MANUSCRIT ACCEPTAT

Raman analysis assessed by Fourier-Transformed infrared and X-ray fluorescence spectroscopies: a multi-analytical approach of ancient chromolithographs from the 19th century

A. Pitarch, A. Álvarez-Pérez, K. Castro, J. M. Madariaga, I. Queralt

Aquest arxiu PDF conté el manuscrit acceptat per a la seva publicació.

Abstract

A set of chromolithographs from the 19th century were analysed to identify the fillers and pigments used for their elaboration. Because of the delicacy of the chromolithographs, the research involved the use of Raman, Fourier-transform infrared and energy dispersive X-ray fluorescence spectroscopies for a complete characterization of the works on paper without removing any microsamples. Despite the high fluorescence of the samples when analyzed by Raman spectroscopy, in this paper, we demonstrated that ink spectra can be successfully enhanced by subtracting the spectra of the supporting background paper. The results of the study showed that, apparently, the lithographer used a limited range of common inorganic pigments from the 19th century (carbon black, chrome yellow, Prussian blue, red ochre, red lead and vermilion) together with organic pigments (indigo blue, gamboge and a red organic pigment). The study also found that despite the fact that during the 19th and early 20th century the use of mixtures of several pigments was a common practice, unusual admixtures were used for the preparation of some colours of the studied chromolithographs.

Introduction

The material characterization of ancient works on paper can provide valuable data relating to many aspects. On one hand, identification and quantification of the raw materials employed in the manufacturing process of the paper support may provide a first indication of its origin, chronology and the technology used for its elaboration. On the other hand, pigment identification can provide useful information to determine the period of time in which the works on paper were performed. Furthermore, material characterization of works on paper can supply helpful information to develop conservation strategies. Good examples of the importance of these studies are the increasing number of references available in the literature in the last few years.[1-13]

Amongst all the available analytical techniques, Raman spectroscopy (RS) has become a powerful tool in the study of works on paper not only because of its noninvasiveness, but also because of its ability to access the low wavenumber regions (<500 cm^{-1}), which is decisive for the identification of many inorganic pigments.[14] However, despite all the advantages in the qualitative identification of inorganic pigments in works on paper, Raman analysis can be thwarted by the natural fluorescence of organic and inorganic materials usually present in artworks (such as binders, varnishes, etc.) or by atomic fluorescence inherent in some materials.[15] The use of extremely long or extremely short wavelength lasers and the application of spectral manipulations such as subtracted-shifted Raman analysis[16] are some of the numerous tools that have been developed to avoid fluorescence. Sometimes, the use of other complementary techniques is advisable, such as Fourier-transform infrared (FTIR) spectroscopy, which provides the necessary information on those organic materials whose Raman signals might be shielded by the fluorescence emission. Another source of difficulties with using RS may arise when analysing metallic paints (which are sometimes applied in

different shades, ranging from silver to gold or a more reddish copper colour). Like many metals, gold does not provide a Raman spectrum, thus it is virtually undetectable by this technique.[17] Once again, the use of complementary techniques (such as X-ray fluorescence, XRF) is compulsory for the proper characterization of the object under analysis. To this end, several papers in the literature have highlighted the necessity of a multi-analytical approach for the complete study of pigments used in different kinds of ancient works on paper. Pessanha et al.[11] analyzed a hand-painted Chinese wallpaper from the 18th century by XRF and confocal RS to identify the pigments used and the fibres in the paper support. Striová et al.[12] studied five polychrome prints from the 18th to 19th century using XRF, reflectance microinfrared and micro-RS. Castro et al.[13] analysed a Dutch map from the 18th century to characterize and evaluate the state of conservation of the paper support as well as to identify the pigments used to embellish the map by using a combination of energy dispersive X-ray fluorescence (EDXRF), FTIR spectroscopy, nuclear magnetic resonance (NMR), RS and scanning electron microscopy coupled to an energy dispersive spectrometer (SEM-EDS).

However, when dealing with the study of coloured lithographs (which were particularly in vogue during the 18th and 19th centuries), the number of analytical papers that describe their chemical characterization is really scarce.[12, 18-24]

The aim of this work is to try to fill the lack of literature on coloured lithographs and to highlight the necessity of a multi-analytical approach in the study of ancient works on paper based on the use of RS. As an example, a full chemical characterization of chromolithographs from the 19th century is presented.

Experimental

Specimen

In comparison with other works on paper, lithography has a relatively young history: it was invented by Aloïs Senefelder in Germany in 1796 after a long experiment and is based on the chemical repellence of oil and water.[25] For the elaboration of a lithograph, the stone was dampened with water and the printing ink was then applied with a roller. This ink adhered only to the greased image but was repelled by the wet parts of the stone. The image could then be taken away from the inked drawing on a sheet of damp paper. By the early 19th century, almost all of the main techniques employed for drawing on stone had been developed; however, in 1840 the 'Lithotint process' was patented, in which a second stone (the tint stone) was used. By using this new technique, the appearance of a wash drawing made by a brush could be obtained. Moreover, by using several stones, ornate designs of dozens of bright colour impressions could be obtained.

The object under analysis, which belongs to a private collection, is the book entitled Les Orchideés. Histoire Iconographique. Organographie – Classification - Géographie – Collections -

Commerce – Emplot - Culture avec une revue descriptive des espècies cultiveés en Europe, written by Paul Émile de Puydt and edited by J. Rothschild in Paris in 1880. This high quality book was elaborated with considerable accuracy (it has a green gilt-lettered label) and contains both engravings printed in black ink and chromolithographs characterized by ornate designs of orchards. Its 50 coloured plates contain subtle gradations in tone and complex overprinting. Once the lithographs were coloured, they were finished by hand, heightening them with varnish.

Although the paper support seems to be in a bad state of conservation (paper made with wood pulp becomes yellow and rapidly loses its original flexibility[26]), the chromolithographs remain in a good state. In this sense, a set of 13 representative lithographs from the book were selected for the present study, considering the whole palette of colours used for its elaboration.

