

Chapter 9

Analysis of Natural and Synthetic Organic Lakes and Pigments by Chromatographic and Mass Spectrometric Techniques



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Abstract This chapter aims to provide an overview of natural and synthetic organic lakes and pigments and of how their analysis by chromatography and mass spectrometry can provide useful information in the examination of works of art. The characteristics of natural organic colourants are reviewed, including information on their provenance and uses in the production of lakes; information on the date of production, availability as paint products and application in artworks of the most important synthetic organic pigments is also provided. This chapter specifically illustrates the state-of-the-art of organic pigments analysis by high performance liquid chromatography with different detectors, and by gas chromatography – mass spectrometry also coupled to analytical pyrolysis. Different mass spectrometry based techniques used both as detector and directly applied on a sample or its extract are also presented. Particular attention is paid to sample preparation; further issues related to difficulties in finding relevant standards or reference materials and understanding photo-degradation processes occurring in degraded organic pigments are also discussed. Several case studies are presented, showing the potentialities of liquid chromatography interfaced with mass spectrometry in determining properties of the samples which can be of assistance for assessing the provenance, dating or even the authenticity of a painting.

Keywords High performance liquid chromatography · Mass spectrometry · Organic lakes · Synthetic organic pigments · Paint materials

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M. P. Colombini et al. (eds.), *Analytical Chemistry for the Study of Paintings and the Detection of Forgeries*, Cultural Heritage Science,
https://doi.org/10.1007/978-3-030-86865-9_9

9.1 Introduction

Organic lakes and pigments have been used in paintings and in ink formulations since pre-history. Their composition is, in some cases, specific to a time period or a geographical area, thus their identification may provide data for dating purposes or even for establishing authorship. Unfortunately, the analysis of organic lakes and pigments in artworks and in painting matrices is particularly arduous for the chemist. In addition to the analytical issues that must be overcome when we deal with the analysis of any microsample from a work of art, such as the small amount and representativeness of the sample available and the low concentration in which analytes are present, several other factors have to be considered, such as the lack of reliable recipes for lake preparation, or the uninformative product names provided by modern manufacturers due to patent wars. Finally, organic colourants are amongst the most fugitive species in works-of-art, and thus their composition as determined today strongly depends on the condition of the painting, which may have undergone irreversible degradation.

Consequently, the study of the composition in terms of colouring molecules of organic dyes and pigments can provide important information on the origin and dating of an object, given that a thorough comparison with reference materials, possibly also subjected to natural and artificial ageing, is correctly performed.

This chapter presents the main natural and synthetic organic lakes along with their most important characteristics for establishing provenance and dating. State-of-the-art methods of detection and identification of organic pigments and lakes based on chromatography and mass spectrometry will be reviewed, and specific issues related to sample treatment and photo-ageing processes will be presented. The level of information achievable by the analysis of organic pigments will be illustrated through selected case studies.

9.1.1 *Natural Organic Lakes*

In antiquity, organic coloured paint materials were obtained from natural sources derived from plant extracts or from the metabolism of insects or molluscs. Ancient Egyptians were the first to develop dye extraction procedures and to document them accurately in hieroglyphics (Zollinger 2003). The introduction of indigo, Tyrian purple, and the reds madder and cochineal were main milestones in the artistic and economical history of natural dyes (Zollinger 2003). Notably, different cultures around the globe developed methods to extract such colours, even if from different autochthonous plants or animal species. These dyes were used for colouring textiles, and for the preparation of organic pigments. Organic dyes and pigments differ in their solubility in water and in other binding media: dyes are soluble in binding media while pigments are insoluble (Colombini and Modugno 2009), and lakes are generally obtained by precipitation as salts, absorption on inert and colourless

substrates and/or complexed as metal salts (Herbst et al. 2004; Kirby et al. 2005a, 2014). By this procedure, coloured insoluble particles are formed (through complexation or absorption phenomena), and can be separated by precipitation and filtration, washed and dried to obtain a solid lake pigment. The most commonly salt used in lake production was alum, and in particular hydrated potassium aluminium sulphate ($KAl(SO_4)_2 \cdot 12H_2O$), which was also employed as a mordant for textile dyeing. Other salts used in lake production were chalk (calcium sulphate, $CaSO_4$) and gypsum (calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$). The metallic cation chosen may change and influence the colour shades that are produced.

Over the centuries, artists have applied lakes with different painting techniques and on several supports. Lakes have performed a less important role in classic painting compared to inorganic pigments because most of them exhibit lower lightfastness and great sensitivity to atmospheric agents and to pH variations. As a consequence, lakes were applied in a great extent for miniatures in illuminated manuscripts, and in a less extent in mural paintings and in easel or canvas painting. Notwithstanding this, evidence of the use for millennia of madder lake, purple and indigo pigments in wall painting and paint decorations on ceramics, and in codices, has been found by scientific examinations. Madder was identified on funerary vessels and in Pompei's pigments (Andreotti et al. 2017; Colombini et al. 2017) while purple was used in Thera wall paintings (Karapanagiotis et al. 2017), in Macedonia and Magna Grecia funerary paintings (Andreotti et al. 2017), and indigo is the main ingredient of Maya blue (Grazia et al. 2020). Finally, yellow organic dyestuffs such as saffron (*Crocus sativus*), Buckthorn/Persian berries (*Rhamnus* spp.), and weld (*Reseda luteola* L.) have been used to produce lake pigments in works of art since antiquity (Ciatti and Marini 2009; Mayhew et al. 2013; Saunders and Kirby 1994).

If a survey is made of the recipes used in Europe between the fifteenth and the nineteenth centuries, the dyestuffs most frequently mentioned are those extracted from redwoods (brazilwood), madder, and the scale insects kermes, cochineal and Indian lac (Kirby and White 1996). Most of these natural sources were available in Europe since antiquity, while some others have been imported since early times from India and South and Central America (Kirby et al. 2014). In Fig. 9.1, the geographical locations of some natural sources of red dyes used to produce lake pigments are depicted. Lakes produced with these materials are characterized by a low colouring power given by the dye and translucency provided by substrate (Kirby and White 1996). From the study of recipes from the European and Mediterranean area and the material analysis of paintings, a timeline can be identified in the use of these materials: up to the early seventeenth century, brazilwood, lac and shearings of cloth dyed with kermes ("cimatura de grana") were the most common sources for lake production. It is worth noting that some confusion can be generated by the inconsistent nomenclature of raw materials and final products reported in ancient treatises and recipes, and the paucity of details provided, which sometimes refer to undefined "common practices". Fake pigments (e.g. "fake purple") are attested since medieval times, and guild regulations were often disregarded by dyers and manufacturers (Saez et al. 2019). From the late sixteenth century onwards, cochineal became more common, because of the increased availability of scale insects

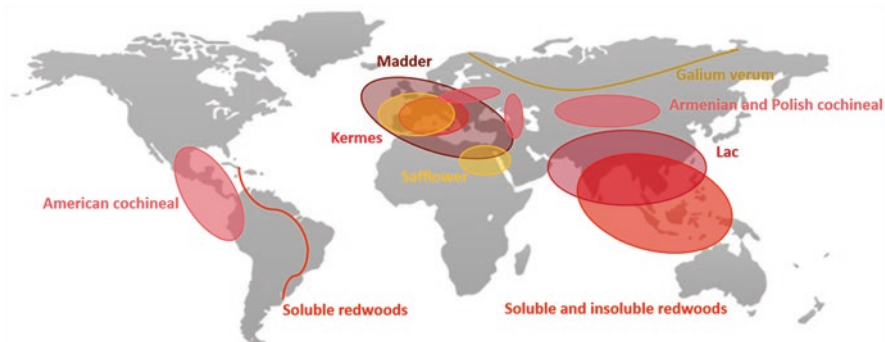


Fig. 9.1 Map showing the geographical location of natural sources of red dyes. (Adapted from Kirby et al. 2014)

from South America, and by the nineteenth century the most important sources have been cochineal and madder, while lac and kermes are barely mentioned. For their low covering propriety, these lakes have been widely employed in glazing on canvas, or to modify the hues of other inorganic red pigments. This technique, exhibited by several European painters of fifteenth and sixteenth century, consisted in the overlapping of coloured paint layers on already dried paint layers in order to achieve different nuances (Kirby et al. 2005a, 2014). Moreover, anthraquinoid lakes were used in illuminating manuscripts, where colours were protected from degradation processes induced by light and external agents. Different species were used to produce organic lakes in the East, such as safflower (Wouters et al. 2010).

Starting from the end of the eighteenth century, thanks to the advances in knowledge of the chemistry of organic substance and the availability of strong acid and bases, progress led to the production of higher quality organic dyes, pigments, and lake pigments. The distinction between natural and synthetic materials becomes blurred due to manufacturers experimentation of new approaches such as the exploitation of natural dyes as pigments, by precipitating the natural extracts as salts in alkaline conditions (Degano et al. 2017). In particular, several methods to extract the colouring materials from madder were already tested at the end of the eighteenth century, yielding products with slightly different names, such as Brown Madder. Later, the availability of sulphuric and sulphurous acids led to the isolation of alizarin and purpurin in 1826. Different modified madder-based products, e.g. garancine (1828), enriched in alizarin and purpurin, Kopp's purpurin (also known in France as "purpurine commerciale"), enriched in both purpurin and pseudopurpurin, or "carmine de garance", supposedly pure madder dyestuff without the addition of an inorganic salt, were then commercialized (Kirby et al. 2007). Several "carmines" based on cochineal are also reported in nineteenth – twentieth century catalogues, in a wide range of hues and prices, prepared using different recipes and inorganic salts (Kirby et al. 2007). New lakes based on brazilwood were also introduced, produced by varying the pH of the reagents used or employing tin in the precipitating agent (Doherty et al. 2021).

Natural organic lakes can be classified based on their colour. The main organic lakes and pigments prepared with natural dyes are listed in Table 9.1.

