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DOI

[10.1016/j.microc.2020.105340](https://doi.org/10.1016/j.microc.2020.105340)

Publication date

2020

Document Version

Final published version

Published in

Microchemical Journal

License

Article 25fa Dutch Copyright Act

[Link to publication](#)

Citation for published version (APA):

Álvarez-Martín, A., De Winter, S., Nuyts, G., Hermans, J., Janssens, K., & Van der Snickt, G. (2020). Multi-modal approach for the characterization of resin carriers in Daylight Fluorescent Pigments. *Microchemical Journal*, 159, [105340].
<https://doi.org/10.1016/j.microc.2020.105340>

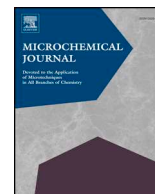
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Multi-modal approach for the characterization of resin carriers in Daylight Fluorescent Pigments



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ARTICLE INFO

Keywords:

Daylight fluorescent pigments
Herb Aach
Melamine-based resin
ATR-FTIR
SPME-GC-MS
Contemporary art conservation
DayGlo

ABSTRACT

Almost seventy years after artists such as Frank Stella (1936), Andy Warhol (1928–1987), James Rosenquist (1933–2017), Herb Aach (1923–1985) and Richard Bowman (1918–2001) started to incorporate Daylight Fluorescent Pigments (DFPs) in their artworks, the extent of the conservation problems that are associated with these pigments has increased progressively. Since their first appearance on the market, their composition has constantly been improved in terms of permanency. However, conservation practices on the artworks that are used in, are complicated by the fact that the composition of DFPS is proprietary and the information provided by the manufactures is limited. To be able to propose adequate conservation strategies for artworks containing DFPS, a thorough understanding of the DFPS composition must be acquired. In contrast with previous research that concentrated on identification of the coloring dye, this paper focuses on the characterization of the resin, used as the carrier for the dye. The proposed approach, involving ATR-FTIR, SPME-GC-MS and XRF analysis, provided additional insights on the organic and inorganic components of the resin. Using this approach, we investigated historical DFPS and new formulations, as well as different series from the main manufacturing companies (DayGlo, Swada, Radiant Color and Kremer) in order to obtain a full characterization of DFPS used by the artists along the years. First, the initial PCA-assisted ATR-FTIR spectroscopy allowed for an efficient classification of the main monomers in the resin polymer. Next, a further distinction was made by mass spectrometry and XRF which were optimized to allow a more specific classification of the resin and for detection of additives. In this paper we show the potential of SPME-GC-MS, never applied for the characterization of artistic materials, at present undervalued for heritage science purposes. We anticipate that this information will be highly relevant in the future stability studies and for defining (preventive) conservation strategies of fluorescent artworks.

1. Introduction

Since the 60s, North American artists frequently used Daylight Fluorescent Pigments (DFPS) in their artworks for various reasons: Frank Stella incorporated them in his minimal paintings for their self-referential, industrial look, as did James Rosenquist and Andy Warhol whose pop art was inspired by commercial billboards, in which DayGlo paints were used to draw more attention to their messages [1]. Other artists such as Richard Bowman and Herb Aach dedicated their careers to exploring the new visual effects specific to DFPS [2,3]. These luminescent, synthetic, modern paints revealed a new dimension in color

that resulted in unseen visual experiences, such as illusory color depth, optical vibration and new contrast effects. Unfortunately, there is a downside to the use of fluorescent paints, in the sense that they age much faster than conventional colors, due to the organic nature of the two groups of materials that DFPS are made: the dyes and the resin carrier. In particular, the fast bleaching of the pigment and strong metamerism problems associated to retouches and fillings have been reported [3]. As it is also impossible to digitally document the luminescent effect of DFPS, the conservation of fluorescent artworks proves an arduous task for the curatorial staff [4]. It is known that a DFP exists mostly of a resin carrier which is colored with a very small percentage

