

CHARACTERIZATION OF SOME ORANGE AND YELLOW ORGANIC AND FLUORESCENT PIGMENTS BY RAMAN SPECTROSCOPY

SCIENTIFIC PAPER

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Raman spectroscopy has become one of the most important vibrational analytical techniques for the investigation of paint samples and notably for organic pigments. For the analysis of modern materials, especially for synthetic inorganic and organic pigments the prospect of using Raman spectroscopy is an alternative to e.g. Py-GC-MS. It provides enough information allowing for a broad characterization of colourants either in raw samples, on cross-sections or in-situ. One of the advantages of Raman spectroscopy over FTIR analysis is that it allows the detection of weak IR frequencies such as stretching vibrations of chemical groups, e.g. the nitro group in azo pigments, which represents the biggest family of organic pigments found in paintings.

The purpose of this paper is, firstly, to complement existing databases with data on both yellow and orange pigments, mainly found in artist paints, and secondly, to introduce the analysis of selected fluorescent pigments. The latter are of aesthetic interest as they are widely employed in the industry (paints, plastics, textiles) and of conservation interest due to their ageing behaviour. A short list of organic pigments has been drawn according to their use in paintings (artwork and industrial paints), to which some inorganic pigments also found in artworks, were added. This has been complemented with some pigments which are mainly found in automotive paints. Analyses were performed with dispersive micro-Raman spectroscopy. The prospect of induced fluorescence background led to the preferential use of a diode laser at 785 nm.

Results show that Raman spectra allow for characterization of various chemical groups in organic pigments. In the case of fluorescent pigments, differentiation is more difficult since the formulations of such pigments/dyes are quite complex. Further research on this topic must be undertaken both to further the knowledge of photostability of these materials and to improve characterization using vibrational analytical techniques. Some of the conclusions drawn from

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this study were used for identification of two fluorescent paint samples taken from a late 20th century Ben (Benjamin Vautier, 1935-) artwork.

1 Introduction

Raman spectroscopy is widely used in cultural heritage science. Over the last decade, it has become an unavoidable analytical technique for the characterization of the molecular structures and compositions of organic and inorganic materials.¹ Raman spectroscopy is now one of the most used vibrational analytical techniques for investigation of paint samples and particularly for analyses of organic pigments.² Both spatial resolution down to 1 μm and the versatility of laser type, in the case of dispersive Raman, make it the preferred choice in conservation science laboratories.

The complementarity of this technique with FTIR remains.³ Indeed, Raman has shown some limitations in the assessment of material degradation processes, and it is probably more appropriate for pigment identification. One of the advantages of Raman spectroscopy over IR is that it allows detection of weak IR frequencies, such as the stretching vibration of chemical groups, e.g. in azo pigments, which represents one of the biggest families of organic pigments found in artist paints.

Gas chromatography coupled to mass spectrometry has also been successfully used for the identification of modern materials, especially for synthetic inorganic and organic pigments.⁴⁻⁶ The prospect of using Raman spectroscopy, as an alternative to chromatography techniques, is promising. It provides sufficient information thereby enabling a broad characterization of the colour-

ing matters, either on raw samples, on cross-sections or in-situ analysis.

Owing to the large variety of organic pigments, it is important to classify the material types according to their chemical structures. The purpose of this paper is, firstly, to complement existing databases with data on both yellow and orange pigments, mainly found in artist paints, and secondly, to introduce the analysis of selected fluorescent pigments. The latter are of aesthetic interest as they are widely employed in the industry (paints, plastics, textiles) and of conservation interest due to their ageing behaviour. Some of the conclusions drawn from this study are used for the characterization of two fluorescent paint samples which have been taken from a late 20th century painting from the artist Ben (Benjamin Vautier, 1935-).

2 Experimental

2.1 Pigments

A short list of organic pigments was drawn according to their use in painting (artwork and industrial paints).⁷ Some additional pigments were used that mainly found use as automotive paints and which were kindly provided by the Forensic Science Laboratory of Marseille, France. However, both the provenance and the origin of these pigments are difficult to trace and therefore, it can be problematic to obtain an accurate composition.

