RESEARCH PAPER

Py-GC/MS applied to the analysis of synthetic organic pigments: characterization and identification in paint samples

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Abstract A collection of 76 synthetic organic pigments was analysed using pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS). The purpose of this work was to expand the knowledge on synthetic pigments and to assess characteristic pyrolysis products that could help in the identification of these pigments in paint samples. We analysed several classes of synthetic pigments not previously reported as being analysed by this technique: some metal complexes, β-naphthol pigment lakes, BONA pigment lakes, disazopyrazolone, triarylcarbonium, dioxazine, anthraquinone, indanthrone, isoindoline and thioindigo classes. We also report for the first time the Py-GC/MS analysis of a number of naphthol AS, benzimidazolone, phthalocyanine and perylene pigments and other miscellaneous pigments including pigments with unpublished chemical structure. We successfully used the Py-GC/MS technique for the analysis of paints by artists Clyfford Still and Jackson Pollock to identify the synthetic organic pigments and the binding media.

Introduction

The rapid development of synthetic chemistry during the nineteenth century, partly driven by the textile dying industry, led to the development of synthetic organic pigments.

Synthetic organic pigments now dominate the colourant market and have partially replaced traditional natural organic colourants.

The term "synthetic organic pigment" refers specifically to those pigments that are synthesised in a laboratory and must be distinguished from natural organic pigments obtained from plants or animal sources.

Synthetic pigments are classified in the Colour Index, a reference record for all the dyes and pigments, created by the Society of Dyers and Colourists. The pigments are recorded by a generic name and a number. In this work, we use the Colour Index names [1] to indicate the pigments analysed. Several classification systems have been proposed for synthetic organic pigments; in this work, we have adopted the one of Herbst and Hunger [2], based on the chemical constitution.

The identification of the pigments in a work of art is of paramount importance to improve the knowledge on the work of art itself, on the historical context, on the artist and on the painting technique. Moreover, in selected cases, it may allow to solve authenticity, attribution and conservation problems.

The main issue in synthetic organic pigments analysis is their difficult detection and identification, particularly in complex matrixes such as paint samples. The main reasons are: the great range of possible analytes (hundreds of such pigments,

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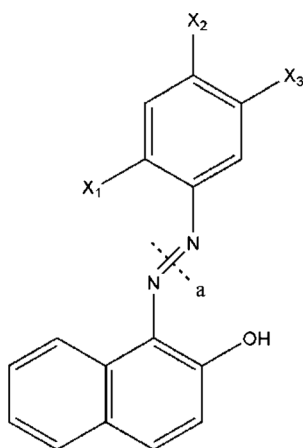
Fig. 1 Structure of β-naphthol pigment lakes with breaking points highlighted

compared to a handful of traditional ones), their small particle size, usually less than 1 μm, and the low concentration of the pigment in paint formulations, sometimes less than 1 % or lower.

Moreover, organic pigments, both natural and synthetic, are subjected to photo-induced degradation, which may further reduce their concentration in the paint sample. Thus, their detection is more challenging, compared to that of inorganic pigments.

Several techniques are used in the analysis of synthetic pigments, mainly FTIR and Raman spectroscopies [3–9], direct temperature mass spectrometry (DTMS) [9–11], laser desorption mass spectrometry (LDMS) [11, 12] and pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) [13–15]. A review by Lomax and Learner focuses on the chemistry, properties, and uses of synthetic organic pigments and examines in depth the analytical techniques currently used for the analysis of these materials [16].

The creation of a library of the chemical-physical properties of synthetic organic pigments is fundamental for their identification in unknown samples. Raman libraries already exist, while an equivalent library prepared with chromatographic techniques is lacking, mainly because authors have analysed only some classes of synthetic pigments. Moreover, the pyrolysis profiles highly depend on the instrumental parameters. The purpose of this work was to expand the knowledge on selected compounds by Py-GC/MS analysis and to integrate the work of other authors by assessing the characteristic pyrolysis products that can be useful in the identification.

In our study, we analysed with Py-GC/MS 76 synthetic pigments, 45 of them never previously reported as being analysed by this technique.

We report for the first time the Py-GC/MS analysis of the following classes of pigments: metal complex, β-naphthol pigment lakes, BONA pigment lakes, disazopyrazolone, triarylcarbonium, dioxazine, anthraquinone, indanthrone, isoindoline and thioindigo. We also analysed three pigments with unpublished chemical structure (PV51, PV52, PV53) and we expanded the data on the naphthol AS, benzimidazolone, phthalocyanine and perylene classes, with respect to the literature.

Our Py-GC/MS procedure for the analysis of synthetic pigments was successful in discriminating between the listed classes of synthetic pigments, and in several cases we were able to identify the pyrolysis products

Table 1 Pyrolysis products of β-naphthol pigment lakes

CI name	Substituents (Fig. 1)			Products of pyrolysis (main m/z)	
	X_1	$X2$	X_3	a	Others
PR49:1	2-Aminonaphthalene-1-sulfonic acid as diazo component				2-Naphthol (144, 115) 1-naphthalenamine (143, 115) dinaphtho[2,1b:1′,2′-d]furan[a] (268, 239, 119) – small peak
PR49:2	2-Aminonaphthalene-1-sulfonic acid as diazo component				2-Naphthol (144, 115) 1-naphthalenamine (143, 115) dinaphtho[2,1b:1′,2′-d]furan[a] (268, 239, 119) – most abundant peak
PR53:1	SO_3^-	Cl	CH_3	a-X_1-X_2: m-toluidine (106, 107, 77) a-X_1: 4-chloro-3-methylaniline (141, 106, 77)	9-chloro-5,6- dihydronaphtho[1,2-c]cinnoline (266, 231, 202)
PO46	SO_3^-	Cl	C_2H_5	a-X_1-X_2: m-toluidine (106, 107, 77)	9-chloro-5,6-dihydronaphtho[1,2-c]cinnoline (266, 231, 202)

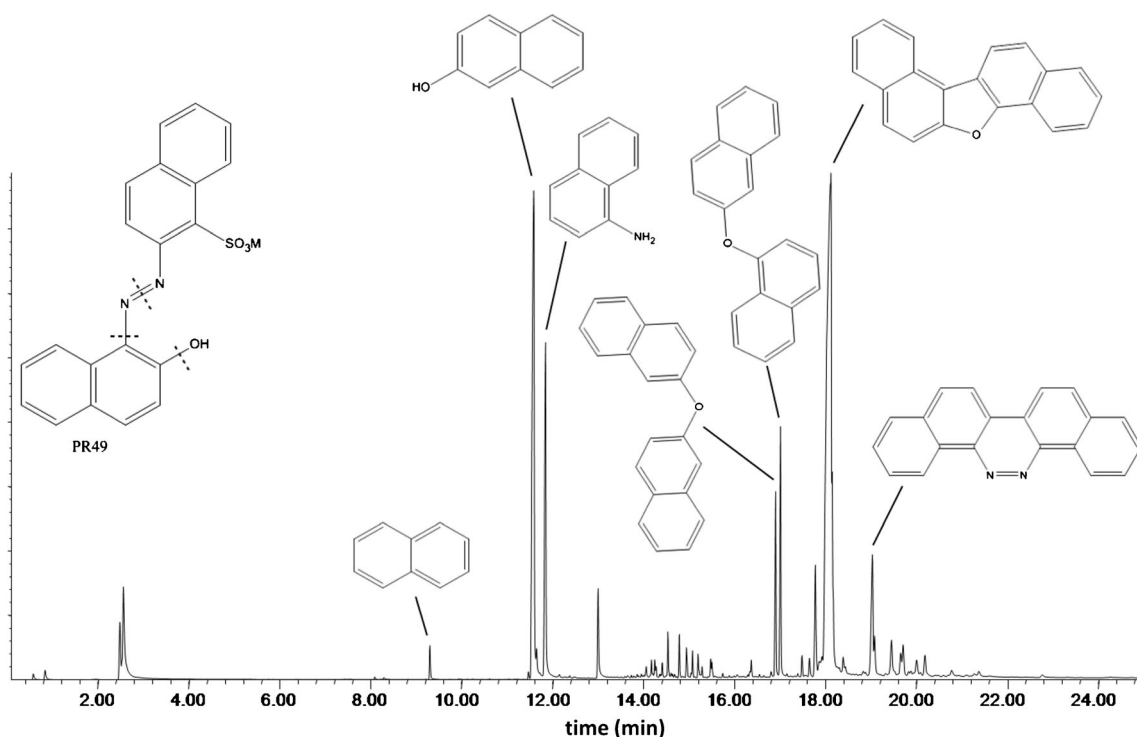[a] And the positional isomer dinaphtho[2,1b:1,2-d]furan

Fig. 2 Structure of PR49 (*left*) and pyrogram of PR49:2 with fragments produced by pyrolysis

characteristic of individual pigments that can be used as markers.