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of dyestuff (0.1–5%). The resin carried is a condensation-type resin, consisting on a large resin structure formed by small monomers carrying polar groups. During the manufacturing of DFPs, dyes and resin are mixed when the latter is still in a monomeric form or in an early stage of condensation. As the resinous medium is not a solvent for the pigment, since the sixties, DFPs were mainly mixed with colorless media such as gouache, acrylic, alkyd and enamel [5]. Next to these two base components, UV-stabilizers, anti-foam agents and optical brighteners are commonly added to the resin matrix to retain the best properties of the dye [3,6]. So far, the lack of information about the composition and properties of DFPs has prevented the formulation of an adequate, standard conservation and restoration treatment [4,7,8]. Nowadays, inpainting is usually based on the application of new DFPs that have been artificially aged to visually match the appearance of the original paint [4]. However, this approach, employing modern DFPs, yields unsatisfactory results on the long-term. Since the formulation of the resin has been constantly modified, the present-day DFPs age in a different manner than the surrounding historical paint, and thus will eventually display a deviant appearance [5]. In the past years, some attempts were made to enhance the understanding of the DFPs composition [9,10]. However, these studies focused on the characterization of the dye composition rather than on the resin and its additives and provided only limited information on the durability of the paint system as a whole. Therefore, the aim of this study was to search for differences in DFPs compositions over the years, by focusing on the resin structure and additives in samples from four different pigment manufacturing companies such as DagGlo Corp. (Ohio, US), Kremer Pigmente GmbH (Aichstetten, Germany), Radiant Color NV (Houthalen, Belgium) and Swada LLC (Stalybridge, UK).

1.1. Art historical background

Initially DFPs were developed during World War II to improve safety signalization and later to increase the visual saliency of commercial images [11]. The earliest found reference on the 'artistic' use of DFPs is an article published in 1970 by an American artist and color engineer Herb Aach (1923–1985), who appears to have played a key role in the introduction of DFPs as artistic materials. In this paper, entitled *On the Use and Phenomena of Fluorescent Pigments in Painting* [3], Aach, who extensively used DFPs in his own artworks [12], describes his first contact with DFP and their *optimal* use in painting. As active member of the Committee of Commercial Standards (CS98-62 of the U.S. Department of Commerce), which governed artists' materials, he often tested new pigments in terms of lightfastness and suitability for art works [3,6]. Aach already noticed an improvement in the longevity between two different sets of DFPs manufactured by DayGlo, the main manufacturer company at that time. Motivated by their lack of permanency, Aach kept working on the stability, consistency and artistic suitability of DFPs throughout his career. For instance, in an attempt to overcome their distinct transparency, he increased the ratio of DFPs in the acrylic medium [3]. This experiment resulted in very saturated, matt, fresco-like paint layers, which is clearly reflected in his *Split Infinity* series (Fig. 1A). Beside the valuable information about his paint compositions, nothing could be found in Aach's paper regarding the nature of the resin used in DFP. After Aach died in 1985, a collection of his DayGlo pigments were conserved in the *Herbert Aach Estate* (New York, US). For this research, 16 different samples were donated to the authors for an in-depth investigation (Fig. 1B-C). As a benchmark for the evolving composition, a number of more recent fabricated samples from Radiant Color, Swada and Kremer were included in this study (Table 1).

1.2. Structure of daylight fluorescent pigments

DFPs are comprised of two main components: (i) a transparent, crystalline organic substance that strongly fluoresces in the solid state

when excited by long-wave UV or visible light and (ii) organic resinous particles and other organic or inorganic excipients, in which the mixture of fluorescent components is dissolved [5]. The ratio of this mixture is in general 5:95, with the fluorescent pigment being the minor component. The most common resin used during the manufacture of DFPs belongs to the amino resin's family, synthesized by reactions involving formaldehyde with a variety of amine functional compounds such as urea, melamine, and benzoguanamine. The combination of these compounds results in resins based on melamine–formaldehyde, melamine-urea–formaldehyde, benzoguanamine-formaldehyde, benzoguanamine-urea–formaldehyde and melamine-benzoguanamine-formaldehyde copolymers [13].

The first commercialized DFPs in the early 1940's were melamine-thermoplastic resins containing fluorescent dyes with moderate solvent and light stability. The main disadvantage of thermoplastic DFPs was their tendency to swelled. To overcome this, thermoset DFPs were developed from the same ingredients but using higher proportion of melamine in an attempt to improve the stability. As a result, new colors were commercialized in a broad variety of applications such as paints and inks, plastics, textile and make-up [5,6].

