

SCIENTIFIC PAPER

FROM BECKMANN TO BASELITZ – TOWARDS AN IMPROVED MICRO-IDENTIFICATION OF ORGANIC PIGMENTS IN PAINTINGS OF 20th CENTURY ART

Karin Lutzenberger, Heike Stege

This paper is based on a presentation at the 8th international conference of the Infrared and Raman Users' Group (IRUG) in Vienna, Austria, 26-29 March 2008.

Guest editor:
Prof. Dr. Manfred Schreiner

Doerner Institut, Bayerische
Staatsgemäldesammlungen,
Barer Str. 29, 80799 München, Germany

corresponding author:
lutzenberger@doernerinstitut.de

Today, synthetic organic pigments play a major role as colorants of excellent light-fastness in artists' paints. Their analytical determination in paintings gains steady importance with respect to attribution and studio practice of certain artists as well as dating and authentication. Synthetic organic pigments have extremely varied chemical structures and properties such as colouring strength, solubility or thermal stability. Therefore, it is a challenging task to fully identify all organic as well as inorganic colorants and fillers in a micro-sample taken from a painting. A complementary sampling and analytical approach is suggested, that combines micro-chemical and solubility tests, Raman microscopy, pyrolysis gas chromatography/mass spectrometry, thin layer chromatography and/or high-performance liquid chromatography on a case-to-case basis. This paper presents results and discusses practical experiences with Raman microscopy as a rapid and minimally invasive technique for the identification of organic pigments in paint samples. Case studies from 20th century German artworks by Max Beckmann, Georg Baselitz, A.R. Penck and Markus Lüpertz illustrate the potential and limitations of Raman microscopy and the need for complementary techniques, especially in the case of mixtures. Selected organic pigments, especially Pigment Green 7, Pigment Violet 23 or Pigment Yellow 83, are briefly discussed with respect to their use in artists' paints.

1 Introduction

For more than 50 years, the identification of inorganic pigments and also of natural plant dyestuffs and lakes has been an established and routine task in art and archaeology. It is thus surprising that analytical research on the use of synthetic organic pigments is still rather in its early stages; however, at the moment, these modern colorants are becoming an increasingly important target of art-technological research, i.e. with respect to questions of studio practice and authenticity. Owing to the variety of synthetic organic pigments, their identi-

received: 30.06.2008
accepted: 30.04.2009

key words:
Synthetic organic pigments, painting
analysis, complementary methodological
approach, Raman microscopy, 20th cen-
tury German art

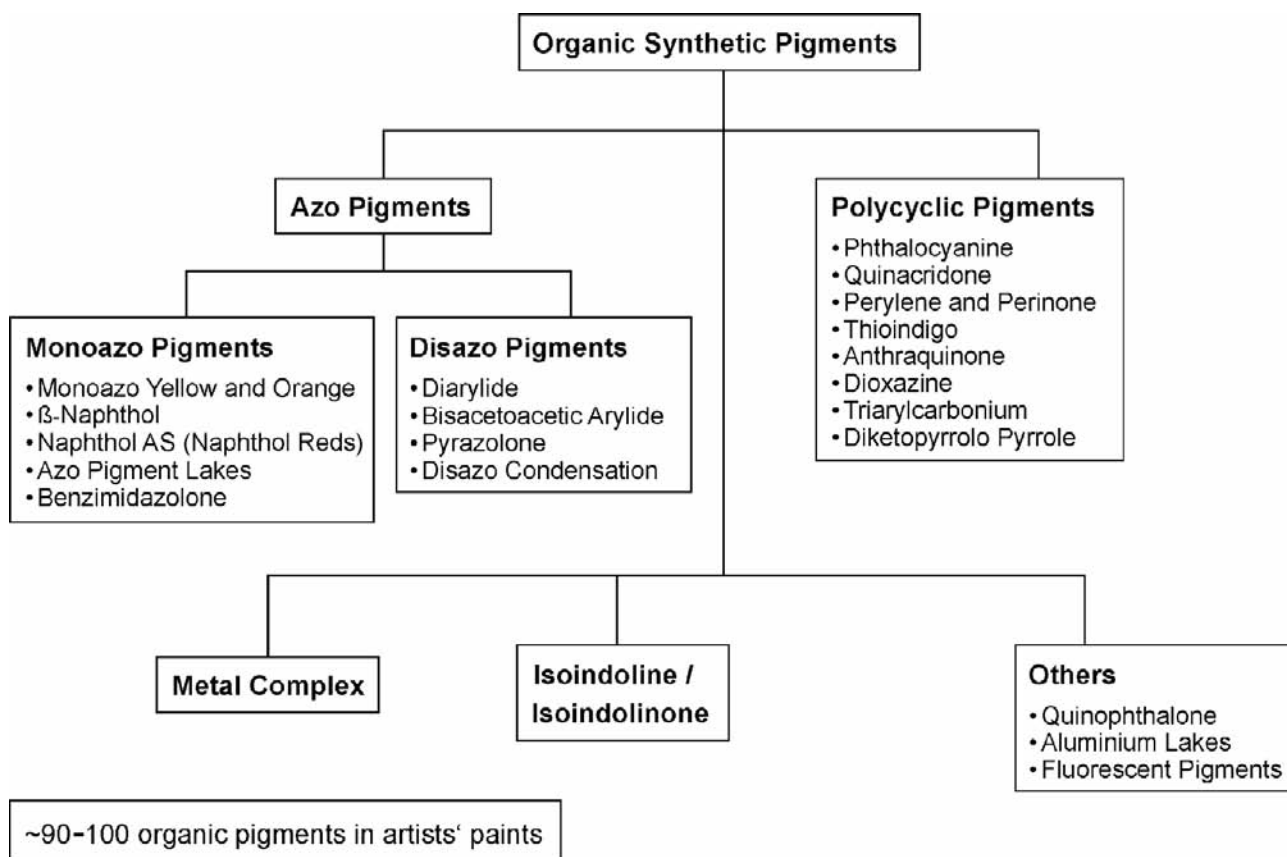


Figure 1: Overview on the classification of organic synthetic pigments.