To further test our method, we applied our procedure to the analysis of selected pigments and paint samples from two 20th century American artists, Clyfford Still (1904–1980) and Jackson Pollock (1912–1956). Py-GC/MS was successful in identifying the synthetic organic pigments present in the analysed paint samples.

Fig. 3 Structure of BONA pigment lakes (*top*), with fragments produced by pyrolysis (*bottom*)
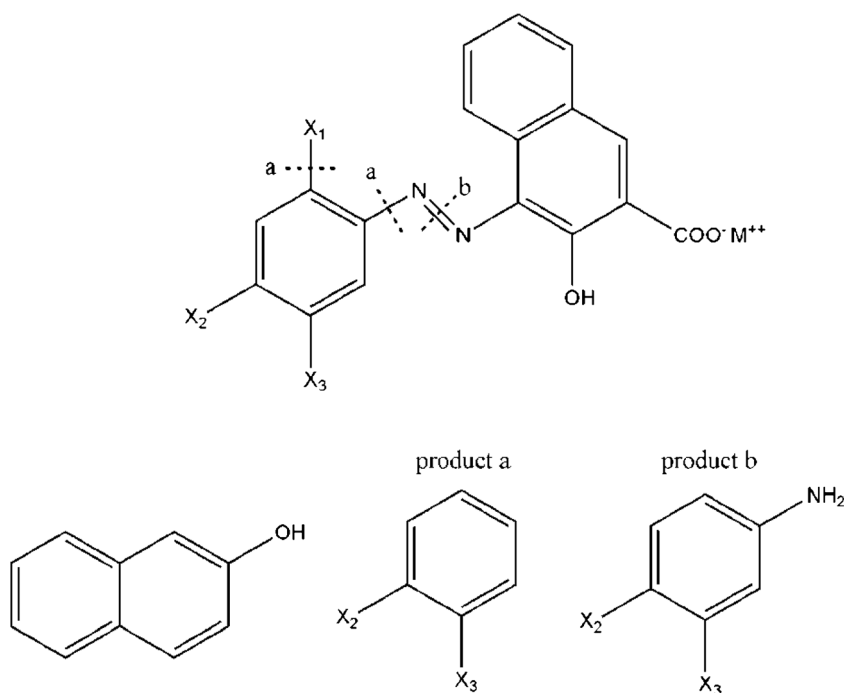
Table 2 Pyrolysis products of BONA pigment lakes

CI name	Substituents (Fig. 3)			Products (main m/z)			
	X_1	X_2	X_3	a	b	2-Naphthol	Others
PR48:1 and PR48:2	SO_3^-	CH_3	Cl		Benzenamine, 3-chloro-4-methyl (140, 141, 106)	(144, 115)	2-Naphthol, 1-amino (159, 130, 103) 8-chloro-5,6-dihydronaphtho[1,2-c]cinnoline(266, 231, 202)
PR52:1 and PR52:2	SO_3^-	Cl	CH_3	Benzene, 1-chloro-2-methyl (91, 126, 63)	m-Toluidine, 4-chloro- (141, 106, 77)	(144, 115)	9-Chloro-5,6-dihydronaphtho[1,2-c]cinnoline(266, 231, 202)
PR57:1	SO_3^-	CH_3	H		p-Toluidine (106, 107, 77)	(144, 115)	5,6-Dihydronaphtho[1,2-c]cinnoline (232, 231, 202)
PR63:1	2-Aminonaphthalene-1-sulfonic acid as diazo component					(144, 115)	1-Naphthalenamine (143, 115)dinaphtho[2,1b:1',2'-d]furan[a] (268, 239, 119) benzo[h]naphtho[1,2-c]cinnoline[a](280, 140, 126)

[a] And the positional isomer dinaphtho[2,1b:1,2-d]furan

[b] Or benzo[f]naphtho[2,1-c]cinnoline

Experimental

Reference pigment samples

Samples of synthetic organic pigments were collected from the Getty Conservation Institute's reference material collection. The pigments analysed are listed in the Electronic Supplementary Material (ESM), Table S1. In this work, we present only the results of the pigments never previously reported as being analysed by Py-GC/MS. For the other pigments, the results were consistent with the ones of other authors [13, 15].

Paint samples

Clyfford Still Ten samples from six different paintings and seven samples from the pigments found in the artist's studio were analysed with Py-GC/MS. The samples from Still's paintings included: three samples from "Untitled", dating 1948 (private collection); one sample from "Untitled" (1948); two samples from "Untitled", dating 1951–1952, one sample from "Untitled" (1954), and two samples from "Untitled" (1974), all owned by the San Francisco Museum of Modern Art; one sample from "Untitled" (1960), owned by the Hirshhorn Museum of Washington.

Jackson Pollock Two samples from "Mural" (1943) were analysed. The painting belongs to the University of Iowa Museum of Art and was from 2012 till 2014 at the Getty Center in Los Angeles, CA, undergoing a technical study and a conservation treatment [17].

Apparatus

Pyrolysis–gas chromatography/mass spectrometry was carried out on a 7890A gas chromatograph, coupled with a 5975C triple axis detector mass spectrometer (Agilent Technologies, USA), coupled with a EGA/PY 3030D multi-shot pyrolyzer (Frontier Laboratories, Japan). The pyrolysis was carried out at 550 °C for 12 s. The chromatographic separation was carried out on a DB-5 ms Ultra Inert column, 40 m×250 µm×0.25 µm (Agilent J&W, USA). The helium (purity 99.9995 %) flow rate was 1 mL/min. The inlet temperature of the GC was 320 °C, the MS transfer line was kept at 320 °C and the ion source at 230 °C. The GC injection program was: pulsed split mode, with an injection pulse pressure of 30 psi until 45 s. The split ratio was 20:1, with a split flow of 20 mL/min. The GC temperature program was: initial temperature 40 °C, held for 2 min, then ramped at 20 °C/min to 320 °C for 14 min.

For the Py-GC/MS analysis, we analysed the neat pigments, without any binder and without any derivatisation step.

Fragments were recognized using the NIST library of standards (the match factor was ≥90 %) and the AMDIS software (US National Institute of Standards and Technology, NIST). The most important unknown products for each pigment are reported and the mass spectra are shown in the ESM.

Results

Azo pigments

β-naphthol pigment lakes Historically, "lakes" referred to the first type of synthetic organic pigments made from water soluble dyes by formation of insoluble Al^{3+} complexes with alum. Today, these compounds are used as pigments after being rendered insoluble by conversion into insoluble alkali earth or manganese salts [2]. β-naphthol pigment lakes originated with the discovery of lithol red by Julius at BASF in 1899. Lithol red is one of the earliest colourants specifically developed as a pigment rather than a dyestuff. β-naphthol lakes, with sulfonic and/or carboxylic functional groups, are used in their insoluble form as alkali earth metals or manganese salts [2]. We analysed four pigments belonging to this class: lithol red PR49 (the barium PR49:1 and the calcium PR49:2 salts), PR53:1 and PO46 (both barium salts). PR49 and PO46 are currently used as inexpensive industrial paints, especially in the USA. PR53:1 is found in inexpensive colour pencils and water colours. Their structure is given in Fig. 1. The results obtained by interpreting the pyrograms achieved by the analysis of these four pigments are reported in Table 1. The pyrogram obtained for PR49:2 is presented in Fig. 2 as an example. The main products of pyrolysis for these pigments in our experimental conditions are those originated from the 2-naphthol structure. Thus, the analysed pigments have many products in common. As a consequence, their identification is very difficult. As an example, 2,2′-dinaphthyl ether is the only characteristic product of PR49, but it is not one of the most abundant. This result is not in
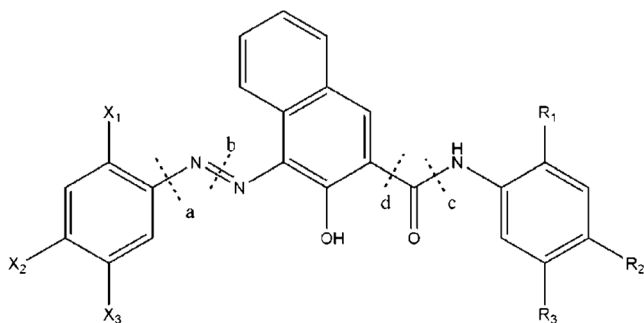