Although, a few manufacturers do provide general information on the formulation, in most of the cases the composition remains proprietary. The characterization of the resin type is in most cases an arduous task since the formulation can greatly vary between manufacturing companies and even between series produced by the same manufacture over the years. In other fields, such as industrial processes or material and polymer chemistry, several analytical techniques have been applied to characterize melamine-based resins. For instance, few studies investigate the thermal behavior of melamine resins by a variety of analytical methods such as FTIR, NMR, differential scanning calorimetry and thermogravimetry [14–17], providing information about critical parameters related to the synthesis and cure process. In heritage science, the only publication dealing with the characterization of the resinous composition of DFPs, used for artistic purposes, applied Py-GC-MS in order to characterize the main fragments of melamine-derivate resins [9]. However, the elevated temperatures of the pyrolysis process prevent this technique to provide information on the additives that are characterized by a low thermal stability.

In this study, we propose a multi-method, three-step approach, combining ATR-FTIR, SPME-GC-MS and XRF, to obtain a more comprehensive analysis of the resin fraction of DFPs, as compared with previous research. First, ATR-FTIR was employed as a screening technique to rapidly distinguish the main resinous fraction type (e.g. melamine-based resin). Next, a further distinction was made by mass spectrometry which was optimized to allow for a more specific classification of the resin and detection of additives. The latter cannot be identified by the preceding FTIR analysis due to their small weight percentage. In particular, Solid Phase Micro-Extraction coupled to Gas Chromatography-Mass Spectrometry (SPME-GC-MS) was considered as a semi-destructive analytical method to avoid the aforementioned breakdown of the resinous fraction by other GC-MS based techniques (e.g. Py-GC-MS). SPME-GC-MS has been widely applied in museum institutions to identify volatile compounds emitted by the objects in the collection [18–20] and to characterize terpene resins in archaeological objects [21,22]. Despite the broad application of this technique, no studies deal with the application of SPME as a screening method for the evaluation of the constituents of artistic materials so far. As such, this research can be considered as a first evaluation of the potential of SPME-GC-MS as one-step preparation technique for screening artworks.

As a final step, XRF analysis was carried out in order to provide information about the inorganic composition of the UV-absorbers added by the different companies.

This study is the first to provide a more complete overview of the resin carrier and the presence of additives on a selection of DFPs. In summary, the new knowledge that is provided by this methodology on the chemical composition of the resin carrier used by manufactures



Fig. 1. (A) Herb Aach, *Split Infinity # 2* (1975), daylight fluorescent acrylic paint on cotton duck (size 188 × 137 cm), private collection (© artwork of Herb Aach); (B) envelop with pigment sample of *Aurora Pink*, from the Herbert Aach estate; (C) preserved daylight fluorescent pigment samples from Herbert Aach donated for this research by his widow, Doris Aach.

along the years, is anticipated to be a vital step towards a full understanding of the fading of DFPs and the parameters affecting this process.

2. Materials and methods

2.1. Reference materials and historical samples

A set of samples was selected for this study, including the samples from the Herbert Aach Estate manufactured by DayGlo between 1965 and 1979 and more recent samples from other manufacturing companies (Swada, Kremer and Radiant), purchased in 2009.

In total, 33 DFP samples were collected for this study (Table 1). 14 historical samples from the 60 s-70 s, listed as *DayGlo* (DayGlo corp., Ohio, USA) and belonging to Herb Aach's private collection were generously donated by his widow Doris Aach. This historical corpus was supplemented with 19 modern 'benchmark' reference samples. In particular, 13 samples, fabricated between 1997 and 2009, were generously provided by Swada (Stalybridge, UK), three samples, fabricated in 2009, were offered by Radiant Color (Houthalen, Belgium) and two samples were purchased in 2009 from Kremer Pigments (New York, USA). In addition, a reference sample of the carrier resin (toluene-sulfonamide-melamine-formaldehyde (P.Y. 0653)) was generously provided in 2012 by Radiant Color (Houthalen, Belgium). Each manufacturer classifies the samples in product series, according to the composition, physical properties and use. For nine samples from Aach's historical DayGlo collection, it was unclear to which series they belonged and therefore remained uncharacterized (see Table 1). Three samples from the AX series, one from the T series and one from the GT series were analyzed. From Swada, six color samples from the T series, two samples from the A series, two samples from the FTX series, one sample from the RTS series and one sample from the LMP series were analyzed. From Radiant Color, a sample of pure resin and three samples from the PS series were selected and from Kremer both pigments