fication in artworks can be a challenging analytical task. Figure 1 gives an overview of the chemical classification of organic pigments according to their chemical constitution. A rough distinction can be made between azo and non-azo pigments; the latter are also known as polycyclic pigments. The commercially important group of azo pigments can be further classified according to structural characteristics, such as the number of azo groups or the type of disazo or coupling component. Polycyclic pigments, on the other hand, can be identified by the number and type of rings that constitute the aromatic structure.¹⁻³

The history of synthetic organic colorants started in 1856. The first synthesis of mauveïn by William H. Perkin ushered in an era of colour chemistry that still continues. Many new organic structures were discovered and introduced as commercial organic dyestuffs and pigments. Around the year 1900, only a few pigments, such as aniline black or monoazos, had already been invented. The commercial development of azo colours began with the discovery of Lithol Red in 1899.^{3(p.47)} In 1909, yellow monoazo pigments were discovered by Meister Lucius & Brüning in Germany (later the Hoechst AG) and they entered the market in 1910 under the trade name of "Hansa Yellows".^{1(p. 214)}

Another milestone in modern pigment technology was the discovery of copper phthalocyanines, which have a relatively complex structure but are easy to synthesise.^{3(p. 47)} Most of today's relevant synthetic organic pigment classes were introduced around 1950; the most important discoveries in the 2nd half of the century were the family of quinacridone pigments, followed by benzimidazolone and isoindolinone pigments. The latest commercialisation of a new pigment family is represented by the diketopyrrolopyrroles, which were discovered in 1983.^{3(p. 47)} It is very difficult to keep track of the huge variety of synthetic organic pigments on the market today. Approximately 100 of them are today used in artists' paints, but modern artists also work with normal household paint, car lacquers or graffiti sprays, which expands the artists' palette significantly.

The identification of organic pigments in paint samples from artworks is hampered by various factors, such as the small amount of sample usually available, the variability of the pigment's chemical structure and physicochemical properties, such as solubility and thermal stability, as well as the low content of organic pigments, which typically possess a high tinting strength. Hence, problems relating to the sensitivity and interfer-

ences with matrix components (binding medium, inorganic pigments or fillers) frequently occur.

In museum laboratories, diverse analytical techniques are applied to synthetic organic pigments, but so far there is no widely recognised strategy for their full identification. De Keijzer proposed micro-chemical spot tests,⁴⁻⁶ which were further developed by Kaalsbek.⁷ Various chromatographic methods have been successfully utilised: thin-layer chromatography (TLC)⁸ for soluble pigments, high-performance liquid chromatography (HPLC) with diode array detection as a more sensitive method⁹ and pyrolysis gas chromatography coupled with mass spectrometry (Py-GC/MS).^{10,11} Py-GC/MS proved to be a fast method for identifying organic pigments that yield pyrolysis products with sufficient volatility to pass through a gas chromatography column. Unfortunately, this technique displays rather low sensitivity to non-azo pigments. Fourier-transform infrared spectroscopy (FTIR) can be used to identify organic pigments,^{12,13} but FTIR spectra of samples of modern artists' paints contain bands from various components of the binding medium and, to some degree, also from inorganic pigments.¹⁴⁻¹⁶ Their relative contributions are dependent upon the quantitative composition of the particular formulations. Therefore, the identification of organic pigments from the complex FTIR spectra of painting samples can be difficult in practice. Furthermore, improvements in the detection of organic pigments have been achieved with laser desorption ionisation mass spectrometry (LDI-MS)¹⁷ and direct temperature-resolved mass spectrometry (DTMS).^{18, 19} Finally, the development of imaging secondary ion mass spectrometry (imaging SIMS) has made high-resolution MS imaging possible. An exciting application for this technique is the mass spectrometric analysis of pigments and binders of individual paint layers within a cross-section.²⁰

In forensic science, Raman microscopy is routinely applied to lacquer particles for the identification of pigments.²¹⁻²³ In art and archaeology, Raman spectrometry – until now more regularly applied to inorganic pigments or natural organic lakes and dyestuffs²⁴⁻²⁷ – has only recently been evaluated for modern organic colorants and it performs surprisingly well.²⁸⁻³¹ For archaeometrical purposes, the Raman technique, especially Raman microscopy, is very advantageous because it is rapid and non-destructive.

In the first part of this paper, a comprehensive and efficient sampling and analysis strategy is suggested for the micro-identification of organic (and

inorganic) pigments in paintings. This strategy was optimised and simplified for routine conditions in museums. Raman microscopy is an indispensable part of this approach and therefore particular attention is given to the discussion of the practical strengths and limitations of this technique with respect to synthetic organic pigments. Selected case studies from paintings by various 20th century German artists are used to evaluate the potential of Raman microscopy to differentiate between and within different classes of organic pigments (phthalocyanines, anthraquinones, dioxazines, naphthol AS, β -naphthols, diarylides, "Hansa Yellows"). Problems associated with mixtures are also addressed. Some of the identified organic pigments are briefly discussed with respect to their history in artists' paints.