Fig. 4 Structure of Naphthol As pigments with breaking points highlighted

Table 3 Pyrolysis products of naphthol AS pigments

CI name	Substituents (Fig. 4)						Products (main m/z)				
	X_1	X_2	X_3	R_1	R_2	R_3	a	b	c	d	Others
PR7[a]	CH_3	Cl	H	CH_3	Cl	H	Benzene, 1-chloro, 3-methyl (91, 126, 63)	Benzenamine, 4-chloro, 2-methyl (106, 141, 140) b – X_2: o-toluidine (106, 107, 77)	Aniline (93, 66)	4-Chloro-o-tolyl isocyanate (167, 138, 132)	
PV44	OCH_3	Benzamide	OCH_3	H	H	H	Benzamide, N- (4-amino-5-methoxy-2-methylphenyl)- (256, 151, 105) a—X_2: benzamide (121, 105, 77) a—X_1-X_3: benzenamide, N-phenyl (105, 77, 197)				Benzoic acid, methyl ester (105, 77, 136) naphthol AS (170, 273, 115, 152)

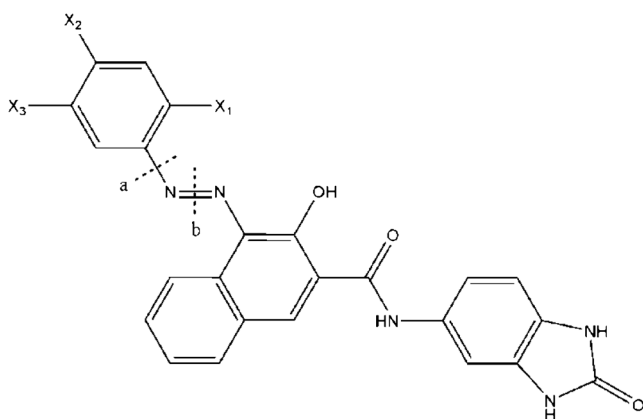[a] A Py-GC/MS analysis of PR7 has already been published by Sonoda [13]

Fig. 5 PV32 structure with breaking points highlighted

Table 5 Pyrolysis products of metal complex pigments

C.I. name	Products (main m/z)		
	a	*b*	Others
PGr8			Quinoline (129, 102) 2-naphthol (144, 115) 11-octadecenoic acid, methyl ester (264, 296, 55)
PGr10	Benzene, chloro- (112, 77, 114)	*p*-Chloroaniline (127, 129, 65)	Benzene, 1,3-dichloro (146, 148, 111) benzenamine, 2,6-dichloro-*N*-phenyl (237, 167, 239)

agreement with the data reported on PR49 by Stenger et al. [18]. In their work, many techniques were used for the analysis of PR49, one being Py-GC/MS. They report two pyrolysis products specific for the unambiguous identification of PR49, 2-naphthol and an unknown compound with m/z 268, 239, 134. We found, however, that 2-naphthol is a common pyrolysis product not only of the β-naphthol pigment lakes class, but of several other classes of synthetic pigments, and thus cannot be used as a marker for PR49. We identified the second compound indicated by Stenger as a characteristic product of PR49 as dinaphtho[2,1b:1′,2′-d]furan or dinaphtho[2,1b:1,2-d-]furan, which we found also in PR52, PR53 and PR63 pyrograms. Two isobaric peaks are present in the chromatogram at 17.7 and 18.0 min, which most probably correspond to the two positional isomers.

BONA pigment lakes These pigments derive their name from Beta-OxyNaphthoic Acid (BONA) which is used as a coupling component in their synthesis. We analysed six pigments belonging to this class: PR48 (the barium PR48:1 and the calcium PR48:2 salts), PR52 (the calcium PR52:1 and the manganese PR52:2 salts), PR57:1 and PR63:1 (both calcium salts). The structure of the BONA pigment lakes sub-class and the fragmentation pattern undergone by these compounds during pyrolysis is shown in Fig. 3, and the products originated from the

pyrolysis are summarized in Table 2. Pyrolysis causes decarboxylation on the naphthol ring and loss of X_1 substituent. Moreover, the azo bond is broken, leading to the formation of 2-naphthol and X_2 and X_3 substituted benzene and benzenamine. As expected, no significant differences were observed in the pyrograms of pigments that differ only for the metal ion.

Naphthol AS pigments Naphthol AS is one of the most important groups of azo pigments in the paint industry; these pigments were first synthesised in 1911.

We have integrated the work of Russell et al. [15] on naphthol AS pigments by analysing PR7 and PV44. The structure and the fragmentation pattern for this class of pigments are reported in Fig. 4.

The results for PR7 are consistent with the ones described by Russell: the pigment shows two characteristic pyrolysis products (products a and b of Russell's scheme) and also *o*-toluidine. The pyrolysis of PV44, instead, yields aniline and 2-naphthol, which are products common to several classes of pigments, but also other characteristic products not attributable to the fragmentation pattern indicated by Russell (see Table 3), for example the product "a" with the loss of X_2 substituent, or with the loss of both X_1 and X_3 substituents.

Table 4 Pyrolysis products of PV32, benzimidazolone violet

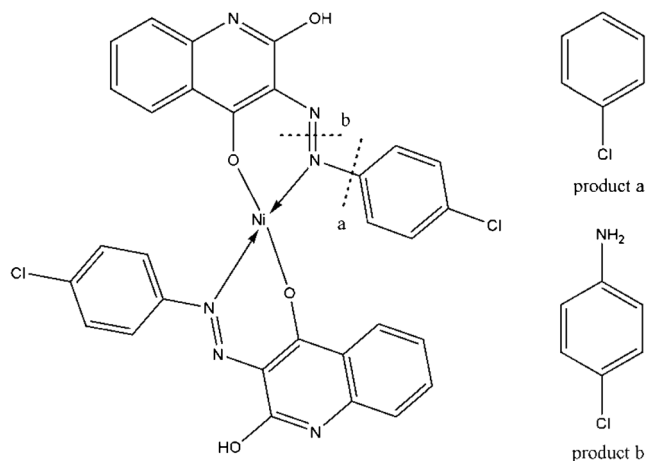| C.I. name	Substituents (Fig. 5)			Products (main m/z)		
	X_1	X_2	X_3	*a*	*b*	Others
PV32	OCH$_3$	SO$_2$NHCH$_3$	OCH$_3$	/	b-X_2: benzenamine, 2,5-dimethoxy (138, 153, 110)	Unknown product (231, 170, 107) unknown product (246, 231, 168, 202)

Fig. 6 *PGr10 with fragments produced by pyrolysis*

Benzimidazolone pigments Developed and patented by Hoechst in 1960, the benzimidazolones are monoazo pigments with the 5-aminocarbonyl benzimidazolone group. The main pyrolysis product of PV32, in Fig. 5, is 2-naphthol. Other characteristic products not attributable to the fragmentation pattern indicated in the literature by Russell [15] for this class of pigments are also present in the pyrogram. Their main *m/z* are listed in Table 4.