Instrumentation

The delicacy of the studied book required analytical techniques that were able to perform an analysis of the whole piece, without any kind of presampling procedure. Raman, FTIR and EDXRF spectroscopies were selected for this purpose.

Raman spectroscopy

The Raman spectra of the inks and paper support were obtained by using an ultramobile innoRam® Raman spectrometer (B&WTEK Inc., Newark, USA) provided with a 785 nm excitation laser with 300 mW laser power at the source and coupled to an Inphotonics Fiber Optic Sampling microprobe (Norwood, USA). The system was calibrated with a 520.5 cm−1 silicon Raman line, and the spectra were acquired at a resolution of 2 cm−1 in the range of 100–2200 cm−1, accumulating several scans for each spectrum to obtain the desirable signal-to-noise ratio. For the measurements, ×20 and × 50 microscope lenses were used to analyse the surfaces in conjunction with a colour TV microcamera that allowed a perfect focusing of the laser. The positioning was controlled by a manual micrometric stage. Several analyses were carried out in different areas of the same colour to obtain reliable results. The interpretation of spectra was performed by comparing the obtained Raman spectra with spectra of pure standard compounds contained in the e-VISARCH Raman spectral database.[27]

Energy dispersive X-ray fluorescence spectroscopy

The elemental analysis of inorganic compounds in the inks and paper support was carried out using an EDXRF system consisting of an XDV–SD spectrometer (Helmut Fischer GmbH, Germany) equipped with a tungsten anode X-ray tube (operating at 10, 30 and 50 kV), a Peltier cooled Si-Pin semiconductor detector, four collimators (0.1 mm up to 3 mm) and five primary filters (nickel 10, molybdenum 70, aluminium 500 and 1000 and titanium 300 μm). The X-rays were collimated by a collimator with a 3-mm diameter to adjust the X-ray focal spot to selected areas of the lithographs. The measurements were carried out at 50 kV, with an anode current of 128 μA, using an aluminium filter 1000 μm in thickness and a counting time of 300 s. During the analyses, the motorized X–Y stage (scan mode) was used to ensure the representativeness of the measurement.

Infrared spectroscopy

The FTIR spectra of some organic compounds and the paper support (including the filler) were collected using a Thermo Scientific Nicolet iN10 MX Infrared Microscope spectrometer by extracting microfibers from selected areas. The sample holder (Spectra-Tech Micro Compression Cell and Diamond Window Option) was used to flatten and crush the samples for efficient transmission analysis by FTIR spectroscopy. To obtain a good signal-to-noise ratio, 64 scans were accumulated for each spectrum at a resolution of 4 cm−1 in the range of 650–4000 cm−1 (mid-IR). The obtained spectra were collected in transmittance mode. Identification was based on a comparison of the recorded spectra with those of the library spectra.[28]

Results and Discussion

The analysis of the chromolithographs involved the identification of the type of fillers used to elaborate the paper support and the characterization of the pigments used for colouring the lithographs. EDXRF analyses orientated us to the most likely pigments and fillers present in the samples. However, because it is an elemental technique, the use of Raman and FTIR was compulsory to clearly identify all the pigments, whether of an organic or inorganic nature. The list of principal colouring materials identified in the selected chromolithographs is summarized in Table 1.

Table 1. Main detected elements and principal colouring materials identified

Pigments identified by Raman spectroscopy	Formula	Raman bands	Lithography
Carbon black	C (amorphous carbon)	1325, 1580 [29]	*PL. XXIII, PL. XLI*
Chrome yellow	$PbCrO_4$ (lead(II)Chromate)	141, 339, **361**, 378, 405, **842**, 864 [30]	*PL.I, PL. V, PL. XXIII, PL. XLI.*
Indigo Blue	$C_{16}H_{10}N_2O_2$ (indigotin)	98, 136, 172, 181, 236, 253, 265, 253, 265, 277, 311, 320, 468, 546, 599, 676, 758, 862, 871, 1015, 1149, 1191, 1226, 1248, 1310, 1363, 1461, 1483, **1572, 1584**, 1626, 1701 [30]	*PL. I*
Prussian blue	$Fe_4[Fe(CN)_6]_3 \cdot 14\text{-}16H_2O$ (iron (III) hexacyanoferrate (II))	282, 538, 2102, 2154 [29]	*PL. I, PL. VI, PL. VII, PL. XIX, PL. XX, PL. XXIII, XXVII, PL. PL. XXIX, PL.*

Pigmentsidentifiedby Raman spectroscopy	Formula	Raman bands	Lithography
			XXX, PL. XXXVI, PL. XLI.
Red ochre	Fe_2O_3 + clay + silica (iron (III) oxide chromophore)	**220, 286**, 402, 491, 601 [29]	*PL. XXIII, PL. XLI.*
Red lead	Pb_3O_4 (lead (II, IV) oxide)	65, **122**, 144, 148, 150, 224, 232, 314, 391, 456, 477, **550** [30]	*PL. I, PL. XX.*
Vermillion	HgS (mercury (II) sulfide)	**253**, 284, 343 [30]	*PL. XXIII, PL. XLI.*

In bold are the bands wavenumber which have strong or very strong relative intensity.

Paper suport

Regarding mineral fillers, no information was obtained using RS. The first attempt at studying the fillers present in the paper support failed because of the strong fluorescence that occurred during the analyses. The fluorescence overlapped with the bands of any mineral fillers present in the support. However, the main features of cellulose were observed in the spectrum where the most intense Raman bands were located: at 1094, 1118 and 1378 cm−1.[31]

According to the EDXRF results (Fig. S1(a)), a common observation in the entire spectrum of the paper support was the presence of calcium, iron, zinc, rubidium, strontium and lead. Concerning the presence of calcium, this element takes part in several steps of the papermaking process, such as a whitener in the fermentation step, during processing of the water supply, etc.[32] Concerning the presence of zinc and lead, these elements have already been reported in ancient papers as coming from white zinc oxide and lead white, respectively; [33, 34] however, none of the techniques used for the study confirmed the presence of these compounds. The presence of iron may be because of impurities added throughout the production process of papermaking. Rubidium is usually present in kaolinite (both substituting potassium or as an impurity), while the presence of strontium is probably linked with calcium because it is usually present in the calcite crystalline lattice.