2 General Analytical and Sampling Strategy for Paintings

Museums housing collections of modern and contemporary art, such as the Pinakothek der Moderne in Munich, are busy places facing large attendance, numerous temporary exhibitions, extremely sensitive objects and the ubiquitous staff shortages. The planning of technological and analytical examinations also has to consider these general practical conditions and try to minimise interference. To give a practical example, every painting in the depository at the Pinakothek der Moderne is wrapped in foil for dust protection so that every examination and sampling step requires un- and re-wrapping and usually also de- and re-framing of the object under investigation by the conservation or depository staff. Examinations of paintings on display are usually restricted to the gallery's closing day. A crucial point is therefore to find a way to manage the technological examinations as well as an appropriate, sampling for material analyses - preferably in a single session.

For the identification of inorganic pigments and fillers in paints, sampling of a few particles for SEM/EDX, light microscopy, Raman microscopy etc. is usually sufficient. This situation is more complicated for organic colorants in unknown paint compositions owing to their diversity and the virtual impossibility of identifying all of them by means of a single analytical method. In this case, micro-chemical spot and solubility tests offer a simple, hence elegant opportunity to obtain preliminary information on the general presence of organic pigments and for decision-making on the required sample size. These micro-chemical tests can be carried out very quickly on a few particles under a stereomicroscope directly in the museum. Part of

this first sample is routinely kept for SEM/EDX analyses (which are not discussed here). Almost all synthetic organic pigments give distinct colour changes in strong acids and alkalines,^{6,7} particularly concentrated sulphuric acid, concentrated nitric acid, potassium hydroxide in ethanol and potassium iodate. Sometimes, preliminary information on the pigment class can be concluded, e.g. phthalocyanine pigments show discolouration in sulphuric acid and characteristic recolouring on addition of a drop of water. Additional micro-chemical tests for solubility are essential: tests with chloroform, methanol/HCl and dimethyl sulphoxide are recommended. The solubility also delivers information on the class of organic pigment and is also helpful when deciding on the applicability of liquid chromatography (TLC, HPLC) for this paint sample. After these tests, in a second sampling step, appropriate amounts can be taken from coloured areas of a painting where the presence of organic pigments has been established. Samples of a few μg are routinely taken from each colour for Raman microscopy. The benefits and weaknesses of this method are described in greater depth below. Within this project, Py-GC/MS was tested as an alternative for the direct analysis of solid micro-samples; however, this method was less effective than Raman microscopy. Although pure pigments from the azo group as well as from diverse polycyclic classes, such as phthalocyanines, diketopyrrolopyrroles and triarylcarbonium, yielded characteristic pyrograms (to be published separately), the results for paint samples were less satisfying. Generally, the main pyrolysis products derived from the medium and the sensitivity for the organic pigments was insufficient in most cases.

For paints containing soluble organic colorants, the application of Raman microscopy and complementary chromatographic techniques (TLC, HPLC) is highly recommendable. A sample of approx. 100 μg is usually sufficient; yet, taking such an amount is often limited to the tacking edges of a painting.

So far, this simplified micro-sampling strategy has been applied to pigment analyses of about 40 paintings at the Pinakothek der Moderne within the research project on selected 20th century German artists - and proved to be of value in the normal course of museum life.

3 Raman Microscopy – Experimental

3.1 Instrumentation and Measurement Conditions

Raman analyses were performed at the Bavarian State Office for Criminal Investigation (LKA), Munich and at the Federal Institute for Materials Research and Testing (BAM), Berlin. At both institutes, a LabRam-HR Raman microscope (Jobin Yvon, Villeneuve d'Ascq, France) fitted with a BH2 Microscope (Olympus, Hamburg, Germany) was used for the measurements. Three excitation sources were available: (i) in Munich, a 532-nm diode laser (Sacher Lasertechnik, Marburg, Germany), a 633-nm He/Ne laser (Coherent Inc., Santa Clara, USA), and a 785-nm Nd:YAG laser (Coherent Inc., Santa Clara, USA), (ii) in Berlin, a 514-nm argon laser (433 Series Ion Laser Melles Griot, Carlsbad, USA), a 633-nm He/Ne laser, and a 785-nm XTRA diode laser (Toptica Photonics AG, Gräfelfing, Deutschland). The power applied to the samples varied between 0.1 and 20 mW. The microscopes were equipped with interchangeable objective lenses with magnifications of 10x, 50x and 100x; the 50x objective was preferred. The detector in Munich was a thermoelectrically cooled CCD4 camera (Jobin Yvon, Villeneuve d'Ascq, France). The Berlin spectrometer was equipped with a nitrogen-cooled CCD camera (Jobin Yvon, Villeneuve d'Ascq, France). The Raman signal was acquired in the wavenumber range between 180 and 2700 cm^{-1} using integration times from 1 to 32 s.

3.2 References and Sample Preparation

As references, so far 48 of the more than 300 synthetic organic pigments from various manufacturers (i.e. BASF, Ciba, Clariant, Bayer, Hoechst) in the artists' material collection of the Doerner Institut have been recorded by Raman microscopy. To date, spectra of 23 reference pigments have been published by Schulte et al.,²⁸ and more are to follow.³² In the following, we use the pigment nomenclature from the Colour Index International.³³

The Raman samples, both references and paint samples, were prepared following the recommendations given by the Bavarian State Office for Criminal Investigation. One particle of each sample (corresponding to a sample size of approx. 5 to 10 μg) was pressed onto aluminium foil between a microscope slide and a glass cover on a heating stage (100 °C, ca. 1 min). The measurements were

done through the glass cover after cooling. This preparation procedure improves heat conductivity and significantly reduces the thermal background in the Raman spectra. The extent of fluorescence strongly varied in the pure pigments and paint samples. To minimise fluorescence bleaching of the sample by exposure to the laser light for 30 min prior to spectrum acquisition proved necessary. The spectra obtained for the paint samples were visually compared to those obtained for the available reference pigments as well as other published or unpublished Raman data.^{29,34}

4 Results and Discussion

4.1 Case Studies – Polycyclic Pigments

Raman microscopy is suited very well for many polycyclic pigments, especially or those of the phthalocyanine, anthraquinone or dioxazine groups. This shall be demonstrated by two samples of the painting “Woman with mandolin in yellow and red” by the German expressionist Max Beckmann (1884-1950) dating 1950 (Figure 2) and one sample from the painting “Roadworker” by Georg Baselitz, dating 1973 (Figure 3).