Metal complex pigments First developed around 1920, many metal complex pigments did not appear on the market until the late 1940s. Only a few azo metal complexes are available as pigments. The chelating metal is usually nickel, and less commonly, cobalt or iron(II). We analysed two green
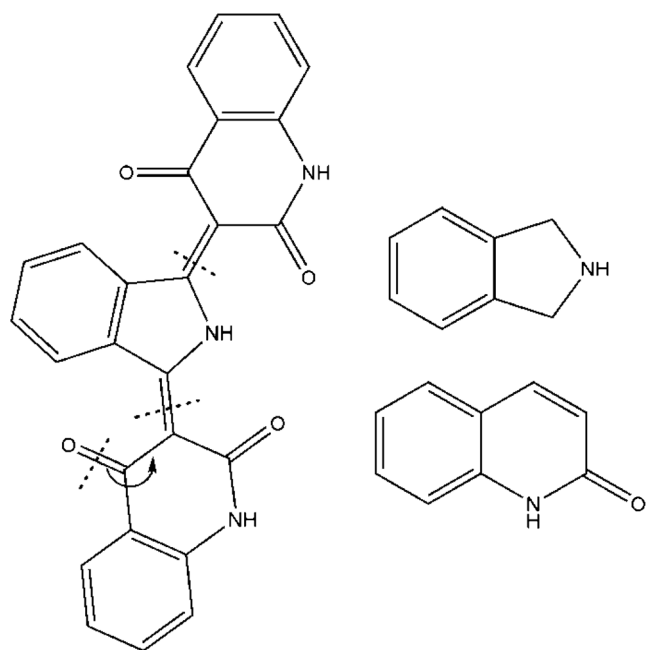
Table 6 Pyrolysis products of PBr38

C.I.name	Products (main *m/z*)
PBr38	2(1*H*)-quinolinone (145, 117, 90) Indole (117, 90, 63) Aniline (93, 66) 1*H*-isoindole-1,3(2*H*)-dione (147, 76, 104)

pigments, PGr8 and PGr10. PGr8 is used in emulsion paints. PGr10, a nickel azo complex that has been known since 1947, is used primarily in high-grade industrial paints [2].

The Py-GC/MS results are listed in Table 5. Interestingly, the pyrogram of PGr8 highlights the presence of the methyl ester of 11-octadecenoic acid, which could have been used in the synthesis of the pigment as in the case of PR83, whose pyrolysis profile will be discussed later on.

The structure of PGr10 is shown in Fig. 6, with the main fragments produced by pyrolysis.

Isoindoline pigments This high-quality products class was introduced in the mid-1960s and is characterized by the
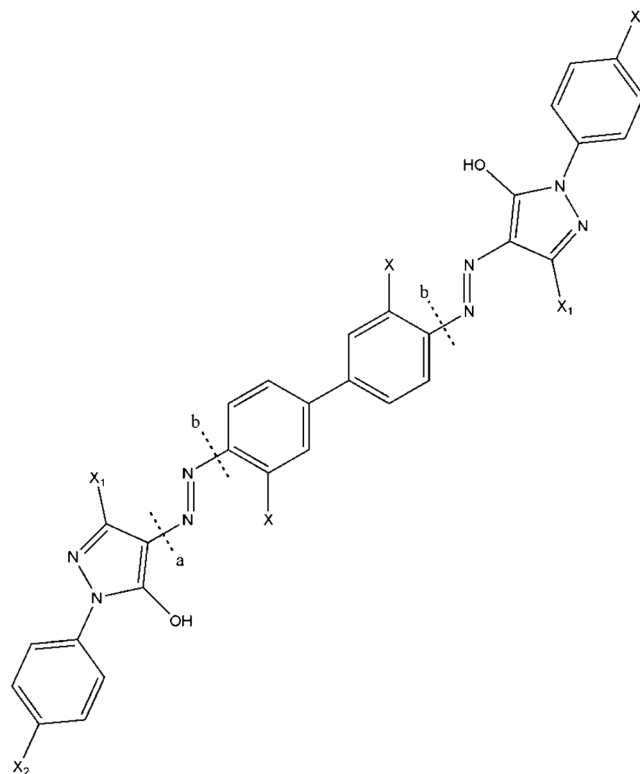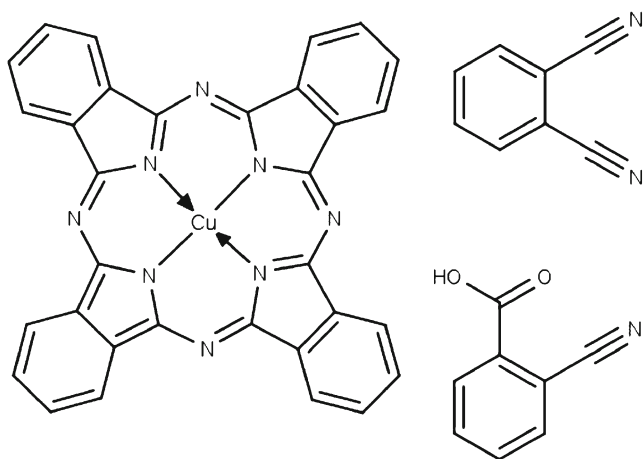

Fig. 7 *PBr38 structure (left), with fragments produced by pyrolysis: indole (top right) and 2(1H)-quinolinone (bottom right)*

Fig. 8 *PR41 structure with breaking points highlighted*

Table 7 Pyrolysis products of PR41

C.I. name	Substituents (Fig. 8)			Products (main m/z)		
	X	X_1	X_2	a	b	Others
PR41	OCH$_3$	H	H	Norphenazone (174, 77, 91)	1,1′Biphenyl, 3,3′dimethoxy (214, 171, 128)	Benzene, isocyanato (119, 91, 64) Aniline (93, 66)

Fig. 9 Structure of phthalocyanine pigments (*left*) with fragments of the PB15 series produced by pyrolysis: 1,2-dicyanobenzene (*top right*) and *o*-cyanobenzoic acid (*bottom right*)

isoindoline ring. We analysed PBr38, a methine-type isoindoline pigment. The commercial type was used as a colourant for plastics, especially for PVC and LDPE, but it was withdrawn from the market [2]. The fragmentation pattern and the pyrolysis products are shown in Fig. 7 and listed in Table 6. The 2(1*H*)-quinolinone is a characteristic pyrolysis product of this pigment.

Disazopyrazolone pigments In the early 1950s, Ciba researchers succeeded in synthesising red disazo compounds of relatively high molecular weight. These products were known as disazo condensation pigments [2]. PR41 is also known as pyrazolone red. The structure is shown in Fig. 8, and the products of pyrolysis are listed in Table 7.

Polycyclic pigments

Phthalocyanine pigments Phthalocyanines are among the most important modern synthetic organic pigments used in artists' paint formulations. Phthalo blues were first introduced in 1935, while phthalo greens in 1938 (chlorinated) and 1959 (chlorinated and brominated) [16]. We extended the work of Russell [15] and Sonoda [13] on phthalocyanine pigments by

Table 8 Pyrolysis products of the phthalocyanine pigments

Product (main m/z)	PB15:0[a]	PB15:1	PB15:2	PB15:3	PB15:4	PB15:6	PB17	PB76	PGr13
Methenamine (42, 140)							X		
Tetrahydrofuran (42, 72)						X			
Benzene, 1,3 dimethyl (91, 106)	X	X							
Benzonitrile (103, 76)	X			X					X
2-Oxepanone (55, 42, 84)					X				
Benzene, 1,2,4 trichloro (180, 182, 144)	X								
Benzene, 1-(1-methylethenyl)-3-(1-methylethyl) (145, 160, 117)				X					
1,2-Dicyanobenzene (128, 101)	X	X	X	X	X	X	X	X	X
o-Cyanobenzoic acid (147, 76, 104)	X	X	X	X	X	X			X
Benzene, 1,1′-(1methylethylidene)bis (181, 196, 103)				X					
Oleic acid (55, 264)					X				
Unknown product (160, 188, 189)						X			
Naphthalene, 1,5-dichloro (196, 198, 200)								X	
Naphthalene, 2,3,6-trichloro (230, 232, 234)								X	
Tetrachloroisophthalonitrile (266, 264, 268)								X	

[a] A Py-GC/MS analysis of PB15 has already been published by Sonoda [13]

analysing PB16, PB17, PB76, PGr13 and all the PB15 crystal modifications: PB15:0, PB15:1, PB15:2, PB15:3, PB15:4, PB15:6. The main products are shown in Fig. 9 and listed in Table 8. We confirmed that 1,2-dicyanobenzene is a characteristic pyrolysis product of the phthalocyanine pigments class. We found also that the pyrograms of the PB15 series contain the characteristic *o*-cyanobenzoic acid that can be considered as a marker and thus can help in the identification of this pigment.

PB15 has been already analysed by Sonoda [13]; he observed only a small peak corresponding to 1,2-dicyanobenzene, while we were able to identify other specific products, listed in Table 8.

As for the other phthalocyanine pigments analysed, PGr13 shows *o*-cyanobenzoic acid as the PB15 series, but it can be distinguished on the basis of its different colour. The pyrogram of PB76 is characterized by products originated from the chlorinated substituents.

Quinacridone pigments Quinacridone pigments have excellent fastness and resistance properties and have been used since their appearance on the market in high-quality artists' materials [2].

