

Raman Spectroscopy for Rapid Analysis of White Household Paints



Introduction

Paint samples can provide valuable evidence in a wide variety of forensic casework, such as associating a suspect and a specific location (in the case of trespass), or a hit and run victim with a particular vehicle. It typically involves optical microscopy, FT-IR and PyGC-MS. Raman spectroscopy is not yet used for routine paint examination, but it has many potential benefits, particularly the speed in which it can be applied and the fact that it is a non-invasive method that can be used to screen paints of all types. This application note focuses on discriminating between “difficult” samples – single layer white architectural paints.

This study investigated 51 single-layer samples of white household paints intended for interior and/or exterior decoration of doors, window frames, etc. At the time the sample set was collected, this represented over 90% of all the paints of this type available (2003) in this geographical region.

The white paint samples varied in manufacturer and finish (gloss, matt, satin), but were all nominally “pure white”. The samples were prepared according to the manufacturers’ instructions, painted onto fresh aluminum surfaces (~1 cm²).

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Experimental conditions

Studies were carried out using a PerkinElmer® RamanStation™ 400 equipped with a 785 nm diode laser. Samples were mounted in a 96 well micro titre plate and the spectrometer was operated in high-throughput screening mode, where it automatically drove to each sample, auto focused and then recorded and co-added spectra from a 3 x 3 grid of points (0.5 mm spacing, 2 x 5 s each point). The exposure times were typically ca. 60 seconds.

Results

The Raman spectra of the 51 paints were recorded at 785 nm; preliminary experiments on a small set of 10 randomly selected paints using 514 and 532 nm excitation showed unacceptable levels of fluorescence and were not continued.

It was found that the 785 nm spectra had much lower levels of fluorescence and they could be divided into 7 groups, i.e. sets of samples whose spectra contained the same bands, although not necessarily with the same relative intensities (Figure 1).

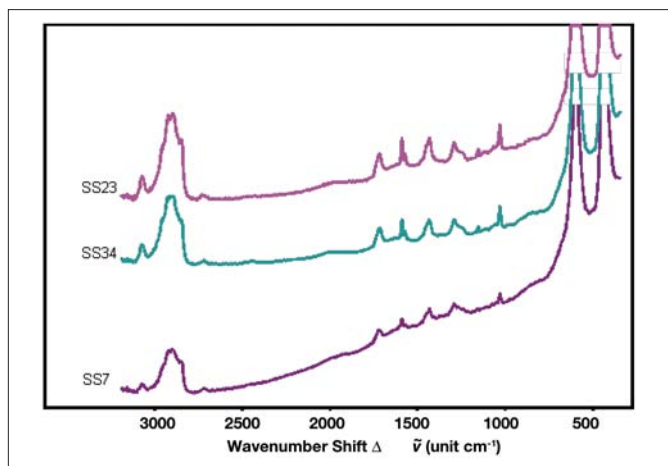


Figure 1. Three Raman paint spectra from group.

In addition, there were six unique Raman spectra. Figures 2 and 3 show representative Raman spectra of samples from each of the seven groups and the six unique spectra, respectively.

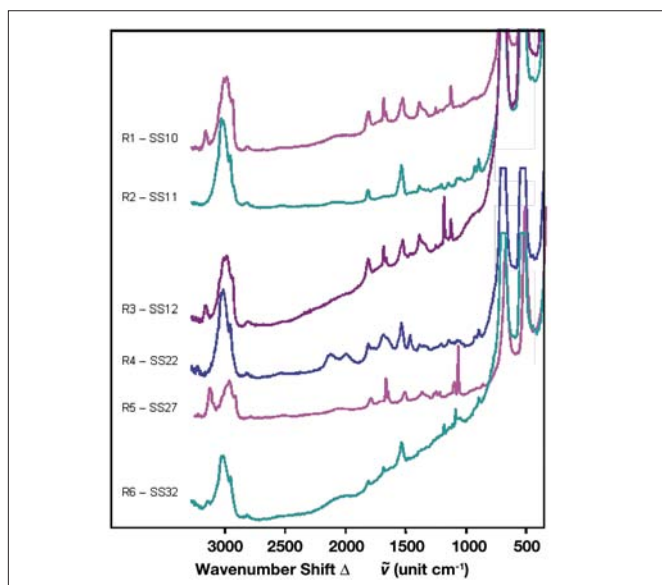


Figure 2. Raman spectra from six of the seven groups.

In fact, both IR absorption and Raman spectra were recorded for all the samples but the individual paint constituents were much easier to identify in the Raman spectra because the narrow line width of both the organic and inorganic components meant there was little band overlap. The high dynamic range of the Raman measurements also meant that it was straightforward to record the large TiO_2 signals (610 cm^{-1}) and much weaker resin bands in a single measurement.^{1,2}

Overall, identification of approximately half the paint samples were straightforward, either because the spectra were unique or because the within-Group variation was sufficiently large, therefore individual members could be distinguished from each other. However, the other half of the samples (25 of the 51 paints examined) were sufficiently similar that they obviously constituted a single group (Group R1, Figure 2). The spectra of the paints within this Group are consistent with a simple drying oil/phthalate base and rutile pigment/extender but there are no other readily identifiable constituents such as CaCO_3 (1086 cm^{-1}), dolomite (1092 cm^{-1}) or styrene/vinyl toluene modifier which give distinctive features that help in discriminating between the other paints.