The pigments were purchased at Sennelier, Kremer and Daler-Rowney (only fluorescent paint). All are named according to their colour index and chemical class (Table 1). A selection of commercial paints were also analysed in the same fashion, and with the aim of identifying unknown acrylic

Pigment Class	Properties	Field	Colour Index
Monoazo yellow (Hansa yellow)	Good light fastness, sensitive to most common organic solvents, poor heat stability	Artist & industrial paint, printing inks	PY1, PY3, PY74
Bisacetoacetarylide & Diarylide yellow	Excellent light fastness properties, good to very good resistance to a variety of organic solvents	Printing inks, in mixture with azo pigments	PY16, PY83
Azomethine: azo metal complex	Poor light fastness, withdrawn from the market (PO59 & PO65)	Industrial & automotive finishes	PO59, PO65(*), PY129
Benzimidazolone	Good light fastness	Artist & automotive paints, printing inks	PO36(*), PY151, PY154
Diazopyrazolone	Good light fastness, good resistance to a variety of organic solvents	Artist paint, printing inks, plastics	PO34
Quinacridone/-quinone & Quinophthalone	Very good light fastness, good resistance to a variety of organic solvents	Artist paint, textile, plastics	PO48(*), PO49, PY138(*)
Flavanthrone	Good light fastness	Automotive & artist paint, plastics	PY24(*)
Perinone	Good light fastness, good resistance to a variety of organic solvents	Automotive & industrial paint, artist paint, leather, plastics	PO43(*)
Isoindoline & Isoindolinone	Good light fastness, good resistance to a variety of organic solvents	Artist & industrial paint, plastics, printing inks	PO61, PO69, PY109, PY139, PY173
DPP Pigment (Diketopyrrolo-pyrrole)	Good light fastness, less stable to some organic solvents	Automotive & artist paint, coatings, plastics	PO73

Table 1: List of pigments studied. (*) pigments from the forensic science laboratory of Marseille.

paint samples from artworks, these paints proved to be of great interest.

Two fluorescent pigments, an orange and a yellow one, were also considered in this project. Chemical data were only partially available for this study, and only commercial names were used. Even though these pigments deserve to be studied more in depth, they were added to this study on purpose because they regularly appear in contemporary paintings. Such paintings may undergo conservation treatments as they often show signs of degradation, especially in areas where the fluorescent paint was used.

Organic pigments are usually of cyclic molecular structure, mostly aromatic, and contain atoms such as hydrogen, carbon, nitrogen, oxygen, sulphur, chloride or can even be organo-metallic compounds.^{8,9} They are mainly divided in two classes: azo and non-azo pigments. The former represents the largest group found both in industrial and in heritage applications. The organic pigments studied in this work include various chemical structures such as monoazo (Hansa yellow), diazo (diarylide, bisacetoacetylde, diazopyrazolone), benzimidazolone, metal complex (azomethine), isoindolinone and isoindoline, and different polycyclics such as flavanthrone, anthraquinone, quinacridone, perinone and perylene, quinophthalone, Diketopyrrolo-pyrrole (DPP). Azo pigments such as diarylide orange PO16 and yellow PY83 are the most commercialized and found in artist paints. The latter is sometimes combined with PY1 Hansa yellow pigment. Assessment of use, health and safety, and environmental aspects of these pigments is usually provided by companies and can sometimes be carried out by governmental bodies.¹⁰

Little is known about fluorescent pigments, especially the ones used in works of art. However, inorganic fluorescent pigments are increasingly used in multimedia (in fluorescent lighting, flat screens...), and organic fluorescent pigments are found in contemporary art, benefitting from research carried out in the industry, both in terms of quality and of use.

Much like other organic pigments, they are classified in two main groups.¹¹ The first one is comprised of crystalline organic substances, which are no subject of this paper. The second group however, is represented by conventional fluorescent pigments and is comprised of organic resinous particles which consist of organic dyes dissolved in a resin matrix. The resin may not always readily dissolve the medium, and fluorescent pigments are commonly mixed with the resin matrix. Brought

down to several microns in size, the mixture can be used as a pigment.¹²

The principle of fluorescence of organic substances, their photo stability and extensive commercial use in plastic, textile, printing and paint industries, is well documented in literature.^{13,14} Azo pigments (orange and yellow) fluoresce when exposed to radiation, resulting in an increased spectral response and brightness. There are radicals that are detrimental to fluorescence such as F, Cl, Br or NO₂. In this work, we are concerned with nitro groups (azo and quinone pigments). They are available in a wide range of colours and can be mixed with other fluorescent pigments and/or small amounts of non-fluorescent toners which tend to enhance the fluorescence. They can also be stabilized by incorporation of some UV light absorber.

2.2 Raman Micro Spectroscopy

Raman spectra were recorded using a Renishaw InVia Raman spectrometer. The instrument is equipped with green excitation (514 nm) of an argon ion laser source and a near infra red excitation line (785 nm) of a diode laser source, a Peltier cooled charge coupled device (CCD 576x400 pixels). A Leica microscope with a XYZ motorized stage is equipped with 200 and 500 magnification objectives which can provide a sample irradiation diameter of up to 1 μm . A polarized unit system is mounted onto the microscope.