We analysed PV19 and PV42. The formulation of PV42, a mixed phase pigment, has never been published yet. The results are shown in Table 9. The pyrogram of PV19 shows an unknown product, while that of PV42 contains several products, one being the characteristic 2-methylacridone (Fig. 10).

Although the pyrolysis profile does not allow us to hypothesise the formulation of PV42 pigment, it might be used for its identification in unknown paint samples.

Anthraquinone and indanthrone pigments This class groups those pigments sharing the 9,10-anthraquinone skeleton. PR83, alizarin crimson, is an hydroxyanthraquinone pigment and the synthetic counterpart of the natural madder lake. The identification of PR83 by Py-GC/MS is possible on the basis of its characteristic fragments (phenanthrene; anthrone; 9,10-anthracenedione; 9,10-anthracenedione-2-hydroxy). The only
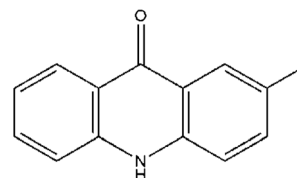

Fig. 10 2-Methylacridone, a characteristic pyrolysis product of PV42

other pigment with a similar fragmentation pattern is an indanthrone blue pigment, PB60, which can be easily distinguished from PR83 because of its blue colour. The products of pyrolysis are listed in Table 10 for both pigments.

The Py-GC/MS analysis of PR83 highlighted an interesting feature: the pyrogram (Fig. 11) shows linoleic acid as the most intense peak, with the presence of other fatty acids. According to Pratt [19], the preparation of PR83 involves the precipitation of a complex made up of the dyestuff, a metal and a fatty acid source such as Turkey Red oil on an alumina hydrate base. The fatty acids peaks in the pyrogram of PR83 could be ascribed to the Turkey Red oil used for the synthesis of the pigment. Turkey red oil, also called sulphonated castor oil, is prepared by adding sulphuric acid to vegetable oils, most notably castor oil. To verify our hypothesis, we analysed PR83 also with GC/MS using TMTFTH (*m*-trifluoromethylphenyl trimethylammonium hydroxide), also called Meth Prep II®, as derivatising agent [20, 21], and a marker of castor oil, methyl ricinoleate, was detected. This result is important and must be considered for the identification of the binding media in the presence of PR83. If a modified vegetable oil is added to the pigment itself, the quantitative analysis of the fatty acids cannot be reliably applied to determine the type of siccative oil used.

Triarylcarbonium pigments These pigments were patented in 1913 and first used as dyes for textiles [16]. As a class, these pigments share the triarylcarbonium structure (Fig. 12). At

Table 9 Pyrolysis products of quinacridone pigments

Pyrolysis product (main *m/z*)	PV19	PV42
Unknown product (233, 262)	X	
Biphenyl (154, 153)		X
Tetrachloroethylene (166, 164, 129, 131)		X
Diphenyl ether (170, 141, 77)		X
Unknown product (195, 167, 139)		X
2-Methylacridone (209, 208, 180)		X
Unknown product (450, 452, 225)		X

Table 10 Pyrolysis products of anthraquinone and indantrone pigments

Pyrolysis product (main *m/z*)	PR83	PB60
Aniline (93, 66)		X
Benzene, nitro (77, 123, 51)		X
2-Naphthol (144, 115)	X	
Phenanthrene (178)	X	
Anthrone (194, 165)	X	X
9,10-Anthracenedione (208, 180, 152)	X	X
Linoleic acid (280)	X	
9,10-Anthracenedione, 1-amino (223, 139, 167)		X
9,10-Anthracenedione, 2-hydroxy (224, 139, 196)	X	
Dinaphtho[2,1*b*:1′,2′-*d*]furan[a] (268, 239, 119)	X	

[a] Or dinaphtho[2,1*b*:1,2-*d*]furan

Fig. 11 Structure of PR83 (left) and its pyrogram with fragments produced by pyrolysis
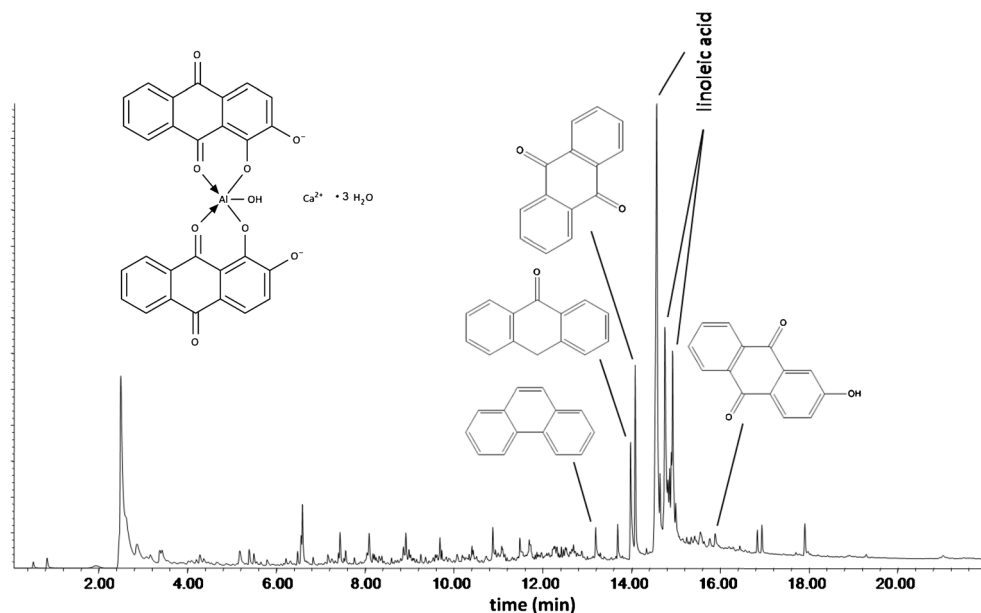
least two of the aryl moieties carry amino groups, which act as electron donating substituents. The compounds are therefore basic and thus capable of combining with acids to form insoluble salts that is the form in which they can be applied as pigments [2]. We have analysed PV1, PV3, PV27, PV39, PB1 and PB62. The results are shown in Table 11.

In some cases, the molecule did not fragment in the pyrolyzer in the adopted conditions: the pyrograms of PV3, PV27, PV39 and PB62 all show the intact molecule peak, as shown in Fig. 13 for PV27 (peak #17). Unfortunately, for PV3 and PV27 the intact molecule of both pigments co-elutes with the de-methylated molecule. This makes the identification of the pigments of this class difficult but not impossible: the different relative abundances of ions in the mass spectra can be exploited to differentiate the pigments, as demonstrated in Fig. 14.

Dioxazine pigments The dioxazine pigments were first synthesised in 1928, but patented as pigments only in 1952 [16].
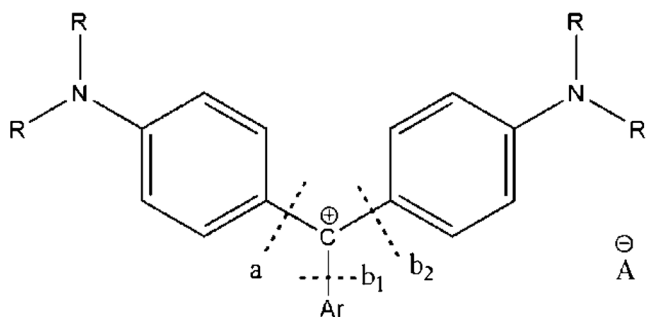

Fig. 12 Structure of triarylcarbonium pigments with breaking points highlighted

The dioxazine molecule is derived from triphenodioxazine, a linear system of five anellated rings.

PV23, Carbazole Violet, is the commercially most important pigment of this class and it is used in almost all media, from coatings and paints to plastics and printing inks [2]. The structure of dioxazine pigments is shown in Fig. 15, and the results are listed in Table 12. Pyrolysis produces chlorinated benzenes deriving from the central structure of the molecule and other smaller aromatic products.

Perylene pigments The group of perylene pigments is derived from perylene-3,4,9,10-tetracarboxylic acid. These compounds have been used as vat dyes since 1913 and were first introduced commercially as pigments in 1950 [2]. We analysed PV29 (Fig. 16), which gives a characteristic product, naphthalimide, a fragment originated from the central polycyclic structure of the pigment. This fragmentation was not observed by Russell [15], who studied substituted perylenes only.

