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# Fourier transform Raman spectroscopic study of pigments present in decorative wallpapers of the middle nineteenth century from the Santa Isabel factory (Vitoria, Basque Country, Spain)<sup>†</sup>

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One of the earliest wallpapers manufactured by the Santa Isabel factory (Vitoria, Basque Country, Spain) (1845) was found at the Torre de los Varona (near Vitoria) during restoration work on the building. As part of this cleaning and restoration work, the identification of the wallpaper's pigments was carried out by Fourier transform (FT) Raman spectroscopy. Fragments of paper were set in a sampler kit for planar surfaces. By moving the paper samples, it is possible to locate the laser beam's spot at the point that it is going to be analysed with a spatial resolution of about 0.5 mm. With this method it is possible to map a surface of several square centimetres without the need for an optical microscope. As FT-Raman analysis is totally non-destructive, the samples were restored and integrated with the whole wallpaper at the end of the analysis. Small particles of pigment were collected for the analysis of the pink and green colours by atomic absorption spectrometry (AAS). In both cases, the damage caused by the pigment sampling was minimal and non-visible. BaSO<sub>4</sub>, CaCO<sub>3</sub>, Pb<sub>3</sub>O<sub>4</sub>, PbCrO<sub>4</sub>, PbO, Prussian Blue, gypsum and an organic black pigment were detected. It is important to take into account the laser beam's penetrative power in order to interpret the spectra correctly. The identification of only eight pigments to make 12 different colours, mostly in two different shades, shows the ability of the wallpaper manufacturer to create a rich palette at low cost. This type of primitive industrial decorative work has become real artwork that it is necessary to preserve and restore. Copyright © 2002 John Wiley & Sons, Ltd.

## INTRODUCTION

Printing on paper was used in the Occident from the end of the fourteenth century to manufacture religious drawings, endpapers and wrappers for books, playing cards, dominoes and so on. However, the great revolution in this kind of art happened around the eighteenth century. Block-printing is a technique that was first introduced for the decoration of textiles, but in the course of the eighteenth century economic circumstances forced many European cotton printers to start printing on paper.

Until the early 1830s, the small factories in which wallpaper was manufactured used small, single sheets of hand-made paper. Modern continuous paper production appeared

in 1832 through the Zuber wallpaper manufacturers. The use of wood pulp provided the possibility of making cheaper wallpapers, so that this decorative technique was then available to a wider number of people, and at the same time allowed manufacturers to use a greater format, becoming very popular particularly in France. Details of the wallpapers manufactured in France, England and the USA are well documented.<sup>1</sup>

In Spain, the Santa Isabel (Vitoria, Basque Country) wallpaper factory began production in 1845 in response to the prohibition of importing wallpapers from foreign countries, such as France.<sup>2</sup> The manufacturing process in this factory was modern, with the use of cylinders to stamp out the colours, mechanical pressure and a continuous paper feed. There were 40–50 workers employed, one of them a chemist, and about 50 000–60 000 rolls of paper were produced per year. In that period, this factory was the only one in all of the north of Spain and supplied wallpapers to the whole country.

One of the earliest wallpapers manufactured by the Santa Isabel factory was found in a room at the Torre de los Varona

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(a tower-palace located in the town of Villanañe, 40 km from the city of Vitoria, in the north of Spain) during restoration of the building, which has belonged to the same family for 1300 years.

As part of the cleaning and restoration work on the wallpaper, the pigments were identified by Fourier transform (FT) Raman spectroscopy and the results obtained are presented and discussed below.

## EXPERIMENTAL

### Description of the wallpaper and samples

The wallpaper covering the whole room is made of continuous paper and the iconography is very rich, with flowers and medallions in undulating arrangements in blue, green, white, red, yellow, orange and grey colours, most of them in two different shades. All these colours were applied over a brilliant white background, indicating the use of mechanical pressure when the wallpaper was manufactured. After the background a given light shade colour was applied followed by the dark one or other different colour.

Figure 1 (top) shows the printing mark of the Santa Isabel wallpaper factory that appears on the back of the continuous papers. Also, some serial numbers were found next to the printing mark, starting with 2117 and finishing with 2139; these figures refer to the manufacturing order of each paper roll. Figure 1 (bottom) shows the sample in detail.

The state of conservation of the wallpaper was very poor. There were moisture and fungi (the tower is located 900 m above sea level and suffers from long, cold winters and hot, moist summers, northern and western winds being dominant

in the area). Furthermore, some pieces of wallpaper had fallen from a wall that was cracked in some areas, and these cracks also promoted the cracking of the paper.

Different pieces of the broken paper were used as samples during the identification process. The samples, each of about 25 cm<sup>2</sup>, were selected from different parts of the room. At least three different samples were used for the same shade of each pigment in order to provide representative results. As the FT-Raman analysis was totally non-destructive, the wallpaper samples were cleaned, restored and integrated with the whole continuous wallpaper at the end of the analytical process.

For the analysis of the pink and green colours, atomic absorption spectrometry (AAS) was also used. In order to achieve this, small chips of pigment (ca 2 mg) were collected with a scalpel from (a) the edge of the wallpaper or (b) from other pieces of paper that appeared below the visible wallpaper. In both cases the damage caused to the art work was minimal and was always located in non-visible parts of the restored wallpaper.