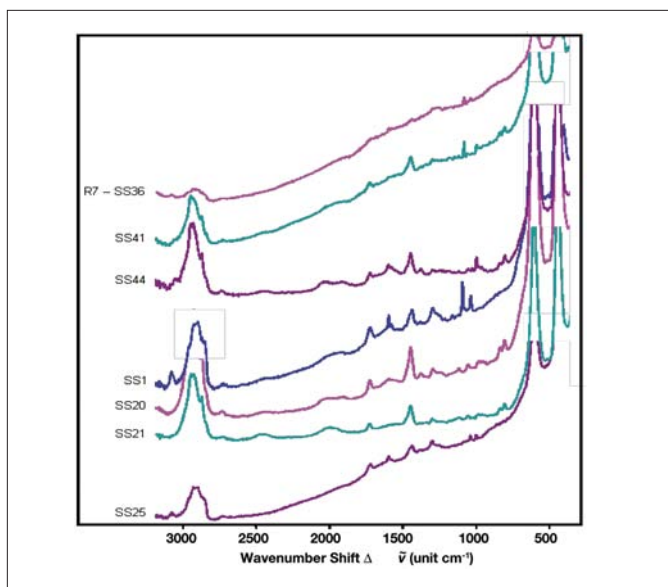


Figure 3. Raman spectra from group 7 and the six unique samples.

Since the relative proportions of the various constituents is different even for the Group 1 paints which contain the same basic components, discriminating between these paints is potentially as simple as measuring the relative band intensity ratios of the most important features, which are the bands characteristic of the rutile, phthalate and aliphatic CH_2 components¹. Raman band intensities can be measured with excellent reproducibility³.

In this case, the measurement was slightly complicated by small sloping backgrounds in some of the spectra and although it would have been straightforward to manually subtract a baseline from each spectrum, this process is prone to bias and/or human error and therefore the first derivative spectra were generated (1st derivative, Savitsky-Golay, 11 points).

Using first derivative spectra reduced the baseline to an acceptably low level without introducing bias. An example is shown in Figure 4. For convenience, the band positions from the conventional spectra are used here even when discussing the bands in the 1st derivative spectra, which lie at different positions.

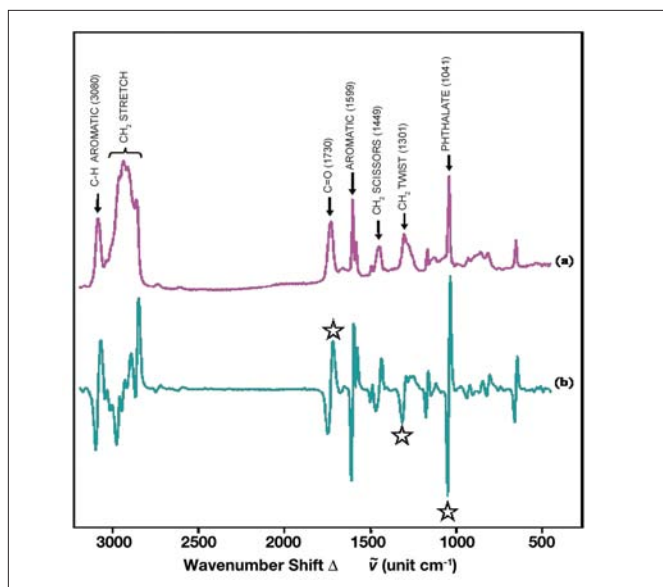


Figure 4. (a) Unprocessed Raman spectrum (b) 1st derivative Raman spectrum.

The intensity of several bands in the differentiated spectra were measured but the largest source of first derivative was the change in the relative intensities of the aliphatic versus the aromatic bands. The band intensities within each spectrum were normalised with respect to the intensity of aliphatic band at 1301 cm^{-1} .

Figure 5 shows such a scatter plot of the intensities of the $\text{C=O } 1730\text{ cm}^{-1}$ and aromatic 1041 cm^{-1} vibrations for the Group 1 paints. The large spread along the diagonal reflects the large changes of both these bands but it is clear that the intensities for these bands were strongly cross-correlated, as were all the other bands measured.

In effect, the cross-correlation means that the data are almost univariate with the aromatic vs aliphatic bands accounting for almost all the variance. Despite this cross correlation it was still possible to divide the 25 spectra in Group 1 into three groups and 5 unique samples.

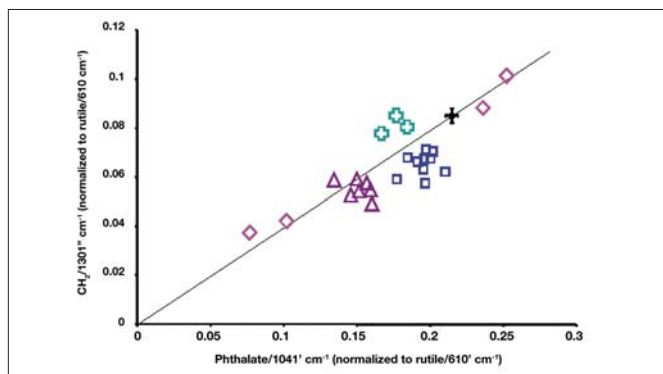


Figure 5. Scatter plot showing the variation within group 1 samples.

Conclusion

This study has shown that Raman spectroscopy has considerable potential for the analysis of white paints. The fact that it is a rapid technique that gives information on both the binder and inorganic constituents already makes it attractive. However, the major advantage of the Raman approach is the high level of reproducibility in the spectra which allows even relatively small difference in relative intensity (rather than simple absence or presence of features) to be used to discriminate between different paints.

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References

1. Bell, S.E. J.; Fido, L.A.; Speers, S.J.; Armstrong, Applied Spectroscopy, 59(1) 100-108 (2005).
2. Bell, S.E. J.; Fido, L.A.; Speers, S.J.; Armstrong, W.J.; Spratt, S., 59(11) 1333-1339 (2005).
3. Bell, S.E. J.; Fido, L.A.; Speers, S.J.; Armstrong, W.J.; Spratt, S., 59(1) 1340-1346 (2005).