Thioindigo pigments Thioindigo pigments were first discovered in 1907 and are structurally related to indigo, the natural dyestuff derived from the plant *Indigofera tinctoria*. We analysed PV36. The structure of the pigment is shown in Fig. 17, with its main pyrolysis product.

Miscellaneous pigments Of the pigments not grouped in the azo or in the polycyclic classes, we analysed PR90. PR90, eosin lake, was used extensively to produce lake pigments (such as geranium lake), where the dyestuff was commonly precipitated with an aluminium hydroxide base or a lead (II, III) oxide [22]. The structure of

the pigment is shown in Fig. 18 and the products of the pyrolysis are listed in Table 13.

Pigments with unpublished chemical structure

We analysed three pigments with an unpublished chemical structure, PV51, PV52 and PV53. The results of the Py-GC/MS analysis are listed in Table 14.
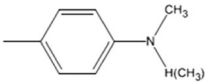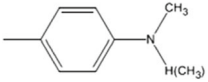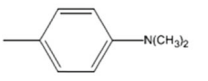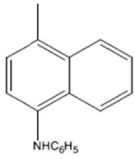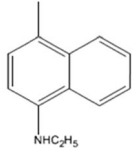
On the basis of the identified fragments, which mainly are rearrangement products, it is not possible to unambiguously hypothesise the structure of PV51, PV52 or PV53.

Nonetheless, they share common fragments with the β-naphthol pigment lakes, BONA pigment lakes and naphthol AS. Thus, their structures most probably contain a 2-naphthol linked by a diazo bond to other aromatic substituents.

Discussion of the analysis of reference pigments

In this work, we expanded the data available on some classes of synthetic pigments already being analysed by other authors [13, 15] and the fragmentation patterns are

Table 11 Pyrolysis products of triarylcarbonium pigments

C.I. name	Substituents (Fig. 12)			Products (main m/z)		
	A*	Ar	R	a	b	Others
PV1	/		/			1H-indole, 1,2,3-trimethyl (158, 159, 144) 1H-Indole, 2,3-dihydro 1,3,3-trimethyl-2-methylene (158, 173, 143)
PV3	PTM PM		CH$_3$	Benzenamine, N,N-dimethyl (120, 121, 77)	b1+b2: Benzenamine, N,N,4-trimethyl (134, 135) b1: Benzenamine, 4,4'-methylenebis N,N-dimethyl (254, 253, 210)	Aniline (93, 66) Aniline, N-methyl (106, 107, 77) PV3 intact molecule (253, 373, 359, 237)
PV27	CF		CH$_3$	Benzenamine, N,N-dimethyl (120, 121, 77)	b1+b2: Benzenamine, N,N,4-trimethyl (134, 135)	Aniline (93, 66) Aniline, N-methyl (106, 107, 77) PV27 intact molecule (239, 359, 345, 253, 373)
PV39	PM PTM		CH$_3$	Benzenamine, N,N-dimethyl (120, 121, 77)	b1+b2: Benzenamine, N,N,4-trimethyl (134, 135) b1:Benzenamine, 4,4'-methylenebis N,N-dimethyl (254, 253, 210)	Aniline (93, 66) Aniline, N-methyl (106, 107, 77) PV39 intact molecule (253, 373, 359, 252)
PB1	PTM PM		C$_2$H$_5$	N,N-Diethyl aniline (134, 106, 149)	b1+b2: Benzenamine, N,N-diethyl-4-methyl (148, 120, 163)	Aniline (93, 66) Benzenamine, N-ethyl (121, 106, 77) 1-Naphthalenamine, N-ethyl (171, 156, 129) 1-Naphthalenamine, N-phenyl (219, 218, 217)
PB62	CF		C$_2$H$_5$	N,N-Diethyl aniline (134, 106, 149)		Aniline (93, 66) Benzenamine, N-ethyl (121, 106, 77) 1-Naphthalenamine, N-ethyl (171, 156, 129) PB62 intact molecule (253, 359, 239, 373, 345)

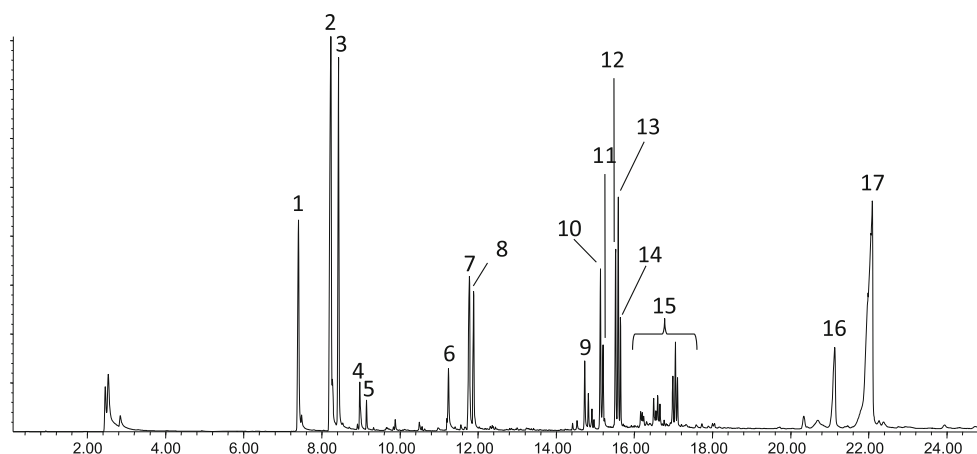*PM* phosphomolibdic acid; *PTM* phosphotungstomolibdic acid; *CF* copper ferrocyanide

Fig. 13 Pyrogram of PV27. (*1*) Aniline; (*2*) aniline, *N*-methyl-; (*3*) benzenamine, *N,N*-dimethyl-; (*4*) benzenamine, *N,*4-dimethyl-; (*5*) benzenamine, *N,N,*4-trimethyl-; (*6*) 4-aminobenzonitrile; (*7*) 4-aminobenzonitrile, *N*-methyl; (*8*) 4-aminobenzonitrile, *N,N*-dimethyl; (*9*) 4,4′-methylenedianiline; (*10*) 4,4′-methylenedianiline, *N*-methyl; (*11*) 4,4′-methylenedianiline, *N,N*-dimethyl; (*12*) 4,4′-methylenedianiline, *N,N*-dimethyl (positional isomer of #11); (*13*) 4,4′-methylenedianiline, *N,N,N*-trimethyl; (*14*) 4,4′-methylenedianiline, *N,N,N,N*-tetramethyl; (*15*) unknown products typical of PV27 (RT 16.99 min: *m/z* 251, 145, 221, 236; RT 17.05 min: *m/z* 265, 221, 159, 144; RT 17.11 min: *m/z* 279, 235, 158, 143) (spectra reported in Figs. S12, S13 and S14); (*16*) 4,4′-((4-aminophenyl)methylene)bis(*N,N*-dimethylaniline); (*17*) intact molecules (4,4′,4″-methanetriyltris(*N,N*-dimethylaniline) coeluting with 4,4′-((4-(methylamino)phenyl)methylene)bis(*N,N*-dimethylaniline)
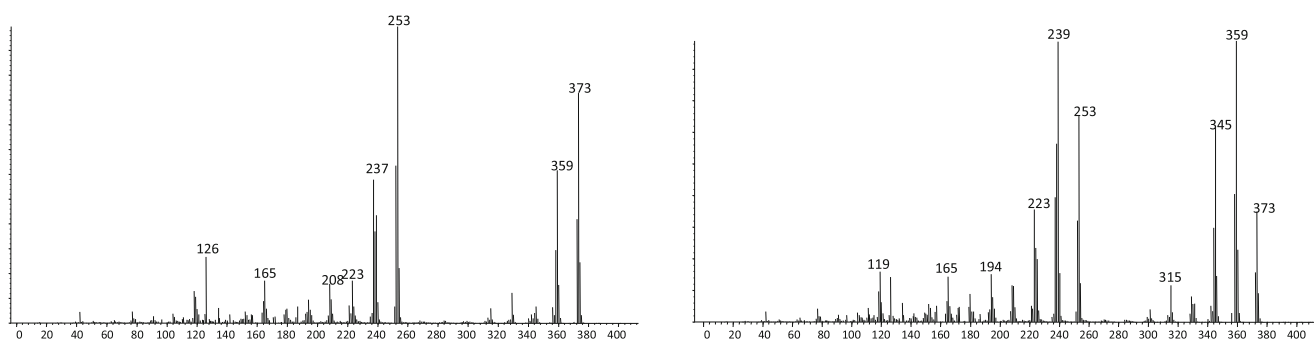