9.1.2 *Synthetic Organic Pigments (SOPs)*

The successful synthesis of molecules responsible for the coloration of natural extracts was performed in 1868 during the synthesis of alizarin by the German chemists Carl Gräbe and Carl Lieberman (Kirby et al. 2005b), leading to the gradual decrease of the production of natural dyes and organic pigments. In an early stage, synthetic and natural pigments were often admixed, but after the 1930s, synthetic pigments totally dominated the market. The following step in the history of organic pigments was the synthesis of completely new formulations from the late nineteenth century, which could be tuned for the desired hue and chemical properties. The first synthetic organic pigments produced was Picric acid. In 1742, the German alchemist Johann Glauber prepared this dye by treating wool or animal horn and resins with nitric acid (Read 2014). Picric acid was rarely used due to its high intense yellow hue and thus the history of synthetic organic dyes officially started in 1856, when William Henry Perkin first synthesized mauveine. He was experimenting under the direction of August von Hofmann at the Royal College of Chemistry in London, and he was trying to produce a synthetic alternative to quinine from coal tar, when he accidentally obtained a purple compound, characterize by a high wash- and lightfastness, that he called mauveine (Lomax et al. 2006). Notably, the advances in synthetic chemistry and the discovery of mauveine occurred during the industrial revolution, a period of great change and expansion for Europe, particularly in the textile trade. The availability of cheaper synthetic dyes made coloured textiles more accessible to the wider population. Mauveine rapidly became the most fashionable colour for Victorian ladies, and Perkin became a rich entrepreneur (Garfield 2011). The commercial success of mauveine, the potential wide variety of hues achievable by slightly modifying the synthetic route, the cheapness, and the availability of the reagents, pushed chemists to experiment with new colorant formulations.

In 1863, the first azo dye, a bright yellow colour named “Field’s yellow”, was synthesized by Fredrick Field (Skelton 1999). Several aniline based dyes, obtained by diazotization reaction and differing by the kind of substituents (Ball 2001), were produced: they are the so called *coal-tar colors* (Lomax et al. 2006). Many of these products were precipitated as lakes (“laked”) to offer new pigments for artists: the availability of synthetic organic pigments in different hues, the possibility to admix them with binding media and additives in paint tubes and the relatively low costs of production, all made these new materials more appealing for manufactures not only of natural organic lakes, but also of traditional inorganic pigments. Unfortunately, many of these products were commercialized without testing for fastness properties and fugitivity in oils and severely faded few years after their application. The experimental trial-and-error strategy showed severe limits and a more reliable approach based on understanding the chemistry of the colorants and extraction processes was

Table 9.1 Classification of the main natural organic lakes

Colour	Chemical class	Raw material	Common lake names	Main components
Blue and purple	Indigoids	Indigo plants (<i>Isatis</i> , <i>Indigofera</i>)	Indigo pigment, Maya blue (in America)	Indigotin, indirubin
		Shellfish purple (<i>Hexaplex trunculus</i> , <i>Bolinus brandaris</i> and <i>Stramonita haemastoma</i>)	Purple pigment, <i>purpurissum</i> (Latin name)	6,6'-dibromoindigotin, 6-bromoindigotin, indigotin (6,6'-dibromoindirubin, 6-bromoindirubin, indirubin)
Red and pink	Homoisoflavonoids	Sappanwood (<i>Caesalpinia sappan</i>), brazilwood (<i>Caesalpinia</i> spp. from South America)	<i>Verzino</i> (Latin, medieval Italy), brazilwood lake	Brazilin, brazilein, urolithin C
	Chalcones	Safflower (<i>Carthamus tinctorium</i>)	Safflower lake	Carthamin
	Anthraquinones	Madder (<i>Rubia</i> spp.)	Madder lake, <i>garanza</i> (medieval Italy), garancine, Kopp's purpurine, <i>carmine de garance</i>	Alizarin, purpurin
		Scale insect <i>Kerria lacca</i>	Indian Lac	Laccaic acid A, Laccaic acid B
		Scale insect <i>Kermes vermilio</i>	Kermes	Kermesic acid, flavokermesic acid (carminic acid)
Scale insects <i>Porpyrophora hemelii</i> , <i>Porphyrophora polonica</i> , <i>Dactylopius coccus</i>	Cochineal lake, carmine	Carminic acid (dcII, kermesic acid, flavokermesic acid)		
Yellow	Carotenoids	Saffron (<i>Crocus sativus</i>)	Saffron lake	Crocin, crocetin
	Flavonoids	Buckthorn/Persian berries (<i>Rhamnus</i> spp.)	Stil de Grain/ Buckthorn lake	Quercetin, rhamnnetin
		Weld (<i>Reseda luteola</i> L.)	Reseda lake, <i>arzica</i> (medieval Italy)	Luteolin, apigenin

developed for producing high performing formulations and adequately meeting market demands. In this regard, the discovery of the benzene structure by Kekulé (Herndon 1974) and the following elucidation of alizarin structure by Adolf Bayer, Carl Grabe and Carl Lieberman in 1868 (Graebe and Liebermann 1879) were fundamental in laying the foundation for the comprehension of colour chemistry.

In 1910, the production of Pigment Yellow 1, alternatively named “Hansa Yellow G”, by Meister Lucius & Brüning, introduced the important class of Monoazo or Hansa pigments on the market (Meister Lucius and Brüning 1909). This very bright yellow pigment was the first of many to be produced with great commercial success (Schulte et al. 2008).

In 1936, phthalocyanines were the first class of organic colorants introduced directly into the market as ‘true’ pigments without prior use as dyes or lakes (De Keijzer 2002). This new class of pigments quickly conquered the blue and green pigment markets in all ranges of applications due to their incredibly high performance in terms of tinting strength, fastness and chemical resistance (Skelton 1999). Phthalocyanines replaced synthetic indigo lake pigments as a popular artists’ pigments. Quinacridones (1950’s) and diketopyrrolopyrroles (1983) were later introduced and used in high-quality artists’ materials due their excellent fastness and resistance properties (Lomax et al. 2006). By the 1990s more pigment classes of synthetic organic origin, such as perylenes and pyrrols, were synthesized and are now sold as artist’s materials.

Synthetic organic pigments now dominate the colorant market and have almost completely replaced traditional natural organic colorants.

Keeping track of the huge variety of currently available SOPs and those used in the past is nearly impossible and an attempt to define the most important classes, based on literature (Herbst et al. 2004; Lutzenberger and Stege 2009), is summarized in the diagram below (Fig. 9.2).

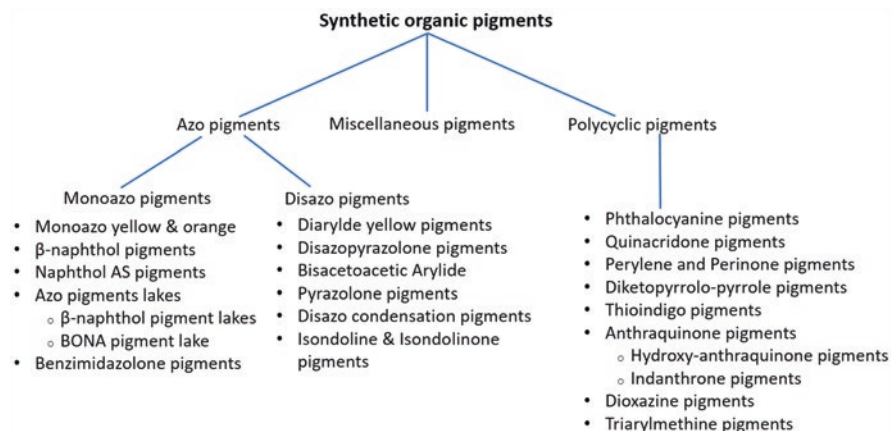


Fig. 9.2 Classification of SOPs. (Adapted from Herbst et al. 2004; Lutzenberger and Stege 2009)

Synthetic pigments can be divided in two main groups: the azo pigments and the polycyclic ones. Amongst each group, pigments are further classified on the basis of their chemical structure. The azo pigments are characterized by the azo functional group (-N=N-): monoazo pigments contain one azo group, while disazo two. The synthetic strategy to produce azo pigments is easy and economical, and based on the reaction of a diazonium compound with a coupling component. The kind of coupling agent selected allows the grouping of monoazo and disazo pigments in subclasses. Conversely, polycyclic pigments can be distinguished by the number or type of rings constituting the aromatic structure (Lutzenberger and Stege 2009). The pigments which cannot be included in one of these two big groups are generally classified as miscellaneous.

Throughout the last 150 years, creative and not informative names have been ascribed to formulations of synthetic organic dyes and pigments by manufacturers and resellers. The total absence of scientific rigour in the naming has led to a general confusion which still does not easily allow the understanding of the composition of the commercialized formulations. Patent wars between manufacturers have compounded such confusion. Indeed, in 1924, the Society of Dyers and Colourists (SDC) and the American Association of Textile Chemists and Colorists (AATCC) recorded the most extensive compendium of dyes and pigments: Colour Index™ (C.I.) (Colour index *n.d.*). A “Colour Index generic name” (e.g. PY1 for Pigment yellow 1) and a “Colour Index constitution number” (e.g. C.I. 11680 for Pigment yellow 1) was assigned to every coloured compound. The first is referred to the application field/coloration method, the latter to the chemical structure (Evans 1990).

A summary of the most important synthetic pigments, along with the year of synthesis and introduction on the market, their use as paint materials and some case studies (paintings and paint fabrics only) in which they were detected are reported in Table 9.2. However, in consulting patents and manufacturers’ logbooks, it should be kept in mind that the commercial nomenclature of synthetic dyes and pigments is often uninformative or undeclared due to patent restrictions, and the recipes of paint tubes often contain mixtures of more than one pigment belonging to the same or different classes. Moreover, the several by-products present in different ratios, as a consequence of the various synthetic strategies adopted to produce the same pigment, have contributed to generate confusion regarding the composition of the starting materials (Lech et al. 2013). Additionally, artists themselves further complicate the composition of the final paint by mixing colours, as well as through the addition of media, thinners, driers, waxes, diluents and extra oils to obtain the desired effects in their artworks (Townsend 1994). Furthermore, artists have experimented with new and old materials, blending highly heterogeneous components, including those that were low cost and not specifically suitable for artistic purposes (Learner et al. 2006).