The induced fluorescence background has led to the preferential use of the diode laser. The collected Raman radiation was dispersed with a 1200 lines/mm grating. Calibration of the Raman microscope was done with the silicon spectral lines at 520.5 cm^{-1} . Spectral data were processed with Renishaw Wire 2.0 software. Raman spectra are all presented with baseline correction. In some cases, photo bleaching was also used to quench the fluorescent background.¹⁵

2.3 Sample Preparation

Sample preparation is necessary for improving the quality and reliability of Raman spectra. For the pigments used in this study, pressure (hydraulic pump) was applied on the powder sample in order to flatten the surface. Then, in order to reduce black body radiation caused by the rise in temperature due to the laser beam, the thin sample (~100 μm of thickness) is transferred onto aluminium foil. A cover glass is used and sealed with an adhesive tape on the glass slide. Materials can be examined

Colour Index	Raman bands (wavenumber/cm ⁻¹)
PO34	1600(vs), 1540(m), 1480(m), 1425(m), 1341(w), 1300(m), 1291(m), 1275(s), 1258(m), 1239(m), 1161(m), 1052(m), 1002(w), 916(w), 769(w), 671(w), 542(w), 395(w), 369(w), 294(w)
PO36	1660(m), 1643(m), 1608(vs), 1570(s), 1487(vs), 1391(vs), 1362(m), 1339(m), 1326(m), 1311(m), 1292(s), 1245(vs), 1196(w), 1141(vs), 1113(w), 1063(w), 1011(m), 950(m), 919(w), 876(w), 833(w), 818(w), 740(m), 708(w), 655(m), 626(m), 602(w), 561(m), 479(w), 420(w), 401(m), 358(w), 340(w), 305(w)
PO43	1703(m), 1615(m), 1591(vs), 1547(vs), 1484(w), 1445(m), 1403(vs), 1385(vs), 1344(w), 1315(m), 1283(w), 1250(vs), 1155(m), 1103(w), 1029(m), 1009(m), 875(m), 807(w), 641(w), 550(w), 523(w), 447(w), 399(m), 338(w), 250(w), 213(m)
PO48 & PO49	1671(vs), 1655(ms), 1616(ms), 1591(ms), 1549(s), 1510(w), 1475(w), 1456(m), 1347(vs), 1318(mw), 1270(w), 1203(m), 1150(w), 1075(w), 1020(w), 937(w), 828(ms), 696(m), 645(w), 523(s), 462(vs), 353(w), 283(w), 241(w)
PO59	1676(m), 1602(s), 1535(m), 1423(w), 1359(s), 1336(vs), 1291(w), 1262(s), 1166(w), 1137(w), 1028(w), 836(w), 782(m), 756(w), 717(w), 544(w), 500(w), 448(w), 371(w), 342(w), 310(w), 256(w)
PO61	1673(w), 1592(s), 1493(w), 1445(s), 1403(s), 1307(w), 1237(vs), 1185(m), 1147(s), 1105(s), 1076(w), 939(w), 842(w), 727(m), 682(m), 564(w), 400(w), 291(m), 243(w), 230(w)
PO65	1620(w), 1605(w), 1595(m), 1580(m), 1533(m), 1486(m), 1428(s), 1415(s), 1394(vs), 1370(m), 1346(m), 1285(w), 1262(w), 1236(s), 1193(w), 1164(w), 1114(w), 1050(w), 989(w), 875(w), 773(w), 749(w), 646(w), 585(w), 330(w), 296(w)
PO73	1668(m), 1612(s), 1586(s), 1554(ms), 1523(w), 1448(m), 1408(m), 1352(vs), 1330(m), 1314(ms), 1268(m), 1220(m), 1207(w), 1115(w), 1057(s), 1020(w), 931(s), 749(w), 730(ms), 690(ms), 650(w), 627(ms), 500(m), 358(m), 323(m)
PY1	1672(m), 1622(vs), 1602(s), 1563(s), 1536(s), 1487(vs), 1451(m), 1389(s), 1339(s), 1325(s), 1312(vs), 1257(s), 1218(s), 1195(w), 1179(w), 1170(w), 1139(vs), 1000(s), 952(ms), 925(m), 847(m), 826(m), 786(s), 616(m), 511(w), 460(m), 391(m)
PY3	1674(w), 1614(vs), 1596(vs), 1568(m), 1546(m), 1496(vs), 1445(m), 1388(vs), 1338(vs), 1311(vs), 1276(ms), 1246(s), 1191(m), 1156(m), 1140(vs), 1106(w), 1063(w), 1037(m), 988(vs), 957(m), 825(w), 746(m), 650(ms), 620(m), 461(ms), 452(ms), 410(m), 394(m)
