Effective identification of paints pigments in hit-and-run cases with confocal Raman microscope

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Abstract

Purpose – The purpose of this paper is to identify different automotive coatings using Confocal Raman microscope which could hardly be differentiated with Fourier transform infrared microscope (FTIR).

Design/methodology/approach – Raman spectroscopy was used to provide extra vibration information to infrared spectroscopy. Paints preparation was not necessary, and only 30 s was needed for each sample in an optimised method. Paints were first analysed by FTIR and then compared with Raman microscope.

Findings – Raman microscope was used to address the lack of ability of FTIR in discriminating four groups of paints in same colours. This study indicated that Raman microscopy is especially effective in sensing pigments and could successfully identify all pigments in the paints.

Research limitations/implications – The two instruments in combination produce accurate results than when used individually, especially in complex and multi-layered paints analysis.

Practical implications – The method proved to be fast, accurate and non-destructive, and it could be easily applied to real cases.

Originality/value – With this method, scientists could discriminate some coating types which were hard to be discriminated by other techniques.

Keywords Pigments, FTIR spectroscopy, Coatings technology, Forensics, Confocal Raman microscope

Paper type Technical paper

Introduction

The development of new methods for Raman spectroscopy of painted works of art has been investigated for many years (Domenech *et al.*, 2011; Weis *et al.*, 2004). These methods proved to be accurate, fast and non-invasive and were successfully applied in pigments' analysis in art. The possible contribution of Raman spectroscopy to forensic science, specifically to analysis of automotive paint samples, has also been evaluated in some cases since 2005. The results revealed that assigning bands to vibrations of the binders is difficult, and identifying the binder is possible only by a full vibrational approach, including infrared (IR) spectroscopy. However, Raman spectroscopy as such is suitable for identification of pigments and extenders in automotive paints, where the identification of organic pigments could especially provide an advantage over IR spectroscopy (Chalmers *et al.*, 2012; De Gelder *et al.*, 2005, Stachura *et al.*, 2007; Skenderovska *et al.*, 2008, He *et al.*, 2013; Suzuki, 2013).

It is estimated that more than 90 per cent of coating samples could be recovered in hit-and-run cases. In these cases, analysis of automotive coatings would be of great help to discriminate coatings from the scene of traffic accident and those collected from automobiles to exclude suspects. It will also be an important trace evidence to find suspects by verifying the similarity between coatings from scene and those from automobiles. Many coatings contained several layers, of which each layer might be only several micrometers in thickness and consists of different composition, and to characterize the coating layers in micrometres thickness, accurate and sensitive analysis method was needed.

Now, Fourier transform infrared microscope (FTIR) and scanning electron microscope/energy dispersive spectrometer (SEM-EDS) are popularly techniques used in coatings analysis. Previous studies suggested these two methods were fast and accurate, and could be applied to daily cases (Tweed *et al.*, 1974; Beam and Willis, 1990; Voskertchian, 1995; Ziêba-Palus, 1999; Thorburn and Doolan, 2005; Flynn *et al.*, 2005; Steven *et al.*, 2005a, 2005b; Ziêba-Palus and Borusiewicz, 2006), so these two methods were chosen as standard methods for forensic coatings analysis in many

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countries (SWGMAT, 2000; ASTM, 2008). Only few coatings were needed for FTIR analysis and high-quality spectra could be obtained in only a few seconds. FTIR has been used in real cases with many advantages (Lv *et al.*, 2012). Raman spectroscopy is complementary to IR spectroscopy, although both of them are vibrational spectroscopic techniques. Their spectra could supply different information derived from different nature of interactions and selection rules (De Gelder *et al.*, 2005). There are three important advantages of Raman spectroscopy over IR spectroscopy. First, Raman spectra generally extend well below 600 cm^{-1}, a region where many inorganic pigments and extenders have important vibrational bands, while IR cannot detect bands below 450 cm^{-1} (Deuterated Triglycine Sulphate detector) or 600 cm^{-1} (Mercury Cadmium Telluride detector). Second, Raman bands do not overlap, while bands in IR spectra do. At last, Raman spectra has no interference of carbon-dioxide and can be used with a water solvent, while IR cannot because of strong absorption capacity of carbon-dioxide and water.