Table 9.2 Compendium of the most common synthetic organic pigments with the year of synthesis and introduction on the market. Their use as paint materials and some case studies (paintings only) in which they have been detected are reported. Adapted from (de Keijzer 2014)

Red and orange pigments	Pigment code		First discoveries	Industrial introduction	Paint materials and paint artworks	Features
	β-naphthol pigments					
	PR1, 12070	1880: England	1899: Farbwerke vorm Meister Lucius und Brüning manufacturer (Germany)	1955: M. Rothko, <i>Red band</i> (Lomax et al. 2014) 1955–1960: F. Melani, <i>Bandiera</i> (Carlesi et al. 2016) 1968: P. Gilardi, <i>Disgelo</i> (La Nasa et al. 2019)	Since 1905: <i>Rouge Japonais Foncé</i> , Lefranc archive paint tube (France) (Degano et al. 2017) 1905: F. Melani's atelier material (Italy) (Carlesi et al. 2013) 1923–1924: V. Huszar, <i>Miss Blanche advertisement</i> (Netherlands) 1927: Royal Talens N.V., list of artists' paints, Rembrandt series (Netherlands) 1964: J. Dubuffet, <i>Chain de mémoire III</i> 1964: J. Dubuffet, <i>Le train de pendules</i> 1970: M. Rothko, Untitled (Lomax et al. 2014) Mid. 1980s: <i>Bright Red and Vermillion Hue</i> , Windsor & Newton, Artists' oil colour and Winton oil colour (England) 1988: <i>Karmin, Krapplack hell, Kadmiunrot dunkel, Zimmoher dunkel</i> , Lukas, A and B quality artists' oil colours (Germany) 1918: E.L. Kirchner, <i>Plastik: Mann and Frau</i> 1929: Missiemuseum Steyl-Tegelen, pigment archive (Netherlands) 1949: M. Rothko, Untitled (Lomax et al. 2014) 1988: <i>Helio-Echtröt, Helio-Echtorange, Kadmiunorange, Zimmoherrot hell</i> , Lukas, A and B quality artists' oil colours (Germany)	Low light and heat fastness, high migration fastness, low tinting strength
	PR3, 12120	1905: Germany				
	PR4, 12085	1906: Germany, France				
	PR6, 12090	1906: Germany, England				

(continued)

Table 9.2 (continued)

Pigment code	First discoveries	Industrial introduction	Paint materials and paint artworks	Features
PO5, 12075	1907: Germany	1908: AGFA (Germany)	1931: Royal Talens N. V., list of artists' paints, Rembrandt series (Netherlands) 1933–1934: W. Kandinsky's Paris palette 1936: M. Beckmann, <i>Stillleben mit Ausblick auf dem Wannsee</i> 1968: P. Gilardi, <i>Disgelo</i> (La Nasa et al. 2019) 2003: A. Harding, <i>Quartet</i> (La Nasa et al. 2020)	
Naphthol AS pigments				
PR2, 12310	1911: Germany		1967: G. Baseltz, <i>Drei Feldarbeiter</i>	Good lightfastness
PR8, 12335	1911: France, Germany, England		1988: <i>Indischgelb</i> , <i>Geraniumlack</i> , <i>Grüner Lack hell</i> , Lukas, A quality artists' oil colours (Germany) 1988: <i>Geraniumlack</i> , <i>Kobaltviolett dunkel</i> , Lukas, B quality artists' pigments (Germany)	
PR5, 12490	1931: Germany, England		1982: G. Baseltz, <i>Orangenesser IV</i>	
PR7, 12420	1921: Germany		1955–1960: F. Melani, <i>Bandiera</i> (Carlesi et al. 2016)	
PR12, 12385	1922: Germany, French			
PR9, 12460	1922: Germany		1970: B. Rancillac, <i>La Suite Américaine</i> 1970–71: D. Hockney, <i>Mr and Mrs Persey</i> 1993: G. Baseltz, <i>Bildsechzehn</i>	
PR112, 12370	1939: Germany		1960s: D.A. Siqueiros, murals of the Polyforum Cultural Siqueiros building (Mexico) (La Nasa et al. 2021) 1975: A.R. Penck, <i>Young Generation</i> (Lutzenberger and Stege 2009) 1987: K. Haring, <i>Necker</i> (Magrini et al. 2017) 1991: <i>Vermiljoen chin.</i> , <i>Talensrood donker and Permanentrood</i> , Royal Talens B. V., list of artists' paints, Rembrandt oil colours (Netherlands) 2013–14: BLU, mural painting on the wall of an old military warehouse (La Nasa et al. 2021)	

PR146, 12485	1953: Germany			
PR170, 12475	1963: Germany		1983: J. Dubuffet, <i>Mire G 137 Kowloon</i> 1985–86: P. Caulfield, <i>Interior with a picture</i>	
β-naphthol pigment lakes				
PR49, 15630	1899: Germany		1961: M. Rothko, <i>Untitled</i> , Harvard Murals (Stenger et al. 2010)	Poor lightfastness, good solvent fastness
PR53, 15585	1902: Germany		1993: M. Lupertz, <i>Männer ohne Frauen. Parsifal</i>	
PO46, 15602	1949: USA			
BONA pigment lakes				
PR57, 15850	1903: Germany, England		1958: F. Winter, <i>Teile</i> 1958: F. Winter, <i>Später Garten</i> 1958: F. Winter, <i>Winterliches Gedächtnis</i> 1991: <i>Geraniumlack, Talensrood purper</i> , Royal Talens B. V., list of artists' paints, Rembrandt oil colours (Netherlands) 1991: <i>Cadmiumrood azo, Vermiljoen, Karmin</i> , Royal Talens B. V., list of artists' paints, Van Gogh oil colours (Netherlands) 1991: <i>Donkerrose</i> , Royal Talens B. V., list of artists' paints, Amsterdam oil colours (Netherlands)	Similar properties to β-naphthol pigment lakes but more lightfast
PR48, 15865	1904: Germany		Late 1920s: <i>Wachung Red</i> , A. Siegel, E.I. du Pont de Nemours & Company (USA) 1991: <i>Cadmiumrood donker azo</i> , Royal Talens B. V., list of artists' paints, Van Gogh oil colours (Netherlands) 2011: A. Pasquini, <i>Untitled</i> (Bosi et al. 2020) 2014: A. Luchko, <i>Straniera</i> (Bosi et al. 2020)	
PR52, 15860	1910: Germany			
PR63, 15880	1906: Germany			

(continued)

Table 9.2 (continued)

Pigment code	First discoveries	Industrial introduction	Paint materials and paint artworks	Features
Benzimidazolone pigments				
PR171, 12512	1960: Germany	1964: Farbwerke Hoechst AG (Germany)		Good lightfastness and solvent fastness
PR175, 12519	1960: Germany	1964: Farbwerke Hoechst AG (Germany)		
PR176, 12515	1960: Germany	1965: Farbwerke Hoechst AG (Germany)	1988: <i>Karmin, Krapplack hell dunkel and dunkelst, Casslerbraun, Septa, Vandyckbraun and Indigo</i> , Lukas, A quality artists' pigments (Germany) 1988: <i>Karminrot, Krapplack hell and dunkel, Casslerbraun and Vandyckbraun</i> , Lukas, B quality artists' pigments (Germany)	
PBr25, 12510	1960: Germany	1966: Farbwerke Hoechst AG (Germany)		
PR185, 12516	1962: Germany	1967: Farbwerke Hoechst AG (Germany)		
PV32, 12517	1963: Germany	1965: Farbwerke Hoechst AG (Germany)		
PR208, 12514	Belgium	1970: Farbwerke Hoechst AG (Germany)		
PO36, 11780	1961: Germany	1964: Farbwerke Hoechst AG (Germany)		
PY120, 11783	Germany	1969: Farbwerke Hoechst AG (Germany)		

Pyrazolone pigments				Versatile fastness properties
PO13, 21110	1910: Germany			
PR38, 21120	1934: Germany	1934: I.G. Farbenindustrie, (Germany)		
PO34, 21115	1934: USA	1934: I.G. Farbenindustrie (Germany)		
PR41, 21200	1935: USA			
Perylene pigments				Excellent lightfastness and solvent fastness
PR123, 71145	1948: USA			
PR149,71137	1956: Germany	1961: Farbwerke Hoechst AG (Germany)	1961: Lefranc (France) 1996: <i>Scarlet</i> , Royal Talens B.V., list of artists' paints (Netherlands)	
PR179, 71130	1913: Germany, England			
Perinone pigments				Excellent lightfastness and solvent fastness
PO43, 71105	1924: Germany	1953: Farbwerke Hoechst AG (Germany)	1978: Royal Talens B.V., list of artists' paints, Rembrandt oil colours (Netherlands) 1978: S. Francis; <i>Untitled</i> 1991: <i>Geraniumlack, Talensrood purper, Cadmiumrood donker</i> ; Royal Talens B.V., list of artists' paints, Rembrandt oil colours (Netherlands) 1991: <i>Cadmiumrood donker azo, Vermiljon, Kammin</i> , Royal Talens B.V., list of artists' paints, Van Gogh oil colours (Netherlands)	

(continued)

Table 9.2 (continued)