### Procedures

The FT-Raman spectra of the pigments were collected with a Nicolet FT-Raman 950 spectrophotometer, with an excitation wavelength of 1064 nm (Nd:YAG laser), and an InGaAs detector. To avoid thermal decomposition of the samples, powers between 12 and 17 mW were used. To obtain a good signal-to-noise ratio, 2000 scans were accumulated for each spectrum with a resolution of 4 cm<sup>-1</sup>. Data acquisition and analysis were carried out with the Omnic software provided by Nicolet.

The 1064 nm excitation wavelength was selected in order to minimize fluorescence effects. Moreover, Burgio *et al.*<sup>3</sup> have demonstrated that less degradation of lead pigments takes place by the use of near-infrared laser beams, such as that at 1064 nm, than with other lasers working at, e.g., 781.8 nm (Renishaw diode laser), 647.1 nm (Coherent I301 krypton ion laser), 514.5 nm or 488.0 nm (Coherent I70 argon ion laser).

The Raman analysis was really non-destructive because the small pieces of the painted papers were set in the sampler kit for planar surfaces. By moving the paper samples, it is possible to locate the laser beam's spot at the point that it is going to be analysed with a spatial resolution of about 0.5 mm. With this method it is possible to map a surface of several square centimetres without the need for optical microscope.

The spectral analysis was performed by comparing the spectrum of each pigment with a home-made database of pigment spectra collected previously using pure pigments supplied by several dealers.

The AAS analysis was performed using an AAnalyst 100 spectrometer (Perkin-Elmer). The small chips of the pink and green paint layers were digested with HCl–HNO<sub>3</sub> (3:1) nearly to dryness, dissolved in water, filtered and diluted to a known volume prior to the analysis.



**Figure 1.** Printing mark of the Santa Isabel wallpapers factory and serial number of the paper roll (top) and sample in detail (bottom).

## RESULTS AND DISCUSSION

The results obtained are presented below, arranged by colours from the background to the front.

### Brilliant white used as the background colour

The white which is present as a background colour through the whole surface of the paper has a brilliant shade given by mechanical pressure (before the colour printing on the paper). As stated before, the other colours were painted over this white. Figure 2(ii) shows the FT-Raman spectrum of this white colour. There are five bands at 986 (vs), 646 (w), 616 (w), 460 (m) and 453 (m)  $\text{cm}^{-1}$ , indicating that the pigment present is  $\text{BaSO}_4$  (abbreviations: s = strong, m = medium, w = weak, sh = shoulder, v = very). The strong band at 986  $\text{cm}^{-1}$  is due to the stretching mode of the S—O bond.<sup>4</sup>

The spectral match was confirmed by comparison with the literature<sup>5</sup> and with a spectrum from a contemporary sample of  $\text{BaSO}_4$  processed in our laboratory [Fig. 2(iii)].

The shoulder at 437  $\text{cm}^{-1}$  and the intensification of the 460  $\text{cm}^{-1}$  band, with respect to the  $\text{BaSO}_4$  signal, are due to the composition of the paper and the weak signals at 964, 519 and 538  $\text{cm}^{-1}$ . These five bands belong to wood pulp, as can be seen in Fig. 2(i).

The  $\text{BaSO}_4$  pigment was introduced in paintings in the eighteenth century and was available in France as a synthetic pigment from the middle of the nineteenth century.<sup>6</sup> The use of  $\text{BaSO}_4$  as a background pigment of paper may be due to aesthetic reasons (this pigment has a brilliant shape when mechanical pressure is applied) or to its low hiding power.<sup>6</sup>

This pigment has been used by preference as a charge mixed with other pigments,<sup>7</sup> but here the manufacturer selected calcium carbonate as the charge to lighten the different colours, as shown below.