Considering the complementary nature of both techniques and also the advantages of Raman spectroscopy listed above, and little work has been done on Raman spectroscopic study of automotive paints, it is worthwhile to deeply explore the possible contribution of Raman spectroscopy to find popular pigments in paints which could not easily be detected by FTIR.

Experimental

A Nicolet iN10 ATR-FTIR system with DTGS detector and Ominc Picta software was used for IR observation. The background was subtracted for every measurement. A Renishaw Invia confocal Raman microscope system with charge-coupled device detector was used to collect Raman spectrum. Before every measurement, crystal silicon with a fixed peak position at 520 cm^{-1} was used to calibrate Raman shifts. The spectra were collected in WIRE3 workstation with 785-nm laser. Four couples of coatings, each couple with the same colour (red, blue, orange and green), were kindly provided by the Ministry of Public Security, China.

Results and discussion

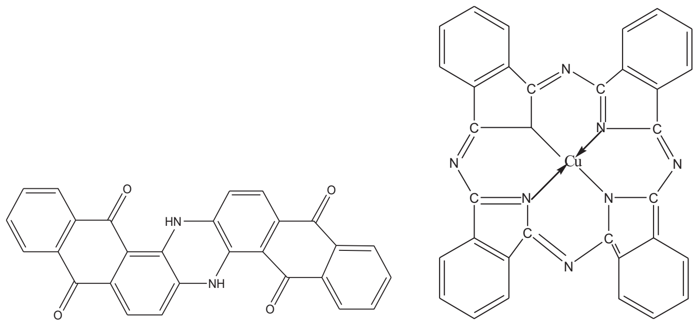
Figure 1 shows the chemical structures of some popular pigments. Phthalocyanine blue and Vat blue RSN are blue pigments low cost. Both of them are widely used in paints, inks, paper, ceramics and seals. Phthalocyanine blue cannot be detected by FTIR for the symmetrical structure; absorption of $-NO_2$ functional group is the main absorption of Vat blue RSN in FTIR which cannot be easily recognized in paints, especially in nitro-paints.

Toluidine Red and Scarlet Powder are two kinds of red pigments with excellent tinting strength and covering capacity. They can not be damaged by water and oil; they also are resistant to light, atmosphere, alkali and acid. Both of these two pigments are widely used in red paints in China now. In many cases, red paints existed, and Toluidine Red and Scarlet Powder can be detected with high frequency.

Blue samples

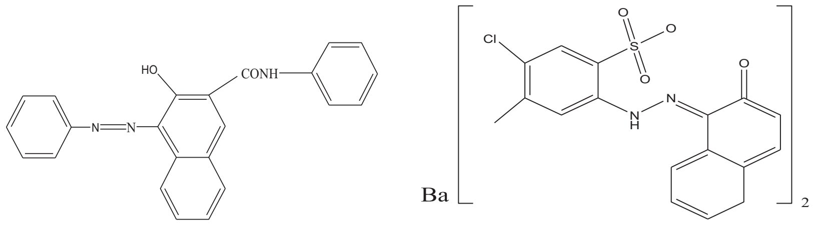
Figure 2 shows the IR spectra of two blue paints. Both blue paints were amino paints. From the synthesis of amino resin paints, the IR spectrum of amino resin paint should be the overlay of spectra of alkyd resin and n-butylated melamine-formaldehyde resin. Bands at 3,075, 1,730, 1,365,