PY16	1673(w), 1633(m), 1592(vs), 1549(ms), 1508(s), 1478(m), 1389(s), 1316(vs), 1276(vs), 1246(m), 1187(w), 1143(m), 1127(m), 1100(w), 1067(ms), 952(m), 940(m), 827(w), 695(m), 661(m), 621(m)
PY24	1663(ms), 1621(m), 1598(s), 1419(m), 1385(vs), 1354(w), 1261(m), 1185(s), 1159(m), 1010(w), 528(m), 456(m), 275(w)
PY74	1673(w), 1596(s), 1516(m), 1403(ms), 1355(s), 1330(vs), 1301(w), 1266(s), 1163(w), 1092(m), 1067(w), 804(m), 647(w), 400(w), 362(w)
PY83	1671(w), 1622(s), 1599(m), 1560(w), 1535(w), 1486(s), 1450(w), 1390(m), 1339(w), 1310(m), 1256(m), 1217(m), 1196(w), 1180(w), 1140(s), 1000(s), 988(s), 952(ms), 926(m), 826(m), 787(s), 616(m), 595(w), 512(m), 461(m), 391(m)
PY109	1671(vs), 1575(m), 1454(w), 1369(m), 1311(m), 1244(s), 1205(m), 1095(w), 1061(w), 820(w), 762(m), 724(m), 623(m), 370(w), 352(w)
PY129	1601(m), 1569(m), 1535(m), 1484(m), 1424(m), 1387(s), 1339(w), 1270(m), 1213(m), 1177(w), 1154(m), 1111(w), 1030(w), 978(w), 939(w), 880(w), 848(w), 604(w), 444(w)
PY138	1787(w), 1672(w), 1486(m), 1462(w), 1418(s), 1371(s), 1353(m), 1282(m), 1188(w), 966(m), 770(w), 655(w), 620(w), 585(w), 525(w), 352(w), 327(w)
PY139	1665(w), 1588(m), 1564(vs), 1381(m), 1259(w), 1246(w), 1185(w), 1141(w), 695(m), 605(m), 294(m), 246-237(ms)
PY151	1715(w), 1653(m), 1628(w), 1603(m), 1582(s), 1516(m), 1497(m), 1455(m), 1388(s), 1320(m), 1292(m), 1273(w), 1249(m), 1202(m), 1145(s), 1070(m), 1044(m), 1023(m), 957(m), 908(w), 876(w), 846(w), 794(w), 703(w), 615(m), 586(w), 475(w), 385(m), 311(w), 225(w), 198(m)
PY154	1660(w), 1615(s), 1589(s), 1503(vs), 1474(m), 1403(s), 1365(ms), 1323(ms), 1298(s), 1266(s), 1160(m), 1134(m), 1070(m), 1038(m), 1006(m), 955(m), 916(w), 878(w), 772(m), 705(w), 612(w), 567(w), 516(w), 480(m), 400(w), 355(m), 285(w)
PY173	1634(m), 1570(m), 1551(m), 1493(m), 1458(m), 1423(w), 1391(vs), 1298(m), 1243(m), 1080(w), 958(w), 903(w), 725(w), 580(m), 375(m)
Fluorescent orange, Sennelier	1590(s), 1550(s), 1511(w), 1428(w), 1363(s), 1233(m), 1204(m), 1158(s), 1094(w), 1049(w), 982(m), 797(w), 773(m), 691(w), 637(m), 289(w)
Fluorescent orange, Kremer	1602(ms), 1551(m), 1509(m), 1429(m), 1381(m), 1368(m), 1310(w), 1234(w), 1205(w), 1153(vs), 1096(m), 1048(w), 977(ms), 798(s), 775(w), 692(m), 660(w), 637(s), 615(w), 544(w), 291(s)
Fluorescent Lumogen orange, Kremer	1711(m), 1596(s), 1573(ms), 1455(m), 1378(s), 1298(vs), 1064(m), 548(m), 451(w), 391(w)
Fluorescent yellow, Sennelier	1697(w), 1599(m), 1587(m), 1383(m), 1366(m), 1156(s), 1094(w), 1049(m), 980(m), 797(m), 691(w), 636(m), 543(w), 291(w)
Fluorescent yellow, Kremer	1695(w), 1602(s), 1548(ms), 1432(m), 1384(m), 1234(m), 1208(m), 1157(vs), 1099(m), 1051(m), 977(ms), 916(w), 801(s), 689(m), 637(ms), 544(m), 474(w), 410(w), 298(ms)
Fluorescent Lumogen yellow, Kremer	1586(vs), 1573(vs), 1525(w), 1464(w), 1355(s), 1314(s), 1301(s), 1227(m), 1125(w), 1083(m), 599(w), 519(m)

Table 2: Pigments and relevant Raman shifts. Relative intensities: vs (very strong), s (strong), ms (medium to strong), m (medium), w (weak).

through glass since the Raman scattering from glass is very weak.

fact that chemical structures are quite similar, the interpretation of Raman frequencies is sometimes difficult.¹⁶ The list of observed Raman bands is in Table 2.

