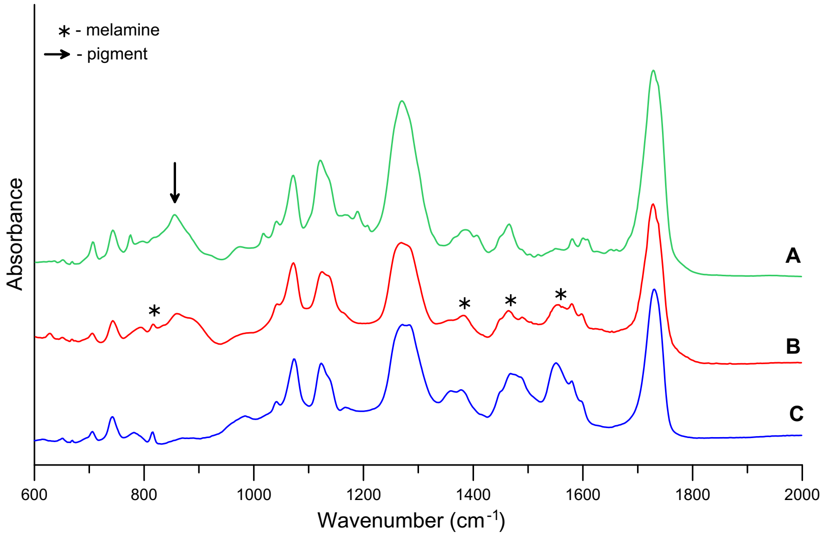

Fig. 1. Infrared spectra of yellow solid paints A, B, and C.