Figure 1 Chemical structures of some pigments



Vat blue RSN

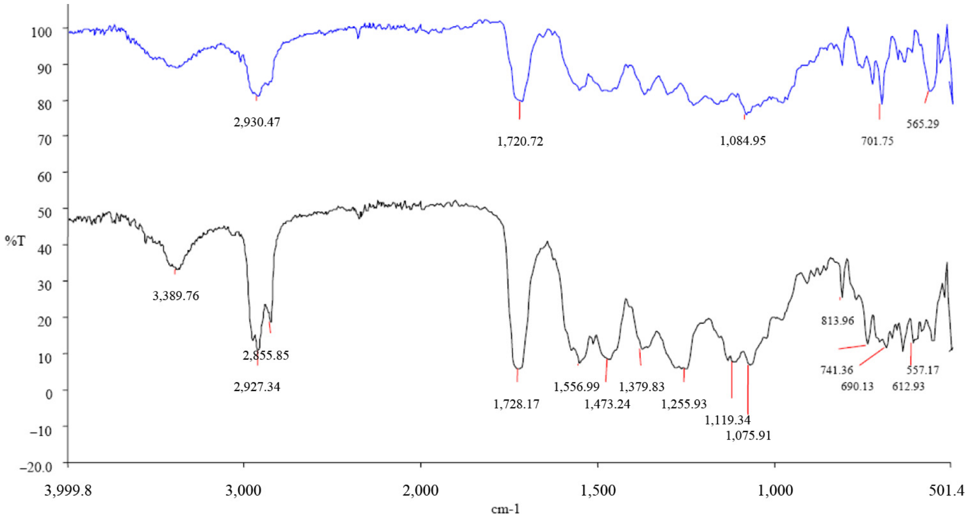
Phthalocyanine blue



Pigment Scarlet Powder

Bronze red C

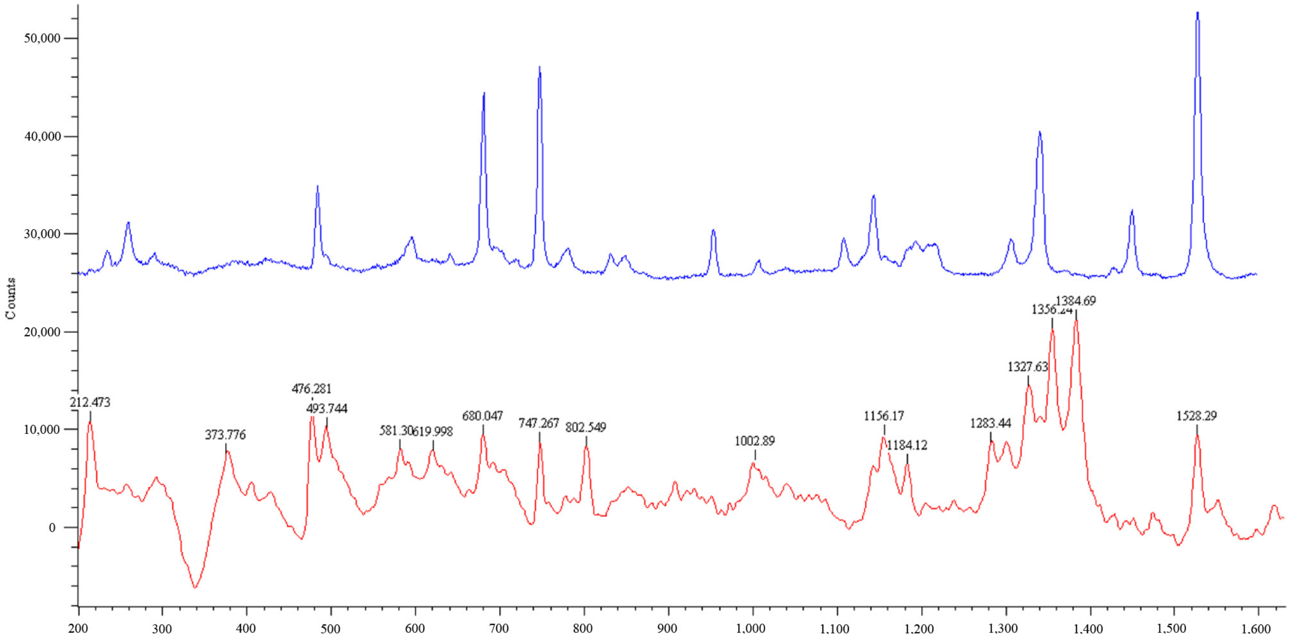
Figure 2 IR spectra of two blue paint samples