3 Results and Discussion

Raman spectra have revealed some distinct fingerprints for all studied pigments. Owing to the

3.1 Organic Pigments

The characteristic feature of orange and yellow azo pigments studied in this work is that their relevant Raman spectra show some expected bands between 1700 and 900 cm^{-1} (Figures 1 and 2).

Hansa yellow (PY1, PY3, PY74, Figure 1) displays an amide I band at 1650 cm^{-1} , a nitro asymmetric stretch at 1630 cm^{-1} , an aromatic ring vibration at 1600 cm^{-1} , an aromatic nitro stretch at 1560 cm^{-1} , an azobenzene ring at 1485 cm^{-1} , a CH_3 deformation at 1451 cm^{-1} (not always present), an $\text{N}=\text{N}$ stretch at 1380 cm^{-1} , an amide III at 1255 cm^{-1} , an aromatic nitro group at 1340 cm^{-1} (with a slight shift), a benzylamide at 950 cm^{-1} (not always significant), and an aromatic scissoring modes at 820 cm^{-1} (medium intensity band).

PY74 (Figure 1) is quite distinguishable from the two previous ones.

The distinction between pigments with the same chemical group is fairly subtle. For instance, Hansa yellow PY3 differs with PY1 by a band at 746 cm^{-1} , which corresponds to C-H bending along with a 650 cm^{-1} band attributed to C-Cl stretching.

Diarylide pigments (Figure 1), PY16 (biacetoacetylide) and more specifically PY83, are usually complex to study since they are sometimes used in mixtures with Hansa pigments. Indeed, PY83 is supposed to be containing some unknown percentage of PY1. This makes the identification of diarylide more difficult. However, the presence of a band at 1280 cm^{-1} , which corresponds to the two carbon bridge of the aromatic function, and especially in the case of PY16, enables the differentiation with Hansa pigments.

Spectra show some significant differences in the 1700-1100 cm^{-1} region while 900-200 cm^{-1} display poor Raman features. 1500-1300 cm^{-1} region is particularly discriminating when comparing PY16 to PY83. The latter presents some medium intensity bands such as amide at 1670 and 1255 cm^{-1} , $\text{N}=\text{N}$ stretch at 1400 and 1540 cm^{-1} , and benzylamide band at 955 cm^{-1} .

Benzimidazolone group can be found in both orange and yellow pigments (Figure 2). Three pigments were studied (PO36, PY151, PY154). They show rich Raman spectra with some distinguishing bands at 1600 cm^{-1} (PO36) and 1145 cm^{-1} (PY151) attributed to aromatic ring vibration, 1505 cm^{-1} (PY154) for azobenzene, and a very intense 1487 cm^{-1} band for azobenzene ring (PO36).

Azomethine pigments (Figure 2) belong to the metal complex group (PO59, PO65, PY129) and

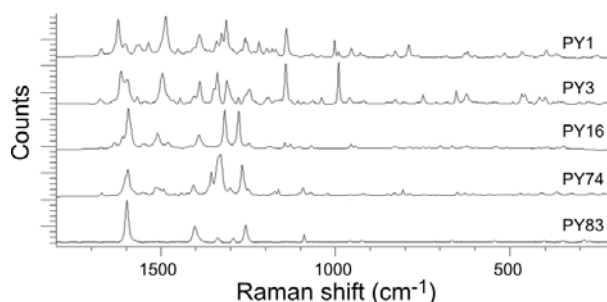


Figure 1: Raman spectra (1800 – 200 cm^{-1}) of Hansa (PY1, PY3, PY74), Biacetoacetylide (PY16) and Diarylide (PY83).

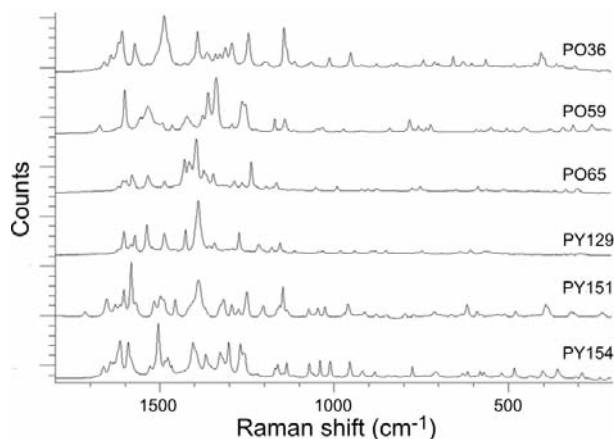


Figure 2: Raman spectra (1800 – 200 cm^{-1}) of Benzimidazolone (PO36, PY151, PY154) and Azomethine (PO59, PO65, PY129).

are chemically close to diarylide molecules. They display some characteristic Raman bands such as $\text{N}=\text{N}$, azobenzene and amide. PO65 has some significantly different Raman bands at 1670 and 1255 cm^{-1} along with $\text{N}=\text{N}$ stretch at around 1400 and 1540 cm^{-1} , a benzylamide band at 955 cm^{-1} .