belonged to the 56000–56450 Fluorescent Pigments series. Beside the manufacturing company, A and AX series are classified as thermoplastic copolymers and T, GT, FTX and PS are classified as thermoset copolymers. All these 33 samples were analyzed by FTI-ATR, based in the result a selection of 12 samples were analyzed by SPME-GC-MS. Finally, 23 samples were analyzed by XRF.

2.2. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR)

































A preliminary characterization of the samples listed in Table 1 was obtained through ATR-FTIR analysis to identify the resin polymer type. Spectra were recorded with OPUS software (Bruker Optics) on a Thermo Nicolet 6700 spectrometer, equipped with a Golden Gate diamond ATR module (single reflection, 45°) and a DTGS detector. All the spectra were acquired from 4000 to 400 cm^{-1} , with 4 cm^{-1} spectral resolution and 64 scans. Samples were pressed directly on the diamond crystal of the ATR accessory. Spectral matching was done using OMNIC (Thermo Scientific™) and ATR-FTIR spectra were identified using the IRUG (Infrared and Raman Users Group) libraries, the HR Hummel Polymer and Additives library as well as the ASTER mineral library. Principal component analysis (PCA) was performed by calculating the singular value decomposition of the data matrix (wavenumber range: 400–2190 cm^{-1}) using Mathematica software. For this analysis, all spectra were baseline corrected, normalized to the highest peak in the wavenumber range, and they had their mean value subtracted.

2.3. Spme-GC-MS

2.3.1. SPME sampling procedure

Three fiber coatings were tested for this study: (i) 75 μm carboxen/polydimethylsiloxane (CAR/PDMS), (ii) 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and (iii) 100 μm

Table 1
List of the investigated DFPs classified by manufacturer company.

Sample No.	Manufacturer			
	DayGlo (Herbert Aach Estate)	Swada	Radiant	Kremer
1	 New AX17/Saturn Yellow			
2	 New GT7/Saturn Yellow			
3			 PS-10/Chartreuse Yellow ^(S)	
4	 (*)/Rocket Red ^(S)			
5		 T/Nova Red 2		
6	 (*)/Arc Yellow			
7	 New AX16/Arc Yellow			
8	 (*)/Fire Orange			
9	 (*)/New Fire Orange			
10	 (*)/Blaze Orange			
11	 (*)/Pink ^(S)			
12	 (*)/Aurora Pink ^(S)			
13	 (*)/Neon Red			
14	 (*)/New Rocket Red			
15	 New AX18/Signal Green			
16	 New T18N/Signal Green			
17			 PS-11/Green	
18			 PS-37/Pink ^(S)	
19		 RTS(1997)/Astral Pink ^(S)		
20		 LMP(1998)/Flame Orange ^(S)		
21		 T/Arc Chrome 6		
22		 FTX/Blaze 5		
23		 T/Laser Red 3		
24		 A/Magenta 10		
25		 FTX/Strong Magenta 21		
26		 T/Comet Blue 60		
27		 T/invisible Blue 70		
28				 56000 White ^(S)
29		 T/Astral Pink ^(S)		
30		 A/Astral Pink ^(S)		
31		 FTX/Flame orange ^(S)		
32				 56400 pink
33				Resin p-y-0653 ^(S)

(*) = product series unknown. These samples belong to Aach's private collection, where samples were not stored in the original containers (see Fig. 1C).
(S) = analyzed by SPME-GC-MS.

polydimethylsiloxane (PDMS). The non-polar PDMS fiber showed the higher extraction efficiency for the analytes of interest due to their molecular weight and polarity, thus was selected for this study. This type of coating has been used in previous studies for the detection of resins in archeological samples [12]. For sampling, 40 mg of sample powder was

placed in a 1.5 ml vial with a PTFE septum. SPME fiber was inserted into the vial through the septum followed by manual exposure of the fiber to the headspace of the sample. Samples were heated in order to facilitate the release of the most volatile analytes. Two sampling conditions were performed: (i) 40 min at 80 °C and (ii) 240 min at 150 °C.