Fig. 14 Mass spectra of intact molecules of PV3 (*left*) and PV27 (*right*): (4,4′,4″-methanetriyltris(*N,N*-dimethylaniline) coeluting with 4,4′-((4-(methylamino)phenyl)methylene)bis(*N,N*-dimethylaniline)

generally consistent with literature data. We also report the pyrolysis profiles of pigments never previously analysed by this technique. Several pyrolysis products
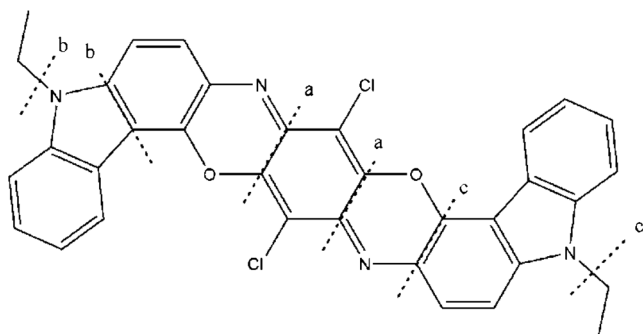

**Fig. 15** Structure of dioxazine pigments with breaking points highlighted

are common to different classes of synthetic pigments, for example 2-naphthol and aniline; thus, these compounds cannot be used in the identification of the pigments. In particular, the pigments belonging to the beta-naphthol and BONA pigment lakes classes cannot be easily distinguished because they share many products in common. Nonetheless, the interpretation of the profile generally allows the identification of the class.

For PGr8, a metal complex pigment, and PR83, an anthraquinone pigment, we assessed the presence in the pyrograms of products derived from vegetable oils, even if the pigments analysed were not expected to contain binding media. Thus, we hypothesised that the fatty acids detected originated from an oil used in the synthesis of the pigments themselves.

With regard to the isoindoline and disazopyrazolone pigments analysed, we found characteristic products, respectively

Table 12 Pyrolysis products of dioxazine pigments

C.I. name	Product (main *m/z*)			
	a	b	c	Others
PV23	Benzene, 1,4-dichloro (146, 148, 111)	Indole (117, 90, 109)	Carbazole (167, 166, 139)	Unknown product (183, 154, 196, 211) Unknown product (182, 195, 210, 181) Unknown product (222, 235, 250, 153)
PV37	Benzene, 1,4-dichloro (146, 148, 111)			Benzonitrile (103, 76) Benzoic acid, ethyl ester (105, 77, 122, 150) Benzamide (105, 77, 121, 51) Benzoxazole, 2-phenyl (195, 63, 167) Unknown product (211, 104)
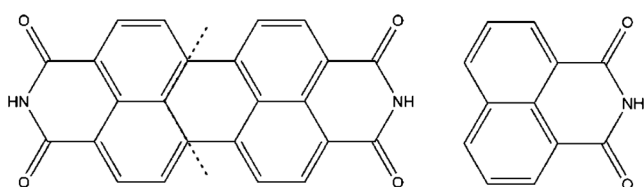
Fig. 16 Structure of PV29 (*left*), with naphthalimide, a fragment produced by pyrolysis (*right*)
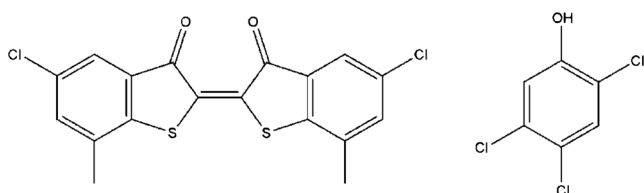
Fig. 17 Structure of PV36 (*left*) with 2,4,5-trichlorophenol, a fragment produced by pyrolysis (*right*)
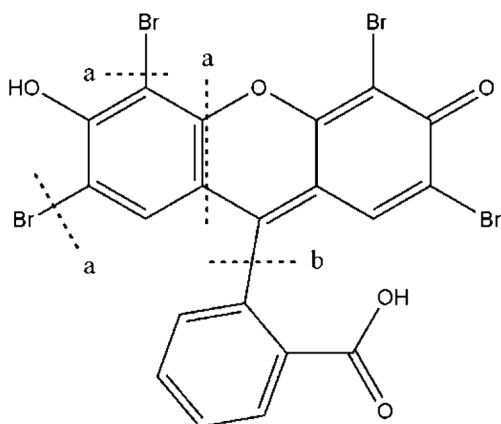
Fig. 18 Structure of PR90 with breaking points highlighted

2(1*H*)-quinolinone and norphenazone, that can help in the identification of these classes.

We confirmed the results of Russell [15] for the phthalocyanine pigments, but we expanded the database analysing another three phthalo pigments and the six crystal modifications of PB15. Py-GC/MS allows us to differentiate between the various PB15 crystal modifications, because they show different pyrolytic profiles.

The pyrogram of PV19, a quinacridone pigment extensively used in paint industry, shows only an unknown product, which can still be used for the identification of this pigment. The other quinacridone pigment analysed, PV42, has 2-methylacridone as characteristic product.

The alizarin crimson PR83 is unambiguously identifiable by Py-GC/MS, and this result is important because this pigment has been widely used in artists' paints.

Another interesting result is the one obtained for the triarylcarbonium class: we found that some of the pigments belonging to this class show in the pyrograms the intact molecule peak.

As for the dioxazine pigments, the products of PV23, one of the most used pigments in paint materials, are unknown, but the *m/z* reported could help in its identification.

We analysed for the first time with Py-GC/MS PV36, a thioindigo pigment, obtaining a peculiar pyrogram with a single peak, the 2,4,5-trichlorophenol.

We also reported for the first time the Py-GC/MS results of three violet pigments with unpublished chemical structure, PV51, PV52 and PV53.

Table 13 Pyrolysis products of PR90

C.I. name	Product (main *m/z*)		
	a	b	Others
PR90	Phenol (94, 66)	Benzoic acid (105, 122, 77, 51)	1,4-Dioxane (88, 28, 58) Biphenyl (154, 153) Unknown product (135, 107, 149, 121) 9H-Fluoren-9-one (180, 152)

Table 14 Pyrolysis products of pigments with unpublished chemical structure

Pyrolysis product (main m/z)	PV51	PV52	PV53
Heptane, 3-methylene (55, 70, 41)			X
2-Propyl-1-pentanol (57, 41, 70, 83)	X		X
Naphthalene (128)			X
Benzenamine, 4-methoxy (108, 123, 80)	X	X	
Phenol, 4-amino (109, 80)	X	X	
2-Naphthol (144, 115)	X	X	X
2-Naphthalenamine (143, 115)			X
Benz[c,d]indol-2(1H)one (169, 114, 141)	X		
Bis(2ethylhexyl) maleate (57, 117, 71, 100)	X	X	
2-Butenedioic acid (E)-bis(2ethylhexyl) ester (70, 112, 57, 211)	X	X	X
Dinaphtho[2,1b:1 2-d]furan (268, 239, 119)			X

Clyfford Still's and Jackson Pollock's paints and works

Clyfford Still

In his studio Clyfford Still had a big collection of pigments that he used to paint his artworks. The paints were prepared by pouring dry pigments onto a palette in a mound and creating a well at the top, where Still poured boiled linseed oil as well as a small amount of turps and driers. He then mixed the ingredients with a palette knife [23].

We analysed ten paint samples and seven pigments from Still's collection. The results are shown in Table 15.

We were able to identify the class of the pigment used in 5 of the 10 paint samples, namely the red azo pigment lakes class. For the pigments in the artist's studio, we identified four pigments as PR49, belonging to the red azo pigment lakes class.

In two paint samples, we identified PR83, anthraquinone red. As an example, we report the pyrogram of a paint sample from "Untitled", 1948 (Fig. 19). Three paint samples and three pigments form the artist's studio showed products common to several classes of pigments or too few products to allow an identification.

The Py-GC/MS analysis also showed that the binder used by Clyfford Still is a vegetable oil [24–26], in fact palmitic, stearic and azelaic acids are the main peaks in the pyrograms for all the paint samples.

Jackson Pollock

"Mural" (247×605 cm), realized in 1943, is an early work by Jackson Pollock. The painting was, from 2012 till 2014, at the Getty Center in Los Angeles, CA, undergoing a technical study and a conservation treatment. Two red paint samples from "Mural" were analysed by Py-GC/MS. Sample #8 was collected from the end of a drip of thin, very fluid red paint that descends from a diagonal brushstroke. Sample #27 was collected from the lower right part of the painting.

