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HPLC-DAD and HPLC-ESI-Q-ToF characterisation of early 20th century lake and organic pigments from Lefranc archives

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Abstract

The characterisation of atelier materials and of the historical commercial formulation of paint materials has recently gained new interest in the field of conservation science applied to modern and contemporary art, since modern paint materials are subjected to peculiar and often unpredictable degradation and fading processes. Assessing the composition of the original materials purchased by artists can guide not only their identification in works of art, but also their restoration and conservation. Advances in characterisation methods and models for data interpretation are particularly important in studying organic coloring materials in the transition period corresponding to the late 19th–early 20th century, when many such variants or combinations were hypothetically possible in their formulations. There is thus a need for reliable databases of materials introduced in that period and for gaining chemical knowledge at a molecular level related to modern organic pigments, by state-of-the-art protocols. This paper reports on the results of a study on 44 samples of historical colorants in powder and paint tubes, containing both lake pigments and synthetic organic pigments dating from 1890 to 1926. The samples were collected at the Lefranc Archive in Le Mans (France) as a part of Project Futurama “*From Futurism to Classicism (1910–1922). Research, Art History and Material Analysis*”, (FIRB2012, Italian Ministry of University and Research), and were investigated using an analytical approach based on chromatographic and mass spectrometric techniques. The focus of the chemical analyses was to reveal the composition of the historical organic lake pigments including minor components, to discriminate between different recipes for the extraction of chromophore-containing molecules from the raw materials, and ultimately to distinguish between different formulations and recipes. High performance liquid chromatography (HPLC) with diode array detector (DAD) or electrospray-Quadrupole-Time of Flight tandem mass spectrometry detector (ESI-Q-ToF) were chosen given their considerable capacity to identify such complex and widespread organic materials. Although the inorganic components of the pigments were not taken into account in this survey, the specific molecular profiles provided invaluable information on the extraction procedures or synthetic strategy followed by the different producers, at different times. For instance, the use of Kopp’s purpurin and garancine was highlighted, and synthetic by-products were identified. The results provided evidence that the addition of synthetic organic pigments to paint mixtures started from 1910 onwards, but they also suggest that in the formulation of high quality (surfin) colorants, natural products were still preferred. Moreover, in one of the samples the use of murexide as the colouring material was confirmed. This paper presents the first systematic and comprehensive survey on organic lakes and pigments belonging to an historical archive, by both HPLC-DAD and HPLC-ESI-Q-ToF. Specific by-products of synthetic production of pigments, which can act as specific molecular markers for dating or locating a work of art, were also identified for the first time.

Keywords: Organic pigments, Lakes, Colorants, Synthetic, Historical industrial pigments, HPLC-DAD, HPLC-Q-ToF, Alizarin synthesis

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Background

The study of the manufacturing and usage of historical and modern organic pigments and dyes is the topic of several research projects using both an artistic and a documentary approach that often focus more on the historical than the chemical–physical point of view. The identification of formulations and production techniques can contribute to solve dating or attribution issues, especially when patented dyes or pigments are involved. A complete picture of the composition of paint components also means optimizing conservation strategies, which are fundamental when dealing with dyes and organic pigments, which are probably the most fugitive materials present in a work of art.

Modern organic pigments have the same conservation issues as other synthetic paint materials: they have been often chosen by artists on the basis of their colour hue and brightness, without sound knowledge of their durability and stability. Thus, many late 19th–early 20th century paintings are nowadays at risk due to the fading or darkening of the organic pigments [1, 2].

Organic pigments and dyes differ in their solubility in the medium in which they are incorporated: organic pigments are often obtained by forming insoluble structures (precipitating them as salts, or adsorbing them onto an inert substrate or even complexing them with suitable metal salts), while dyes are inherently soluble in the medium [3]. Lakes or lake pigments are organic pigments historically prepared as complexes following specific recipes, while the production of synthetic organic pigments started in the late 19th century and has been flourishing since the beginning of the 20th century. The distinction between natural and synthetic materials is complicated by the fact that since the beginning of the 19th century, the manufacturers experimented with new ways to exploit natural dyes as pigments, by precipitating the natural extracts as salts in alkaline conditions. After the synthesis of alizarin (1868), several synthetic analogues of natural dyes were produced and used to obtain both lake pigments and organic pigments. At first, synthetic and natural pigments were often admixed, and after the 1930s, synthetic pigments completely dominated the market [4]. A short review about natural and synthetic pigments produced at the end of the 19th and at the beginning of the 20th century follows.

Since ancient times the three most commonly employed natural dyes for making red lake pigments have been madder, cochineal and Brazilwood (the latter, being fugitive, was mostly used for illuminating manuscripts or in mixtures), while unripe buckthorn berries, quercitron and weld were used for yellow lakes [5]. In the course of the 18th and 19th centuries, the demand for dyes increased, as well as knowledge on dyeing processes.

In the last decades of the 19th century, the efforts in understanding the chemistry of the colorants and extraction processes had a strong influence on the preparation of a wider variety of new colours for paint materials. An important role was played by the availability of reagents that allowed reactions to be performed in strong acidic or alkaline environments, such as sulphuric acid and synthetic sodium carbonate (thanks to the LeBlanc process, potassium carbonate formerly obtained from ashes was replaced by sodium carbonate). As a result, the first organic pigments in the form of insoluble salts appeared on the market [4]. Another development was the introduction of tin salts (in addition to aluminium and iron salts) for preparing lake pigments or as counterions for the precipitation of organic pigments. In this article, those products obtained by employing synthetic routes to modify natural materials are referred to hereafter as “modified natural” products.

A typical example is madder. At the end of the 18th and during the 19th century, German and English chemists tried to imitate Turkey red, also known as Rouge d’Andrinopole [4], based on madder. Various extraction methods from the raw material were tested, yielding products with slightly different names, such as Brown Madder (obtained in 1840 by using copper and iron sulphates instead of alum and potassium/sodium carbonate as a substrate for the precipitation of the lake pigment). The availability of sulphuric and sulphurous acids allowed further experiments to be performed, leading to the isolation of alizarin and purpurin in 1826. By modulating the extraction process, it became possible to obtain different modified madder-based products, e.g. garancine (1828), enriched in alizarin and purpurin, and Kopp’s purpurin (also known in France as “purpurine commerciale”), enriched in both purpurin and pseudopurpurin [4]. Fermenting madder prior to treatment in diluted sulphuric acid yields the so-called “carmine de garance”, supposedly pure madder dyestuff without the addition of an inorganic salt.

With regard to cochineal, depending on the recipe and inorganic salt added, several “carmines” are reported in the 19th–20th century catalogues, with a wide range of prices and colours [4].

Another red lake pigment whose production was modified during the 19th century was brazilwood: various extraction procedures of the raw material were tested by varying the pH of the reagents used. In addition, tin-containing pigments based on brazilwood were available in France and have been identified in pigments used by Vincent van Gogh [4].

New means of modifying natural red colours were made available in the same period, e.g. processing natural sources with synthetic reactants. The pigment called

murexide was first reported in 1776 by Scheele (Karl Wilhelm, 1742–1786), who obtained it by processing excrement from boa constrictors. Such excrement contains 90% ammonium acid urate, the synthetic precursor of murexide [6, 7]. The reaction to obtain it was studied again in the late 1830s by Justus von Liebig (1803–1873) and Friedrich Wöhler (1800–1882). After the introduction of Peruvian guano as a fertilizer on the market, murexide was successfully crystallized from that material, and commercial production started in England in 1853.

Unlike red colours, not much information is available on the treatment of natural raw materials to obtain specific modified yellow lake pigments.

The synthesis of analogues of natural compounds was the next step in the development of new materials for the dyeing industry. Alizarin was the first dye whose structure was determined, thus enabling its synthesis in 1868. The first synthesis of alizarin was patented by Graebe and Liebermann and was a milestone in the industrial production of dyes and pigments [8, 9]. It entailed the dibromination of anthraquinone, followed by fusion with sodium hydroxide. The second, much cheaper, synthetic path was developed in 1869 by Graebe, Liebermann and Caro and independently by Perkin in the same year. It entailed the treatment of anthraquinone with fuming sulphuric acid, followed by a treatment with sodium hydroxide and potassium chlorate.

Shortly afterwards, the first azoic dyes and pigments appeared on the market. In the early 20th century, the production began of β -naphthol pigment lakes, BON pigment lakes, Hansa Yellows, pyrazolones, diarylides, and Naphthol Reds. The history of synthetic organic pigments discovered and produced in the 19th–20th centuries have been reviewed by de Keijzer [10], and all the different classes of industrial organic pigments are discussed in detail in [3].

While the chemical characterisation of historical and synthetic dyes has been the topic of several studies [11], there are few papers that describe the investigation of organic pigments from an analytical chemical point of view. The study of historical red and yellow lakes (organic dyes precipitated on inert substrates or as insoluble complexes with suitable metal salts, in order to act as pigments) was pioneered in the 1990s at the National Gallery of Art in London [4] and more recently tackled at the KIK-IRPA in Brussels [12]. Interest in the characterisation of modern organic pigments has only gained momentum in the scientific literature in the last 10 years. Early synthetic dyes have been studied extensively [2, 13–16]. However, relatively little has been published on organic pigments used in paintings—several projects have revealed van Gogh's painting materials in Europe

[16, 17] and extensive work has been carried out at the Getty Institute for Conservation in the US [18].