FTIR spectroscopy proved to be essential in studying the paper support. As illustrated in Fig. S1(b), apart from the most important functional groups of cellulose fibres (3408 and 3343 ν(OH), 2902 ν(CH), 1637 δ(OH), 1434 δ(CH), 1372 δ(CH), 1338 δ(CH2)) wagging, 1322 δ(CH), 1282 δ(CH2) twisting, 1236 (δ(C–OH) out-of-plane, 1205 δ(C–OH) δ(C–CH)), 1161 ν(CC) asymmetric ring breathing, 1112 ν(C–O–C) glycosidic, 1060 ν(C–OH) 2º alcohol, 1036 ν(C–OH) 1º alcohol, 1002 (shoulder) ρ(–CH–) and 898 cm−1 (shoulder) ν(C–O–C) in plane symmetric,1 the presence of kaolinite (Al2O3·2SiO2·2H2O) was observed. Thus, the presence of kaolinite explains the presence of rubidium as previously determined by EDXRF. Absorbance values at 3696 and 3618 cm−1 were assigned to the vibrational modes of hydroxyl groups of kaolinite. An absorption band at 1111 cm−1 is associated with ν(Si–O), while those at 1034 and 1008 cm−1 (shoulder) are due to Si–O–Si and Si–O–Al lattice vibrations. Bands at 936 and 913 cm−1 can be attributed to OH-bending vibration mainly caused by Al–OH groups. As can be seen, some of these vibrations are overlapped by those of cellulose. The absorbance values from the lower frequency wavenumbers observed (788 (sh), 755 (sh) and 697 (sh) cm−1) can be largely attributed to different Si–O vibrations.[35, 36] This clay mineral was widely used in paper manufacturing for both filling and coating from the second half of the 19th century.[37, 38] Its use made paper heavier, whiter and more receptive to ink.

Inks

Most of the Raman analyses of the pigments used for the elaboration of the lithographs were unsuccessful because of the high fluorescence of the samples. Moreover, the contribution of the paper support while analysing the coloured regions was very strong, causing the hiding of the ink spectra. For a proper characterization of the colouring substances, a subtraction of the spectrum of the paper support from the spectrum taken in the coloured areas had to be

carried out. We could successfully enhance the spectrum of the ink over the signals from the paper matrixes in which they were held, obtaining the spectrum of the ink (Figs 1(a)–(c)).
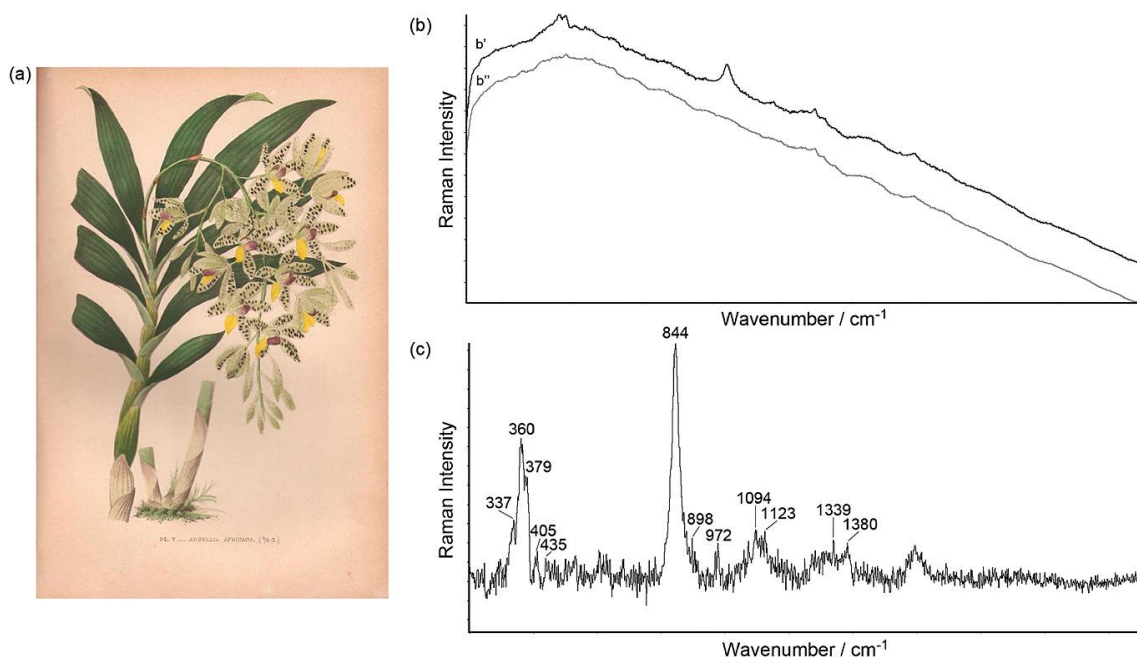

Figure 1. Subtraction process: (a) picture of the analysed lithography (PL V); (b) Raman spectra of the yellow area –(b') and the paper support –(b''); and (c) Raman spectrum of chrome yellow achieved after the subtraction process.

Yellow colour

This colour appears in four of the 13 analysed lithographs (PL. V, PL. VI, PL. VII, and PL. XXXVI). The preliminary EDXRF analyses showed the presence of chromium and lead and the Raman results denoted that only one yellow pigment was used: chrome yellow, $PbCrO_4$ (Fig. 1(c)).[29] The spectrum shows a strong band located at 844 cm−1 and a group of several peaks centred at 360 cm−1 (337, 360, 380 and 405 cm−1). Moreover, the lack of any sulphate peaks (especially the very narrow stretching peak at ~1000 cm−1) demonstrates that pure lead chromate, without any addition of lead sulphate, had been used.[3] According to the literature, this pigment was introduced into the market in the early 1800 s.[39] In fact, its use had already been reported in different kinds of works on paper support from the same chronology.[3], [19] In addition, bands located at 379, 898, 972, 1094, 1123, 1339 and 1380 cm−1 are due to cellulose from the background.