“Woman with mandolin in yellow and red” – impressive in its vivid colourfulness and strong contrasts – is one of Max Beckmann's last works, which he created three years after his emigration to the United States of America. Here, the copper phthalocyanine Pigment Green 7 (PG 7) was identified in a green sample taken from the background of the painting using a diode laser source ($\lambda_{exc} = 532 \text{ nm}$).

The sample spectrum in Figure 4 shows various bands that are characteristic of phthalocyanines: first of all, the most intense band between 1520 and 1540 cm^{-1} from stretching vibrations of the C=C pyrrole group and the C-N aza group. Furthermore, bands of medium intensity at approx. 690 cm^{-1} from breathing vibrations of the macrocycle and another one at approx. 1340 cm^{-1} that can be assigned to C-C stretching vibrations of the pyrrole group.³⁵

The commercially important group of blue and green phthalocyanine pigments can be identified by Raman spectroscopy with high discrimination power in paint samples. Two blue (PB 15 with several polymorphs and PB 16) and two green pigments (PG 7 and PG 36 with different degrees of chlorine and bromine substitution) are used in artists' paints. In the green sample, the Raman band at 1084 cm^{-1} can be assigned to aromatic



Figure 2: Max Beckmann, “Woman with mandolin in yellow and red”, 1950, canvas, 92 x 140 cm, Bayerische Staatsgemäldesammlungen (Inv. No. 1532).



Figure 3: Georg Baselitz, “Roadworker”, 1973, canvas, 200 x 162 cm, Bayerische Staatsgemäldesammlungen (Inv. No. WAF PF 3).

chlorine compounds present in PG 7.^{36(p. 203)} It is not present in unsubstituted, blue phthalocyanine pigments, such as PB 15. Generally, SEM/EDX is not sufficiently sensitive to detect the copper content derived from phthalocyanines in paint samples; however, the halogen substituents in the two green representatives of the group often provide an additional discriminatory information. The chemical development and industrial production of phthalocyanine pigments started in 1935/37.^{37(p. 21)} and this is indeed one of the earliest findings so far of a phthalocyanine pigment in a work of art. Interestingly, none of the many other investigated paintings by Max Beckmann contained this newly introduced, intense green pigment, which he apparently started to use – either voluntary or

involuntary - only during his last years in the United States and not before his emigration from Amsterdam in 1947.³⁸

A red sample from “Woman with mandolin” was analysed with a diode laser source ($\lambda_{\text{exc}} = 785 \text{ nm}$). The main bands in the spectrum at 1328, 1482 and 1292 cm^{-1} (Figure 5) can be assigned to the anthraquinone compound alizarin (all ring vibrations³⁶(pp. 122,165)). The strong Raman band at 254 cm^{-1} as well as the weaker band at 344 cm^{-1} are characteristic of the pigment vermilion, which is admixed.

Alizarin, 1,2-dihydroxyanthraquinone, is the main dyestuff of natural madder lake colours, but in this case, the deep red aluminium lake is probably its synthetic equivalent. Synthetic alizarin (Pigment Red 83) cannot be differentiated from natural alizarin by its Raman spectrum, but it is known that after the start of its industrial production in 1869 the cultivation of madder strongly declined.³⁹ In the early period of synthetic organic pigments

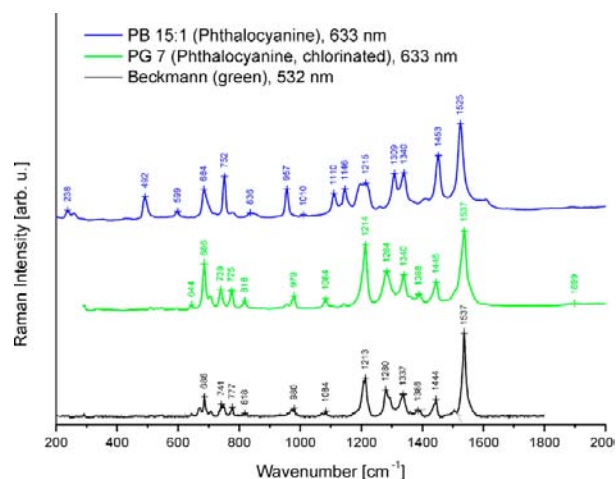


Figure 4: Spectra comparison of a green sample from “Woman with mandolin in yellow and red” (measured with laser 532 nm) with PG 7 (examined with laser 633 nm) and PB 15:1 (examined with laser 633 nm).

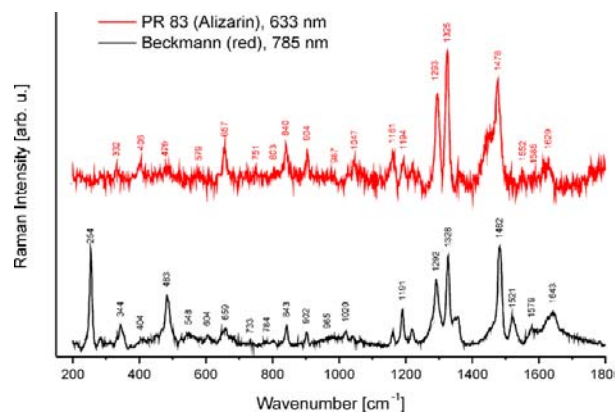


Figure 5: Spectra comparison of the red sample from “Woman with mandolin in yellow and red” (measured with laser 785 nm) with PR 83 (examined with laser 633 nm).

shortly after 1900, when many of the newly-developed colorants had only poor light-fastness and thus met with serious objections from artists and colour traders, alizarin was the only synthetic colorant of sufficient stability and over long-time declared as light-fastness standard for coal-tar colours.^{40, 41} Since then, commercial interest in PR 83 has declined considerably. However, although its fastness to light and solvents leaves much to be desired by modern standards, alizarin has a useful and pleasing mass-tone not equalled by the recent, more permanent and cleaner blue reds. For this reason, it is still a regular component of artists' colours¹(p. 496),⁴²(p. 431) and can be found in various contemporary paintings.