Due to the poor solubility of organic lake pigments and synthetic pigments in any medium (including water or organic solvents), the most commonly used approaches for their detection and characterisation exploit Raman spectroscopy or, whenever possible, surface-enhanced Raman spectroscopy (SERS) [18–28], thanks to the availability of dedicated spectral libraries. Whenever sampling has been permitted, analytical pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC/MS) [1, 29–32] has been successfully applied. Direct temperature mass spectrometry (DTMS) [25, 33, 34] and laser desorption mass spectrometry (LDMS) [34, 35] have also been used, but have not yielded positive identification when isomers are present, which is often the case when organic pigments are concerned.

Unfortunately, none of the above-mentioned techniques yield relevant information on minor components, or easily allow the identification of unknown products, which are fundamental in clarifying the synthetic pathways used to produce and modify colorants. Moreover, although bulk techniques can assess changes related to ageing, they do not clearly highlight the degradation pathways. Separation techniques coupled with spectrophotometric and mass spectrometric detection have shown great potential to address these issues, when sampling and dissolution of the analyte have been possible. Although a definitive characterization of the material can only be achieved when a multi-analytical approach is applied, only in few cases has it been possible to perform organic and inorganic analyses, leading to the complete information on the samples under study [14, 26].

The present study summarises the results of the characterisation of the organic chromophore-containing constituents in 44 samples of historical colorants in powder and tube paint containing organic lake pigments and synthetic pigments (dating from 1890 to 1926), provided by the Lefranc Archive in Le Mans (France). This involves using high performance liquid chromatography with diode array detector (HPLC-DAD) and with Electrospray-Quadrupole-Time of Flight tandem mass spectrometry detection (HPLC-ESI-Q-ToF). The samples were collected through a collaboration with the Lefranc Archives in the framework of the project *Futurama "From Futurism to Classicism (1910–1922). Research, Art History and Material Analysis"*, (FIRB2012, Italian Ministry of University and Research [36]), coordinated by Dr. Mattia Patti (Dipartimento di Civiltà e Forme del Sapere of the University of Pisa).

The samples of pigments in the form of powder were collected from jars belonging to the Lefranc's laboratories, and thus correspond to test formulations that may

not actually have been included in commercialized products. Amongst the collection of test formulations, this study deals with those samples whose jars were labelled as lakes or organic pigments. Some commercial paint tubes were also sampled, which also contained binding media and other additives. Some preparations were dated—the oldest one was dated 1890 and the most recent 1926. The complete characterisation of the organic chromophore-containing compounds found in the materials belonging to the Lefranc archives should provide conservators, restorers and conservation scientists with a database of chromatographic profiles, DAD spectra and mass and tandem mass spectra, which can be used as a reference for future studies of artists' studio materials, other archives and modern paint samples. The study of these materials has already been complemented by the characterisation of the inorganic components of a selection of the powders [26]. It will be further improved by the characterisation of the organic binding media employed in the paint tubes in the frame of a JPI European project dealing with the study of modern oils in painting materials [37].

Experimental

Reagents

All the solvents were HPLC grade and were used without any further purification.

The eluents for the HPLC-DAD analyses were: bi-distilled water (Carlo Erba, Italy) and acetonitrile, HPLC grade (Sigma-Aldrich, USA), both with 0.1% trifluoroacetic acid [TFA, 99% purity, from Fluka (Milan, Italy)].

The eluents for HPLC-ESI-Q-ToF analyses were water and acetonitrile, both LC-MS grade (Sigma-Aldrich, USA) with 1% formic acid (98% purity, J. T. Baker).

Samples

The samples were collected from the Lefranc Archive in Le Mans (France) by Diane Kunzelman and Mattia Patti in the framework of the Italian Project Futurama "From Futurism to Classicism (1910–1922). Research, Art History and Material Analysis", financed by the Italian Ministry of University and Research (MIUR)—*Futuro in Ricerca* 2012 program [36]. They comprise both powders contained in closed jars and paint tubes. The complete list of the samples is provided in Table 1. Further information on the contents of Lefranc Archive can be found in [38].

Apparatus and protocol

For HPLC-DAD analyses, an HPLC system 2089 Quaternary Gradient with a diode array spectrophotometric detector MD-2010 was used, equipped with an AS-950 autosampler (Jasco International Co, Japan). Injection

volume was 20 μ L. ChromNav software was used to carry out data acquisition and data analysis. The chromatographic separation was performed on an analytical reversed-phase column TC-C18 [2] (150 \times 4.6 mm, 5 μ m) with a TC-C18 [2] pre-column (12.5 \times 4.6 mm, 5 μ m), both Agilent Technologies (Palo Alto, CA, USA). The eluents were A: trifluoroacetic acid (TFA 0.1% v/v) in bidistilled water and B: trifluoroacetic acid (TFA 0.1% v/v) in HPLC grade acetonitrile. The flow rate was 1.0 mL/min and the program was 15% B for 5 min, then to 50% B in 25 min, then to 70% B in 10 min and then to 100% B in 1 min and then hold for 5 min; re-equilibration took 13 min. The separation took place at room temperature (25 °C). The detector operated with spectra acquisition in the range of 200–650 nm every 0.8 s with 4 nm resolution.

For HPLC-ESI-Q-ToF analyses, an HPLC 1200 Infinity coupled to a Jet Stream ESI-Q-ToF 6530 Infinity detector was used, equipped with an Agilent Infinity autosampler (Agilent Technologies, Palo Alto, CA, USA). Injection volume depended on the sample concentration and ranged between 1 and 10 μ L. MassHunter[®] Workstation Software (B.04.00) was used to carry out mass spectrometer control, data acquisition, and data analysis. The chromatographic separation was performed on an analytical reversed-phase column Zorbax Extend C18 Rapid Resolution column (50 \times 2.1 mm, 1.8 μ m), with a Zorbax Eclipsed Plus C18 Analytical Guard Column pre-column (12.5 \times 4.6 mm, 5 μ m), both Agilent Technologies (Palo Alto, CA, USA). The eluents were A: formic acid (FA 1% v/v) in LC-MS grade water and B: formic acid (FA 1% v/v) in LC-MS grade acetonitrile. The flow rate was 0.2 mL/min and the program was 15% B for 1 min, then to 50% B in 5 min, to 70% B in 2 min, to 90% B in 7 min, to 100% B in 5 min and then hold for 2 min; re-equilibration took 10 min. During the separation, the column was maintained at 30 °C in a thermostatic oven. The mass spectrometer operated in ESI ionization in negative mode and the working conditions were: drying gas (N_2 , purity >98%) temperature 350 °C and 10 L/min flow; capillary voltage 4.5 kV; nebulizer gas pressure 35 psig; sheath gas temperature 375 °C and 11 L/min flow; fragmentor voltage 175 V. High resolution MS and MS/MS spectra (CID voltage 30 V) were acquired in negative mode in the range $m/z = 100$ –1000 at a scan rate of 1.04 spectra/s (collision gas N_2 , purity 99.999%). Auto-calibration was performed daily using Agilent tuning mix HP0321 (Agilent Technologies) prepared in acetonitrile.

Samples were prepared by adding 100 μ L dimethyl sulfoxide (DMSO) to a few mg of powder or paint, and sonicating (ultrasonic bath Sonorex Supra 10P, Bandelin Electronics, Germany) for 5 min at 60 °C. DMSO extraction was chosen as it has proven a good solvent for

Table 1 Sample list, with identification codes and texts appearing on the labels of the powder jars or paint tubes (samples identified by "F" or "P", were from pigment powders, while samples identified as "T" were sampled from paint tubes) and summary of results obtained by HPLC analyses, along with the hypothesised dating of the powders and tubes (or at least, a post quem)