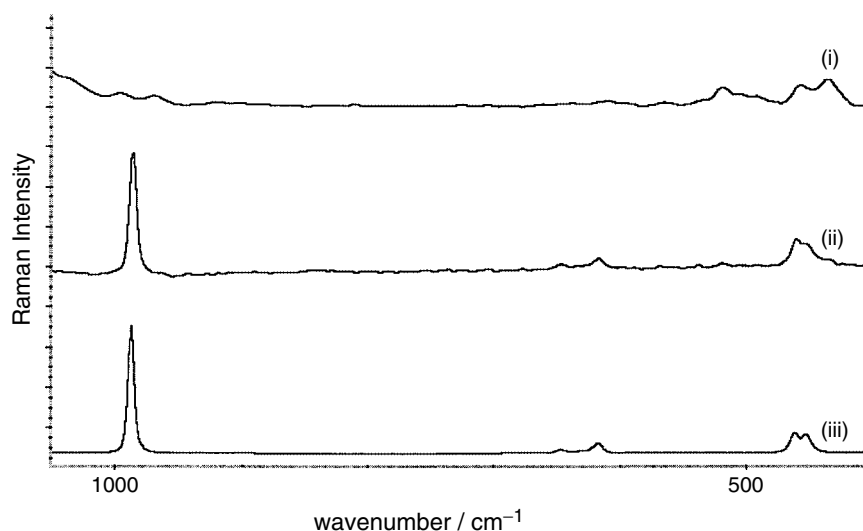
### Grey

Two different types of greys can be found on the wallpaper, one light and the other dark. The light grey is always found over the  $\text{BaSO}_4$  background layer and the dark grey is found over the light grey. The FT-Raman spectra of the two types of greys are shown in Fig. 3. In both spectra there are two broad bands centred at 1597 and 1340  $\text{cm}^{-1}$ . The light grey shows another three peaks at 1085 (s), 711 (vw) and 280 (vw)  $\text{cm}^{-1}$ , which are consistent with calcium carbonate (see below). By contrast, in the dark grey colour only a small signal of the strongest band of calcium carbonate, at 1085 (vw)  $\text{cm}^{-1}$ , can be observed. Comparison with the FT-Raman spectrum of modern lamp black and ivory black recorded in our laboratory, also shown in Fig. 3, indicates that the black pigment used to make the grey colour is one of these two carbon black pigments. The other compound used to prepare the grey colour is calcium carbonate.

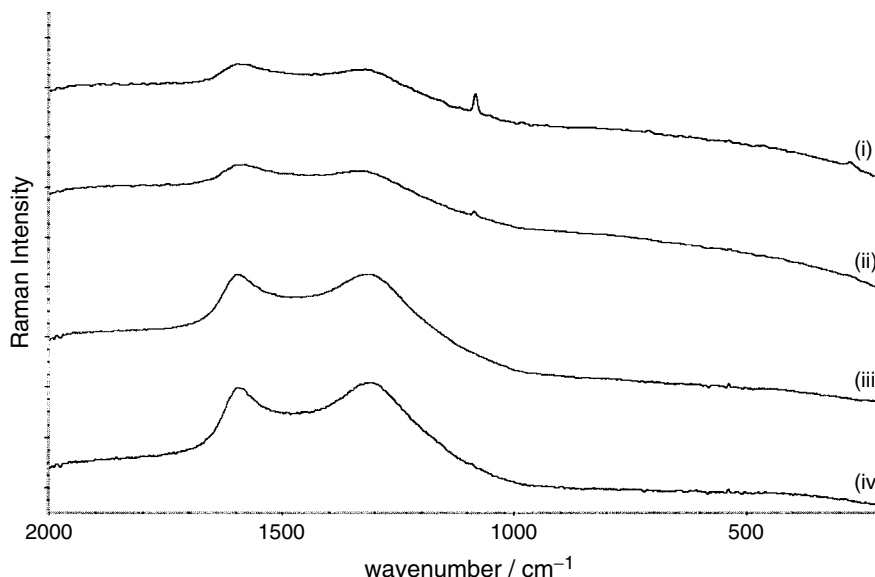
Semi-quantitative measurements of the ratio  $I(\text{CaCO}_3)/I(\text{grey})$ , at 1084  $\text{cm}^{-1}$  for  $\text{CaCO}_3$  and 1597  $\text{cm}^{-1}$  for grey, indicate that there is approximately four times more  $\text{CaCO}_3$  in the light grey than in the dark grey colour.

### Blue

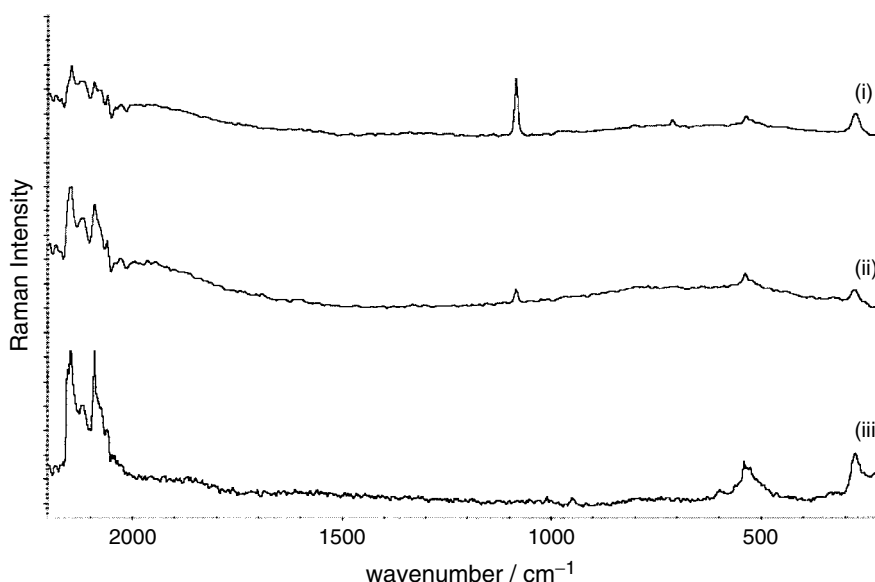
This colour is present in two shades, light blue and dark blue and Fig. 4(i) and (ii) show their FT-Raman spectra. The spectrum of the light blue colour shows bands at 2147 (s), 2123 (w), 2097 (w), 2078 (sh), 2063 (w), 1085 (vs), 711 (w), 537 (w) and 279 (s)  $\text{cm}^{-1}$ . The first five bands are assigned to C—N stretching vibrational modes of the hexacyanoferrate ion, which agrees with the region given for cyano ligands by Nakamoto.<sup>8</sup> All these bands and the band at 537  $\text{cm}^{-1}$  indicate the presence of Prussian Blue. The bands at 1085 and 711  $\text{cm}^{-1}$  are assigned to calcium



**Figure 2.** FT-Raman spectrum of a wood pulp (i), the brilliant coating white colour (ii) and standard barium sulphate (iii); 4  $\text{cm}^{-1}$  spectral resolution.