White colour

The EDXRF analyses performed on white areas (not shown) revealed the presence of calcium, iron, zinc, rubidium, strontium and lead, the same elements found on the paper support. In the same way, Raman analysis provided the spectrum of the paper itself with the characteristic

bands at 381, 435, 1056, 1094, 1121 and 1380 cm−1 because of the cellulose. In these kinds of works on paper, the white colour is, in fact, the background paper support.

Orange colour

This colour appears in different tonalities (from deep orange to yellowish orange) in two of the analysed lithographs (PL. I and PL. VII). EDXRF analysis of PL. I revealed the presence of lead, while the spectrum of PL. VII showed the presence of lead and chromium. Raman analyses performed on deep orange areas of PL. I demonstrated the presence of red lead (Pb_3O_4). The Raman bands at 122, 150, 224, 314, 391, 456 and 548 cm−1 observed in the spectrum (not shown) would be from the presence of this pigment. On the other hand, analyses carried out in the yellowish orange areas of PL. VII revealed the presence of chrome yellow (Raman bands at 361 and 843 cm−1). It seems that only a small amount of pigment was necessary to obtain the desired colour, such that the more pigment was used, the deeper it was.

Pink, red and purple colours

Three reddish shades can be observed on the lithographs: pink (on PL. XX), deep red (on PL. XXXVI) and purple (on PL. V, PL. VI, PL. VII and PL. XXVII).

Concerning the pink shades, by analysing them using EDXRF, the main element identified was lead. In fact, by using RS, red lead was determined. The use of FTIR spectroscopy was not conclusive neither for the use of an organic red compound nor for the use of red lead (because it presents IR bands below 500 cm−1, while the range limit of the used FTIR spectroscopy apparatus is about 700 cm−1).

When dealing with the deep red areas present in some of the lithographs, strong fluorescence appeared from them. The subtraction process described previously did not allow a clear identification of the pigment responsible for this colour. According to the literature,[40], [41] coprecipitation of organic pigments with white fillers was a frequent technique in the preparation of artists' materials (because these white compounds were used as substrates or mordants). Thus, the presence of barite ($BaSO_4$), calcium carbonate ($CaCO_3$), calcium sulphate ($CaSO_4$) or gypsum ($CaSO_4 \cdot 2H_2O$) could suggest the possible presence of an organic pigment. However, none of these typical white fillers were determined either by Raman or EDXRF spectroscopy. The only elements identified by EDXRF were iron and lead. FTIR analysis of the deep red colour revealed the presence of bands at 1574, 1251, 1151, 1104, 1020 and 905 cm−1 (see Fig. S2). Moreover, there is a group of bands centred around 2900 cm−1 whose positions were obtained after decomposition of the spectrum in a sum of Gaussian curves at 2969, 2940, 2905 and 2866 cm−1. All these bands belong to an organic compound, probably the pigment responsible for the deep red colour. Unfortunately, the closeness and the overlapping of the bands of the background cellulose with those of the pigment at 1151, 1104, 1020 and 905 cm−1 made it impossible to identify the pigment. However, the position of the

bands are quite close to those of some lake pigments such as red alizarin[42] or even some kind of betalaine (natural organic pigments extracted from vegetables such as beetroot red and also used as natural pigments). This red organic pigment was also used in the purple colour mixed with Prussian blue.

As with what happened with the deep red colour, the EDXRF analyses of purple areas only determined the presence of iron. Again, a strong fluorescence occurred in these areas when analysed using RS. Nevertheless, in this case, some bands were observed in the Raman spectrum because of the presence of Prussian blue (273, 534, 2091 and 2153 cm−1). This finding was corroborated by the FTIR analyses, where the typical band corresponding to the vibration of $C \equiv N$ (2095 cm−1) was recorded in the spectrum. Additional FTIR bands were observed in the spectrum. These bands were located at the same position as those of the deep red colour. Unfortunately, as with what happened with the red colour, it was not possible to attribute them to any compound or to find out the red compound needed to obtain the purple colour.