Results are shown in Table 16. The program of sample #27 is shown in Fig. 20.

Sample #27 shows all the characteristic pyrolysis products of alizarin crimson PR83, confirming that Pollock used this

Table 15 List of the Clyfford Still's paint samples and pigments analysed

Type	Paint	Sample no	Py-GC/MS results
Paint sample	Untitled, 1948 (a)	339_8	/
	Untitled, 1948 (a)	339_11	PR83
	Untitled, 1948 (a)	339_12	PR83
	Untitled, 1948 (b)	322_11	Red azo pigment lakes class
	Untitled, 1951–1952	968_1	Red azo pigment lakes class
	Untitled, 1951–1952	968_2	Red azo pigment lakes class
	Untitled, 1954	969_2	Red azo pigment lakes class
	Untitled, 1960	693_4	Red azo pigment lakes class
	Untitled, 1974	920_1	/
	Untitled, 1974	920_2	/
Pigment from the artist's studio		18	PR49
		21	PR49
		31	/
		35	/
		38	PR49 or PR63
		39	/
		40a	PR49

Fig. 19 Pyrogram of Clyfford Still paint sample 339_12, from Untitled (1948). (*1*) caprylic acid; (*2*) azelaic acid; (*3*) phenanthrene; (*4*) palmitic acid; (*5*) anthrone; (*6*) 9,10-anthracenedione,2-hydroxy; (*7*) stearic acid
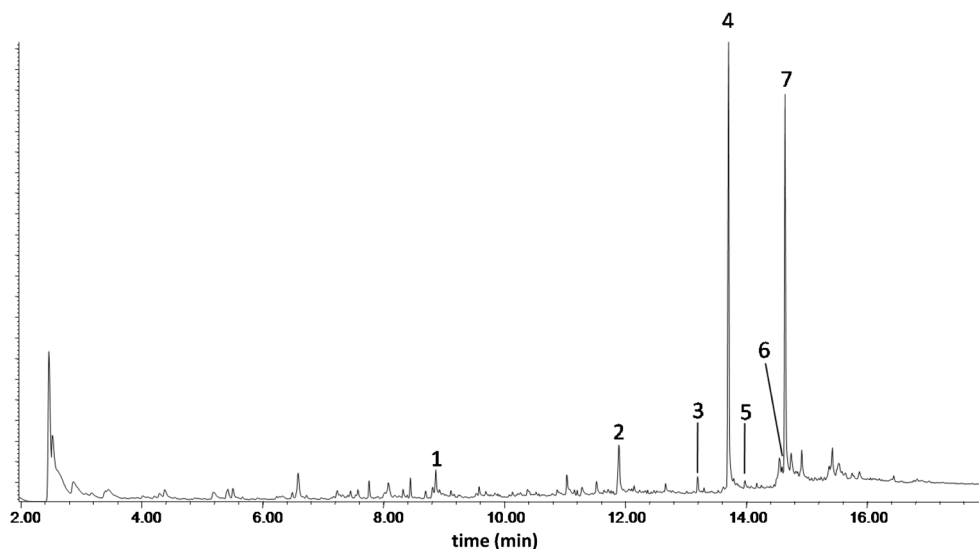

Table 16 Results of the Py-GC/MS analysis on two paint samples from Jackson Pollock's *Mural*

Product	Time (min)	m/z	Marker of	JP #8	JP #27
Naphthalene	9.2	128	Generic		X
2-Naphthol	11.5	144, 115	Generic	X	X
Phenanthrene	13.1	178	PR83		X
Anthrone	13.9	194, 165	PR83		X
9,10-Anthracenedione	14.1	208, 180, 152	PR83		X
9,10-Anthracenendione, 2-hydroxy	15.8	224, 139, 196	PR83		X
Unknown PR3 product	17	275, 246, 128	PR3	X	
Dinaphtho[2,1b:1′,2′-d]furan[a]	17.9	268, 239, 119	PR83		X

[a] Or dinaphtho[2,1b:1,2-d]furan

Fig. 20 Pyrogram of Jackson Pollock paint sample 27, from Mural (1943). (*1*) *n*-butyl methacrylate; (*2*) 2-naphthol; (*3*) diethyl phthalate; (*4*) azelaic acid; (*5*) phenanthrene; (*6*) palmitic acid; (*7*) anthrone; (*8*) stearic acid; (*9*) linoleic acid; (*10*) 9,10-anthracenedione,2-hydroxy
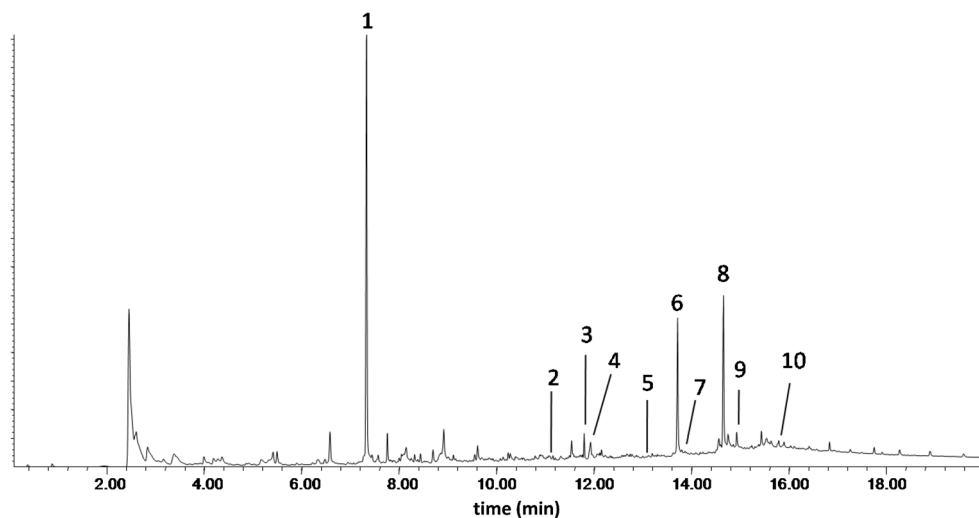
synthetic pigment. The typical PR83 products are all present in the painting sample: phenanthrene; anthrone; 9,10-anthracenedione; 9,10-anthracenedione-2-hydroxy, while naphthalene and 2-naphthol are common products of many synthetic pigments. The pyrogram of this sample also shows several peaks due to fatty acids (azelaic, palmitic, stearic and linoleic), thus indicating that Pollock used an oil paint. The pyrogram of sample #8 shows a product (unknown) at 17.0 min characteristic of toluidine red PR3, but other expected products of PR3, such as the peak corresponding to the intact molecule, are absent. Thus, the identification of the pigments as PR3 is only tentative.

The two paint samples analysed show also *n*-butyl methacrylate as the most abundant peak at 7.3 min. The painting has undergone a restoration during which a varnish named Soluvar (Liquitex) has been applied. Soluvar varnishes are composed of a mixture of *n*-butyl and isobutyl methacrylate (Paraloid B-67 and F-10) resins. The presence of the restoration varnish may thus account for the detection of *n*-butyl methacrylate in the pyrogram [27–30].

Conclusions

The application of Py-GC/MS technique has proven to be a useful tool for the identification of synthetic pigments and for their detection in paint samples. In this work, we expanded the database of pyrolysis products by analysing classes of synthetic pigments never previously analysed by this technique. The publication of a complete database of pyrolysis products derived from the analysis of synthetic pigments is fundamental to unambiguously identify the pigments in paint formulations and in paint samples.

As for the reference pigments analysed, Py-GC/MS in some cases produces the same fragments for more than one pigment, but the overall pyrolysis profile generally allows the identification of the individual pigment.

In the analysed paint samples, only the most abundant products were detected, in most cases due to the low concentration of the pigment compared to the binding medium. Moreover, in many cases, these products were not the specific markers of individual pigments. Nonetheless, in most cases, we were able to identify at least the class of the synthetic pigment used, as in the case of five of the Clyfford Still paint samples.

The identification of PR83 alizarin crimson, instead, is rather easy, because this pigment is the only synthetic anthraquinone used in paint formulations. We identified the characteristic pyrolysis products that can be considered as markers of PR83 and we used them to identify the pigment both in the Jackson Pollock paint sample and in two Still paint samples.

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