**Figure 3.** FT-Raman spectrum of light grey colour (i), dark grey colour (ii), standard ivory black (iii) and standard lamp black (iv);  $4\text{ cm}^{-1}$  spectral resolution.



**Figure 4.** FT-Raman spectrum of light blue colour (i), dark blue colour (ii) and standard Prussian Blue (iii);  $4\text{ cm}^{-1}$  spectral resolution.

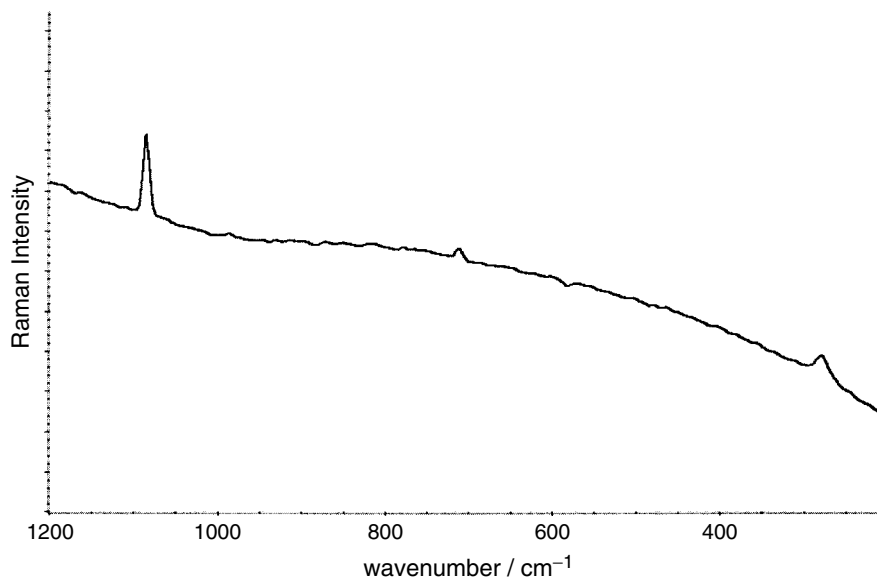
carbonate, whereas the band at  $279\text{ cm}^{-1}$  has a contribution of both Prussian Blue and calcium carbonate. However, the spectrum of the dark blue colour only shows those bands assigned to Prussian Blue and the strongest band of  $\text{CaCO}_3$  at  $1085\text{ cm}^{-1}$ .

Semi-quantitative measurements of the ratio  $I(\text{CaCO}_3)/I_{\text{(blue)}}$ , at  $1084\text{ cm}^{-1}$  for  $\text{CaCO}_3$  and  $2147\text{ cm}^{-1}$  for Prussian blue, indicate that there is 10 times more  $\text{CaCO}_3$  in the light blue than in the dark blue colour. Figure 4(iii) shows the FT-Raman spectrum of a contemporary sample of Prussian Blue, a pigment introduced in 1724 by Woodward.<sup>6</sup> Therefore, the results obtained for the blue colour are historically consistent.

### Rose

The spectrum of this colour (Fig. 5) has bands at  $1085\text{ (s)}$ ,  $711\text{ (w)}$  and  $279\text{ (w)}\text{ cm}^{-1}$ . These bands are representative of calcium carbonate, which is probably the white pigment used to make the pink colour from a red colour. There are no other bands in the spectrum. This could be due to the low concentration of the red pigment in the sample, the use of a red pigment with a very weak Raman spectrum and/or to the low power of the laser used to avoid the thermal decomposition of the sample.

Although there is no spectral confirmation of which is the red or the pink pigment, it could be the same



**Figure 5.** FT-Raman spectrum of rose colour;  $4\text{ cm}^{-1}$  spectral resolution.

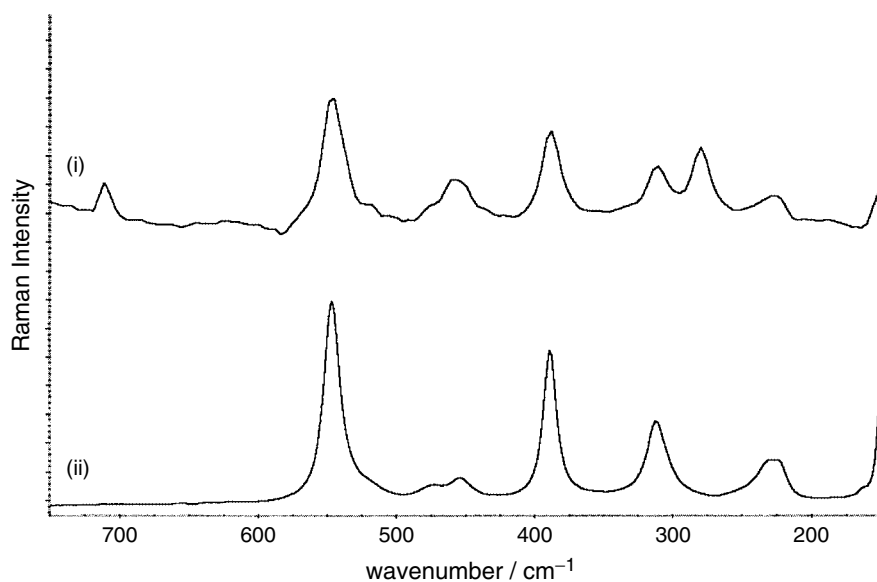
pigment as that employed to make the orange and the red colours,  $\text{Pb}_3\text{O}_4$  (see below). Semi-quantitative measurements of the pink colour layer made using AAS support this view.