Samples code	Date	Label	Tentative translation	Colorants identified	Dating/recipe
F1*	1899	Echantillon de Carmin B (2 Mars 99)	Sample of carmine B (2 March, 1899)	Carminic acid ^(a) + carminic acid NH ₃ ^(c) + Acid Red 73 ^(a)	AR73 since 1882
F2*		Laque de garance 334 B4 981 15-11-21	Madder lake 334 B4 981 15-11-21	Pigment Red 84 ^(c)	PR84 since 1884
F3*		Laque de garance Cramoisie N° 3	Crimson madder lake N° 3	Purpurin ^(a) + pseudopurpurin ^(a)	Kopp's purpurin
F4*		Garance PMC5 nouvelle 3464 serie 902 AZ	New madder PMC5 3464, series 902 AZ.	Pigment Red 84 ^(c)	PR84 since 1884
F5*	1914	Assiette à Dorer Rouge vif. 1914	Bright red gilding bole. 1914	Acid Red 9 ^(c) or Acid Brown 6 ^(c)	AR9 since 1877, AB6 since 1878
F6		Laque de garance Rose S. N° 1	Rose madder lake S. N° 1	Alizarin ^(a) + purpurin ^(a)	Garancine since 1828
F7*	1899	Laque de garance Ponceau N° 1 Nov. 1899	Poppy red madder lake N° 1 November 1899	Pseudopurpurin ^(a) + purpurin ^(a) (+anthragallo ^(a) + alizarin ^(a))	Natural from madder
F8*	1905	Laque de Garance Rose Prun pour aquarelle Mars 1905.525	Plum pink madder lake for watercolours March 1905.525	Alizarin ^(a)	Most probably synthetic alizarin (available since 1868)
F9*		Garance PTF. N° 2 nouvelle 635	New madder PTF. N° 2.635	Pigment Red 84 ^(c)	PR84 since 1884
F10*	1900	Carmin fin Mai 1900	Excellent carmine, May 1900	Carminic acid ^(a) + carminic acid NH ₃ ^(c) + Acid Red 73 ^(a)	AR73 since 1882
F11		Pourpre Impérial (...) B	Imperial purple (...) B	Insoluble in DMSO and in acidic or alkaline water solutions	
F12*		Laque de garance Brun. Rouge	Dark red madder lake	Alizarin ^(a) + purpurin ^(a)	Garancine since 1828
F13		Vermillon pur N° 1 pour filets (orléans) 2038	Pure vermilion N° 1 for «nets?» (Orléans) 2038	HgS [26]	
F14		Pourpre Impérial C [aniline?]	Imperial purple C [aniline?]	Insoluble in DMSO and in acidic or alkaline water solutions	
F15*	1895	Carmin huile 1895 d'après modification de 1892	Carmine oil 1895 after the 1892 modification	Carminic acid ^(a) + carminic acid NH ₃ ^(c)	Special extraction of carminic acid
F16*		Laque Carminée rose N° 1	Pink carmine lake N° 1	Carminic acid ^(a) + carminic acid NH ₃ ^(c)	Special extraction of carminic acid
F17*	1890	Purpurine G 1890	Purpurin G 1890	Pseudopurpurin ^(a) + munjistin ^(a) + alizarin ^(a) + purpurin ^(a)	Kopp's purpurin? or madder?
F18*	1910	Laq. Carminée Surfin Violette Juin 1910.1170	Carmine lake of superior quality June 1910.1170	Carminic acid ^(a) + dclV ^(a) + kermesic acid ^(a)	Natural from cochineal
F19*	1895	[La]que de Garance Série Rouge N° 1. 1895	Madder [la]ke Red series N° 1. 1895	Pseudopurpurin ^(a) + purpurin ^(a) (+alizarin ^(a))	Kopp's purpurin
F20*		Laque d'office N° 6	Lake for office N° 6	Redwood marker type A [39]	Natural from brazilwood
P5		Carmin N° 6	Carmine N° 6	Carminic acid ^(a) + carminic acid NH ₃ ^(c)	Special extraction of carminic acid
P8	1926	Laque Geranium 2 B. 131. N° 816 III April 1926 [laque d'aniline]	Geranium lake 2 B. 131. N° 816 III April 1926 [aniline lake]	Phloxine B (Acid Red 92) ^(c) + ethyl ester of eosin (Pigment Red 90) ^(a)	Eosin (PR90) since 1871; Phloxine B (AR92) was in use in 1901 [27]
P9		Stil de grain Brun employable surfin	Dark brown Stil de grain usable of superior quality	3,4-Dihydroxybenzoic acid ^(a) + morin ^(a) + maclurin ^(a) (+ thamnatin ^(a) + emodin ^(a))	Natural from old fustic mixed with buckthorn berries

Table 1 continued

Samples code	Date	Label	Tentative translation	Colorants identified	Dating/recipe
P:10		Laque de Garance clair PMC N° 5	Purple madder lake medium light PMC N° 5	Pseudopurpurin ^(a) + purpurin ^(a)	Kopp's purpurin
P:11	1910	Laq. Brune d'Alizarine p. Pastels C4970 Jul.i.1910.1580	Brown alizarin lake for pastels C4970 July 1910.1580	Alizarin ^(a) + Mordant Yellow 1 ^(b)	Mordant Yellow 1 since 1887
P:20		Laque de Garance V	Madder lake V	2,6-Dihydroxy-9,10-anthraquinone ^(b,c) + alizarin ^(a) + mono-hydroxyanthraquinone ^(c) + flavopurpurin ^(b,d)	Synthesis of alizarin 1868
P:22	1929	Laque de Garance Rose clair N° 6 ancien Type épuisé Remplacé en 1929 par Ton 2521 de 1911 ou 1925 un peu crayeuse	Light pink madder lake N° 6 ancient type, finished, replaced in 1929 by shade 2521 made in 1911 or 1925, a little chalky	Insoluble in DMSO and in acidic or alkaline water solutions	
P:23	1890	Purpurine B 1890	Purpurin B 1890	Pseudopurpurin ^(a) + murexistin ^(a) + alizarin ^(a) + purpurin ^(a)	Kopp's purpurin
P:24	1890	Murexide Cristallisée 1890	Crystallized murexide 1890	Murexide ^(b,c)	From guano since 1853
P:25		Laque de Garance N° 101	Madder lake N° 101	2,6-dihydroxy-9,10-anthraquinone ^(b,c) + alizarin ^(a) + mono-hydroxyanthraquinone ^(c) + flavopurpurin ^(b,d)	Synthesis of alizarin 1868
P:26		Laque de Garance Rxo 2783 nouvelle	Madder lake "Rxo" 2783 new	Imminated Pigment Red 84 + Pigment Red 84	PR84 since 1884
P:27		Laque de Garance N° 100	Madder lake N° 100	2,6-Dihydroxy-9,10-anthraquinone ^(b,c) + alizarin ^(a) + mono-hydroxyanthraquinone ^(c) + flavopurpurin ^(b,d) + alizarin-9-imine ^(c)	Synthesis of alizarin 1868
P:29		"Excréments de Serpents" contenant en notable proportion la Murexide, matière colorante du Jaune Péruvien et du Pourpre Impérial	"Snake dung", containing murexide in a notable proportion, which is the colouring matter in Peruvian yellow and Imperial purple	Insoluble in DMSO and in acidic or alkaline water solutions	
T1		Laque de Smitine foncée	Dark Smitine lake	Alizarin ^(a) + purpurin ^(a)	Garancine
T6		Vert Japonais	Japanese green	Insoluble in DMSO and in acidic or alkaline water solutions	
T9		Vert Anglais N° 4	English green N° 4	Pigment Yellow 3 ^(a)	PY3 since 1910
T10		Vert Anglais N° 5	English green N° 5	Pigment Yellow 3 ^(a)	PY3 since 1910
T15		Vert Anglais N° 2	English green N° 2	Pigment Yellow 3 ^(a)	PY3 since 1910
T17		Lac Carmineé fixe	Fixed carmine lake	Pigment Red 115 ^(c) + alizarin ^(a)	Synthesis of alizarin 1868
T18		Lac Fine (Gar.Andr.)	Fine lac (Andr. Madder)	Alizarin ^(a) + flavopurpurin ^(b,d)	Synthesis of alizarin 1868
T19		Vert Japonais Clair	Japanese light green	Pigment Yellow 3 ^(a)	PY3 since 1910
T25		Rouge Japonais Foncé	Dark Japanese red	Pigment Red 3 (toluidine red) ^(c)	PR3 since 1905
T26		Vert Anglais N° 3	English green N° 3	Pigment Yellow 1 ^(c) + Pigment yellow 3 ^(a)	PY3 since 1910 (while PY1 was available since 1909)
T30		Rose erythrine	Erythrine pink	Insoluble in DMSO and in acidic or alkaline water solutions	

The colorants were identified ^(a) by comparison to reference materials, ^(b) based on matching data found in the literature, or ^(c) based only on a proposed structure reasonably deduced from sound chemical reasoning when considering the DAD and MS data collected. Samples marked with an asterisk were also analysed by Raman spectroscopy, XRF and mid-IR, and the results are reported in [26]

synthetic dyes and pigments [32], and was preferred over alkaline or acidic extraction solvents in order not to alter the composition of the components of the pigments. The solubilisation of the powders in DMSO was complete, while the extraction from the paint materials was incomplete, but sufficient for the qualitative interpretation of their composition. The supernatant was filtered with PTFE syringe filters (0.45 µm pore size), and diluted with 500 µL bidistilled water.

Blank analyses were run between different samples to rule out memory effects or cross-contamination.

Results and discussion

The powders and paint tubes were completely soluble in DMSO, except for seven samples that are discussed below. The results are discussed in the following sections according to the chemical class of the components detected. The chemical structures of the synthetic dyes and pigments are reported in Additional file 1: Table S1.

Some of the colorants were identified by comparison with standard or reference materials, some based only on matching data found in the literature, while a few were based only on proposed structures deduced from the DAD and MS data collected. The means of identification is reported in Table 1.

Insoluble, unidentified powders and paint tubes

A few samples were insoluble in DMSO, and nor could they be dissolved in acidic or alkaline media (diluted HCl and concentrated NH₃ were tested). This group contains the following samples: F11 “Pourpre Impérial (...) B”; F14 “Pourpre Impérial C [aniline?]”; P.22 “Laque de Garance Rose clair N° 6 ancien Type épuisé Remplacé en 1929 par Ton 2521 de 1911 ou 1925 en peu crayeuse”; P.29 “Excréments de Serpents contiennent en notable proportion la Murexide, matière colorante du Jaune Péruvien et du Pourpre Impérial”; and the paint tubes T6 “Vert Japonais” and T30 “Rose erythrine”. These materials were thus not characterized by HPLC related techniques and nor could they be identified by Raman or FTIR.

On the other hand, F13 “Vermillon pur N° 1 pour filets (orléans) 2038”, was insoluble but was identified as vermilion thanks to the detection of mercury by XRF [26].