1,262, 1,122, 1,069, 743, 706 and 648 cm^{-1} were from absorbance of alkyd resin, and peaks at 2,931, 1,553, 1,490 and 815 cm^{-1} were from n-butylated melamine-formaldehyde resin. More specifically, absorption at 3,381 cm^{-1} should be assigned as NH absorbance in the stretching mode; 3,075 cm^{-1} =C-H stretching mode; 2,931 cm^{-1}, 2,859 cm^{-1} CH$_3$, CH$_2$ stretching mode; 1,730 cm^{-1} C=O stretching mode; 1,365 cm^{-1} methine bending mode; 1,262, 1,122 cm^{-1} C-O stretching mode; 1,069 cm^{-1} O(CH$_2$)$_2$ stretching mode; 743 cm^{-1}, 706 cm^{-1} =C-H in ortho substituents of benzene in alkyd resin out-plane bending mode. Further, 1,553 cm^{-1} should be assigned as a combination of N-H bending mode in –NH$_2$, –CONH$_2$ and C-N stretching mode, and 815 cm^{-1} as the vibration of triazine ring. FTIR did not offer further vibrational information on pigments. It is hard to discriminate these two paints just from resin information from FTIR.

Figure 3 shows Raman spectra of these two blue paints. The samples were clearly discriminated from those in Figure 3. Phthalocyanine blue was the main pigment in the first sample. Peaks at 1,528 cm^{-1} should be assigned to benzene stretching; 1,338 cm^{-1} to C-C stretching and C-N stretching; 1,141 cm^{-1} to C-C-C bending and C-N stretching; 1,036 cm^{-1} to CH in-plane wagging; 1,003 cm^{-1} to benzene breathing; 746 cm^{-1} to CH and C-C-C bending; 678 cm^{-1} to ring breathing; 593 cm^{-1}to benzene bending; 255, 230 and 171 cm^{-1} to transition of Cu ion in crystal. Main peaks of Vat blue RSN near 420, 483, 592, 681, 748, 834, 953, 1,041, 1,109, 1,143, 1,164, 1,184, 1,198, 1,303, 1,329, 1,344, 1,358, 1,372, 1,382, 1,451, 1,472, 1,486, 1,532 and 1,608 cm^{-1}. The peaks at 1,303, 1,329, 1,344, 1,358, 1,372 and 1,382 cm^{-1} were significantly different from the other sample.

Figure 3 Raman spectra of two blue paint samples (phthalocyanine blue and Vat blue RSN)



Orange samples

Figure 4 shows the IR spectra of two orange paints. Both of them were alkyd resin paints. Peaks at 1,599 and 1,580 cm^{-1} were assigned as skeleton vibration of benzene rings in phthalate structure of alkyd resin. These two peaks were weak but characteristic in spectrum and could be used as an indicator of alkyd resin paint. It is hard to discriminate these two paints just from FTIR spectra as illustrated in Figure 4.

Figure 5 shows the Raman spectra of these two orange paints. Significant difference was shown in Figure 5. Peaks at 830, 348 and 138 cm^{-1} revealed that $PbCrO_4$ was used as the main pigment, while peaks at 1,400, 1,369, 548, 389, 312 and 223 cm^{-1} hinted that $Fe_2O_3{\cdot}H_2O$ was used in the other sample.

Green samples

Figure 6 showed the IR spectra of three green paints. These paints were identified as phenolic aldehyde, vinyl perchloride and epoxy paints. For phenolic aldehyde paint, the band 3,468 cm^{-1} was the stretching vibration of OH; 2,927 and 2,854 cm^{-1} were the stretching vibration of C-H; 1,416 cm^{-1}, stretching vibration of O-CH_2; 1,269 and 1,173 cm^{-1}, stretching vibration of C-O; and 909-667 cm^{-1}, substituent of the benzene. For vinyl perchloride paint, 1,723, 1,600, 1,580, 1,263, 1,124, 1,074 and 743 cm^{-1} were from alkyd resin as the matrix. C-Cl stretching included 616, 636 and 686 cm^{-1}. For epoxy paint, indicative peaks were found at 1,611, 1,508 and 827 cm^{-1}. The FTIR spectra further suggested that Prussian Blue ($Fe_4[Fe(CN)_6]_3{\cdot}K_4Fe(CN)_6$) might exist in the first two samples (2,090 and 2,101 cm^{-1}).