### Red

The red colour is always found covering a pink colour. Figure 6(i) shows the FT-Raman spectrum of this colour. The most intense bands are situated at 1085 (s) (not shown), 711 (w), 547 (s), 459 (w), 389 (s), 313 (m), 280 (m), 225 (w), 152 (m) and 120 (m) (not shown)  $\text{cm}^{-1}$ . The band at  $547\text{ cm}^{-1}$  is due to the  $\nu(\text{PbO})$  vibrational mode and the band at  $225\text{ cm}^{-1}$  is due to the  $\delta(\text{PbO}_2)$  vibrational mode.<sup>9</sup> All these bands can

be assigned to minium ( $\text{Pb}_3\text{O}_4$ ), which is red in colour. Also in Fig. 6(ii) the spectrum obtained in our laboratory from a contemporary sample of minium is shown.

The bands at 1085, 711 and  $280\text{ cm}^{-1}$  are assigned to calcium carbonate. In order to ascertain if this  $\text{CaCO}_3$  was systematically mixed with the red minium, several spectra of different red layers were collected and the ratio  $I(\text{CaCO}_3)/I(\text{Pb}_3\text{O}_4)$ , at  $1085\text{ cm}^{-1}$  for  $\text{CaCO}_3$  and  $547\text{ cm}^{-1}$  for  $\text{Pb}_3\text{O}_4$ ,<sup>5,10</sup> was calculated. This ratio should be constant if both pigments are mixed in the red layer. However, this ratio is not constant, indicating that  $\text{CaCO}_3$  is not mixed with the red minium. Hence we conclude that the  $\text{CaCO}_3$  signals observed in the spectrum of the red sample belong to the



**Figure 6.** FT-Raman spectrum of red colour (i) and standard red lead (ii);  $4\text{ cm}^{-1}$  spectral resolution.

background paint layer of the pink colour and are only due to the penetration of the laser beam.

### Orange

This colour always appears over the red and pink colours and the spectrum is shown in Fig. 7(i). In this case, the bands are located at 547 (vs), 476 (sh), 453 (w), 386 (m), 310 (m), 225 (m), 148 (m) and 119 (vs)  $\text{cm}^{-1}$ . The band at 547  $\text{cm}^{-1}$  is due to a  $\nu(\text{PbO})$  vibrational mode and the band at 225  $\text{cm}^{-1}$  is due to a  $\delta(\text{PbO}_2)$  vibrational mode.<sup>9</sup> All these bands can be assigned to minium ( $\text{Pb}_3\text{O}_4$ ), which is red in colour.

To obtain an orange colour it is necessary to mix a yellow with a red pigment. The most suitable option would be to use a pigment compatible with minium ( $\text{Pb}_3\text{O}_4$ ), such as massicot,  $\text{PbO}$  (yellow). This last pigment has bands at 385 (w), 289 (s) and 143 (vs)  $\text{cm}^{-1}$ ,<sup>5</sup> which would be overlapped by those of minium, if the quantity of  $\text{PbO}$  is relatively low. The same mixture of pigments has been found elsewhere.<sup>11,12</sup> Moreover, in the preparation of  $\text{Pb}_3\text{O}_4$ , consisting of the calcination of white lead for a long time at an elevated temperature,  $\text{PbO}$  can also be formed.<sup>13</sup> In Fig. 7(ii) the spectrum obtained in our laboratory from a contemporary sample of minium mixed with massicot (80:20), which is orange in colour, is shown.

Both pigments have been widely studied.<sup>9–12,14–18</sup>  $\text{Pb}_3\text{O}_4$  is one of the oldest pigments and was used by Romans and Greeks.<sup>6</sup> Even though it is fairly resistant, it turns black if it is mixed with pigments containing sulphide, such as yellow cadmium sulphide, or by air polluted with  $\text{SO}_x$  or  $\text{H}_2\text{S}$ , and light can also promote degradation.<sup>7,15</sup> This could be the reason for using the yellow  $\text{PbO}$  to make the orange colour, instead of other yellow pigments such as  $\text{CdS}$ .