Brown colour

The EDXRF analyses carried out on the brown-coloured areas detected the presence of chromium, iron, mercury and lead. In this case, two complex mixtures were identified using RS. In PL. XXIII, for example, a mixture of chrome yellow (Raman band at 840 cm−1), Prussian blue (Raman bands at 273, 531 and 2155 cm−1), carbon black (C, broad bands centred at 1300 and 1600 cm−1), red ochre (mainly Fe_2O_3, Raman bands at 290 and 408 cm−1) and vermilion (bands at 251, 290, 341 cm−1) was determined (Fig. 2). On the other hand, in PL. XLI a combination of chrome yellow, Prussian blue, carbon black, red ochre and red lead (bands at 121 and 544 cm−1) was identified (Fig. 3). There are reports on the use of complex pigment mixtures in other artworks from the same chronology,3, [43] but if we keep in mind the reports on the scientific analysis of works on paper, we can see that a few of them report the existence of these admixtures: Sarmiento et al.[44] found an admixture of calcite, Prussian blue, indigo blue ($C_{16}H_{10}N_2O_2$) and red ochre on Finnish wallpapers from the 18th to 19th century. Vandenabeele et al.[45] detected a mixture of carbon black and hematite on porcelain cards from the 19th century and Castro et al. identified burnt sienna (mainly Fe_2O_3), chrome yellow, carbon black, red lead and calcite mixed together on the brown areas of a 19th century wallpaper from a tower-palace in Villanañe, Spain.[46]
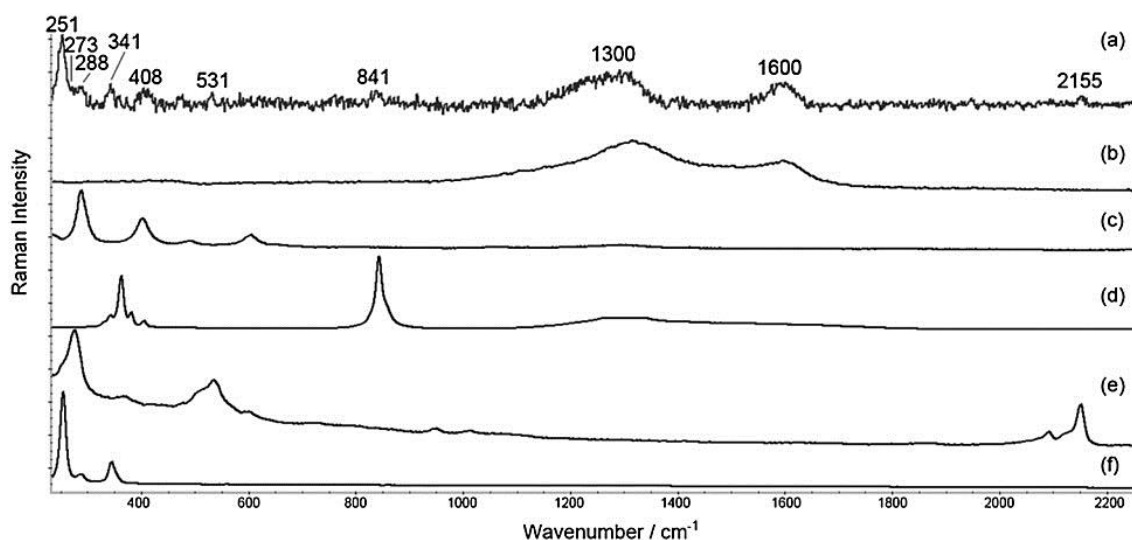
Figure 2. Raman spectrum of brown colour from the PL. XXIII and spectra of reference materials. Spectra of (a) PL. XXIII after the subtraction process and baseline correction; (b) carbon black; (c) red ochre; (d) chrome yellow; (e) Prussian blue; and (f) vermilion.
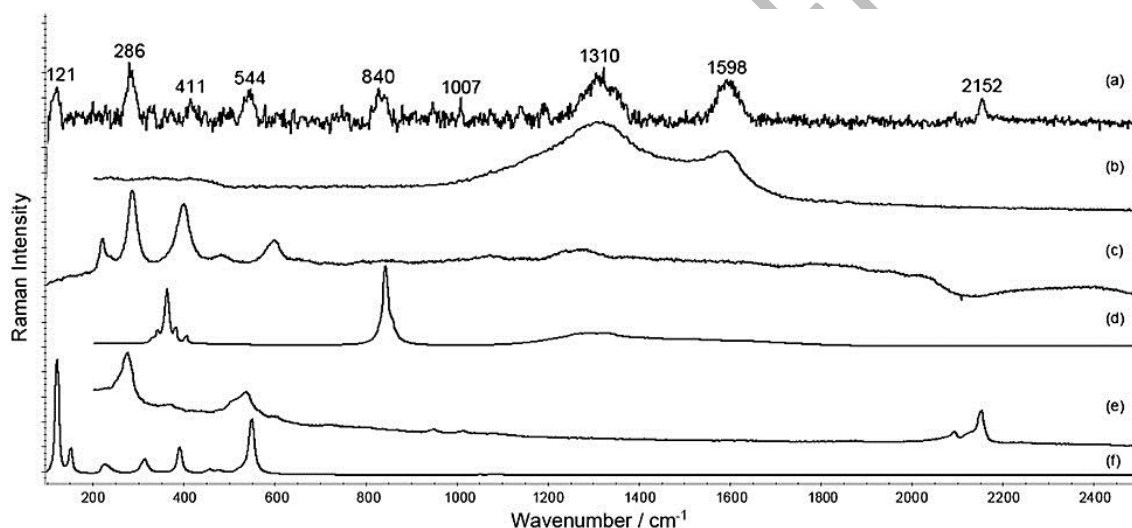

Figure 3. Raman spectrum of brown colour from the PL. XLI and spectra of reference materials. Spectra of (a) PL. XLI after the subtraction process and baseline correction; (b) lamp black; (c) red ochre; (d) chrome yellow; (e) Prussian blue; and (f) red lead.

Blue colours

PL. XXIII, PL. XXVII, PL. XXIX and PL. XXX have blue colour in their palette. In all of them, the Raman analyses seemed to indicate the use of Prussian blue as the pigment responsible for this colour because bands at 280, 382, 535, 600, 2093 and 2155 cm−1 were observed in the spectra, with 2155 cm−1 being the most characteristic band (from the ν(CN) stretching vibration) of Prussian blue. Prussian blue was first synthesized in Berlin between 1704 and 170747 but was not much used until the middle of the 18th century. The presence of iron on the EDXRF spectrum was in agreement with the Raman analyses.

Green colours

Three elements were identified by EDXRF: chromium, iron and lead. According to the Raman and FTIR spectra collected from the green areas, we can say that instead of green pigments, mixtures of blue and yellow pigments were used. For example, the Raman spectrum from PL. I (Fig. 4) contained the characteristic bands of Prussian blue (278, 541, 2091, 2123, 2151 cm−1) with many bands of indigo blue (252, 541, 599, 679, 766, 1226, 1250, 1464, 1485, 1576, 1632 cm−1), a natural pigment first synthesized in1870 and commercially produced in 1897.[47] In addition, bands at 1093 and 1378 cm−1 are due to cellulose. Unfortunately, in this case no yellow pigment could be clearly identified.
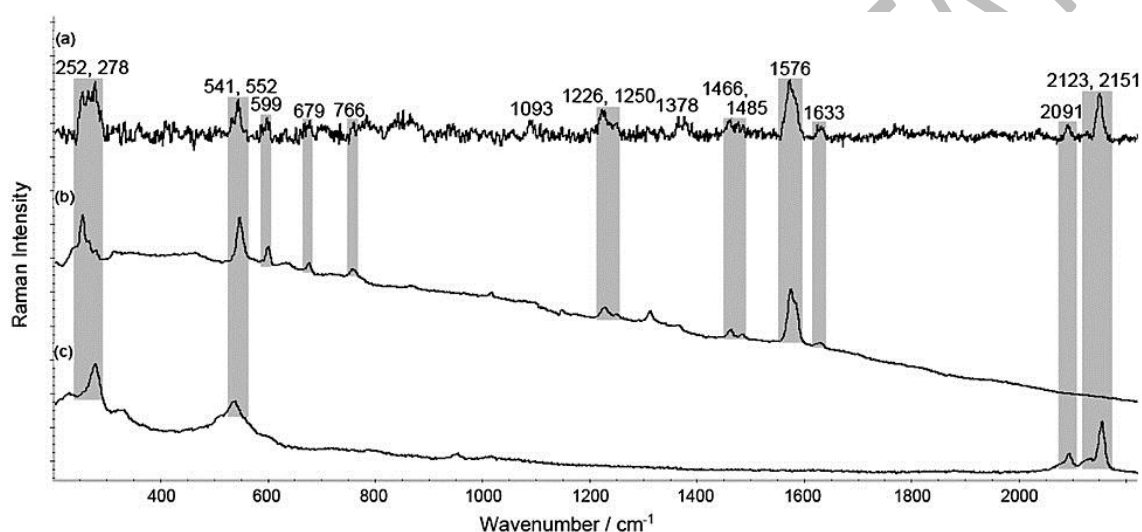