Pigment code	First discoveries	Industrial introduction	Paint materials and paint artworks	Features
Quinacridone pigments				
PR122, 73915	1958: USA		1974: Royal Talens B. V., list of artists' paints, Rembrandt oil colours (Netherlands) 1978: S. Francis, Untitled 1991: <i>Rembrandtrose</i> , <i>Permanentviolet</i> , <i>Permanent troodviolet</i> , Royal Talens B. V., list of artists' paints, Rembrandt oil colours (Netherlands) 1991: <i>Permanenrose</i> , <i>Permanent roodviolet</i> , <i>Permanent blauwviolet</i> , Royal Talens B. V., list of artists' paints, Van Gogh oil colours (Netherlands) 1991: Violet, Royal Talens B. V., list of artists' paints, Amsterdam oil colours (Netherlands) 2013–14: BLU, mural painting on the wall of an old military warehouse (La Nasa et al. 2021)	Excellent lightfastness and solvent fastness
PR192, 739155	1958: USA			
PR202, 73907	1958: USA		1982: G. Baselitz, <i>Orangeness IV</i>	
PR206, 73900+73920	1958: USA			
PR207, 73900+73906	1958: USA			
PR209, 73905	1958: USA			
Diketopyrrolo-Pyrrole pigments				
PR254, 56110	1982: Switzerland		1996: Royal Talens B. V., list of artists' paints, Rembrandt oil colours (Netherlands) 2000: Schmincke, MUSSINI (Germany) 2003: Schmincke, PRIMAcryl (Germany) 2004: Lukas (Germany)	Excellent lightfastness and solvent fastness

PR255, 561050	1982: Switzerland	1996: Royal Talens B.V., list of artists' paints, Rembrandt oil colours (Netherlands) 2000: Schmincke, MUSSINI (Germany) 2003: Schmincke, PRIMAryl (Germany) 2004: Lukas(Germany)	1996: Royal Talens B.V., list of artists' paints, Rembrandt oil colours (Netherlands) 2000: Schmincke, MUSSINI (Germany) 2003: Schmincke, PRIMAryl (Germany) 2004: Lukas (Germany)
PR264, 561300	1982: Switzerland		
PO71, 561200	1982: Switzerland		
PO73, 561170	1982: Switzerland		
Anthraquinone pigments			
PR83, 58210	1868: Germany		Since 1804: Lefranc archive paint tube (France) (Degano et al. 2017) Since 1900: <i>Laque de garance rose</i> , Felice Alman (Italy) (Christiansen et al. 2017) Since 1900: P. Picasso's atelier material, Ripolin (Netherlands) (Gautier et al. 2009) 1947: M. Rothko, Untitled (Lomax et al. 2014) 1950: M. Beckmann, <i>Frau mit Mandoline in Gelb und rot</i> (Lutzenberger and Stege 2009)

(continued)

Poor lightfastness and solvent fastness

Table 9.2 (continued)

Yellow pigments	Pigment code	First discoveries	Industrial introduction	Paint materials and paint artworks	Features
	Monoazo yellow pigments				
	PY1, 11680	1897: Germany		<p>Since 1909: <i>Vert Anglais n. 3</i>, Lefranc archive paint tube (France) (Degano et al. 2017)</p> <p>Since 1909: F. Melani's atelier material (Italy) (Carlesi et al. 2013)</p> <p>1912: Schmincke (Germany)</p> <p>1919: A. Rodchenk, <i>Konstruktivistische Komposition</i></p> <p>1919: L. Meidner, <i>Der Krieg</i></p> <p>1924: Daler-Rowney (England)</p> <p>1925: M. Ullmann, <i>Komposition mit zwei Akten</i></p> <p>1926: <i>Pigment Fast Yellow HGL</i>, J.W. Leitch and Co. (England)</p> <p>1931: Royal Talens B. V., list of artists' paints, Rembrandt series (Netherlands)</p> <p>1935: <i>Sumproof Yellow 1</i>, Gouache paint-outs, Schmincke (Germany)</p> <p>1948: V. Pasmore, <i>Abstract Design for a Poster</i></p> <p>1958: A. Pellán, <i>Jardin Vert</i></p> <p>1958: H. Frankenthaler, <i>Basque Beach</i></p> <p>1960s: D.A. Siqueiros, murals of the Polyforum Cultural Siqueiros building (Mexico) (La Nasa et al. 2021)</p> <p>1968: P. Gilardi, <i>Disgelo</i> (La Nasa et al. 2019)</p> <p>1982: F. Bacon, <i>Figure with cricket pads</i> (Russell et al. 2011)</p> <p>1982: S. Polke, <i>Stairwell (Treppenhaus)</i></p> <p>2003: A. Harding, <i>Quartet</i> (La Nasa et al. 2020)</p> <p>2013–14: BLU, mural painting on the wall of an old military warehouse (La Nasa et al. 2021)</p>	Good lightfastness and poor solvent fastness

PY3, 11710	1909: Germany	<p>Since 1909: F. Melani's atelier material (Italy) (Carlesi et al. 2013)</p> <p>Since 1909: <i>Vert Anglais n. 3</i>, Lefranc archive paint tube (France) (Degano et al. 2017)</p> <p>1927: <i>Talens Groen Licht</i>, Royal Talens B.V., list of artists' paints, Rembrandt tempera paints (Netherlands)</p> <p>1935: <i>Sunproof Yellow II</i>, Gouache paint-outs, Schmincke (Germany)</p> <p>1935: V. Vytlačil, <i>Construction No. 3</i></p> <p>1936: A. Calder, <i>From against yellow</i></p> <p>1936: M. Beckmann, <i>Stilleben mit Ausblick auf den Wannsee</i></p> <p>1938: P. Picasso, <i>Portrait of Dora Marr</i></p> <p>1939: V. Vytlačil, <i>Construction</i></p> <p>1945: J. Pollock, <i>There were seven in eight</i></p> <p>1945: J. Pollock, <i>Summertime number 9A</i></p> <p>1949: B. Newman, <i>Dionysius</i></p> <p>1953: E. Briggs, <i>Untitled</i></p> <p>1957: Y. Klein, <i>Monochrome Vert</i></p> <p>1958: A. Pellam, <i>S'abstenir</i></p> <p>1965: T. Wesselmann, <i>Study for First illuminated Nude</i></p> <p>1968: Lucebert, <i>Baby elephant</i></p> <p>1968: P. Gilardi, <i>Disgelo</i> (La Nasa et al. 2019)</p> <p>1970: P. King, <i>Dunstable Reel</i></p> <p>1973: B. Riley, <i>Cantus Firmus</i></p> <p>1982: T. Setch, <i>Once upon a time there was oil III</i></p> <p>1985: P. Caulfield, <i>Interior with picture</i></p> <p>1989: K. Fritsch, <i>Display stand with Madonnas</i></p> <p>2003: A. Harding, <i>Quartet</i> (La Nasa et al. 2020)</p>
PY65, 11740	1936: Germany, England	<p>Before world war II: IG. Farbenindustrie (Germany)</p>

(continued)

Table 9.2 (continued)

Pigment code	First discoveries	Industrial introduction	Paint materials and paint artworks	Features
PY73, 11738	1961: USA, Germany, England			
PY74, 11741	1959: USA	1958: E.I. du Pont de Nemours & Company (USA) 1961: Sherwin Williams Comp. (USA) 1961: Farbwerke Hoechst AG (Germany)	1973: A. Jensen, <i>The sun rises twice (Per I, Per II, Per III, Per IV)</i> 1994: G. Ayres, <i>Sundark blues</i> 2011: A. Pasquini, <i>Untitled</i> (Bosi et al. 2020)	
PY97, 11767	1950: Germany	1960: Farbwerke Hoechst AG (Germany)		
PY98, 11727	1960: Germany	1960: Farbwerke Hoechst AG (Germany)		
PO1, 11725	1925: USA			
Benzimidazolone pigments				
PY151, 13980	1960s	1971: Farbwerke Hoechst AG (Germany)		Good lightfastness and solvent fastness
PY154, 11781	1960s	1975: Farbwerke Hoechst AG (Germany)	1996: <i>Permanent Yellow, light, medium and dark, Permanent Green light, medium and dark, Permanent Yellowish Green, Cinnabar Green light and medium</i> , Royal Talens B. V., list of artists' paints, Rembrandt oil colours (Netherlands)	
PY175, 11784	1960s	1980: Farbwerke Hoechst AG (Germany)		

Diarylide yellow pigments					1988: <i>Indischgelb, Geraniumlack, Gruner Lack hell</i> , Lukas, A quality artists' oil colours (Germany) 1988: <i>Geraniumlack</i> , Lukas, B quality Artists' oil colours (Germany)	Moderate lightfastness and good solvent fastness
PY12, 21090	1911: Germany					
PY13, 21100	1911: Germany					
PY14, 21095	1911: Germany					
PY17, 21105	1911: Germany					
PY81, 21127	1958: Germany					
PY83, 21108	1949: Germany	1958: Farbwerke Hoechst AG (Germany)			1993: M. Lüpertz, <i>Parsifal or men without women</i> (Lutzenberger and Stege 2009) 2006: Peeta, <i>Writings</i> (La Nasa et al. 2021) 2006: Deban and M. Ment, <i>Writings</i> (La Nasa et al. 2021)	
PY127, 21102	1964: Germany					
Isoindoline and isoindolinone pigments						
PY109, 56284	1956: Germany				1980: Royal Talens B. V., list of artists' paints, Rembrandt oil colours (Netherlands)	Excellent lightfastness and solvent fastness
PY110, 56280	1977: Germany				1978: <i>Inditan Yellow</i> , Royal Talens B.V., list of artists' paints, Rembrandt oil colours (Netherlands)	
PY139, 56298	1980: Germany					
Phthalocyanine pigments						
Blue pigments						
PB15, 74160	1928: England	1935–1936: I.G. Farbenindustrie (Germany) 1937: E.I. du Pont de Nemours & Company (USA)			1937: Winsor & Newton, artists' paint (England) 1940: Royal Talens B.V., list of artists' paints (Netherlands) 1953: G. Capogrossi, <i>Cinema Airone</i> (La Nasa et al. 2021) 1967: B. Newman, <i>Who is afraid of red, yellow and blue III</i> 1975: A.R. Penck, <i>Young generation</i> 1989: K. Haring, <i>Tutto mondo</i> (Cucci et al. 2016) 2011: A. Pasquimi, <i>Untitled</i> (Bosi et al. 2020)	Excellent lightfastness and solvent fastness