Perinone (PO43) (Figure 3) is a class of pigments which is chemically close to perylene molecules. It displays characteristic intense features at 1591 cm^{-1} for azobenzene ring, at 1547 cm^{-1} for NO_2 stretching, a conjugated 1403 and 1385 cm^{-1} attributed to asymmetric NO_2 stretching. Another very intense band is noticeable at 1250 cm^{-1} .

Quinacridone (PO48 & PO49) (Figure 3) are very difficult to differentiate. Their Raman spectra are very similar. Significant bands occur within the 1700-1300 cm^{-1} region and two main bands at 523 and 463 cm^{-1} corresponding to $\text{C}=\text{O}$ stretch. Perinone, quinacridone and flavanthrone (PY24) (Figure 3) have these Raman bands in common. A main Raman band at 1341 cm^{-1} is also present and assigned to asymmetric NO_2 stretching, and a 1290 cm^{-1} band is also detected for aromatic ring vibrations.

Flavanthrone (PO24) (Figure 3) is a polycyclic pigment. The Raman spectrum displays a pattern of bands which are mainly related to aromatic vibra-

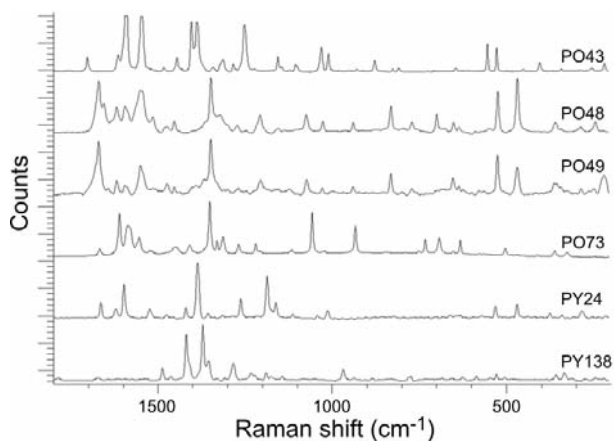


Figure 3: Raman spectra (1800 – 200 cm^{-1}) of polycyclic pigments: Perinone (PO43), Quinacridone (PO48, PO49), DPP (PO73), Flavanthrone (PY24) and Quinophtalone (PY138).

tions notably at 1598 cm^{-1} . Amide I band at 1650 cm^{-1} and nitro asymmetric stretch at 1630 cm^{-1} are present. Very strong 1385 and 1261 cm^{-1} bands should be attributed to the amide group rather than N=N stretching. Aromatic ring vibration is seen at 1185 cm^{-1} , and an expected carbonyl bending vibration was detected at 525 and 456 cm^{-1} .

Quinophtalone (PY138) displays two main conjugated Raman bands at 1418 and 1371 cm^{-1} which could be attributed to azobenzene vibration, and a 1282 cm^{-1} band assigned to the amide group. The presence of chloride atom in the molecule of quinophtalone is shown in a very weak C-Cl bond at 655 and 620 cm^{-1} .

The DPP pigment (Diketopyrrolo-pyrrole) (PO73) is shown in Figure 3. Quinacridone are sometimes used with DPP which could mislead the interpretation of spectra. The Raman spectrum shows a significant band at 1352 cm^{-1} due to aromatic ring vibration. Despite some weaker bands present, this pigment displays a similar Raman spectrum to that of quinacridone pigments. The main difference is a weak band at 1400 cm^{-1} which corresponds to an aromatic group. The expected carbonyl bands are not visible in the spectrum.

In Figure 4, Raman spectra of isoindoline (PO69, PY109, PY139), isoindolinone (PO61, PY173) and diazopyrazolone (PO34) are shown. It is particularly of interest with isoindoline and isoindolinone groups that Raman spectra show some different pattern for the five different pigments even though they are chemically close molecules. All spectra almost display as expected some distinct bands corresponding to carbonyl, C-C stretching, CH deformation, C-N stretching and C-Cl. Isoindolinone pigments show a few different Raman features, especially in the case of PO61.