Figure 4. (a) Raman spectrum of a green area on the lithograph PL. I (after subtraction process and baseline correction) and comparison with reference spectra from (b) indigo blue and (c) Prussian blue.

Another combination found in some lithographs is the mixture of chrome yellow (323, 341, 355, 379, 841 cm−1) and Prussian blue (280, 372, 512, 536, 945, 2093, 2155 cm−1) in the Raman spectrum of PL. VII. The combination of these pigments has already been reported in the literature.[19, 40, 44, 45, 48] This mixed green could be the one known as chrome green, a 19th century pigment synthesised through coprecipitation of Prussian blue and chrome yellow upon addition of barium white.[49] However, no indication of the presence of barium white was found in the chromolithograph with the techniques used in this work. Chrome green has been also used to describe the compound Cr_2O_3. However, to describe this oxide, the term chrome oxide green should be used.[50]

The FTIR spectrum of PL. XIX revealed the presence of an organic yellow compound mixed with Prussian blue. A representative spectrum is reported in Fig. S3, where we can observe a characteristic band of Prussian blue at 2087 cm−1 and the bands at 2970, 2929, 1735, 1687, 1646 (sh), 1632, 1592, 1337, 1261 cm−1, which are consistent with the vibrational modes of gamboge.[51] The peaks shown in Fig. S3 that may stem from the cellulose and kaolin are marked with an asterisk (at 2902, 1632, 1427, 1371, 1321, 1203, 1162 and 1062 cm−1) and plus (at 1111, 1034 and 912 cm−1), respectively. Gamboge is a yellow gum-resin of vegetable

origin in which the chromophore responsible for the yellow colour resides in the resin component.[12], [49] The use of gamboge was common from the 17th century in Europe.[52] In fact, in the 19th century, the botanical artist William Hooker created a special pigment to yield a green tone suitable for colouring leaves (known as Hooker's green) by mixing Prussian blue and gamboge.[52] The combination of blue and yellow colouring substances has been reported in studies of wallpapers by Castro et al.[53] and in polychrome prints by Striová et al.,[2] both works on paper from the 19th century.

Golden substances

Some of the lithographs (PL. VII) had gold-coloured details, which were also analysed by RS, but this study did not yield any ascribable spectrum. Like many metals, gold is undetectable by RS17 such that further investigations such as using EDXRF were necessary here. EDXRF analysis of the golden areas on this lithograph revealed that gold and copper had indeed been used. The presence of chromium and lead is due to the chrome yellow underneath (which was determined by RS). A spectrum of one of the analysed spots are shown in Fig. 5.
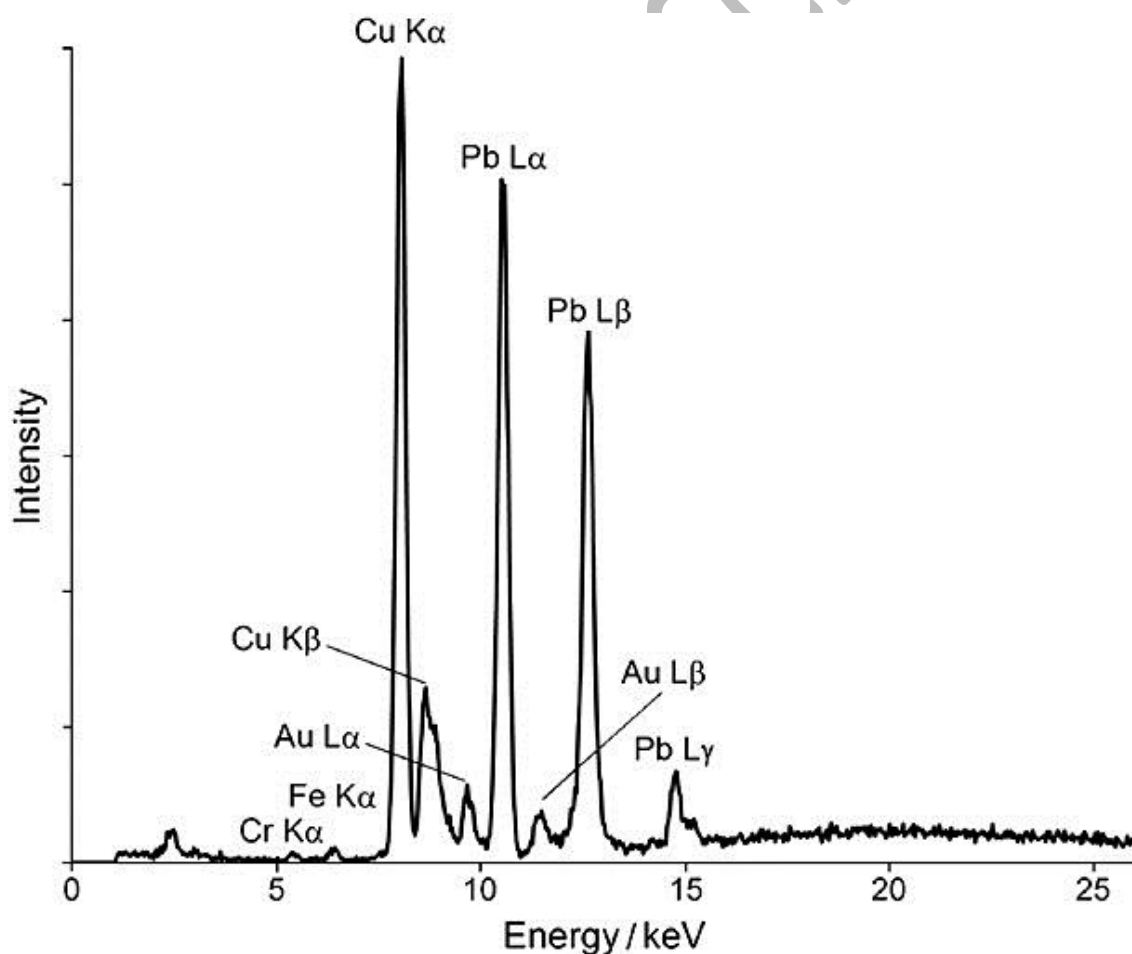