Within this project, pigment analyses were performed on several paintings by Georg Baselitz, born 1938 and considered to be one of the most important representatives of modern German art. A purple sample taken from the tacking margin of the painting “Roadworker” from 1973 yielded the Raman spectrum depicted in Figure 6, recorded with a Nd:YAG laser source ($\lambda_{\text{exc}} = 514 \text{ nm}$). The dioxazine Pigment Violet 23 (PV 23) was unambiguously identified - its most prominent Raman bands are a triplet at approx. 1345 cm^{-1} , 1390 cm^{-1} and 1430 cm^{-1} . The middle band can be assigned to C=C and C=N in-plane vibrations of pyrroles as well as ring vibrations of alkyl pyrroles, the other two can be ascribed to ring vibrations of benzene.³⁶(p. 181) PV 23 is the only pigment of the dioxazine group that found its way into artists' paints and, to our knowledge, this is the first reported finding of this pigment in a painting. The pigment exhibits a unique blue-violet shade of exceptional intensity and is currently employed in a diversity of paint formulations. PV 23 was developed in 1928, but a promising field of application was not found until 1952, the year in which it was patented by

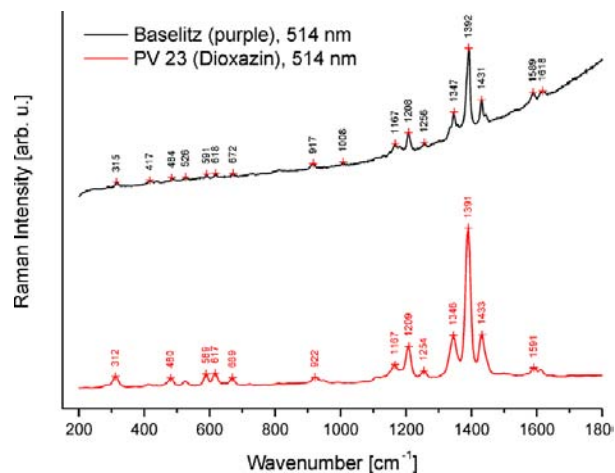


Figure 6: Spectra comparison of a purple sample from “Roadworker” (examined with laser 514 nm) with PV 23 (measured with laser 514 nm).

Hoechst;⁴³ its industrial production commenced in 1953. The first entries of the pigment in the 2nd edition of the Colour Index International are found in 1963 and 1965,⁴⁴ and they already mention its use in artists' colours. The earliest recipe from an artists' paint manufacturer found so far dates back to 1967 – in this year, the Schoenfeld company in Düsseldorf was already using PV 23 in oil, tempera and gouache coloursⁱ.

4.2 Case Studies – Naphthol AS and β -naphthol (Monazo) Pigments

The numerous azo pigments, subdivided into monoazo and disazo compounds and their sub-groups, are an important pigment class used in modern paints and therefore the success of Raman microscopy for their identification is essential. Most of the azo pigments can be dissolved in diverse organic solvents and, for this reason, liquid chromatography can (and should) be applied as a complementary method.

Raman microscopy is applicable to all sub-groups of monoazo pigments; however, the identification and also differentiation of pigments from only two monoazo groups, naphthol AS and β -naphthol pigments, are discussed in the following. These two were selected because they are frequently used in artists' paints.

β -naphthol colourants, which are based on the coupling of substituted aniline with β -naphthol, are among the oldest synthetic dyes. Th. and R. Holliday (at Read, Holliday & Sons in the UK) applied for the patent in 1880. In 1885, Gallois and Ullrich obtained Para Red (PR 1) by coupling β -naphthol with diazotised 4-nitroaniline. The resulting pigment – first manufactured in 1889 – is even considered to be the oldest of all known synthetic organic pigments. With respect to their light-fastness, a number of β -naphthols fall below modern standards.¹(pp. 271-274) Therefore, hardly any of them can be found on current colour charts. Nevertheless, within this project, β -naphthol pigments were still found on German paintings dating into the 1990s.

The naphthol AS pigments are a class of about eighty 2-hydroxy-3-naphtharylide azo pigments, their coupling component being 2-hydroxy-3-naphtholic acid, known as naphthol AS. The first group was patented as Grela Reds in 1911.⁴⁵(p.18) Owing to their high costs, naphthol AS pigments were not

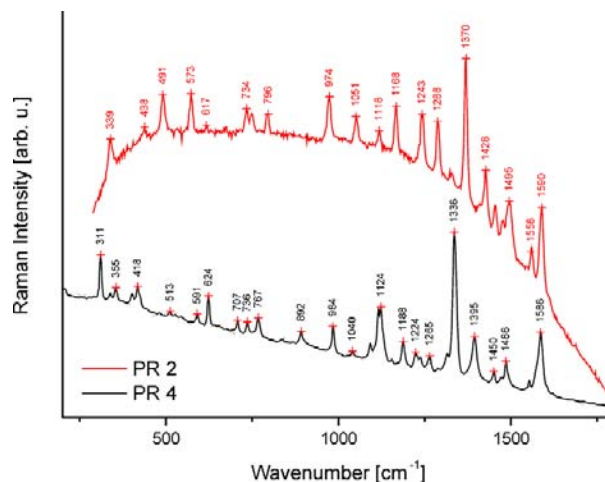


Figure 7: Spectra comparison of the naphthol AS pigment PR 2 (examined with laser 633 nm) with the β -naphthol pigment PR 4 (examined with laser 633 nm).