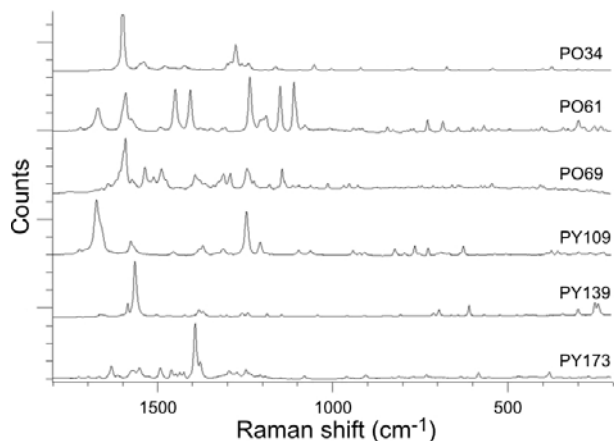


Figure 4: Raman spectra (1800 – 200 cm^{-1}) of Diazopyrazolone (PO34), Isoindoline (PO69, PY109, PY139) and Isoindolinone (PO61, PY109, PY173).

Diazopyrazole (PO34) belongs to the diazo pigment type. It shows two significant bands, a very intense band at 1600 cm^{-1} for aromatic ring vibration, and a strong band at 1270 cm^{-1} corresponding to amide III. A pattern of weaker bands makes this pigment distinguishable.

3.2 Fluorescent Pigments

Fluorescent pigments of three different origins and of different nature, have been studied. One fluorescent (orange and yellow) pigment from the Sennelier company (material data sheet unavailable), and two pigments from Kremer: one fluorescent perylene type pigment and one lumogen dye/pigment. According to the manufacturer, the latter represents a new type of dye/colouring matter and is supposed to have some improvement in fluorescence under black light, as well as being excellently applicable in synthetic resins. In the case of perylene pigments, the comparison of Raman spectra between fluorescent pigments of this type and perinone PO43 showed some major differences.

As far as our research is concerned, the composition of these fluorescent pigments is not accurately known and is a commercial secret. The manufacturers provide data on light fastness, which is strongly dependent on the composition of binders, pigment concentration and organic colourants which may be dissolved in amino resins. Owing to the fact that fluorescent pigments do not contain any azo or nitro bonds, they do not contain any metal ions or inorganic phosphorus. The resulting Raman spectra may display some misleading features.

This part of the work focuses on a few pigments amongst a very intensive variety of fluorescent

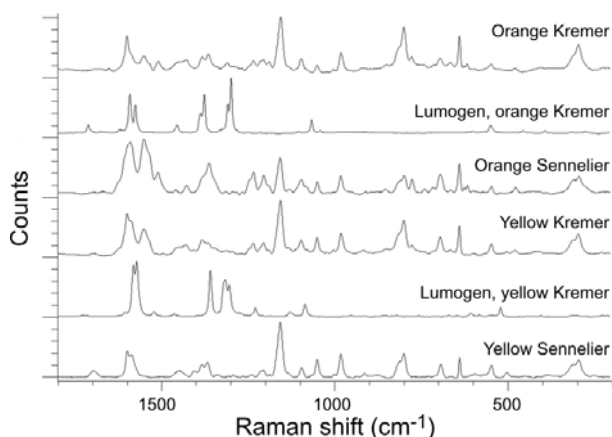


Figure 5: Raman spectra (1800 – 200 cm^{-1}) of fluorescent orange & yellow: Kremer and Sennelier pigments.

colorants/pigments found in the market. In Figure 5 the three different types of both orange and yellow pigments display some characteristic Raman features. The unknown fluorescent pigments (Sennelier and Kremer ones) show very similar Raman spectra with differences in band intensity. However, lumogen dyes show some distinct Raman bands.

The drawback is that the orange and yellow pigments cannot easily be differentiated by Raman spectroscopy. More complementary fluorescent dyes/pigments must therefore be studied.

3.3 Paint Tubes

Raman analyses of commercial paint tubes of both organic yellow and fluorescent pigments was undertaken and two trade marks, Daler-Rowny and Sennelier, were investigated. In both cases, pigments are mixed with an acrylic resin containing unknown solvent and additives.

The analysis of paint tubes gave rise to Raman spectra (Figure 6) with much less significant features than the corresponding standards. Both yellow and fluorescent commercial paint tubes show some significant bands indicating the presence of C=C stretching, deformation CH_3 and stretching C=O. Azo N=N bands at 1380 cm^{-1} are also present along with a significant Raman band at 1080 cm^{-1} , which is attributed to carbonate from the extender.

In the case of azo pigments, the differences between standard pigments and those in an acrylic medium are very slight. The two fluorescent paints display some similar Raman features which indicate that orange and yellow pigments belong to the same chemical group.