Figure 5. EDXRF spectrum of the golden regions on PL. VII.

Conclusions

This work presents the chemical characterization of a set of 13 chromolithographs from the 19th century. The analytical techniques allowed the identification of the fillers from the paper matrix and determining almost all the pigments present in the book. The necessity of a multi-analytical approach for the proper characterization of such kind of works on paper has been demonstrated.

This work has also presented a successful methodology for the determination of inks on paper when Raman analyses of the pigments are frustrated because of the high fluorescence of the samples. In this sense, ink spectra can be enhanced by subtracting the spectra of the paper support from the spectra taken from the coloured areas.

Concerning the analysed book, the study showed that, notwithstanding that the lithograph's palette is extensive, the range of substances used for its elaboration was relatively limited. In fact, it has to be highlighted that to obtain some of the colours observed in the chromolithographs, the use of some complexes and unusual admixtures of primary pigments were identified.

From the 18th century until the end of the 19th century, the pigment industry experienced important innovations, being a period of time in which new inorganic pigments such as Hooker's Green, chrome yellow or chrome green, amongst others, became available in the market. While a few inorganic pigments were introduced during this period, the main development was the invention of synthetic organic pigments after 1856, which led to the introduction of more than a hundred new pigments and many more dyes that revolutionized not only the printing industry, but also the textile and other industries. Some organic pigments were determined in the analysed samples. Thus, the analysed lithographs are not only evidence of the technical developments in colour illustration that took place during that period, but also reflect how the industry was incorporating new materials in their work and designs.

Acknowledgements

References

1. K. Castro, E. Princi, N. Proietti, M. Manso, D. Capitani, S. Vicini, J. M.Madariaga, M. L. Carvalho, Nucl. Instr. and Meth. in Phys. Res. B2011, 269, 1401–1410.
2. P. Colomban J. Raman Spectrosc. 2011, 42, 192–194.
3. M. C. Caggiani, P. Colomban, J. Raman Spectrosc. 2011, 42, 790–798.
4. S. M. Doncea, R. M. Ion, R. C. Fieracui, E. Bacalum, A. A. Bunaciu, H. Y.Aboul-Enein, Instrum. Sci. and Tech. 2010, 38,96–100.
5. S. Pessanha, M. L. Carvalho, M. I. Cabaço, S. Valadas, J.-L. Bruneel,M. Besnard, M. I. Ribeiro, J. Raman Spectrosc. 2010, 41, 1510–1516.
6. A. Duran, J. L. Pérez-Rodríguez, T. Espejo, M. L. Franquelo, J. Castaing,P. Walter, Anal. Bioanal. Chem. 2009, 395, 1997–2004.
7. C. Frausto-Reyes, M. Ortiz-Morales, J. M. Bujdud-Pérez, G. E. Magaña-Cota,R. Mejía-Falcón, Spectrochim. Acta Part A 2009, 74,1275–1279.
8. R. Ganzerla, A. Gambaro, E. Cappelletto, M. Fantin, S. Montalbani,M. Orlandi, Microchem. J. 2009, 91,70–77.
9. M. Manso, M. L. Carvalho, Spectrochi m. Acta Part B 2009, 64(6),482–490.
10. M. Manso, S. Pessanha, F. Figueira, S. Valadas, A. Guilherme,M. Alfonso, A. C. Rocha, M. J. Oliveira, I. Ribeiro, M. L. Carvalho, Anal.Bioanal. Chem. 2009, 395, 2029–2036.
11. S. Pessanha, A. Guilherme, M. L. Carvalho, M. I. Cabaço, K. Bittencourt,J. L. Bruneel, M. Besnard, Spectrochim. Acta Part B 2009, 64, 582–586.
12. J. Striová, G. Coccolini, S. Micheli, C. Lofrumento, M. Galeotti, A. Cagnini,E. M. Castellucc i,Spectrochim. Acta Part A 2009, 73,539–545.
13. K. Castro, N. Proietti, E. Princi, S. Pessanha, M. L. Carvalho, S. Vicini,D. Capitani, J. M. Madariaga, Anal. Chim. Acta 2008, 623, 187–194.
14. H. G. M. Edwards, J. H. Chalmers, In Raman Spectroscopy in Archaeol-ogy and Art History, (Ed: N. W. Barnett), The Royal Society of Chemistry,Cambridge, 2005.
15. G. D. Smith, R. J. H. Clark, J. Arch. Sci. 2004, 31, 1137–1160.
16. S. E. J. Bell, E. S. O. Bourguignon, A. C. Dennis, J. A. Fields, J. J. McGarvey,K. R. Seddon, Ana l. Chem. 2000, 72,234–239.
17. L. Burgio, R. J. H. Clark, V. S. F. Muralha, T. J. Stanley, J. Raman Spec-trosc. 2008, 39, 1482–1493.
18. P. Vandenabeele, P. De Paepe, L. Moens, J. Raman Spectrosc. 2008,39, 1099–1103.
19. S. A. Centeno, V. L. Buisan, P. Ropret, J. Raman Spectrosc. 2006, 37,1111–1118.
20. K. Castro, P. Vandenabeele, M. D. Rodríguez-Laso, L. Moens, J. M.Madariaga, Anal. Bioanal. Chem. 2004, 379, 674–683.
21. O. Hahn, D. Oltrogge, H. Bevers, Archaeometry 2004, 46(2), 273–282.
22. J. L. Ferrero, C. Rold, D. Juanes, J. Carballo, J. Pereira, M. Ardid, J. L.Lluch, R. Vives, Nucl. Instr. and Met. in Phys. Res. B 2004, 213, 729–734.
23. H. G. Wiedemann, Chemie in Unserer Zeit 2001, 35, 368–381.
24. C. Marcolli, H. G. Wiedemann, J. Therm. Anal. Calorim. 2001, 64,987–1000.
25. A. Senefelder, The invention of lithography. Translated from the originalGerman by J.W. Muller. The Fuchs & Lang Manufacturing Company,New York, 1911.