(continued)

Table 9.2 (continued)

	Pigment code	First discoveries	Industrial introduction	Paint materials and paint artworks	Features
	PB16, 74100	1931: England	1939: I.G. Farbenindustrie (Germany) 1939: Imperial Chemical Industries Ltd. (England)	1962: G. Baselitz, <i>Der Zwerg</i> 1964: E. Kelly, <i>Blue green red I</i>	
	Triarylmethine pigments				
	PV39, 42535	1884: Germany		1886: V. van Gogh, <i>Glass with yellow roses</i> (Van Bommel et al. 2005) 1888: V. van Gogh, <i>Montmajour drawing</i> (Confortin et al. 2010) 1956–1959: <i>Ultramarine</i> , Yang Tse permanent inks, L. Fontana's atelier material, J.M. Paillard (France) (Zaffino et al. 2017) Since 1960: felt-tip pen, L. Bo Bardi's atelier material, Johann Faber (Germany) (Moretti et al. 2019) 1965: G. Turcato, <i>Composizione-Superficie Lunare</i> (Sabatini et al. 2020c)	Poor lightfastness
	Phthalocyanine pigments				
Green pigments	PG7, 74260	1935: Germany, England	1936: Imperial Chemical Industries Ltd. (England) 1938: I.G. Farbenindustrie (Germany) 1940: E.I. du Pont de Nemours & Company (USA)	1940: Royal Talens B.V., list of artists' paints (Netherlands) 1950: M. Beckmann, <i>Frau mit Mandoline in Gelb und Rot</i> (Lutzenberger and Stege 2009) 1956–1957: F. Bacon, <i>Study for a portrait IV</i> (Russell et al. 2011) 1961: M. Louis, <i>Alpha Phi</i> 1962: G. Baselitz, <i>Der Zwerg</i> 1964: E. Kelly, <i>Blue green red I</i>	Excellent lightfastness and solvent fastness
	PG36, 74265	1935: England			

	Triarylmethine pigments		
	PG1, 42040	1887: Germany	1960s: D.A. Siqueiros, murals of the Polyforum Cultural Siqueiros building (Mexico) (La Nasa et al. 2021) Since 1960: felt-tip pens, L. Bo Bardi's atelier material, Johann Faber (Germany) (Moretti et al. 2019)
Violet pigments	Quinacridone pigments		
	PV19, 46500	1955: USA 1955: E.I. du Pont de Nemours & Company (USA)	1965–1970: Royal Talens B.V., list of artists' paints, Rembrandt oil colours (Netherlands) 1980: Schmincke (Germany) 1983: G. Richter, <i>Bild 525, Prag</i>
	Dioxazine pigments		
	PV23, 51319	1928: Germany 1953: Farbwerke Hoechst AG (Germany)	1938: G. Baselitz, <i>Roadwarker</i> 1973: G. Baselitz, <i>Straßenbauarbeiter</i> 1974: Royal Talens B.V., list of artists' paints, Rembrandt oil colours (Netherlands) 1988: J. Schnabel, <i>Ri de pomme</i> (E. Ghelardi et al. 2015)

(continued)

Table 9.2 (continued)

Pigment code	First discoveries	Industrial introduction	Paint materials and paint artworks	Features
Triarylmethine pigment				
BV14, 42510	1859: France			
PR90, 45380	1873: Germany		1888–1890: V. van Gogh paintings (Geldof et al. 2013) 1889: V. van Gogh, <i>Two white butterflies</i> (Claro et al. 2010) 1890: V. van Gogh, <i>Wheat field under clouded sky</i> (Claro et al. 2010) 1890: V. van Gogh, <i>La maison blanche, la nuit</i> (Sabatini et al. 2020a) 1888: V. van Gogh, <i>Landscape with Snow</i> (Pozzi et al. 2021)	Poor lightfastness
BV10, 45170	1887: Germany		Since 1905: <i>Rouge Japonais Foncé</i> , Lefranc archive paint tube (France) (Degano et al. 2017) 1955–1960: F. Melani, <i>bandiera</i> (Carlesi et al. 2016)	
PR81, 45160	1887: Germany		1956–1959: <i>Natural Sienna earth</i> , Yang Tse permanent inks, L. Fontana's atelier material J.M. Paillard (France) (Zaffino et al. 2017) 1955–1960: F. Melani, <i>bandiera</i> (Carlesi et al. 2016)	

9.2 Analysis: Methods, Instrumentation, and Specific Issues

9.2.1 *High Performance Liquid Chromatography (HPLC) and Ultra Performance Liquid Chromatography (UPLC)*

Liquid Chromatography has been widely employed in the analysis of organic materials in Heritage Science objects. In particular, it can be considered the method of choice because of its reliability and performance for the analysis of organic colorants whenever sampling is allowed. The first applications were based on Thin Layer Chromatography (TLC) that was gradually supplanted by High Performance Liquid Chromatography (HPLC) due to higher selectivity and sensitivity, great chromatographic efficiency, and the possibility of performing quantitative analysis (if analytical standards are available), or semiquantitative evaluations (Degano 2019). Reversed-phase chromatography (RP-HPLC) has been applied for the last 30 years for the characterization of organic dyes and pigments, which are most often complex mixtures of organic molecules that are mostly aromatic and polar, generally water soluble and characterized by a strong absorption in the UV-Vis range (Degano and La Nasa 2016). While natural colorants are inherently composed by mixture of different compounds, synthetic dyes were often admixed to obtain specific hues, or contained synthesis by-products whose identification can provide interesting information on the manufacturer. Thus, the identification of materials is usually achieved by comparing the chromatographic profiles of extracts of unknown samples to those obtained for known reference materials.

The analytical column is the core of the chromatographic separation. Amongst the several columns available, the most commonly used in the analysis of organic pigments and lakes are constituted by C8 or C18 stationary phase, with sizes of 150×4.6 or 150×2 mm, with 3 or 5 μm particle size. UHPLC (Ultra High-Pressure Liquid Chromatography) allows the use of sub-2- μm particle size, bearing relatively higher back-pressures. While HPLC can operate continuously at high pressure, up to 6000 psi, UHPLC can operate up to 10,000 psi. The recent success of UHPLC is given by its higher chromatographic efficiency and sensitivity, shorter runtimes and thus faster analysis, saving solvent cost and waste (Serrano et al. 2013; Taujenis and Olšauskaite 2012; Troalen et al. 2014). The solvent flow generally ranges between 0.2 and 10 mL/min, while for nano-LC setups a flow 0.002 mL/min is required. For an efficient separation of mixtures of differently polar compounds, the fine-tuning of a suitable elution program in gradient mode is fundamental. Binary systems of water and methanol or acetonitrile acidified with formic acid or trifluoroacetic or acetic acids are generally selected (Halpine 1996). For the analysis of some classes of synthetic pigments, counter ion chromatography making use of ion pair reagents such as tetrabutylammonium hydroxide may be more efficient in achieving a better separation and improved peak symmetry (van Bommel et al. 2007). When dealing with strongly polar dyes or uncoloured degradation compounds, the use of a RP-amide i.e. a polar embedded reversed-phase column, may be effective (Restivo et al. 2014). Finally, 2D-HPLC, entailing the use of two columns exploiting

different retention mechanisms, can be employed as a universal system to separate both extremely polar and relatively less polar organic dyes (Pirok Bob et al. 2016, 2019a, b).

For the detection of separated compounds, the most commonly employed detectors are spectrophotometric (UV-Vis, Diode Array and Fluorescence Detectors) and mass spectrometric (ESI-MS, APCI-MS) detectors. Whenever possible, the use of both spectrophotometric and mass spectrometric detectors in series is advisable, to exploit the ability of the first to assess the colour of the eluted components through the acquisition of the UV/Visible spectrum, and the sensitivity and selectivity of the latter. Fluorimetric detection is extremely sensitive and selective (van Bommel 2005; Colombini et al. 2004; Surowiec et al. 2003) due to the high sensitivity of fluorescence in low concentrations. On the other hand, the fact that only a few chromophores exhibit fluorescence can be a drawback in the application of this method of detection. Thus, in most cases, pre- or post-column derivatisation is applied; particularly using aluminium and gallium salts in post-column derivatisation (van Bommel 2005; Szostek et al. 2003). In recent years, the application of high resolution mass spectrometry has aided the resolution of complex mixtures containing unknown species (including degradation products and synthetic by-products) in replicas, in atelier materials and in paint samples (Chieli et al. 2019; La Nasa et al. 2020; Sabatini et al. 2018, 2020b, c).

9.2.2 Gas Chromatography – Mass Spectrometry (GC/MS) and Analytical Pyrolysis (Py-GC/MS)

In the study of natural dyes, gas chromatographic techniques have not been exploited extensively, due to the relatively high-molecular mass and polarity of target compounds. Derivatization of coloured compounds is thus mandatory. Although uncommon, GC/MS based methods have been proposed mainly for dyed textiles and objects, based on the extraction of colouring molecules followed by their derivatization with a silylating agent, both by Colombini (Colombini et al. 2007) and Degani (Degani et al. 2014). Poulin instead developed a procedure for the simultaneous extraction and derivatization of molecules by TMTFTH (Poulin 2018). To bypass any sample pre-treatment, pyrolysis coupled with gas chromatography has been used. While for natural colours research is limited (Andreotti et al. 2004; Casas-Catalán and Doménech-Carbó 2005; Fabbri et al. 2000), several studies tackled the analysis by Py-GC/MS of synthetic organic pigments (SOPs), which are often insoluble or bound in synthetic binders that prove difficult to solubilize. Synthetic pigments are usually analysed without any derivatising reagent; recently, several libraries, listing the characteristic pyrolysis products of several classes of SOPs, have been created (Germinario et al. 2017; Ghelardi et al. 2015b; Learner 2005; Rehorek and Plum 2007; Russell et al. 2011; Sonoda 1999).