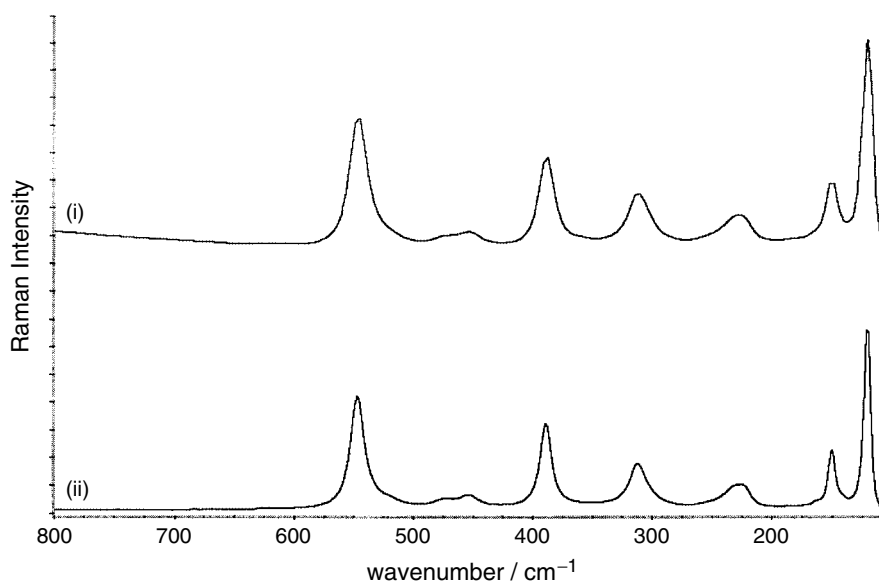
### Green

This colour is present in two different shades. The dark green is always over the light green and this is over the background white. Although the spectrum of the light green colour [Fig. 8(i)] has a poor signal-to-noise ratio, the bands at 2147 (s), 2123 (w), 2097 (s), 2063 (w), 985 (s), 841 (w), 615 (vw), 537 (m), 459 (m), 381 (w), 360 (w) and 282 (w)  $\text{cm}^{-1}$  can be detected. As described above, the bands at 2147, 2123, 2097, 2063, 537 and 282  $\text{cm}^{-1}$  are assigned to Prussian Blue. In this case, an intensification in the signal of the peak at 2097  $\text{cm}^{-1}$  is observed with respect to that of Prussian Blue.

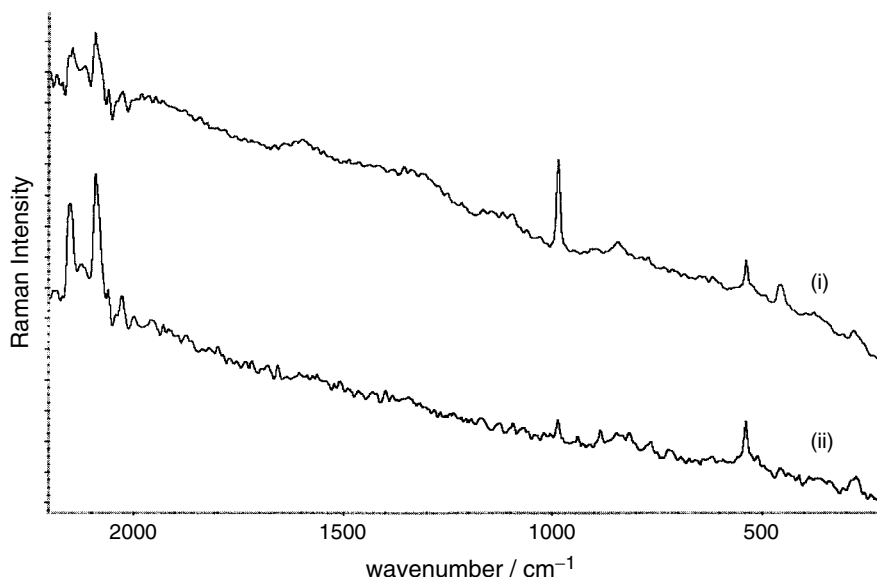
The bands at 985, 615 and 459  $\text{cm}^{-1}$  are assigned to the vibrational modes of  $\text{BaSO}_4$ . The presence of this white pigment's bands in the spectrum is due to the penetration by the laser beam. Thus, the  $\text{BaSO}_4$  detected in is certainly due to the white background colour. The band at 381  $\text{cm}^{-1}$  has not been identified, but could be due to cellulose. There are another two small bands at 841 and 360  $\text{cm}^{-1}$  that belong to  $\text{PbCrO}_4$  (yellow), as described below.

The spectrum of the dark green colour [Fig. 8(ii)] has a very poor signal-to-noise ratio too, but it is possible to see some characteristic bands of Prussian Blue, the same as for the light green colour, at 2147, 2123, 2097, 2063, 537 and 282  $\text{cm}^{-1}$ . However, there is no clear evidence for the presence of  $\text{PbCrO}_4$  in the dark green colour owing to the poor signal-to-noise ratio and/or to the smaller amount of that yellow pigment.

Severe oxidation of the papers below the green colours was observed. This oxidative process was so intense that it can also be seen on the mortar of the wall. Moreover, the resistance of both green shades to be removed with a scalpel was much lower than that shown by the other pigments within the wallpaper, indicating that the binder had also degraded. This degradation is not visible in the blue



**Figure 7.** FT-Raman spectrum of the orange colour (i) and a mixture of red lead and massicot (ii); 4  $\text{cm}^{-1}$  spectral resolution.