2.3.2. GC-MS conditions

After sampling, the fiber was manually inserted into the injector port where the analytes were thermally desorbed and transferred onto the chromatographic column for separation and further detection with the mass spectrometer. The desorption temperature was 250 °C. GC-MS analysis was performed with an Agilent 6890 GC coupled to a 5975 MSD (Agilent Technologies, Wilmington, DE, USA). Chromatographic separation was performed on a 30 m × 0.25 mm id, 0.25- μ m-thick film of DB-5 ms capillary column (Agilent Technologies, Wilmington, DE, USA). The injector was used in splitless mode with an injection time of 5 min. The initial oven temperature program was set at 40 °C (hold for 1 min), then ramp rate of 9 °C/min to 130 °C (hold for 1 min), and 2 °C/min to 230 °C which was held for 1 min. The temperature of the interface and the source were set at 280 and 230 °C, respectively. Mass spectra were acquired under electron ionization mode (EI) at 70 eV and recorded from m/z 40–500 with a scan time of 0.19 s. Data processing was performed using Masshunter® qualitative analysis (version B.07.00, Agilent). Chromatographic peaks were identified by using the NIST library 2011 Mass spectra Library V.2.0.

2.4. XRF analysis

XRF is one of the most cited analytical methods in literature dealing with the investigation of cultural heritage artefacts. The technique owes its popularity to the fact that it allows collecting elemental and spatially-resolved information in a non-destructive way on major and minor constituents of a variety of materials [23]. Small amounts of the pigment powder were put on a mylar foil in a Teflon sample cup. XRF spectra were acquired with a PW4025 Minipal 25 fm (Panalytical) spectrometer, equipped with a low power, air-cooled Rh-anode X-ray tube and a Si-PIN detector. The Minipal has a maximum power, current and voltage of respectively 9 W, 1000 μ A and 30 kV. All samples were measured with a live time of 600 s by applying a voltage of 30 kV and current of 20–75 μ A and using a 50 μ m Al filter between the X-ray tube and the sample. All spectra were analyzed using the bAXIL software package (BrightSpec NV) [24]. The net peak intensities of the Zn and Ti $K\alpha$ were determined for each sample and normalized by the net peak intensity of the Rh $K\alpha$ incoherent scatter peak. The incoherent scatter peak gives an indication on the amount of low Z material present. In our case it is an indication of the amount of pigment powder on the mylar foil. No (semi)-quantification of the data was performed but the normalized net peak intensities give an indication on the relative amounts of Ti and Zn.

3. Results and discussion

3.1. ATR-FTIR spectroscopy

ATR-FTIR spectroscopy was carried out to determine the primary components of the resin (Fig. S1). Of the 33 samples analyzed, 31 were initially classified as resins based on melamine–formaldehyde or melamine-urea–formaldehyde according to the HR library. The two resins with a deviating resin polymer are Swada LMP (1998)/Flame Orange (sample 20, type A) and Swada RTS (1997)/Astral Pink (sample 19, type B). The spectra of the remaining 31 samples with a melamine-based resin were analyzed using principal component analysis (PCA) to support classification of the materials (Fig. 2). The score plot of the second and third principal components suggests that these 31 samples can be further divided into four distinct groups.

The main features of the total of six resin types of resin are discussed using their representative spectra shown in Fig. 3.

Resin type A, the Swada LMP (1998)/Flame Orange (Fig. 3), described by the manufacturer as a polyamide-polyester thermoplastic copolymer, stands out with a clear ester carbonyl band at 1720 cm^{-1} and a set of amide bands at 1630 and 1530 cm^{-1} . This spectrum also showed more intense alkyl vibrations at 2920 cm^{-1} than any other of