In spite of its ability to detect pigments which are not soluble in any extraction solvent, pyrolysis does not provide information on the chemically and thermally stable pigments. Moreover, many families of pigments have a common skeletal structure, differing only in the nature or position of the substituents on the aromatic rings, and thus they often yield common pyrolysis fragments. Notwithstanding this, differences between pyrograms of unaged and artificially aged paint model systems have been detected and have allowed the hypothesis of degradation pathways (Ghelardi et al. 2015a).

9.2.3 Mass Spectrometry Based Techniques

Mass spectrometry based techniques can be applied as detectors for liquid or gas chromatography, or as self-standing analytical tools. For liquid chromatography, the most widely used systems are based on electrospray ionization (ESI) tandem mass spectrometry. ESI allows the interfacing of a high pressure system such as HPLC with a mass spectrometer, which requires high vacuum, and performs the ionization of the analytes. Being a soft ionization technique, for small molecules as dyes ESI mostly produces monocharged molecular ions, whose mass to charge ratio corresponds to $[M+H]^+$ or $[M-H]^-$ ions, for positive and negative analysis modes, respectively. A second stage of analysis after a further fragmentation of the molecular ion in a collision chamber is thus required to perform qualitative analysis and ultimately to improve sensitivity. Consequently, tandem mass spectrometry is employed in most applications, including ion traps, triple quadrupoles and quadrupole-time of flight analysers.

Other mass spectrometry based techniques used to detect organic dyes and pigments without any prior separation of the sample components are: direct temperature mass spectrometry (DTMS); laser-desorption/ionization (LDI) and matrix assisted laser desorption/ionization (MALDI) mass spectrometry; direct analysis in real time (DART) and surface acoustic wave nebulization (SAWN). Through the rapid acquisition and observation of positive and negative ion spectra, acidic, basic and neutral natural and synthetic colorants can be distinguished and characterized by their m/z values. The absence of preliminary separation means that the detection of minor components is quite difficult, but the features of these techniques make them suitable for the analysis of poorly soluble organic pigments and for the screening of large collections of samples.

DTMS was pioneered by Boon and Learner, but has essentially been abandoned in the last 10 years (Boon and Learner 2002; Lomax et al. 2007; Menke et al. 2009) in favour of more robust and more widely available techniques. LDI and MALDI-MS have been widely used for the analysis of synthetic organic pigments (Boon and Learner 2002; Kirby et al. 2009), but also applied to the detection of natural organic lakes (Boon et al. 2007; Sabatini et al. 2016; Soltzberg et al. 2007).

DART has been tested on organic dyes, even directly on textiles (Armitage et al. 2015, 2019), while it has only been applied to the detection of organic lakes on paint

mock-ups in the recent publication by Alvarez-Martin on eosin lake (Alvarez-Martin et al. 2019).

SAWN has been employed by Astefanei for the identification of synthetic dyes in reference powder materials and historical textiles (Astefanei et al. 2017).

9.2.4 Sample Preparation

The application of liquid chromatography, gas chromatography and some of the direct MS techniques requires the preliminary extraction of the chromophore containing molecules from the matrix. The selection of the most suitable extraction method is crucial, considering the uniqueness of samples and the tiny amount of colorant they often contain (Bacci et al. 2006). The effectiveness of the pretreatment is strongly dependent on the solubility and stability of the colorants in solvents and the nature and the ageing of the matrix (Padfield *n.d.*). Thus, there is as yet no universal method of extraction applicable to all the many dye classes in every kind of heterogeneous matrix. The most commonly used extraction methods for the analysis of organic pigments are listed below:

- Boiling mixture of organic solvent and strong acid: this is the strongest and more aggressive extraction method, the organic solvent usually used is methanol (MeOH) and the acid is hydrochloric (HCl) or sulfuric acid (H₂SO₄) (Abrahart 1977; Halpine 1996). HCl 0.5 M and MeOH (1:1) (Halpine 1996) solution or 2 HCl: 1 MeOH: 1 H₂O (v/v/v) (Wouters 1985) are the most effective and used methods. Nevertheless, some undesired effects such as the cleavage of labile bonds, esterification of carboxylic compounds and oxidation of moieties limit its utilization (Ferreira et al. 2002). Moreover, HCl is corrosive and difficult to evaporate;
- Transmethylation with boron trifluoride and methanol (BF₃/MeOH): a suitable method for disrupting highly polymerized painting films and extracting dyes from lake pigments. If BF₃ is highly concentrated, interactions among compounds in the matrix and esterification may occur (Kirby and White 1996);
- Hydrofluoric acid (HF): a weak acid and, in its dissociated form, also a strong aluminium-complexing agent as efficient as a strong acid (Sanyova 2008). This is a mild extraction preferable for unstable colorants and applicable to a wide range of colorant classes and mixtures precipitated with different metal cations, applied on different supports and in various matrices (Padfield *n.d.*; Sanyova and Reisse 2006). It allows working at much milder pH (c.a. 1.5) than with HCl (Sanyova 2008) obtaining high yields for many colorants. The drawbacks of this method consist in the precautions for manipulation and treatment of HF. Its toxicity both for contact and for inhalation requires protections and its corrosive power, especially toward glass, requires the use of Teflon laboratory ware;

- Formic acid (HCOOH): a weak acid which is used in an extracting solution of 5 HCOOH: 95 MeOH (v/v) which enable a mild extraction of the chromophore containing molecules (Zhang and Laursen 2005);
- Complexation agents: ethylenediaminetetracetic acid (EDTA) is used for its capability as a strong chelator of aluminium and of other ions, enabling the release of dyes molecule without decomposing them. An efficient extracting solution used is 2 H₂EDTA: 10 ACN: 88 MeOH (v/v/v) (Zhang and Laursen 2005). Finally, in order to improve the extraction yields of complexation agents, it is also possible to use an organic solvent such as dimethylformamide (DMF) (Surowiec 2008). Another method exploiting a complexing agent entails the use of oxalic acid in a mixture of oxalic acid/MeOH/acetone/H₂O (1:30:30:40, v/v/v/v) (Guinot and Andary 2006; Manhita et al. 2011);
- Organic solvent: pyridine, dimethylsulfoxide, or dimethylformamide (Kirby and White 1996; Wouters 1991) are commonly used, heating at maximum 100 °C for short times (Manhita et al. 2011).

9.2.5 Data Interpretation

The interpretation of chromatographic and mass spectrometric data relies on the identification of specific molecules, typical of organic dyes, based on their retention time, mass spectra and possibly spectroscopic properties (e.g. UV-Vis or fluorescence spectra). The unambiguous identification of the source of colour is a much more complex task, since minor components and in some cases even the ratio between different molecules can enable the distinction between different species, or synthetic routes. Thus, data can only be interpreted by comparing both the qualitative and semi-quantitative profile of the extract of an unknown sample with that of reference materials, possibly subjected to artificial ageing. Comparison with published data should be performed by keeping in mind that different extraction protocols may lead to slightly different results, thus extra caution is needed whenever using novel sample treatments. Finally, multivariate statistical data analysis can be successfully employed to discriminate between closely related materials, such as the dyes and organic pigments extracted from scale insects, as demonstrated by Serrano et al. in extensive research on cochineal (Serrano et al. 2011).

9.3 A Further Analytical Issue: Photo-Degradation of Coloured Compounds

Organic lakes and pigments are among the most labile materials used in works-of-art. They are coloured, which means that they absorb light in the UV-Visible range and are susceptible to photochemical reactions i.e. photo-oxidation processes that

lead to a change in colour or even to bleaching. The photo-oxidation of synthetic organic pigments already heavily affects the appearance of modern and contemporary paintings; therefore, specific storage and display conditions need to be designed to minimize reactions leading to the degradation of chromophore-containing molecules. Thus, improving our comprehension of photooxidation chemical pathways and fading mechanism is the only way to develop suitable preventive conservation strategies.

The stability of materials to photo-oxidation and damages induced by light is defined as photostability (Anghelone et al. 2018). The absorption of photons of suitable energy by an organic molecule provides an electronically excited state, which is the starting point for the subsequent reactions (Weyermann et al. 2009). The presence of oxygen frequently accelerates the degradation via radical-initiated oxidation and only in a few cases it can retard dye-fading by re-oxidizing reduced molecules.

Artificial accelerated ageing of reference materials is commonly used to mimic and study the degradation process undergone by colorants and of other materials present in artworks. In most cases, accelerated ageing procedures are performed in order to assess rates of fading and identify the factors that lead to lightfastness. Accelerated ageing is based on the reciprocity principle: degradation is assumed to be proportional to net exposure calculated as the product of intensity of illuminance and exposition time (Feller 1994). There are many examples of deviations from the reciprocity principle in natural materials. Furthermore artificial accelerated ageing is not able to accurately reproduce natural ageing due to the impossibility to recreate the variety of different conditions an artwork might be exposed during its life (Weyermann and Spengler 2008). Nonetheless, artificial ageing is the only tool available to simulate photo-oxidation. The cross-checking between results collected from the analysis of artificially aged reference materials with historical samples is mandatory to validate the reliability of accelerated ageing procedures.

With regard to natural lake pigments, the most studied chromophores in terms of photo-stability are flavonoids (Colombini et al. 2007; Ferreira et al. 1999, 2002; Saunders and Kirby 1994); degradation products have been identified in aged specimens that were prepared in the laboratory and sampled from works of art. Hydroxybenzoic acids were detected in the extracts from aged specimens, the presence of which may be due to the photo-oxidation of the double bond C2-C3 of the flavonoids, leading to the formation of a depside. This latter is formed by condensation of two or more hydroxybenzoic acids whereby the carboxyl group of one molecule is esterified with a phenolic hydroxyl group of a second molecule. Cleavage also yields low-molecular mass products, such as dihydroxybenzoic acids and trihydroxybenzoic acids (Fig. 9.3). Some of these degradation products were identified in historical and archaeological samples as well (Ferreira et al. 2003; Zhang et al. 2007).