26. L. Laguardia, E. Vassallo, F. Cappitelli, E. Mesto, A. Cremona, C. Sorlini,G. Bonizzoni, Appl. Surf. Sci. 2005, 252(4), 1159–1166.

27. K. Castro, M. Pérez-Alonso, M. D. Rodríguez-Laso, L. A. Fernández,J. M. Madariaga, Anal. Bioanal. Chem. 2005, 382, 248–258.

28. K. Castro, M. Pérez, M. D. Rodríguez-Laso, J. M. Madariaga, Anal.Chem. 2003, 75, 214A-221A.

29. L. Burgio, R. J. H. Clark, Spectrochim. Acta Part A: Mol. Biomol. Spec-trosc. 2001, 57, 1491–1521.

30. I. M. Bell, R. J. H. Clark, P. J. Gibbs, Spectrochim. Acta Part A: Mol. Bio-mol. Spectrosc. 1997, 53(2), 159–2179.

31. C. Boileau, S. Pessanha, C. Tardif, K. Castro, N. Proietti, D. Capitani,S. Vicini, J. M. Madariaga, M. L. Carvalho, E. Princi, J. Appl. Polym.Sci. 2009, 113, 2030–2040 .

32. P. Reynard, Pap. Conserv. 1989, 13,7–27.

33. V. F. Hanson, In Preservation of Paper and Textiles of Historic andArtistic Value II, (Ed: J. C. Williams), Advances in Chemistry Series,American Chemical Society, Washington D.C., 1981, 143–168.

34. M. Manso, M. Costa, M. L. Carvalho, Spectrochimica Acta Part B:Atomic Spectrosc. 2008, 63, 1320–1323.

35. M. Hoch, A. Bandara, Colloids Surf. A: Physicochem. Eng. Aspects 2005,253, 117–124.

36. R. E. Martinez, P. Sharma, A. Kappler, J. Colloid Interface Sci. 2010,352(2), 526–534

37. K. Beazley, The Paper Conservator 1991, 15,17–27.

38. D. van der Reyden, E. Mosier, M. Baker, Triennial meeting (10th),Washington DC, 22–27 August 1993: preprints. Paris: ICOM, 1993.

39. N. Eastaugh, V. Walsh, T. Chaplin, R. Siddal, Pigment Compendium, adictionary of historical pigments. Elsevier Butterworth-Heinemann,Oxford, 2004.

40. K. Wehlte, The materials and techniques of painting. Van NostrandReinhold Company, England, 1975.

41. K. Castro, P. Vandenabeele, M. D. Rodríguez-Laso, L. Moens, J. M.Madariaga, Anal. Bioanal. Chem. 2004, 379, 674–683.

42. C. Clementi, B. Doherty, P. L. Gentili, C. Miliani, A. Romani, B. G.Brunetti, A. Sgamellotti, Appl. Phys. A 2008, 92,25–33.

43. A. M. Correia, R. J. H. Clark, M. I. M. Ribeiro, M. L. T. S. Duarte, J. RamanSpectrosc. 2007, 38, 1390–1405.

44. A. Sarmiento, U. Knuutinen, K. Castro, J. M. Madariaga, Proceedingsof Interim Meeting of the ICOM-CC Graphic Documents WorkingGroup, Copenhagen, 6–8 October 2010.

45. P. Vandenabelee, P. De Paepe, L. Monees, J. Raman Spectrosc. 2008,39, 1099–1103.

46. K. Castro, P. Vandenabeele, M. D. Rodríguez-Laso, L. Moens, J. M. Madariaga,Spectrochim.ActaPartA:Mol.Biomol.Spectrosc.2005, 61,2357–2363.

47. R. D. Harley, Artist's pigments c. 1600–1835: a study in English docu-mentary sources, Butterworth Scientific, London, 1982.

48. T. D. Chaplin, A. Jurado-López, R. J. H. Clark, D. R. Beech, J. RamanSpectrosc. 2004, 35, 600–604.

49. R. J. Gettens, G. L. Stout, Painting Materials. Courier Dover Publica-tions, Dover, 1966.

50. R. Newman, in Artists's Pigments: A Handbook of Their History andCharacteristics,:vol. 3 (Ed: E. W. Fitzhugh), Oxford University Press,Washington, 1997, 273–294.

51. P. Vandenabeele, B. Wehling, L. Moens, H. Edwards, M. DeReu, G. VanHooydonk, Anal. Chim. Acta 2000, 407, 261–274.

52. J. Winter, in Artists' Pigments: A Handbook of Their History and Char-acteristics, vol. 3, (Ed: E. W. Fitzhugh), Oxford University Press,Washington, 1997, 143–155.

53. K. Castro, A. Sarmiento, E. Princi, M. Pérez-Alonso, M. D. Rodríguez-Laso,S.Vicini,J.M.Madariaga,E.Pedemonte,Trends Ana l. Chem. 2007, 26,347–359.