Cochineal-based lake pigments

Several samples contained carminic acid, the molecular marker of cochineal dyestuff. Among them, F18 (dated 1910) also contained kermesic acid and dCIV, known minor components of cochineal dyes and lake pigments [26]. All the other samples containing carminic acid also included a derivative of carminic acid obtained when cochineal is treated with ammonia solution, possibly an imine derivative of carminic acid [see “Madder, garance,

and synthetic alizarin (and derivatives)” section on alizarin-9-imine]carminic acid (. Acid stable carmine was excluded since the compound here observed has a different retention time and DAD spectrum than the one described in [28]. The samples containing this component were the following: F1, dated 1899; F10, dated 1900; F15, dated 1895; F16—chromatograms already published in the Supplementary Information of [26]—and P.5. No minor components were detected in their chromatograms. In two cases (F1 and F10), a diazo colourant was detected, and unambiguously identified as Acid Red 73 (Cotton Scarlet, patented in 1882) thanks to the availability of a pure standard. Most probably it was added to the cochineal-based lake pigment in its insoluble form as a barium salt (barium sulphate bands were detected by IR spectroscopy as discussed elsewhere [26]). All cochineal-based samples except for F18 are thus modified natural pigments, with some even mixed with synthetic pigments. The results are detailed, along with a comparison with Raman and Raman SERS results, elsewhere [26], and are included here for completeness.

Other natural dyes

A molecular marker of Brazilwood, generally known as redwood marker type A [39], was detected in one powder sample, F20, labelled “Laque d’office N° 6”, in the form of its tin lake pigment, see [26].

Natural flavonoid compounds were detected in sample P.9, containing as the main components 3,4-dihydroxybenzoic acid, morin and maclurin, molecular markers of old fustic, and traces of rhamnetin and emodin, molecular markers of buckthorn berries. Interestingly, the jar containing the powdered samples was labelled as “Stil de grain Brun employable surfin”, which is usually obtained by treating unripe buckthorn berries [40]. Thus, a mixture of different natural sources can be hypothesised for the production of this material.

Xanthene pigments

Sample P.8 was labelled as “Laque Geranium”, the name historically given to eosin-containing pigments [41, 42]. The chromatographic analysis yielded unexpected results. The HPLC-DAD chromatogram was not easy to interpret, but HPLC-ESI-Q-ToF allowed the identification of the main component of the sample. Besides the presence of the ethyl-ester of eosin (Pigment Red 90), the main chromatographic peak was associated with a tetrachloro derivative of eosin (Pigment Red 90), named phloxine B (Acid Red 92).

Figure 1 presents the base peak chromatogram obtained by HPLC-ESI-Q-ToF (the base peak chromatogram was preferred to the total ion current chromatogram in order to enhance the signal to noise ratio), along with the

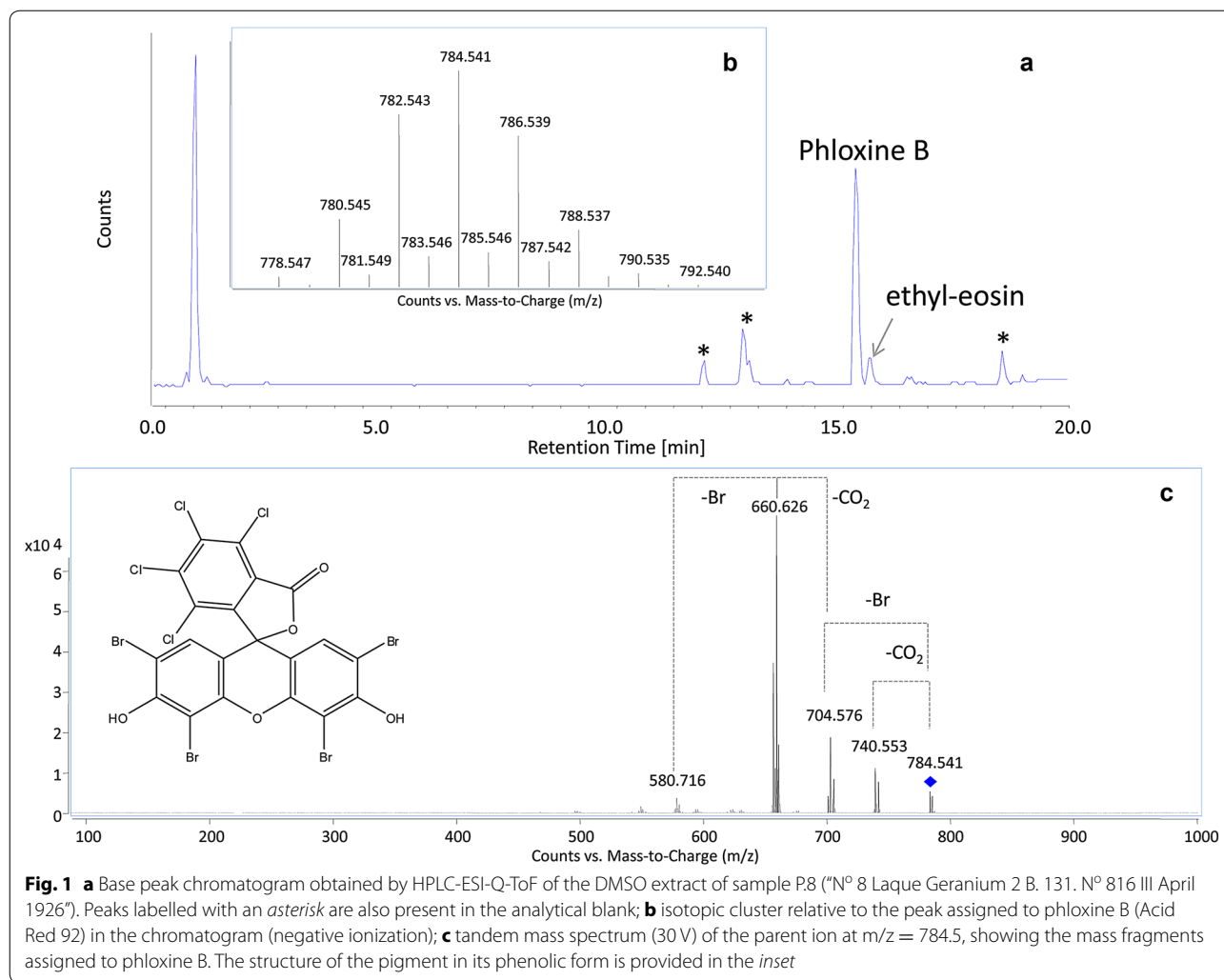


Fig. 1 **a** Base peak chromatogram obtained by HPLC-ESI-Q-ToF of the DMSO extract of sample P8 (“N° 8 Laque Geranium 2 B. 131. N° 816 III April 1926”). Peaks labelled with an *asterisk* are also present in the analytical blank; **b** isotopic cluster relative to the peak assigned to phloxine B (Acid Red 92) in the chromatogram (negative ionization); **c** tandem mass spectrum (30 V) of the parent ion at $m/z = 784.5$, showing the mass fragments assigned to phloxine B. The structure of the pigment in its phenolic form is provided in the *inset*

isotopic cluster relative to the peak assigned to phloxine B (Acid Red 92) in the chromatogram (negative ionization) and its tandem mass spectrum. The isotopic cluster of phloxine B is distinctive, since the relative amount of the different isotopes corresponds to the presence in the molecule of four atoms of chlorine and four atoms of bromine.