Raman spectra of these three green paints in Figure 7 revealed that all the green-coloured samples were a mixture of blue and yellow. The yellow colour was from $PbCrO_4$ (830, 348 and 138 cm^{-1}), and the blue colour was from Prussian Blue (the first two samples) and phthalocyanine blue (the third sample) separately.

Figure 4 IR spectra of two orange paint samples

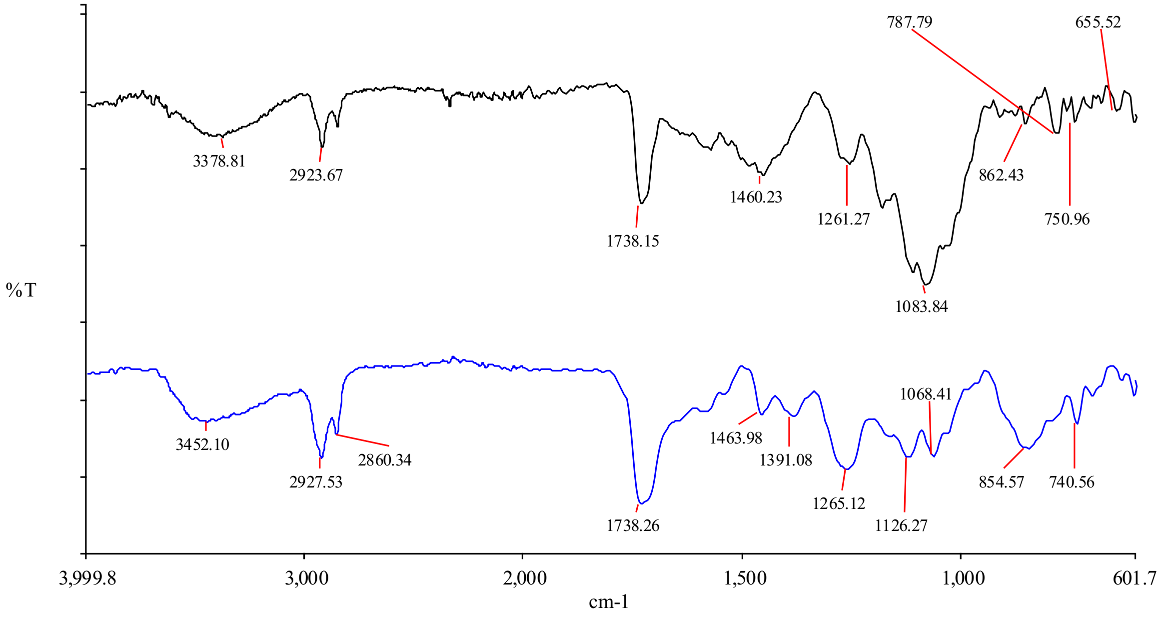


Figure 5 Raman spectra of two orange paint samples ($PbCrO_4$ and Fe_2O_3)