Madder degradation has been extensively investigated, due to its wide occurrence in works of art (Ahn and Obendorf 2004; Clementi et al. 2007; Saunders and Kirby 1994). Ahn and co-workers worked on alizarin in water solution and identified possible degradation products such as phthalic acid and phthalic anhydride, and benzoic acid. However, Clementi and co-workers did not identify any degradation products after accelerated ageing of wool yarns dyed with madder.

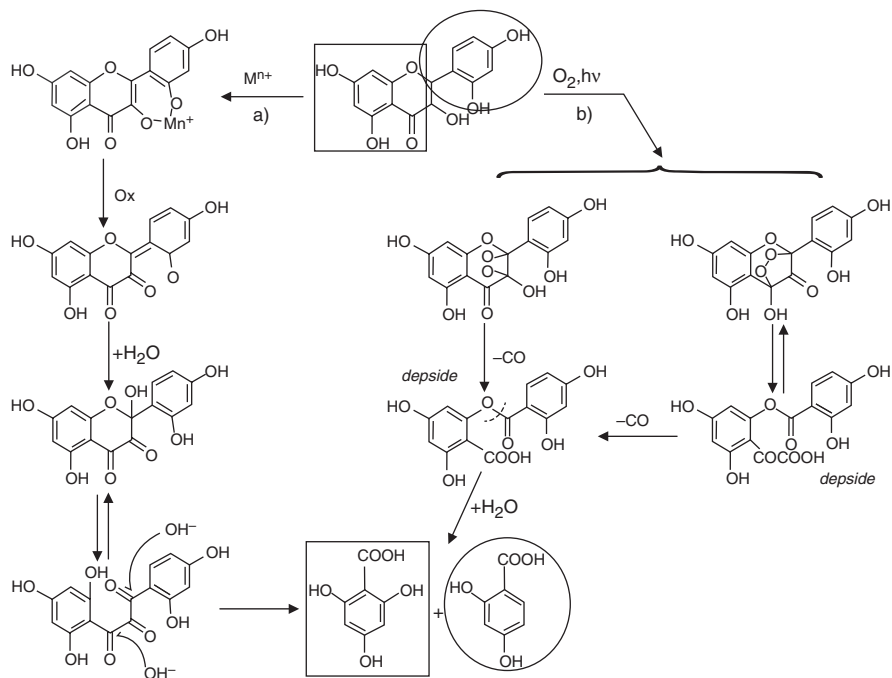


Fig. 9.3 Suggested degradation pathway for morin: (a) oxidation catalysed by a metallic ion (Mn^{2+}) and (b) oxidation by atmospheric oxygen activated by light (O_2 , $h\nu$). The square and the circle evidence the fates of the two aromatic rings (Colombini et al. 2007)

Many studies have been carried out on the synthetic dyes and pigments characterization while few have been performed on their artificial ageing and in particular on the identification of the relative degradation compounds in paintings, drawings or historical textiles (Alvarez-Martin and Janssens 2018; Anghelone et al. 2018; Burnstock et al. 2005; Confortin et al. 2010, n.d.; Crews 1987; Dunn et al. 2003; Favaro et al. 2012; Ghelardi et al. 2015a; Weyermann et al. 2006, 2009). Extensive publications describe the detection of synthetic dyes in wastewaters along with remediation strategies, whereas only few discuss in detail the photodegradation pathways in solution (Pirok Bob et al. 2019a, b; Sabatini et al. 2021). Thus, the database of reference systems and case studies analysed needs to be enlarged in order to reveal degradation processes of SOPs.

9.4 Case Studies

In the previous section, the potential of chromatography-mass spectrometry and several of the analytical issues involving the analysis of synthetic organic pigments were discussed. In this section, some case studies will be described to highlight

how chromatography-mass spectrometry allows the analyst to overcome analytical challenges and to produce data that can be used for authentication purposes.

9.4.1 Commercial Paint Materials: Database of Manufacturers

One of the main causes of confusion on the effective composition of commercial paint materials is the use of creative and non-informative names by the manufacturers, who even used the same name for defining formulations with different compositions. An explicative example of this latter case is constituted by three red historical colorants from LeFranc Archive in Le Mans (France) and one paint tube, dated to the early twentieth century. The three powders were all labelled as *Laque de Garance*, while the paint tube was named *Lac Fine*. The containers of the powders and the paint tube are shown in Fig. 9.4, along with the chromatograms acquired on the extracts of microsamples (Degano et al. 2017).

In all the chromatograms a peak ascribable to alizarin was detected but, while in the paint tube alizarin was the main colorant, in the three powders it was present in

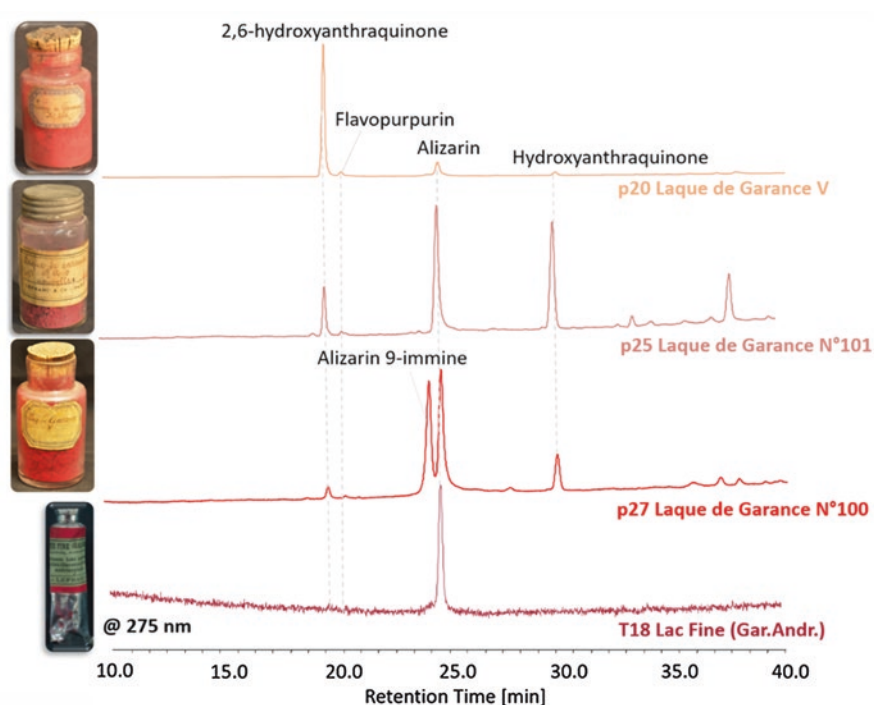


Fig. 9.4 HPLC-DAD chromatograms (extracted at 480 nm) of the extracts of one Lefranc paint tube and three powders (from the bottom to the top): *Lac Fine* (Gar. Andr.); *Laque de Garance* N°100; *Laque de Garance* N°101; *Laque de Garance* V (Degano et al. 2017)

variable amounts and together with other abundant coloured compounds. These species were identified by chromatography with high resolution tandem mass spectrometry (HPLC-ESI-Q-ToF) as 2,6-dihydroxyanthraquinone, flavopurpurin and a hydroxyanthraquinone (possibly 2-hydroxyanthraquinone), which are synthetic species and plausible by-products in the synthesis alizarin, as suggested on the basis of the process reported in (Degano et al. 2017; Fieser 1930). “Laque de Garance Number 100” also contains alizarin-9-imine, possibly formed by treating synthetic alizarin with ammonia. The qualitative and quantitative differences in composition of the three powders from the same period, manufacture and labelled with the same name highlight how important it is to characterise reference materials in order to build rich databases. At the same time, this example clarifies how extensive knowledge of commercial paint formulations may allow the scientist to trace specific manufacture on the basis of the profile collected for a sample from a disputed work of art. Therefore, this information can be correlated with the dating of the artwork and the information related to paint suppliers.

9.4.2 *Commercial Paint Materials: Comparison of Yellow Formulations*

Four case studies have reported the detection of Hansa Yellow pigments by chromatography with spectrophotometric and mass spectrometric detection (HPLC-DAD and HPLC-ESI-Q-ToF), in materials and works-of-art dating from the beginning of the twentieth century to 2003. The chromatographic profiles obtained for the extracts of a LeFranc green paint tube labelled as *Vert Anglais N°3* (Degano et al. 2017), a yellow powder from Fernando Melani’s archive (1907–1985, *yellow 3_Melani*) (Carlesi et al. 2013), a red sample taken from the pop-art sculpture *Disgelo* by Piero Gilardi (1942) (La Nasa et al. 2019) and a yellow sample taken from the painting *Quartet* by Alex Harding (2003) (La Nasa et al. 2020) are provided in Fig. 9.5.

The combined information provided by the two detectors disclosed the composition of these four formulations. Even if the four samples are coloured in different hues, the yellow base for all of them is a Hansa Yellows (PY1, PY1 isomer and PY3) suggesting a common trend to use these pigments together. Nevertheless, the relative amount of PY1 and PY3 differs in the samples suggesting different recipes that were possibly adapted on the basis of the other organic and/or inorganic pigments present in the formulations. In particular, the LeFranc tube, *Quartet* and *Disgelo* chromatograms are richer in PY3 while the *yellow 3_Melani* in PY1. Considering the good lightfastness of Hansa Yellow pigments and their stability in time, the ratio between these two pigments may be used to discriminate formulations of different paint manufactures detected in artworks. If the painter’s atelier materials are available, the evaluation of the authenticity of artworks may be performed by comparing not only the qualitative but also the semi-quantitative composition of the pigments identified.