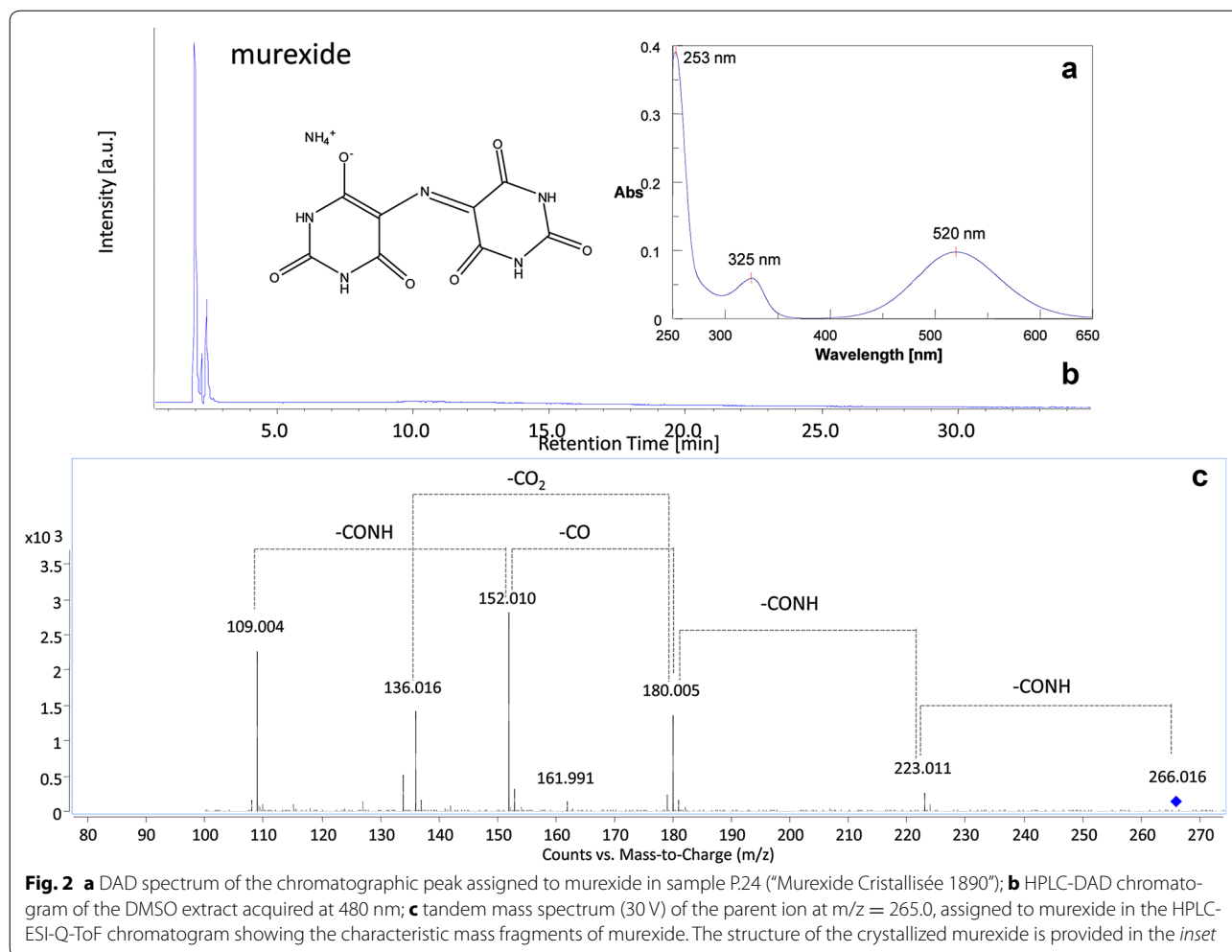
Mixing eosin (Pigment Red 90) and phloxine B (Acid Red 92) is mentioned in the historical treatise *The Dyeing of Paper Pulp* by Julius Erfurt, a practical manual, dated 1901, for use by papermakers, paper stainers, students and others, and phloxine B was detected by FT-Raman in one of the samples of actual dyed papers included in the book to illustrate each recipe [27]. In this case, it can be hypothesised that phloxine B was present in the powder as its aluminium lake, known as Pigment Red 174.

Azoic dyes

The two Hansa yellow pigments Pigment Yellow 3 and Pigment Yellow 1 (patented in 1910 and 1909,

respectively [10]) were identified in the green tube paint samples, along with Prussian blue (detected by FTIR). PY3 was the yellow component in the samples labelled as “Vert Anglais N° 2, 4, 5” (samples T15, T9 and T10 respectively) and in sample T19, labelled as “Vert Japonais Clair”, while T26 (“Vert Anglais N° 3”) contained both PY3 and PY1. The identification was based on the interpretation of UV-Vis spectra, high resolution mass spectra and tandem mass spectra [43].

Pigment Red 3, also known as Toluidine Red, patented in 1905 [10], was the colouring material in the tube T25 labelled “Rouge Japonais Foncé”. Pigment Red 115 was detected along with alizarin also in the paint tube T17 “Lac Carmineé fixe”. The identification was based on the interpretation of the UV-Vis spectrum, high resolution mass spectrum and tandem mass spectrum of the peak in the chromatogram [43]. Sample F5 (“Assiette à Dorer Rouge vif. 1914”) contained a pigment with molecular formula $C_{20}H_{14}O_4N_2S$, consistent with Acid Red 88 or



Acid Red 9 (both synthesised in 1877), or Acid Brown 6 (synthesised 1878). AR88 was excluded by comparison with a standard, and it was not possible to assign the compound to either AR9 or AB6 [26]. Most probably the pigment was prepared in an insoluble form by adsorption on an inert substrate such as kaolin (detected by IR spectroscopy as discussed elsewhere [26]).

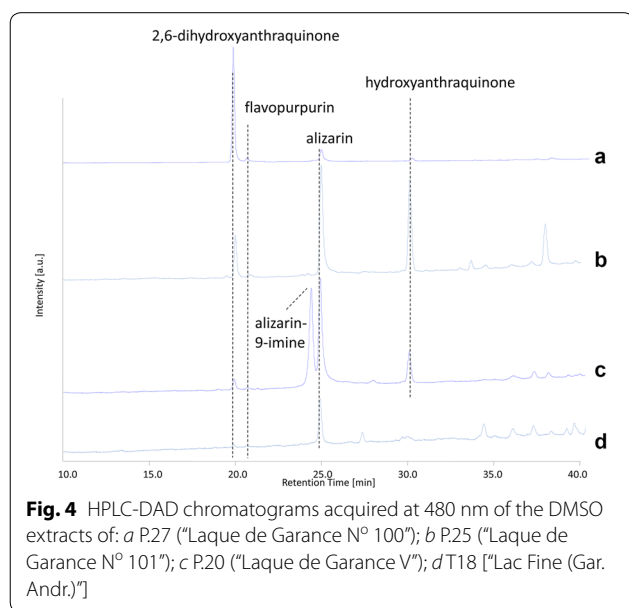
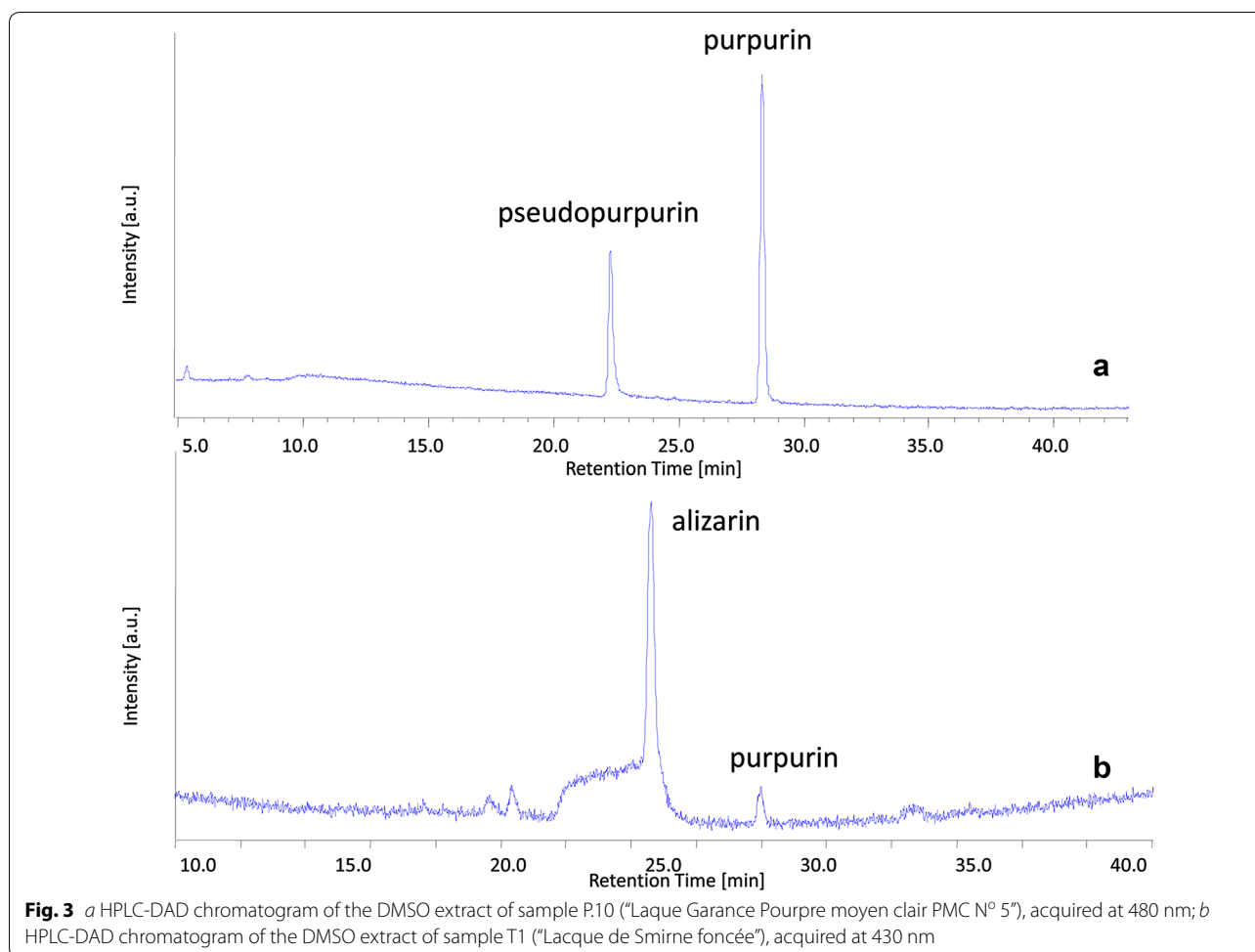
Murexide

Murexide was identified, according to its UV-Vis spectrum and the interpretation of the tandem mass spectrum, in the powder sample P.24, labelled as “Murexide Cristallisée” and dated 1890. This is the first case described in the scientific literature where murexide has been detected in a historical sample. The chromatogram, UV-Vis, MS and tandem MS spectra are provided in Fig. 2, and the fragmentation pattern entailing subsequent losses of isocyanic acid due to Retro Diels-Alder reactions is highlighted [44].