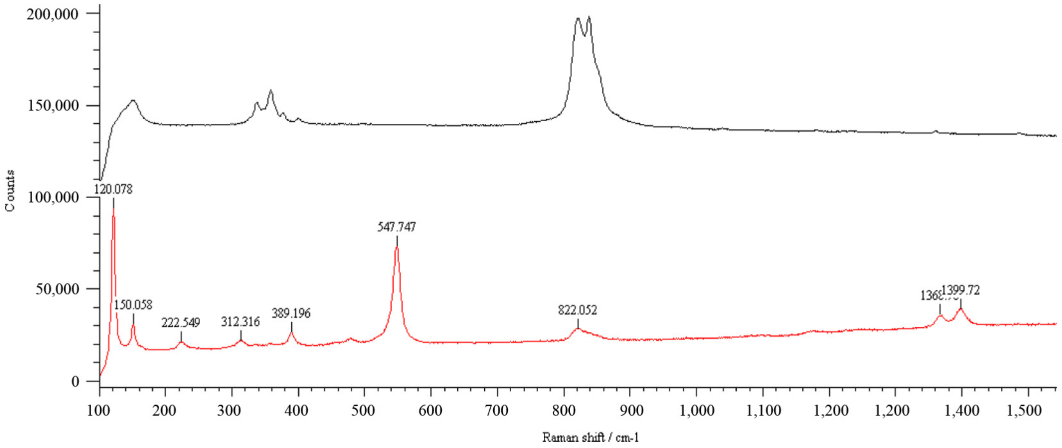


Figure 6 IR spectra of three green paint samples

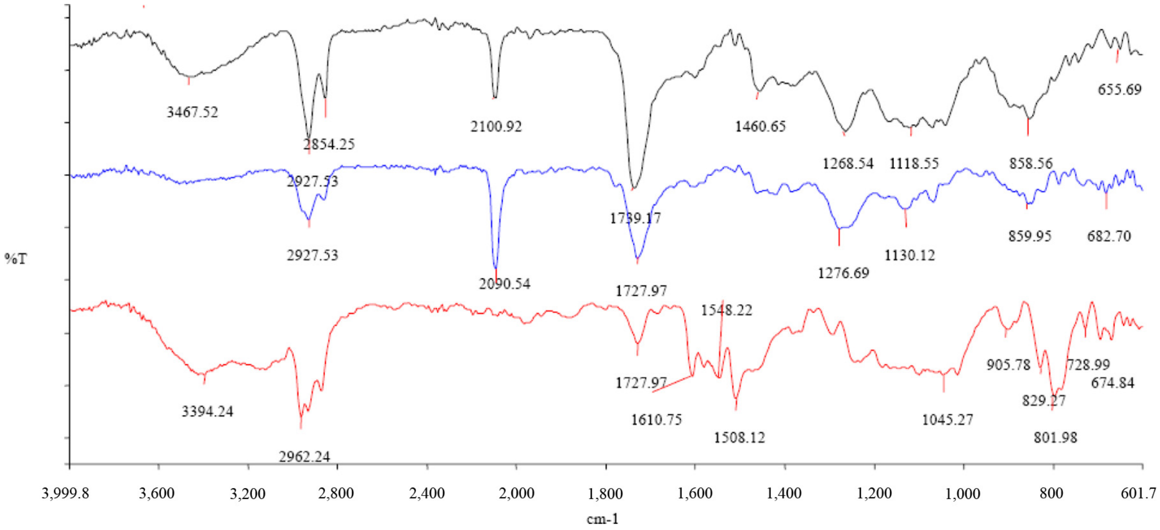
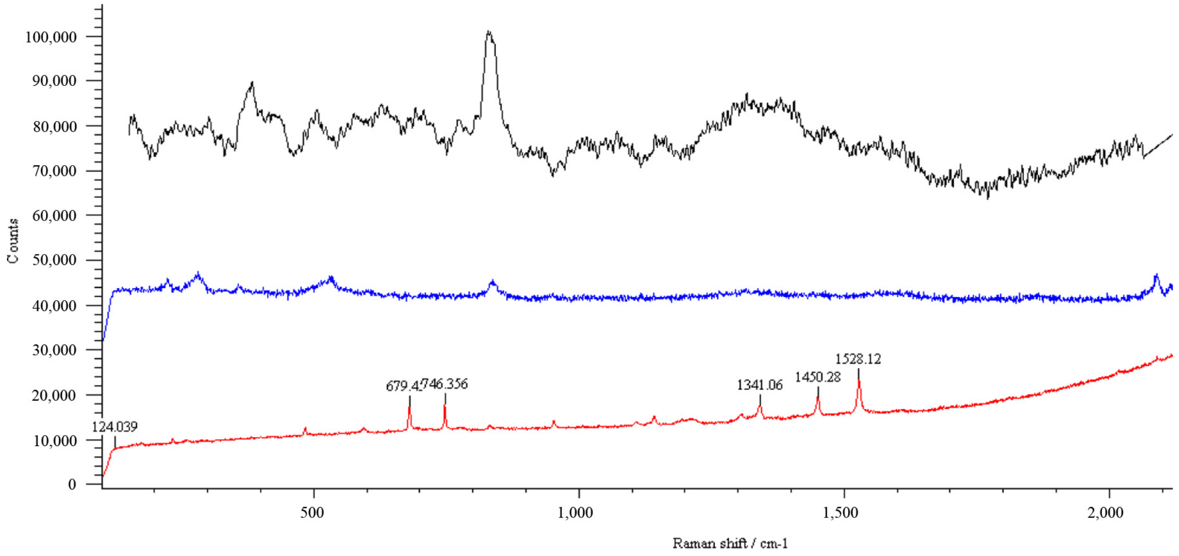