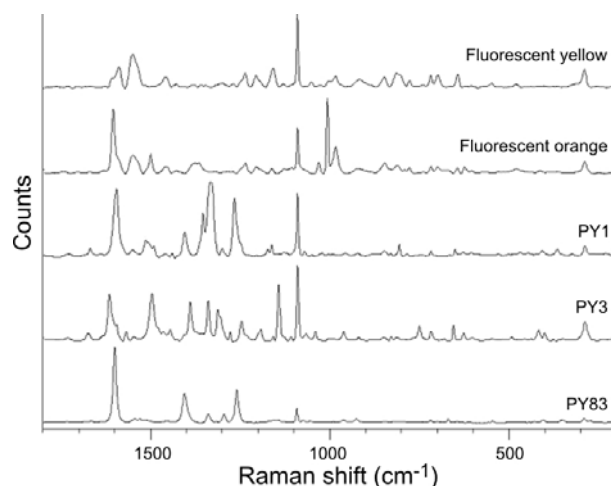


Figure 6: Raman spectra (1800 – 200 cm^{-1}) of paint tubes: Daler-Rowny fluorescent paint, Sennelier (PY1, PY3, PY83).

4 Case Study

A 1985 painting “J'ai rêvé” by the artist Ben has been studied. This painting is composed of six wooden panels which include various plastic objects and acrylic paint. Conservation reports revealed some alterations such as cracks and depletion on some areas covered with orange and yellow fluorescent paints. Prior to undergoing conservation, characterization of paint materials has been carried out in the decayed areas. Samples were taken and analyzed by Raman and FTIR spectroscopy, and completed by elemental analysis using EDXRF.

Raman spectra (Figure 7) revealed that orange and yellow pigments did not display different spectra (Figure 7). A pattern of Raman signals is related to organic and/or fluorescent pigments: 1600 and 1382 cm^{-1} for azo stretching vibration, 1453 cm^{-1} for CH_3 deformation, and $1004/981/792/692 \text{ cm}^{-1}$ for aromatic ring vibration with 1042 cm^{-1} ortho- ring vibration. Additionally, 1150 cm^{-1} is attributed to SO_2 symmetric stretch due to CaSO_4 extender.

FTIR spectra gave some complementary results, enabling us to identify the acrylic binding medium. EDXRF analyses showed the presence of silicon, sulphur, chloride, calcium, titanium and zinc. These elements confirm the identification of extenders, while chloride may indicate the presence of an azo pigment.

Results have shown that both orange and yellow samples contain some significant vibrational bands that can be attributed to azo pigments studied in this work as well as to fluorescent pigments. Although an accurate composition of the two samples cannot be suggested, Raman spectra showed some similarities with those of fluorescent pig-

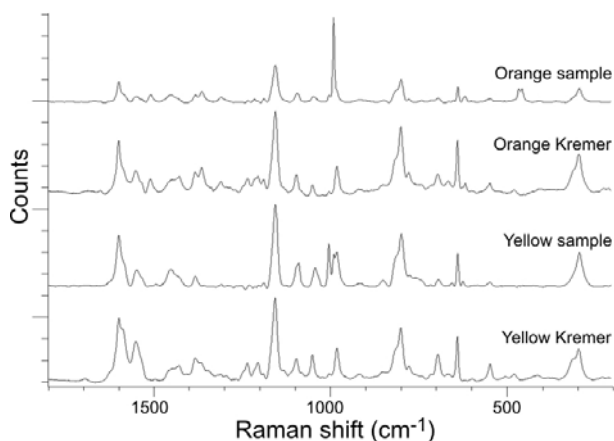


Figure 7: Raman spectra (1800 – 200 cm^{-1}) of Ben samples and fluorescent standard pigments (Kremer).

ments. The hypothesis that the fluorescent paint is composed of an azo pigment mixed in with some fluorescent agent in an acrylic binding medium, cannot be discarded.

5 Conclusions

This work has shown that identification of organic pigments is feasible using Raman spectroscopy. The difficulty arises when distinguishing strong bands from weaker bands, which make the differentiation between pigments of the same chemical class fairly subtle. The expected chemical differences between all pigments did show up in Raman spectra.

The analysis of commercial paint tubes brought up some interesting information, as characteristic Raman bands attributed to main chemical groups are present. However, spectra lack information in comparison to standard pigments. The presence of a binding medium (acrylic) plus additives can be misleading and can overshadow the spectra of standard pigments. Therefore, it is difficult to build a database on the basis of pigment colour.

Fluorescent pigments have shown how difficult it is to obtain more accurate information data from manufacturers. In the next step we will analyse more types of fluorescent pigments found in works of art, and the behaviour of these materials under conditions of photo degradation.¹⁷

The study of the Ben painting using Raman spectroscopy and complemented by FTIR, has enabled us to suggest the type of fluorescent pigment. Obviously, the artist himself could also provide advice leading to more accurate characterization of the colouring matter, and to a better understanding of what the painting might have suffered.

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