Madder, garance, and synthetic alizarin (and derivatives)

Two samples were labelled as “purpurine” and were obtained directly by extracting madder root (F17) or from purified madder root according to Kopp’s purpurin process (P.23) [4]. For these two samples, the labels correspond to the content of the sample, since “purpurine commerciale” typically refers to Kopp’s purpurin and/or a madder that has been partially purified.

A total of 15 samples were labelled as “garance” (which generally corresponds to a lake pigment extracted from madder root). Of these, only seven were characterised by a chromatographic profile consistent with a natural origin of the dye. In particular, F3, 7, 19, and P.10 had a profile enriched in purpurin and pseudopurpurin, pointing to the use of the recipe that was used at that time to obtain Kopp’s purpurin [4]. The chromatogram of sample P.10 is shown in Fig. 3a. F6, 8, and 12 yielded a chromatographic profile showing mainly alizarin, with a lower amount of purpurin and other minor natural



anthraquinones, suggesting that in these cases the recipe to obtain garancine was adopted. Garancine is again most probably the pigment contained in sample T1, as suggested by a high content of alizarin and a low content of purpurin, only partially matching the label of the tube, which is “Laque de Smirne foncée” (the chromatogram is shown in Fig. 3b).

The other eight samples labelled as “garance” were of synthetic origin, since they contained in higher or lower amounts other anthraquinoid components, which are not of natural origin, in addition to alizarin. Three of them (P.20, P.25, P.27) contained alizarin at relatively low purity levels and one paint tube, namely T18 “Lac Fine (Gar. Andr.)”, contained alizarin and a very low amount of another product (see chromatograms in Fig. 4). The interpretation of the chromatograms of these samples and the identification of the above mentioned non-natural anthraquinones were based on the known synthetic pathways of alizarin [9], shown in Fig. 5, and on the interpretation

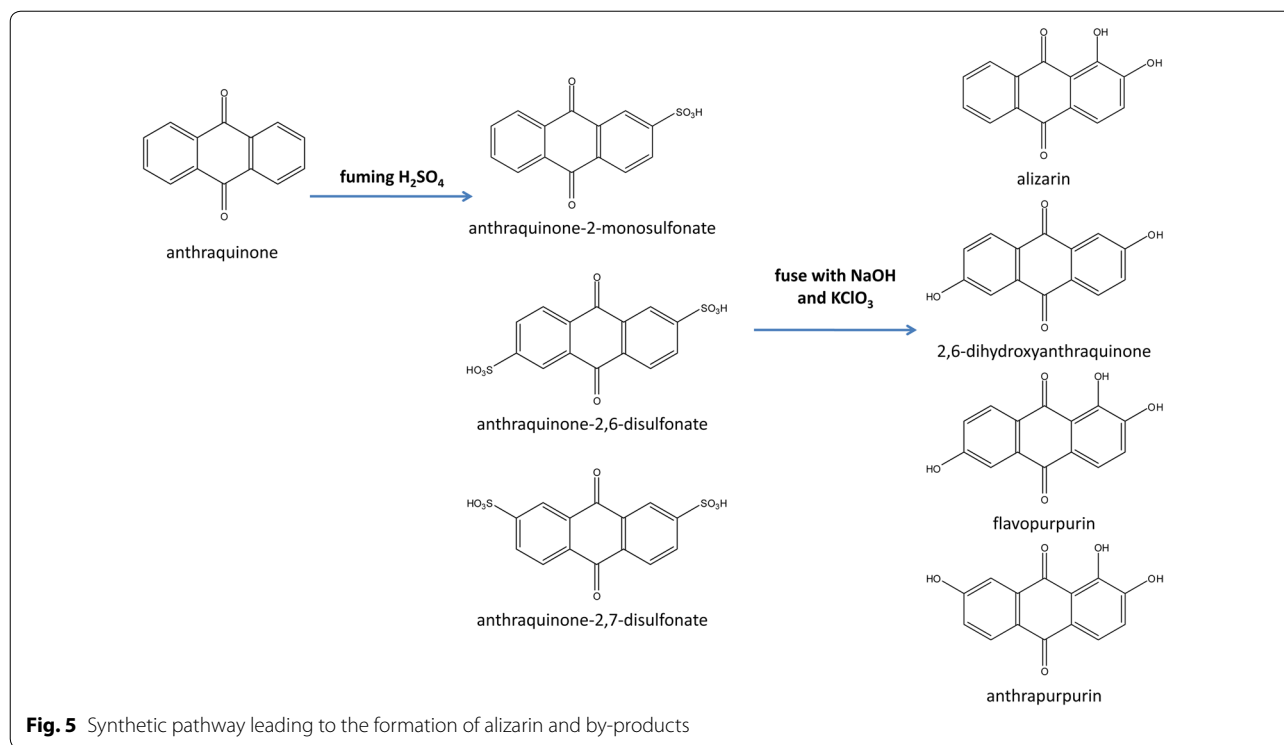


Fig. 5 Synthetic pathway leading to the formation of alizarin and by-products

of UV–Vis spectra [45, 46] and tandem mass spectra, reported in Fig. 6.

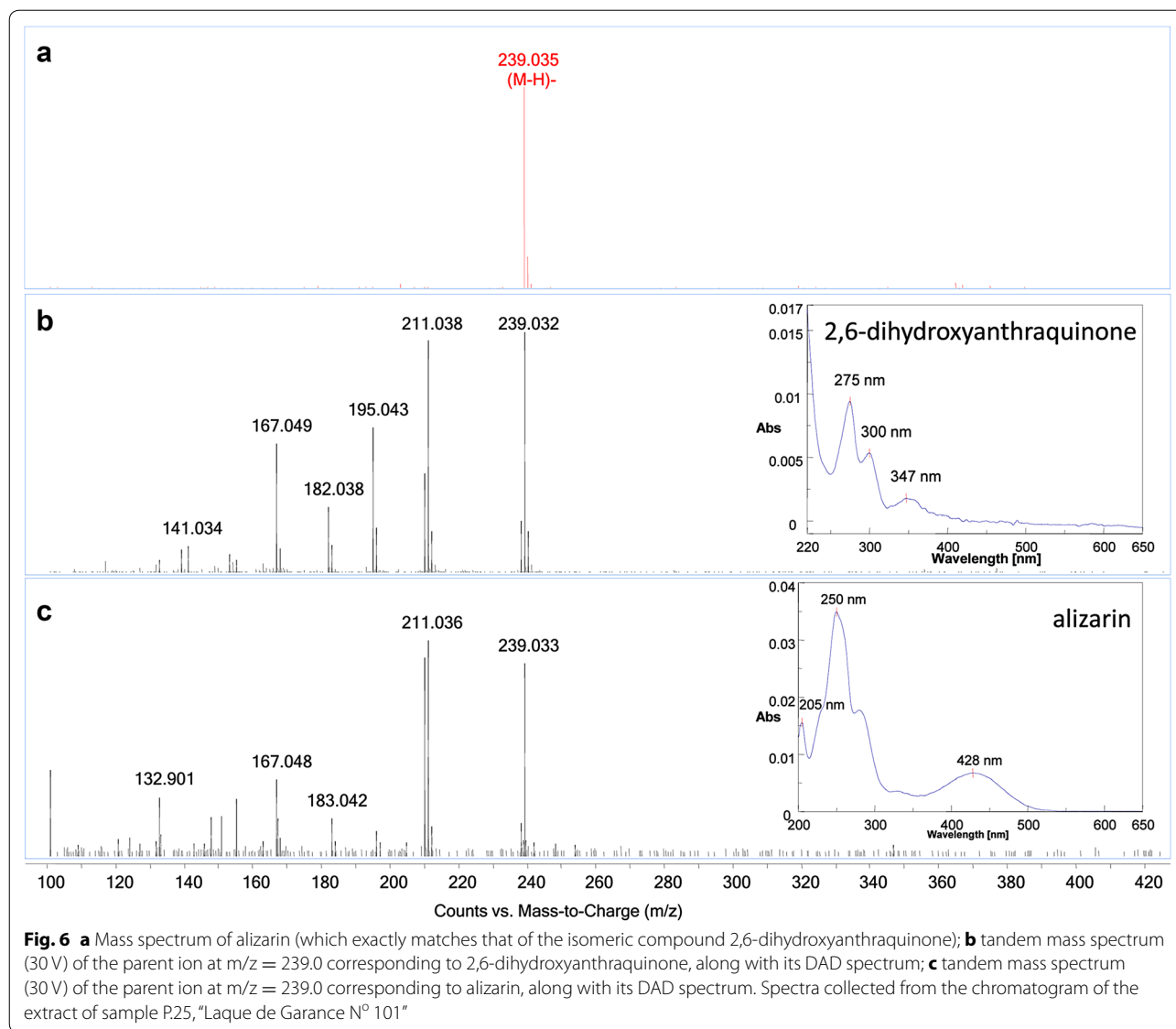
The acquisition of the exact mass and tandem mass spectra using the ToF spectrometer was an important tool for identifying interesting synthetic by-products, such as the yellow compounds 2,6-dihydroxyanthraquinone, flavopurpurin and a hydroxyanthraquinone (possibly 2-hydroxyanthraquinone, based on [9]). The presence of anthrapurpurin or other anthraquinones with hydroxyl substituents in 7-position was excluded by performing target mass spectrometric analyses in all the samples suspected to be synthetic alizarin. These findings may point to the application of specific synthesis conditions favouring the 2,6-substitution and thus leading to an excessive amount of by-products with respect to the target species. Flavopurpurin was detected by other authors in late 19th century textiles from the China National Silk Museum [15]. A mono-hydroxyanthraquinone was also identified in the samples from the Lefranc collection, but neither the UV–Vis nor the mass spectra located the position of the substituent unambiguously. One sample, namely P.20 (“Laque de Garance V”), also contained the imine form of alizarin (alizarin-9-imine). This species is easily formed when alizarin is treated with ammonia and one of its keto groups undergoes condensation; the imine form is in equilibrium with alizarin. Note that if the sample is extracted in acidic solution, the peak corresponding to the imine form disappears from the chromatogram.