Figure 7 Raman spectra of three green paint samples ($PbCrO_4$, Prussian Blue and phthalocyanine blue)



Red samples

Figure 8 shows the IR spectra of two red paints. The first one was alkyd resin paint from Figure 8. Peaks at 1,743, 1,597, 1,453, 1,381, 1,261, 1,070, 752 and 706 cm^{-1} were typical absorption of alkyd resin; 1,652, 1,385, 1,277, 1,072 and 844 cm^{-1} were from cellulose nitrate absorption.

Scarlet Powder was identified in the first paint by FTIR. Peaks of Scarlet Powder should be assigned as follows: 1,673 cm^{-1} C=O stretching; 1,594, 1,493 and 1,453 cm^{-1} were the skeleton vibration of the benzene ring; 1,545 cm^{-1}, combination of N-H bending and C-N stretching vibration; 1,014 cm^{-1} =C-H in ortho substituents of benzene in-plane bending vibration; and 752 and 706 cm^{-1}, the out-plane bending vibration. No pigment information in the second sample was presented by FTIR.

Figure 9 shows the Raman spectra of these two red paints. Raman spectra verified that Scarlet Powder exists in the first paint by comparison with the standard spectra. Furthermore, the pigment in the second sample was tentatively identified as Bronze red C. The main peaks were observed at 1,590, 1,493, 1,445, 1,393, 1,332, 1,282, 1,185 and 1,151 cm^{-1}. Peak at 1,590 cm^{-1} represented benzene stretching; 1,493 cm^{-1}, CCH bending in benzene ring and C=O stretching; 1,393 cm^{-1}, stretching of naphthalene ring; and 1,332 cm^{-1}, C-C stretching, N-N or C-N stretching. Peaks at 1,185, 1,332, 1,393 and 1,445 cm^{-1} in Raman spectra clearly discriminated the sample from the other.

Conclusions

Four couples of samples were compared by using FTIR and Raman in combination. FTIR presented organic composition well. Amino, polyurethane, epoxy paints were identified by indicative peaks which were further tentatively assigned. For paints with the same resin and that which could not easily be discriminated by FTIR, Raman microscopy offers extra peak