Figure 8: A. R. Penck, "Young Generation", 1975, canvas, 281 x 284 cm, Bayerische Staatsgemäldesammlungen (Inv.No. WAF PF 20).

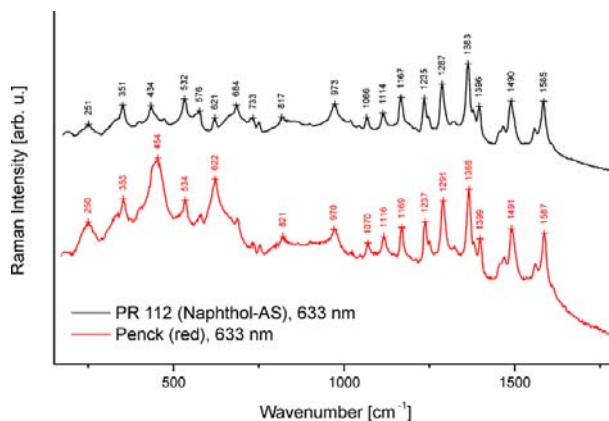


Figure 9: Spectra comparison of a red sample from "Young Generation" (measured with laser 633 nm) with PR 112 (with laser 633 nm).

ⁱ Personal communication by Dr. Annette E. Kleine, LUKAS, Dr. Fr. Schoenfeld GmbH & Co., Düsseldorf (Germany).

commercially successful until the 1930s, when they were produced by IG Farben. Today, roughly 20 naphthol AS pigments, mainly red, are used in artists' paints.

Generally, all azo compounds show distinct Raman bands in the functionality region between 1000 and 1700 cm^{-1} , which can be assigned to diverse deformation, aromatic and stretching vibrations. All red-coloured monoazo pigments have a naphthol group in their structure, which gives rise to an intense naphthalenic symmetric ring vibration^{46(p. 34)} and therefore a prominent band between approx. 1330 and 1375 cm^{-1} . Representatives of the naphthol AS-pigments, as well as the red azo pigment lakes and the benzimidazolones, have a common band at around 1365 cm^{-1} as well as bands of medium intensity at approx. 970 cm^{-1} (benzylamide amide coincident with a naphthalene band) and approx. 1590 cm^{-1} (benzene quadrant stretch).^{29(p.515)}

In comparison, the most intense Raman peak for the β -naphthol group occurs between 1330 and 1350 cm^{-1} . Figure 7 compares the spectra of the red naphthol-AS representative PR 2 and the red β -naphthol PR 4. Therefore, compounds of the β -naphthols can easily be recognized in unknown samples by the position of its most intense band. Such band shifts in wavenumber (and also intensity) are caused by conjugation effects, hydrogen bonding and molecular tautomerism, and depend on neighbouring groups.^{29(p.514)} Of course, they also occur for bands of weak and medium intensity, which were usually found to be still visible in the spectra of paint samples containing monoazo pigments, thus allowing further differentiation. As an example, we chose the painting "Young Generation" (Figure 8) by the German painter, graphic artist and sculptor A.R. Penck (born 1939), dating 1975. A red sample was analysed with a He/Ne neon laser source ($\lambda_{\text{exc}} = 633 \text{ nm}$) giving the spectrum depicted in Figure 9. This led to the unambiguous identification of the red naphthol AS azo pigment PR 112, a bright yellowish red pigment patented in 1939 and still used extensively.

4.3 Case Study – Diarylide (Disazo) Pigments

Azo pigments containing two azo groups are called disazo pigments. Diarylides are an important class of disazo pigments and now account for approximately 80 percent of all yellow pigments. They are formed by the coupling of tetrazotised benzidines with an acetoacetarylide. Diarylide pigments have

been known since 1911, but they were not widely used until almost twenty-five years later.^{45(p.22)}

We frequently found diarylide pigments in the examined paintings, for instance in the works of Markus Lüpertz, a German painter and sculptor of high international reputation, born 1941. As an example, let us consider the spectrum of an ochre-yellow sample of "Parsifal or men without women", dating 1993 (Figure 10). Raman microscopy was carried out with a Nd:YAG laser source ($\lambda_{\text{exc}} = 785 \text{ nm}$) to give the spectrum depicted in Figure 11. Despite the weak Raman signals, the bands at 1255 cm^{-1} , 1398 cm^{-1} and 1597 cm^{-1} can be assigned to a diarylide pigment.



Figure 10: Markus Lüpertz, "Parsifal or men without women", 1993, canvas, 162 x 130 cm, Bayerische Staatsgemäldesammlungen (Inv. No. HST1844).

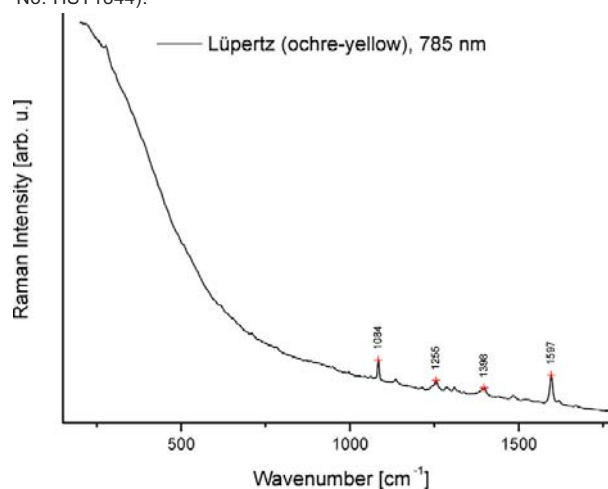


Figure 11: Raman spectrum (examined with laser 785 nm) of an ochre-yellow sample from "Parsifal or men without women".