The three powder samples F2, 4 and 9 and the paint sample P.26 contained a sulphonated purpurin, PR84 (available on the market since 1884). P.26 also contained the imine form of PR84 (also in this case, if the sample is extracted in acidic solution, the peak due to the imine form disappears from the chromatogram). The UV–Vis spectra and the tandem mass spectra of both PR84 and of the corresponding imine are reported in Fig. 7.

Finally, sample P.11, labelled as “Laq. Brune d’Alizarine”, contained not only alizarin (most probably of synthetic origin), but also Mordant Yellow 1, an early synthetic dye available on the market since 1887, known also as alizarin yellow. This species was identified based on the interpretation of the DAD and tandem mass spectra, and by comparison with the data presented in [47]. Since the sodium salt of Mordant Yellow 1 water is soluble, it was most probably incorporated into sample P.11 in an insoluble form, precipitated onto an inert substrate or most probably as its aluminium lake [48].

Conclusions

The chromatographic analysis of historical pigments and paint materials conserved in the Lefranc archives has provided information at a molecular level of the composition of the organic pigments in terms of main and minor components. The results enabled a comparison between the actual chemical composition of the pigments and the information reported on the labels of jars



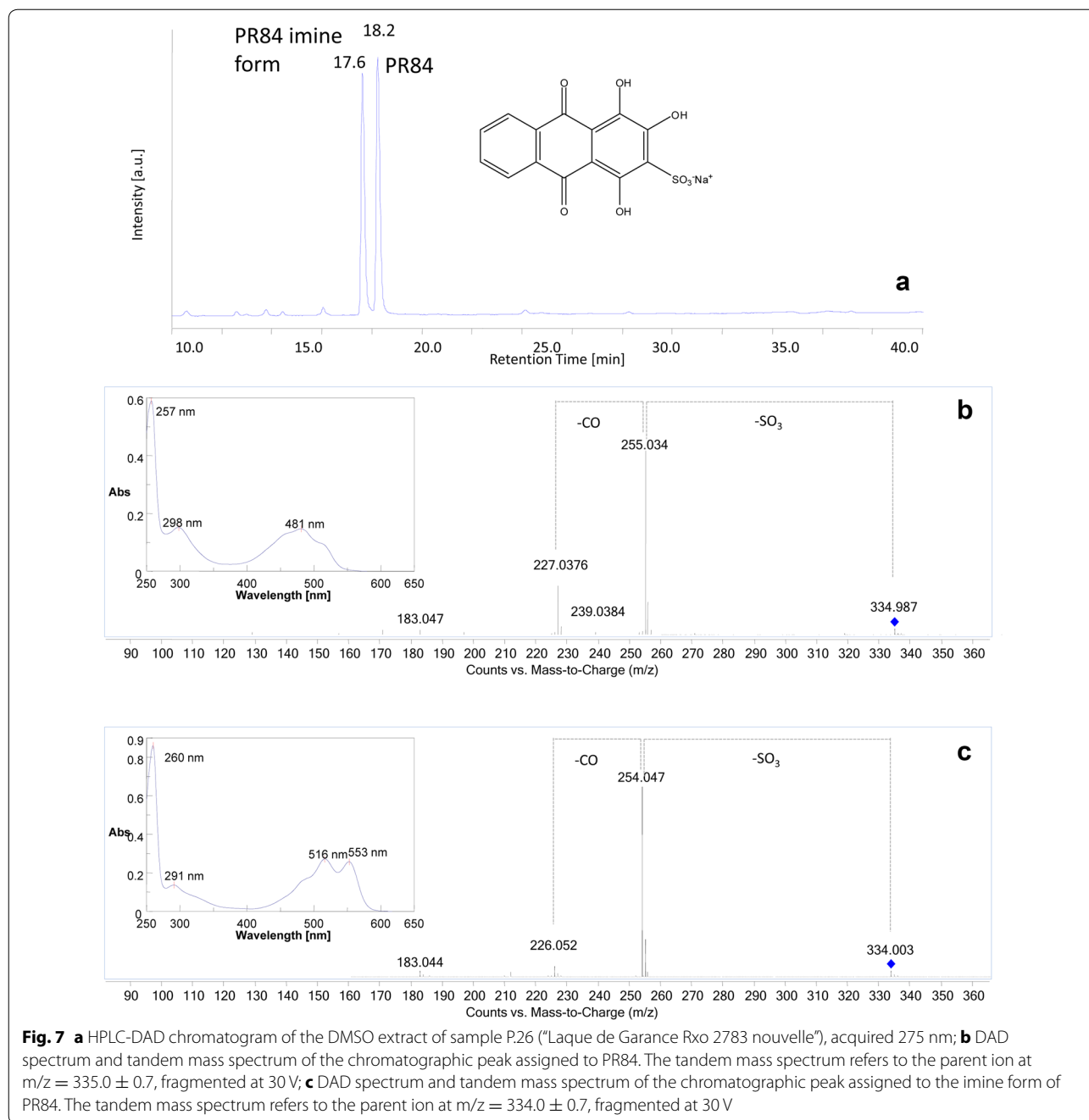
or paint tubes to be performed. Insights into the strategies used in Lefranc laboratories to produce the pigments were obtained, such as admixing natural and synthetic products and/or modifying natural products through targeted extraction procedures or treatments.

The results allowed a timeline to be proposed for the production of specific pigments in the laboratories of one of the main European producers of paint materials in the period of the revolution of paint formulations, between the late 19th and the first decades of the 20th century. In particular, it was possible to date most of the specimens analysed, or at least to determine the earliest time they could have been manufactured. The results are summarised in Table 1.

The results of the chemical analysis show that the labels on the powders reflected the expected colour of

the specimens more than the actual composition of the lake pigment. It is important to note that these materials were the results of experiments aimed at substituting or improving certain existing products, as highlighted in some of the labels (e.g. P.22). Moreover, the labels on the paint tubes carried only partial information.

Although a complete picture can only be achieved when the chromatographic data are integrated with those obtained by elemental analysis and vibrational spectroscopies, as in [26], thanks to the chromatographic analysis, specific recipes to obtain selected hues were hypothesised for several samples, namely to obtain garancine and Kopp's purpurin. Written sources are currently being studied by art historians in the framework of the Futurhama project, since the interpretation of the information within the laboratory notebooks related to the archive



materials can be exploited to complement the analytical results. So far this aspect of the research has been hampered due to the incompleteness and ambiguity of these notebooks [38].

In any case, it is still possible to conclude that since 1910 the synthetic pigments were present in almost all the formulations, but natural red pigments were not abandoned immediately, especially in the “surfin” (of superior quality) colors. Only the best performing powders were included in the commercial paint tubes. For

instance, high amounts of synthesis by-products of alizarin were present in three powders, but only traces of one by-product (flavopurpurin) were detected in one paint tube containing alizarin. This by-product can thus be used as a molecular marker to assess the presence of synthetic alizarin in actual paint samples.

The results obtained in this study represent a starting point for the further characterization of other manufacturers’ archives, the study of artist’s studio materials, and of actual paint samples. A comparison of the

chromatographic profiles of the Lefranc pigments with those of historical/contemporary/modern paint samples can be an excellent tool for solving dating and attribution issues. A database of chromatographic profiles and spectra was created, which can be exploited in future comparisons with other archival or atelier materials and with results obtained from samples from artworks.

Finally, knowledge of the formulations used by the producers and introduced in artworks between the end of the 19th century and the first decades of the 20th century plays a fundamental role in understanding degradation and fading phenomena observed as a result of ageing.

Additional file

Additional file 1: Table S1. Molecular structures of mentioned compounds (6)(10).