Figure 8 IR spectra of two red paint samples

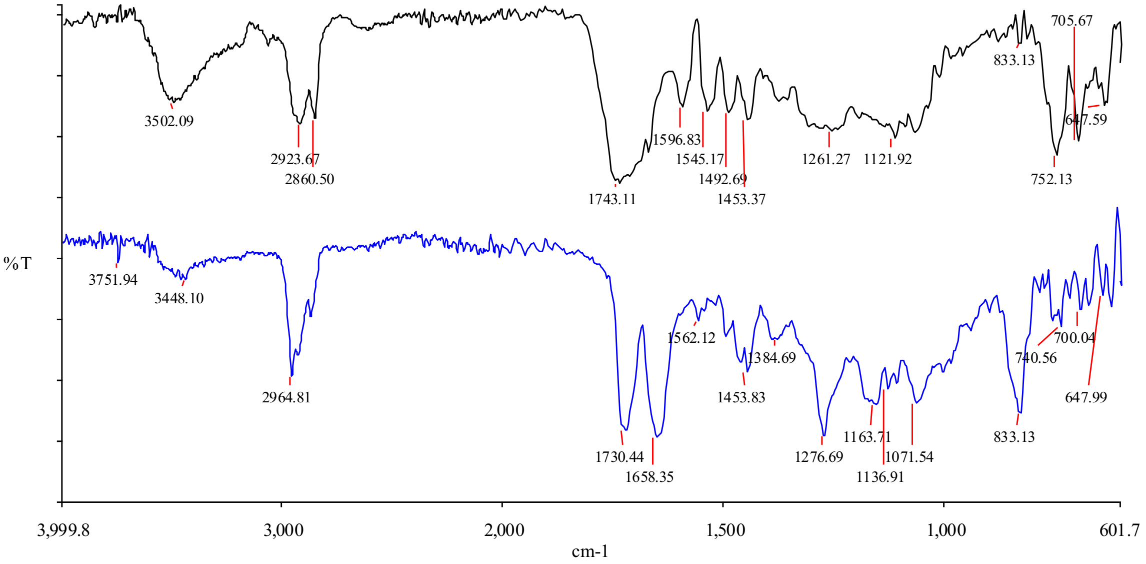
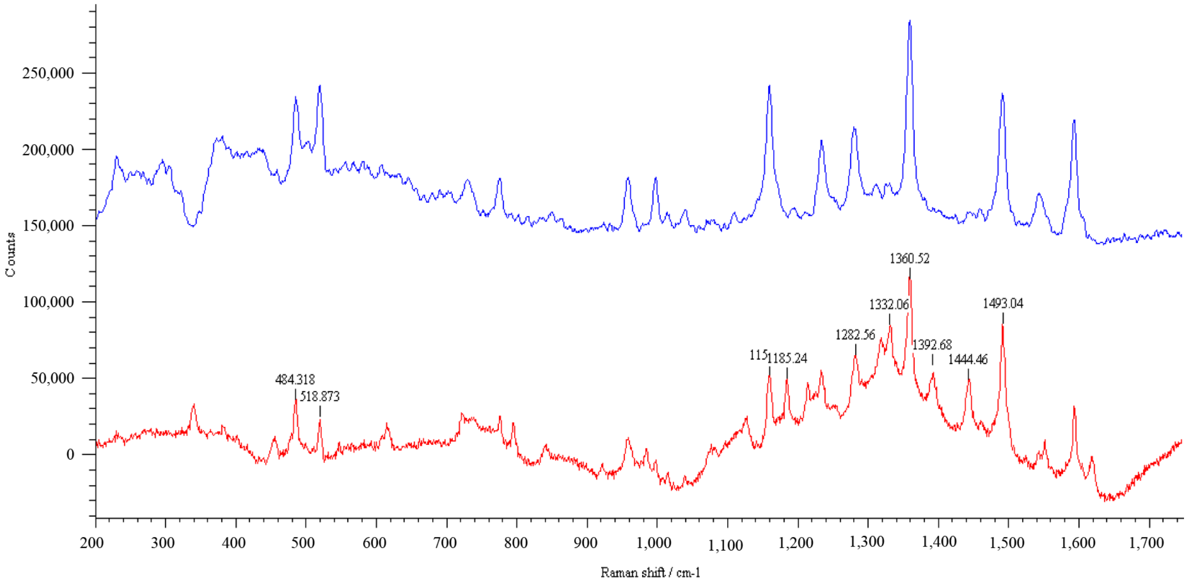


Figure 9 Raman spectra of two red paint samples (Scarlet Powder and Bronze red C)



information on pigments. Phthalocyanine blue and Vat blue RSN, Pigment Scarlet Powder and Bronze red C, Fe_2O_3 and $PbCrO_4$, Prussian blue and phthalocyanine blue were all successfully identified and discriminated in Raman spectra. The results hinted that confocal Raman microscopy could be used as an effective tool in identification of paints pigments in hit-and-run cases. Estimation of recipe concentrations of pigments and additives and new strategies combining more structural information and multidimensional mathematical analysis is suggested for future studies.

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