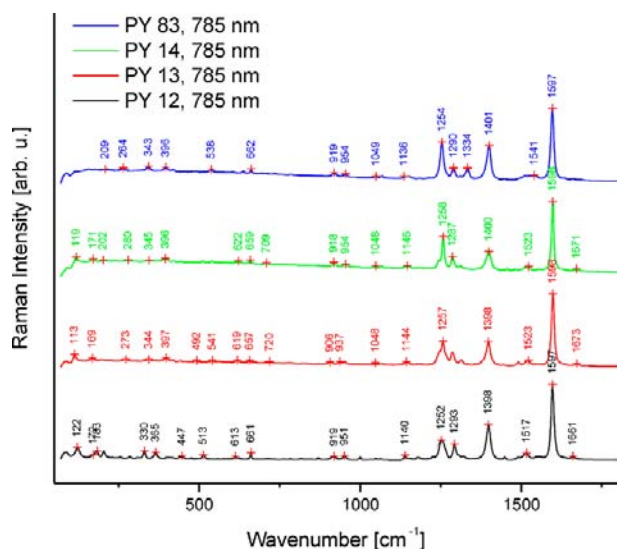


Figure 12: Spectra comparison of four diarylide pigments (examined with laser 785 nm), measured at the Straus Center for Conservation, Boston.

Diarylide disazo pigments usually show these three prominent bands, all other peaks are rather weak. A comparison of the Raman spectra of the most important diarylide pigments for artists' paints, measured at the Straus Centre for Conservation, Boston, indicates that diarylide pigments can hardly be differentiated by their Raman spectra within the group (Figure 12). In the yellow sample from the Lüpertz painting, only additional TLC and HPLC (not discussed here) were able to unambiguously identify the yellow diarylide pigment PY 83 as a component of the sample. PY 83 possesses excellent fastness properties, which makes it almost universally applicable. It was introduced in 1958 by Hoechst under the trade name Permanent Yellow HR.^{44, 45(p.23)}

4.4 Case Studies – Mixtures of Organic Pigments

The previously discussed results from various painting samples illustrate that the proportion of binding medium and often also that of the inorganic pigments was found to be negligible or minor in the Raman spectra. However, the success of identifying mixtures of two or more organic pigments in paint samples by Raman vary from case to case, as demonstrated by two samples from works by Markus Lüpertz.

Starting with a positive result, a green sample of a painting without a title (Figure 13) was found to contain a mixture of a green and a yellow organic colorant. The sample was analysed with a He/Ne laser source ($\lambda_{exc} = 633 \text{ nm}$). All bands (Figure 14) can be clearly assigned to either the copper

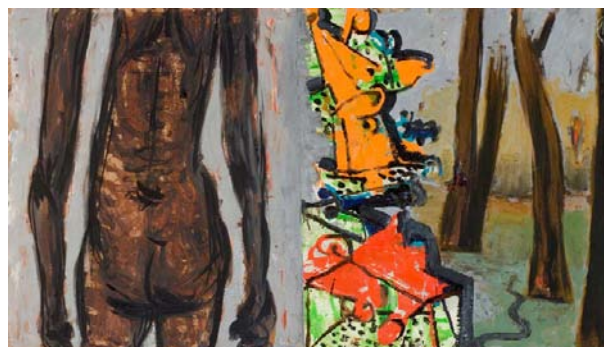


Figure 13: Markus Lüpertz, "Without Title", end of the 20th century, wood, 71 x 125 cm, Bayerische Staatsgemäldesammlungen (Inv. No. HST1804).

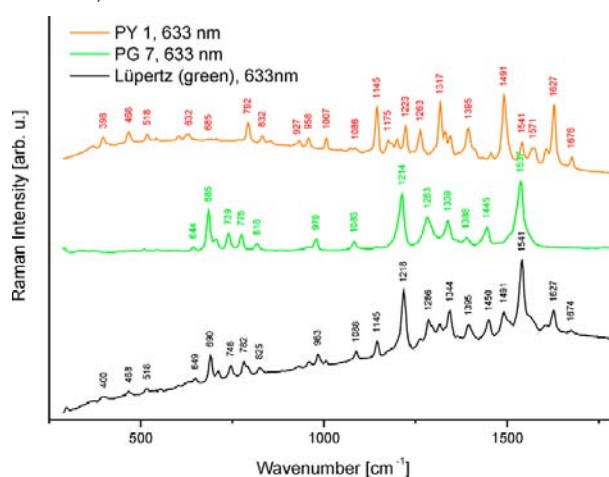


Figure 14: Raman spectrum (examined with laser 633 nm) of a green sample taken from the painting "Without Title".

phthalocyanine PG 7 (see Section 4.1) or the monoazo yellow pigment PY 1. The very weak band at 1674 cm^{-1} is an amide I band that does not occur in phthalocyanine spectra. A second amide band of PY 1 (amide III band at 1260 cm^{-1}) is overlapped by bands of PG 7. The four characteristic Raman bands of PY 1 at 1145 cm^{-1} (C-N symmetric stretch vibration), 1317 cm^{-1} (aromatic ring vibration), 1491 cm^{-1} (aromatic ring vibrations) and 1627 cm^{-1} (ring stretches of benzene derivatives) are clearly visible in the sample spectrum.^{29(p.514), 36(p.157-197)} PY 1 is the oldest representative of the "Hansa Yellow" pigments and its importance for artists' paints is unbroken since 1909.