Authors' contributions

ID interpreted the mass spectra and drafted the manuscript; PT prepared the samples, ran the chromatographic analyses and interpreted the data; FM supervised the project and edited the manuscript; DK provided the samples and cooperated in the historical interpretation of the analytical data. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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References

- Ghelardi E, Degano I, Colombini MP, Mazurek J, Schilling M, Learner T. A multi-analytical study on the photochemical degradation of synthetic organic pigments. *Dyes Pigments*. 2015;123:396–403.
- de Keijzer M, van Bommel MR, Keijzer RHD, Knaller R, Oberhumer E. Indigo carmine: understanding a problematic blue dye. *Stud Conserv*. 2012;57:87–95.
- Herbst W, Hunger K. *Industrial organic pigments*. Weinheim: Wiley; 2004.
- Kirby J, Spring M, Higgitt C. The technology of eighteenth- and nineteenth-century red lake pigments. *Natl Gallery Tech Bull*. 2007;28:69–95.
- Saunders D, Kirby J. Light-induced colour changes in red and yellow lake pigments. *Natl Gallery Tech Bull*. 1994;15:79–97.
- Society of Dyers and Colourists. *Colour index 1971*. 3rd ed. Bradford: Society of Dyers and Colourists; 1971.
- Cooksey C. <http://www.chriscooksey.demon.co.uk>, <http://www.chriscooksey.demon.co.uk/murexide/index.html>. Accessed 20 Nov 2016.
- Dronsfield A, Brown T, Cooksey C. Synthetic alizarin—the dye that changed history. *Dyes Hist Archaeol*. 2001;16(17):34–8.
- Fieser LF. The discovery of synthetic alizarin. *J Chem Educ*. 1930;7:2609–33.
- de Keijzer M. The delight of modern organic pigment creations. In: van den Berg KJ, Burnstock A, de Keijzer M, Krueger J, Learner T, de Tagle A, et al., editors. *Issues in contemporary oil paint*. Cham: Springer International Publishing; 2014. p. 45–73.
- Degano I, Ribechini E, Modugno F, Colombini MP. Analytical methods for the characterization of organic dyes in artworks and in historical textiles. *Appl Spectrosc Rev*. 2009;44:363–410.
- Sanyova J, Reisse J. Development of a mild method for the extraction of anthraquinones from their aluminum complexes in madder lakes prior to HPLC analysis. *J Cult Herit*. 2006;7:229–35.
- van Bommel MR, Vanden Berghe I, Wallert AM, Boitelle R, Wouters J. High-performance liquid chromatography and non-destructive three-dimensional fluorescence analysis of early synthetic dyes. *J Chromatogr A*. 2007;1157:260–72.
- Liu J, Zhou Y, Zhao F, Peng Z, Wang S. Identification of early synthetic dyes in historical Chinese textiles of the late nineteenth century by high-performance liquid chromatography coupled with diode array detection and mass spectrometry. *Color Technol*. 2016;132:177–85.
- Sousa MM, Melo MJ, Parola AJ, Morris PJT, Rzepa HS, Seixas de Melo JSA. Study in mauve: unveiling Perkin's dye in historic samples. *Chem A Eur J*. 2008;14:8507–13.
- van Bommel MR, Geldof M, Hendriks E. An investigation of organic red pigments used in paintings by Vincent van Gogh (November 1885 to February 1888). *ArtMatters*. 2005;3:111–37.
- de Keijzer M, van Bommel MR, Geldof M. Early synthetic organic lake pigments used by Vincent van Gogh at the end of his lifetime. In: *EU-Artech symposium on Vincent van Gogh and contemporaries*, Amsterdam; 2009.
- Lomax SQ, Learner T. A review of the classes, structures, and methods of analysis of synthetic organic pigments. *J Am Inst Conserv*. 2006;45:107–25.
- Rosi F, Grazia C, Fontana R, Gabrielli F, Pensabene Buemi L, Pampaloni E, et al. Disclosing Jackson Pollock's palette in *Alchemy* (1947) by non-invasive spectroscopies. *Herit Sci*. 2016;4:18–31.
- Pozzi F, van den Berg KJ, Fiedler I, Casadio F. A systematic analysis of red lake pigments in French Impressionist and Post-Impressionist paintings by surface-enhanced Raman spectroscopy (SERS). *J Raman Spectrosc*. 2014;45:1119–26.
- Burgio L, Clark RJH. Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. *Spectrochim Acta Part A*. 2001;57:1491–521.
- Ropret P, Centeno SA, Bukovec P. Raman identification of yellow synthetic organic pigments in modern and contemporary paintings: reference spectra and case studies. *Spectrochim Acta Part A*. 2008;69:486–97.
- Scherrer NC, Stefan Z, Francoise F, Renate K. Synthetic organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection. *Spectrochim Acta Part A*. 2009;73:505–24.
- Vandenabeele P, Moens L, Edwards HGM, Dams R. Raman spectroscopic database of azo pigments and application to modern art studies. *J Raman Spectrosc*. 2000;31:509–17.
- Fremout W, Saverwyns S. Identification of synthetic organic pigments: the role of a comprehensive digital Raman spectral library. *J Raman Spectrosc*. 2012;43:1536–44.
- Lomax SQ, Schilling M, Learner T. The identification of synthetic organic pigments by FTIR and DTMS. In: Learner T, Smithen P, Krueger JW, Schilling MR, editors. *Modern paints uncovered*. London: Getty Conservation Institute, Tate Modern; 2007. p. 105.

27. Gabrieli F, Doherty B, Miliani C, Degano I, Modugno F, Uldank D, et al. Micro-Raman and SER spectroscopy to unfold Lefranc's early organic pigment formulations. *J Raman Spectrosc*. 2016;47:1505–13.
28. Casadio F, Mauck K, Cheftiz M. R. F. Direct identification of early synthetic dyes: FT-Raman study of the illustrated broadside prints of José Gaudalupe Posada (1852–1913). *Appl Phys A*. 2010;100:885–99.
29. Chieli A, Sanyova J, Doherty B, Brunetti BG, Miliani C. Chromatographic and spectroscopic identification and recognition of ammoniacal cochineal dyes and pigments. *Spectrochim Acta Part A Mol Biomol Spectrosc*. 2016;162:86–92.
30. Ghelardi E, Degano I, Colombini MP, Mazurek J, Schilling M, Learner T. Py-GC/MS applied to the analysis of synthetic organic pigments: characterization and identification in paint samples. *Anal Bioanal Chem*. 2015;407:1415–31.
31. Learner T. *Analysis of modern paints*. Los Angeles: Getty Conservation Institute; 2005.
32. Russell J, Singer BW, Perry JJ, Bacon A. The identification of synthetic organic pigments in modern paints and modern paintings using pyrolysis-gas chromatography–mass spectrometry. *Anal Bioanal Chem*. 2011;400:1473–91.
33. Carlesi S, Bartolozzi G, Cucci C, Marchiafava V, Picollo M, La Nasa J, et al. Discovering “The Italian Flag” by Fernando Melani (1907–1985). *Spectrochim Acta Part A Mol Biomol Spectrosc*. 2016;168:52–9.
34. Menke CA, Rivenc R, Learner T. The use of direct temperature-resolved mass spectrometry (DTMS) in the detection of organic pigments found in acrylic paints used by Sam Francis. *Int J Mass Spectrom*. 2009;284:2–11.
35. Boon JJ, Learner T. Analytical mass spectrometry of artists' acrylic emulsion paints by direct temperature resolved mass spectrometry and laser desorption ionisation mass spectrometry. *J Anal Appl Pyrol*. 2002;64(2):327–44.
36. Kirby DP, Khandekar N, Sutherland K, Price BA. Applications of laser desorption mass spectrometry for the study of synthetic organic pigments in works of art. *Int J Mass Spectrom*. 2009;284:115–22.
37. <http://www.futurahma.it/en/home/>. Accessed 5 Dec 2016.
38. Cleaning modern oil paints. <http://www.tate.org.uk/about/projects/cleaning-modern-oil-paints>. Accessed 5 Dec 2016.
39. Buzzegoli E, Kunzelman D, Patti M. Colori nuovi per una pittura moderna. In: Nuanciers e dossier di laboratorio dall'archivio storico Lefranc. vol. 27. Firenze: OPD Restauro. 2016; p. 92–113.
40. Nowik W. The possibility of differentiation and identification of red and blue 'soluble' dyewoods: determination of species used in dyeing and chemistry of their dyestuffs. *Dyes Hist Archaeol*. 2001;16(17):129–44.
41. Colombini MP, Andreotti A, Baraldi C, Degano I, Łucejko JJ. Colour fading in textiles: a model study on the decomposition of natural dyes. *Microchem J*. 2007;85:174–82.
42. Lech K, Wilicka E, Witowska-Jarosz J, Jarosz M. Early synthetic dyes—a challenge for tandem mass spectrometry. *J Mass Spectrom*. 2013;48:141–7.
43. Kamel AM, Munson B. Collisionally-induced dissociation of substituted pyrimidine antiviral agents: mechanisms of ion formation using gas phase hydrogen/deuterium exchange and electrospray ionization tandem mass spectrometry. *J Am Soc Mass Spectrom*. 2007;18:1477–92.
44. Szostek B, Orska-Gawrys J, Surowiec I, Trojanowicz M. Investigation of natural dyes occurring in historical Coptic textiles by high-performance liquid chromatography with UV–Vis and mass spectrometric detection. *J Chromatogr A*. 2003;1012:179–92.
45. Khan MS, Khan ZH. Electronic absorption spectra of hydroxy-substituted anthraquinones and their interpretation using the ZINDO/S and AM 1 methods. *Can J Anal Sci Spectrosc*. 2002;47:146–56.
46. da Costa Nogueira Souto CS. Analysis of early synthetic dyes with HPLC-DAD-MS. An important database for analysis of colorants used in cultural heritage. Thesis for the Master Degree in Conservation and Restoration of Textiles. Lisbon; 2010.
47. Ihara K, Hasegawa SI, Naito K. The separation of aluminium (III) ions from the aqueous solution on membrane filter using Alizarin Yellow R. *Talanta*. 2008;75:944–9.
48. Kirby J. The reconstruction of late 19th-century French red lake pigments. In: Clarke M, Townsend JH, Stijnman A, editors. *Art of the past—sources and reconstructions, ATSR proceedings*. London: Archetype Publications; 2005. p. 69–77.