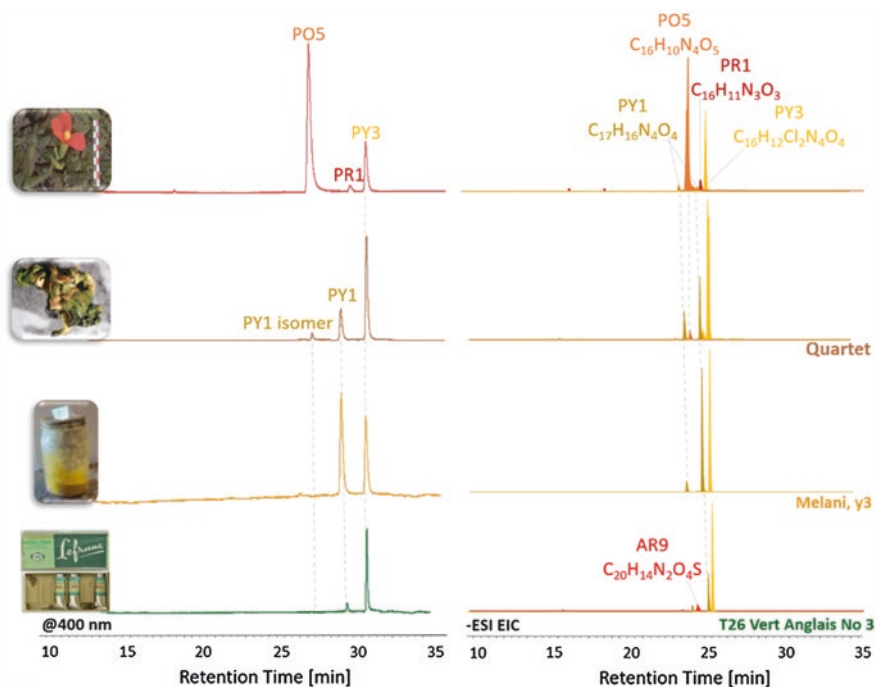


Fig. 9.5 HPLC-DAD chromatograms (extracted at 400 nm) on the left, HPLC-ESI-Q-ToF Extract Ion Chromatograms (EIC) (acquired in negative ionization mode) of $C_{17}H_{16}N_4O_4$, $C_{16}H_{10}N_4O_5$, $C_{16}H_{11}N_3O_3$ and $C_{16}H_{12}Cl_2N_4O_4$ of the extracts of atelier materials and artworks (from the bottom to the top): *Vert Anglais N°3* (Degano et al. 2017), *yellow 3_Melani* (Carlesi et al. 2013), the painting *Quartet* (Alex Harding 2003) (La Nasa et al. 2020); the pop-art sculpture *Disgelo* (Piero Gilardi, 1942) (La Nasa et al. 2019)

9.4.3 Ageing and a Cautionary Tale

Unfortunately, the evaluation of the relative pigment ratio cannot be used as a reliable criterion for all classes of pigments. Many of them, such as triarylmethines and xanthenes, exhibit poor lightfastness, resulting in degradation and consequent modification of the chromatographic profiles. Methyl violet, a triarylmethine pigment, was one of the colours employed by Giulio Turcato to create the effect of a lunar surface in his painting *Composizione-Superficie Lunare* (1965) (Sabatini et al. 2020c). The artwork was overheated and damaged by fire. The HPLC-ESI-Q-ToF analysis of two samples collected from two areas of the painting suggested the use of methyl violet, even though different profiles were obtained: sample 1 shows lower amount of hexa-N-methyl pararosaniline (hexa MP) and an increase in intensity of the respective demethylated compounds (Fig. 9.6).

Methyl violet is a complex mixture generally constituted by tetra, penta and hexa-N-methyl pararosaniline (tetra MP, penta MP, hexa MP, respectively) but many formulations were available that vary based on the synthetic strategy adopted.

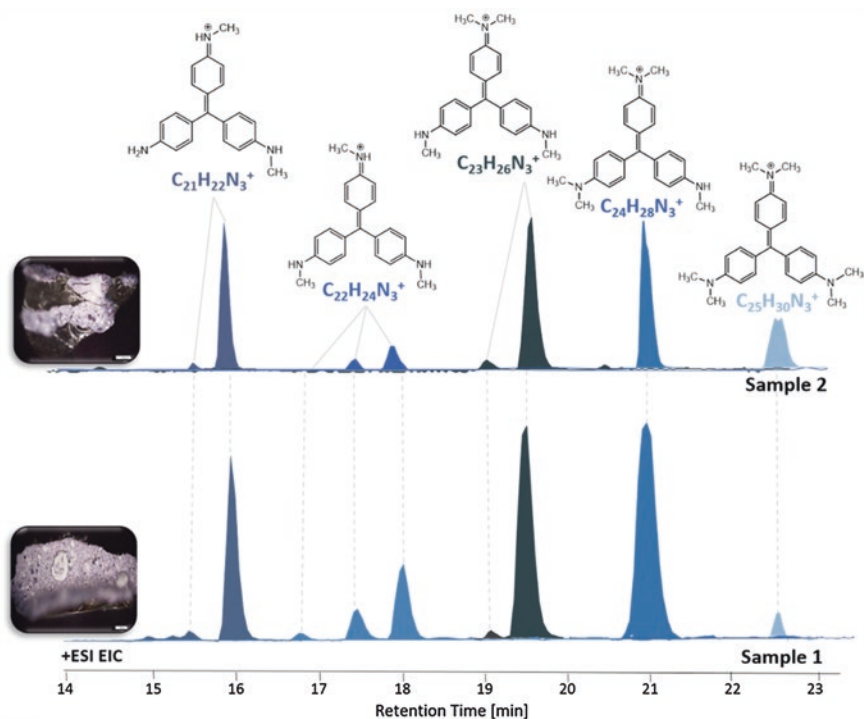


Fig. 9.6 HPLC-ESI-Q-ToF Extract Ion Chromatograms (EIC) (acquired in positive ionization mode) of $C_{19}H_{18}N_3^+$, $C_{20}H_{20}N_3^+$, $C_{21}H_{22}N_3^+$, $C_{22}H_{24}N_3^+$, $C_{23}H_{26}N_3^+$, $C_{24}H_{28}N_3^+$ and $C_{25}H_{30}N_3^+$ of the extracts of two samples (1 and 2) taken from the painting *Composizione-Superficie Lunare* (Giulio Turcato, 1965) (Sabatini et al. 2020c)

Moreover, the composition of methyl violet formulations might be altered by degradation, proceeding via demethylation (Confortin et al. 2010). Thus, the relative ratio of the different N-methyl pararasaniline products is not distinctive for a specific formulation. Finally, the only conclusion to be drawn for the present case study is that sample 1 is more degraded than sample 2.

9.4.4 Ageing and a Tale of Success

Artificial ageing of reference materials may be a reliable simulation of the natural ageing possibly occurring in an artwork, as demonstrated in the following case study. The drawing *Montmajour* by Vincent Van Gogh (1888) appears brownish but purple shades are present on the edges where the ink has been protected from light by the frame (Confortin et al. 2010). The purple ink resembled that used for drawings and letters produced in the same period by the artist, in which methyl violet had been already found. The positive matching between the chromatographic

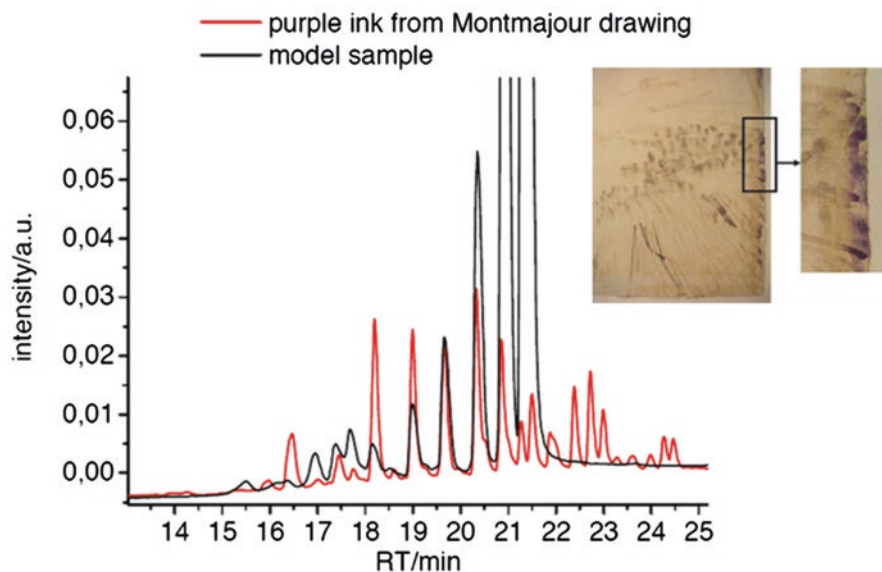


Fig. 9.7 HPLC-PDA chromatograms (extracted at 590 nm) of model sample of crystal violet faded on paper and of purple ink from the drawing *Montmajour* (Vincent Van Gogh 1888). Adapted from (Confortin et al. 2010)

(HPLC-PDA) profile collected for aged model samples of historical crystal violet (mainly constituted by hexa-*N*-methyl pararosaniline) faded on paper (irradiated by UV light for 340 h) and a sample from a purple ink area of *Montmajour* (Fig. 9.7) gave evidence of the reliability of the model samples prepared, at the same time, validating the authenticity of the drawing.

9.5 Conclusions

The review of scientific publications and the case studies presented demonstrate the ability of chromatographic and mass spectrometric techniques to provide qualitative and even semi-quantitative information on the complex mixtures constituting organic lakes and pigments. Such detailed information, if corroborated by a comparison with a suitable set of reference materials, can be used to supplement other scientific data to refute a specific historical period, or identify paint materials or additions that may be consistent with a particular period or artist's practice.

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