**Figure 8.** FT-Raman spectrum of light green colour (i) and dark green colour (ii);  $4\text{ cm}^{-1}$  spectral resolution.

and yellow areas, so only the presence of Prussian Blue or  $\text{PbCrO}_4$  cannot explain it. In our opinion, a third unknown pigment must be present, the same as that which causes the intensification in the signal at  $2097\text{ cm}^{-1}$ , probably with a CN group.

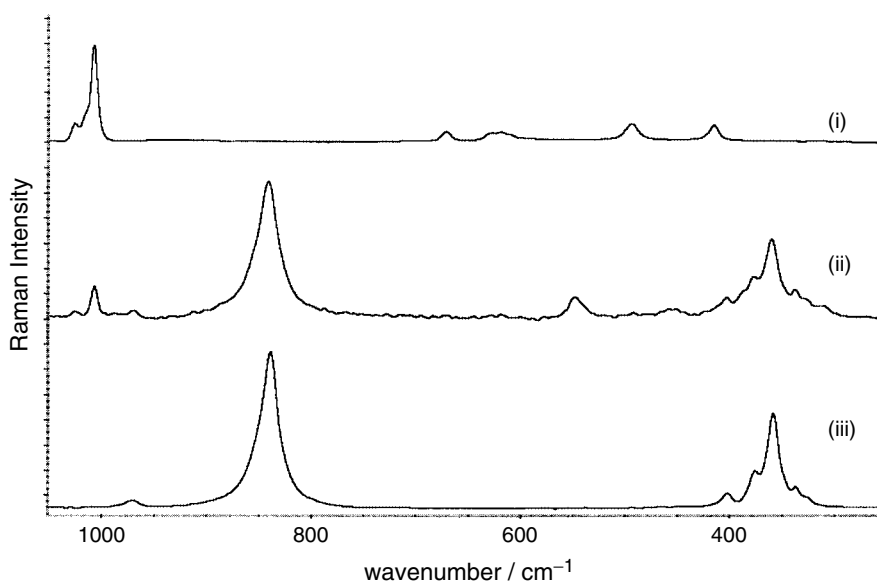
### Yellow

This colour is present in a small quantity over a green and grey background. The FT-Raman spectrum of this colour is shown in Fig. 9(ii). The spectrum shows peaks at 1025 (w), 1007 (m), 969 (vw), 841 (vs), 547 (m), 454 (vw), 402 (w), 384 (vw)  $377\text{ (w)}$ ,  $360\text{ (s)}$ ,  $337\text{ (w)}$  and  $311\text{ (vw)}\text{ cm}^{-1}$ . The peaks at 969, 841, 402, 377, 360 and  $337\text{ cm}^{-1}$  are ascribed to lead

chromate, the FT-Raman spectrum of which obtained from a modern sample in our laboratory is shown in Fig. 9(iii). The spectrum found in the literature bibliography for lead chromate has the same bands.<sup>5</sup>

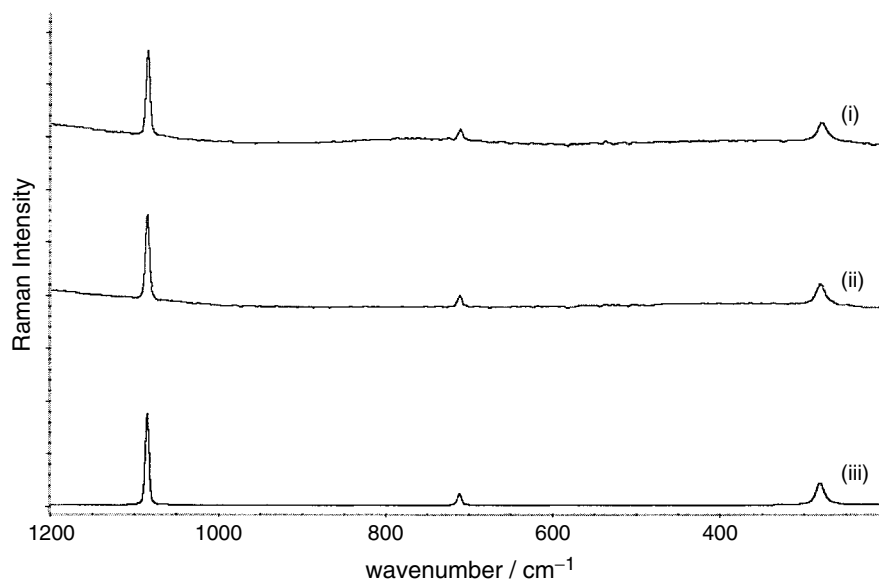
The peaks that appeared at 547, 454, 384 (shoulder) and  $311\text{ cm}^{-1}$  are due to  $\text{Pb}_3\text{O}_4$ . The small amount of this pigment is not clear, but could be due to contamination of the yellow pigment during the manufacture of the wallpaper or could have been added by the manufacturers to obtain the shade they wanted.

Two bands can be found at 1025 (w),  $1007\text{ (m)}\text{ cm}^{-1}$  and another three very weak peaks at 670, 493 and  $420\text{ (shoulder)}\text{ cm}^{-1}$  that are consistent with the presence of



**Figure 9.** FT-Raman spectrum of standard gypsum (i), the yellow colour (ii) and standard  $\text{PbCrO}_4$  (iii);  $4\text{ cm}^{-1}$  spectral resolution.