In a similar green sample from "Parsifal or men without women" by Markus Lüpertz (Figure 10), Raman microscopy did not deliver complete information on the presence of three organic pigments. Raman analysis with a He/Ne laser source ($\lambda_{exc} = 633 \text{ nm}$) again enabled the identification of the green phthalocyanine pigment PG 7 while two further yellow pigments remained undetected, probably mainly due to lacking sensitivity. Solubility tests have previously shown that the sample was partly soluble in dimethyl sulphoxide and chloro-

form. Therefore, both TLC and HPLC were performed as complementary methods for full identification. TLC showed the presence of two yellow organic pigments, and HPLC confirmed the TLC result. The monoazo pigment PY 1 and the diarylide compound PY 12 were identified on the basis of the retention time and the UV/VIS-spectrum (not discussed here).

4.5 General Comparison of Raman Microscopy for Synthetic Organic Pigments

The presented case studies only apply to selected pigment classes, thus Table 1 attempts to summarise the overall sensitivity and differentiation power of Raman microscopy with regard to the studied pigment groups. The given judgements are based on the authors' practical experience with painting samples. There are still gaps to be filled by reference measurements (e.g. for isoindolines or thioindigos), but the general picture is becoming fairly clear:

Most synthetic organic pigments or at least pigment groups can be identified by their Raman spectrum, but effects of the excitation wavelength, such as resonance effects (Raman enhancement or fluorescence), instrument response as well as matrix interferences caused by the binding medium and fillers, can always influence the relative intensity of the peaks and therefore the resulting spectrum. In particular, variations in fluorescence necessitated the use of different excitation lines. In this study, good results were often achieved with the He/Ne laser source (633 nm); however, there are also pigments for which it is impossible to get a discernable Raman spectrum using this red laser.

In the case of paint samples, the recorded spectra are, of course, generally weaker than those of the reference pigments. Nevertheless, the prominent sensitivity found for phthalocyanines and the dioxazine pigment is noteworthy. For these groups, Raman microscopy seems to be the method of choice for pigment identification in paint samples.

However, the diverse pigments do not scatter with the same intensity, and even the reference spectra of pure pigments from some groups, i.e. the quinacridones or perylenes, exhibit mainly weak bands so that identification of an unknown pigment in a paint sample is unlikely to be successful. For other subgroups, such as those from the azo pigments, the pure compound may exhibit distinct

spectra, but experience shows that its identification in paints is strongly dependent on the respective sample composition.

Regarding the possibility of differentiating between certain pigments within a subgroup, it was established that even for classes with high Raman sensitivity this may be restricted. Especially for disazo compounds, identification of the type of subgroup (i.e. pyrazolones, diarylide and disazo condensation pigments) was usually successful in paint samples, but the differences between representatives of the subgroup are so minor that identification of a specific pigment by Raman microscopy alone is not possible.

Pigment Group	Pigment Class	Sensitivity	Differentiation within the Group
Monoazo	Monoazo Yellow and Orange	++	+
	β -Naphthol	+	+
	Naphthol-AS	+	+/-
	Azo Pigment Lake	++	+
	Benzimidazolone	++	+/-
Disazo	Pyrazolone	+	-
	Diarylide	+	-
Polycyclic	Disazo Condensation	++	-
	Phthalocyanine	+++	+
	Quinacridone	0	+/-
	Perylene and Perinon	-	-
	Dioxazine	+++	only PV 23 relevant
	Diketopyrrolo Pyrrole	+	+/-
	Triarylcarbonium	-	-
	Anthraquinone	++	+
Other	Metal Complex	++	+

Table 1: Overview of the analytical potential of Raman microscopy for the different groups of synthetic organic pigments in artists' paints. Sensitivity: excellent (+++), very good (++), good (+), only weak peaks (0), some pigments without spectrum (-). Differentiation within the group: possible (+), sometimes possible (+/-), not possible(-).

5 Conclusions

Generally, Raman microscopy clearly offers major advantages for the identification of synthetic organic colorants in artworks mainly in terms of sample size, in-situ application, facile or no sample preparation, low interferences from the medium as well as high sensitivity for synthetic organic pigments and the possibility of simultaneous detection of inorganic compounds. Comparison and interpretation of Raman spectra is still hampered by the lack of available digital reference databases shared within the conservation community, but hopefully this problem can be overcome in the very near future. Fluorescence problems may

occur in paint samples, although they can usually be overcome with a different wavelength or by bleaching. The use of three different laser wavelengths and the sample preparation method described in this paper gave a discernable Raman spectrum for nearly all the 250 painting samples examined in this project. In any case, the application of Raman microscopy to the identification of organic pigments should be accompanied by other tests and techniques. Preliminary spot and solubility tests are highly recommended along with the combination with TLC and/or HPLC to avoid incomplete identification of pigment mixtures.

6 Acknowledgements

The authors are indebted to the Deutsche Forschungsgemeinschaft (DFG), Bonn, for the generous support of this project under the grant no. KO 291/1-2.

We are very grateful to Ulrich Panne and Janina Kneipp at the Federal Institute for Material Testing and Research (BAM) in Berlin and Johann Rott, Bavarian State Office of Criminal Investigation, Munich, for making the Raman measurements possible. Jens Stenger from the Straus Centre for Conservation in Boston kindly provided their reference spectra of synthetic organic pigments, which were measured by Jessica Arista, for comparison and permitted reproduction of Figure 12. Last, but not least, our sincere thanks go to our colleagues at the Bayerische Staatsgemäldesammlungen Elisabeth Bushart, Susanne von Arnim-Willisch and Michael Szoltys for their support and invaluable practical help during the examinations and samplings at the Pinakothek der Moderne.

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