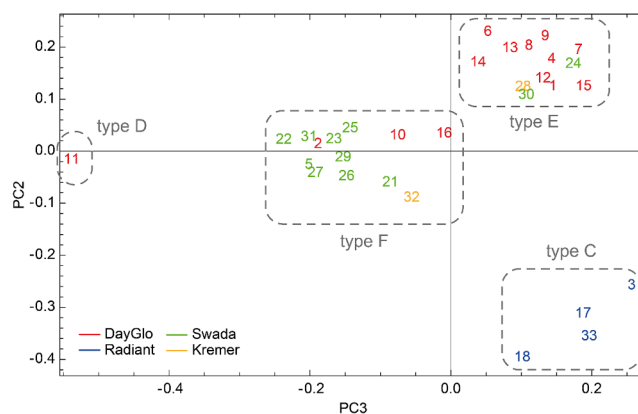


Fig. 2. PCA score plot showing the contributions of the second and third principle component in the ATR-FTIR spectra shown in Fig. S1. The indicated numbers correspond to the samples in Table 1, while their colors refer to the manufacturing company.

the 32 samples (alkyl vibrations not shown). Resin type B, the Swada RTS (1997)/Astral Pink sample, distinguishes itself by a set of bands at 780 and 825 cm^{-1} that indicate the presence of benzoguanamine monomer [5,25], as indicated by the manufacturer in the safety data sheet. Benzoguanamine can also be identified by the vibrations of its triazine ring around 1535 cm^{-1} . Resin types C–F all show a strong band at 1150 cm^{-1} (C–O–C ether stretch) [26]. All samples manufactured by Radiant Color (type C) display spectra that are similar to the uncolored toluene-sulfonamide-melamine–formaldehyde resin sample, donated by the company. In particular, the distinct band at 1015 cm^{-1} is likely caused by the presence of toluene-sulfonamide. The bands at 810 and 1545 cm^{-1} , present in nearly all spectra, are both caused by the vibrations of the triazine ring in melamine [27]. All samples clustered in type C are described by Radiant Color as thermoset-sulphonamide-melamine-paraformaldehyde resin. The pink color from the DayGlo series (sample 11, type D) seems to be similar in formulation to the other DayGlo samples, except that it has been prepared with benzoguanamine rather than melamine as monomer. Since this sample belongs to Aach's private collection, and no information was provided in the container, it was not possible to assign it to a specific pigment series within the DayGlo product range. The final two resin types that can be distinguished with PCA show only subtle differences in the IR spectra that are difficult to ascribe to a specific resin composition with ATR-FTIR spectroscopy. Interestingly, type E corresponds to the samples classified as thermoplastic copolymers from DayGlo and Swada (serie AX and A, see Table 1), while type F consist of thermoset copolymers (serie GT, FTX and T, see Table 1). Based on these clusters, we can conclude that the unclassified samples from Aach's private collection (Table 1) are thermoplastic copolymers with the exception of sample 10, which belongs to the thermoset group (type F). While Kremer specifies both DFPs as thermoset, we observed that one sample lies in the thermoplastic group (sample 28, type E).

3.2. SPME-GC-MS analysis

SPME-GC-MS analysis was used to point out subtle differences in the composition between manufacturer companies. For this reason, a total of 12 samples was analyzed by SPME-GC-MS: three samples from DayGlo, five samples from Swada, three samples from Radiant and one sample from Kremer (Table 1). The selection of these samples was based on the differences encountered by ATR-FTIR spectroscopy explained in the previous section.

SPME is based on the partition of volatile or semi-volatile organic analytes between the headspace of the sample and the polymeric coating of the fiber, integrating sampling, extraction, and concentration of the analyte in a single step [28]. Due to the high temperatures of