**Figure 10.** FT-Raman spectrum of white colour over grey colour (i) white colour over rose colour (ii) and standard calcium carbonate (iii); 4 cm<sup>-1</sup> spectral resolution.

a small amount of gypsum (calcium sulphate), as shown in Fig. 9(i). The band at 1007 cm<sup>-1</sup> is assigned to the  $\nu_1$  vibrational mode of sulphate.<sup>19</sup> These bands were also compared with other spectra in literature<sup>5</sup> and with one obtained in our laboratories. Its presence in this layer could be due to the use of this white pigment as a filler in the lead chromate, to make this cheaper, or to obtain a desirable colour variation.

### White over the pigments

Figure 10(i) and (ii) show the spectra obtained from the white colour situated over the grey and the pink colours, respectively. The samples show bands at 1086 (vs), 711 (w) and 280 (w) cm<sup>-1</sup>. The band at 1086 cm<sup>-1</sup> is due to the  $\nu_1(\text{CO}_3^{2-})$  vibrational mode, and that at 711 cm<sup>-1</sup> to the  $\nu_4(\text{CO}_3^{2-})$  vibrational mode, whereas the band at 280 cm<sup>-1</sup> is due to cooperative lattice modes.<sup>20</sup> All these bands are identical with those which can be observed in the FT-Raman spectra obtained in our laboratory from a modern sample of CaCO<sub>3</sub> [Fig. 10(iii)]. The same bands can be found in the literature.<sup>4,5,21</sup> This pigment has been employed since antiquity, and is very resistant to normal environmental conditions<sup>7</sup> and to light and it is compatible with almost all pigments. It was available when the paper was manufactured in the middle of the nineteenth century.<sup>22</sup> CaCO<sub>3</sub> has mainly been used as a filler mixed with other pigments because of its low hiding and tinting power,<sup>22</sup> but in this wallpaper it was employed as a pigment itself.

### CONCLUSIONS

This work shows the applicability of FT-Raman spectroscopy in the identification of pigments used in old decorative

wallpapers. No other references were found in the literature concerning the use of FT-Raman spectroscopy for this purpose although there have been several studies using this technique to identify pigments in paper works of art such as illuminated manuscripts, cantoralis, etc.<sup>12,15-17,23-25</sup>

The special sample device used in the spectrometer allows an optimal identification of several pigments for each sample without the need of using a more expensive technique such as FT-Raman microscopy, if there is a sufficient amount of sample, and if it is not necessary to analyse a single grain.

The non-destructive characteristic of this instrumental technique makes it possible to use the broken parts of the wallpapers as samples to identify the pigments as a previous step in the cleaning and restoration. Knowledge of the pigments allows the conservators to select the optimum cleaning solvents and the most suitable method for restoration and conservation.

All the pigments have been identified except one of the green layers. We think that the green colour is a mixture of Prussian Blue, PbCrO<sub>4</sub> and a green pigment. Analysis by AAS of this colour layer reveals a high quantity of Cu together with small amounts of Fe, Cr and Pb, but it was impossible to define the original pigment precisely. The destructive influence of copper pigments is common knowledge,<sup>26</sup> as well as that of polysaccharides and monosaccharides with free glucoside hydroxyl groups that react easily with Cu<sup>2+</sup>. The result of this reaction is the breakdown of sugars to simple organic acids<sup>27</sup> which destroy both the binder and the paper.<sup>16</sup> The reaction takes place under high humidity conditions. The destruction caused by green pigments has been reported elsewhere<sup>28-30</sup> (G. Banik, ICOM Committee for Conservation Working Group on Paper and Graphic Documents. Jerusalem Meeting on Parchment, October

26–30, 1992). In our case, it is believed that the binder is a gum (K. Castro, M. A. Olazabal, M. D. Rodriguez-Laso and J. M. Madariaga. presented at the 4th National Congress of Archeometry, October 15–17, 2001, Valencia, Spain), so this is a satisfactory explanation of the degradation observed at the back of the green areas on the paper sample.

It would be interesting to use another experimental approach to investigate the chemical reactions responsible for the oxidation process and to identify the final products in order to predict the original pigment and binder. This information would be of great interest to the conservators in their decision-making processes to select the restoration steps and chemicals in order to restrict the current damage to the paper and to stop future destruction of both the affected paint layers and binding media of the decorative wallpapers.

It is interesting to note the presence of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) in the yellow layer. In our opinion, the yellow pigment had been mixed with gypsum by the pigment manufacturer (this was very common to make the pigments cheaper) and used as such in the factory. If the wallpaper manufacturer had wanted to use a light yellow colour he would have mixed the  $\text{PbCrO}_4$  pigment with  $\text{CaCO}_3$ . This is supported by the use of (a)  $\text{CaCO}_3$  to obtain all the light colours and (b)  $\text{BaSO}_4$  to obtain the brilliant background white, as the only two white pigments in the wallpaper manufacturing process.

The presence of only eight pigments to make 12 different colours, most of them in two different shades, shows the ability of the manufacturer to mix the pigments and create a rich palette with the lowest possible cost. This makes sense considering that these types of works were of industrial or semi-industrial origin. As the years have gone by, these types of primitive industrial decorative works have become real artwork that it is necessary to preserve and restore.

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