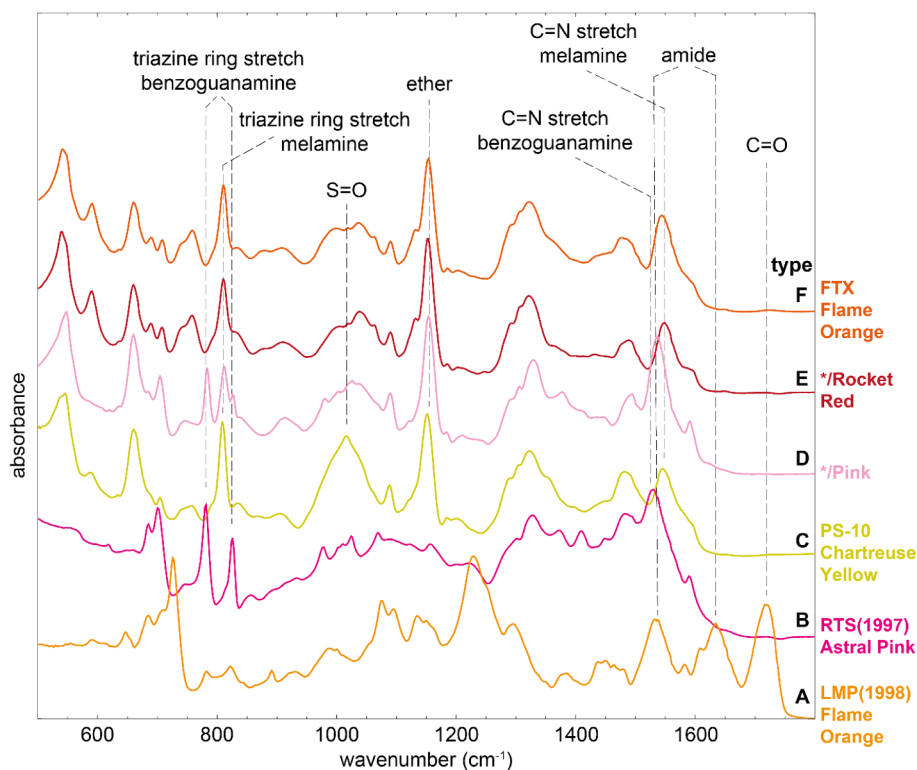


Fig. 3. Normalized ATR-FTIR spectra of the different types of DFPs within the investigated set.

decomposition of synthetic resins, a slight heating of the sample will facilitate the detection of the volatile fraction without causing the total fragmentation of the polymer and without causing any noticeable damage on the sample.

Previous studies have shown the efficiency of heating, over sampling at room temperature for the extraction of archeological resins [21,22,29]. To facilitate the extraction of volatile analytes from the bulk of the sample, a level of heating is required to increase the transport to the coating of the fiber. However, the temperature has to be the appropriate to allow the analytes to reach the fiber coating but without causing the total breakdown of the thermolabile analytes. Since the optimization of a minimal-destructive method is of importance when dealing with historical samples, the first sampling condition was tested at 80 °C for 40 min [22]. The chosen temperature was kept below the thermal degradation point of all samples without altering their appearance.

After exposing the samples to this mild condition, most of the detected compounds can be classified as alkanes, alkenes and alcohols related to additives or residual compounds originating or added during the manufacturing process. Although these are not helpful for identification of the resin, a number of 'target compounds' was identified that can be considered as specific for each manufacturing company, as discussed in the next few paragraphs. It is important to note that the following description is solely based on qualitative analysis, quantitative analysis was not possible due to sampling conditions (e.g. no control of the volume of the headspace and equilibrium time).

As shown in Figs. 4, 5 and 6, a large group of linear alkanes and alkenes has been detected. The presence of n-alkanes was also reported in previous analysis of synthetic resins [30] and these may have been included as additives for improving the durability of the mixture. Interestingly, (Z) and (E) alkenes were exclusively detected in Swada samples.

The synthesis of urea–formaldehyde-based resins proceeds via the methylation of urea and condensation of the methylol groups. Thus, the detection of alcohols in all samples may be related to the

fragmentation of methylol groups present in the polymeric resin [31]. However, only three aldehydes were identified (decanal, nonanal and pentadecanal) in two Swada series: T and FTX. The detection of a larger number of alkanes and alkenes over alcohols and aldehydes is directly related to the high volatility of the first two chemical families, facilitated during the (heated) sampling conditions. In addition to this, the type of fiber used during the analysis (PDMS, 100 μm) might have an influence on the detected analytes as it shows more affinity for low molecular weight and volatile compounds [28].

Toluene sulfonamide derivatives (TSA) were detected in those samples previously classified by ATR-FTIR as melamine-based resins (peaks 2, 3, 5, 6 in Fig. 4 and Fig. 5). The introduction of TSA during the synthesis of polymeric resins was not until 1951 [5]. However, resins only constituted by TSA were not suitable for DFP because of their low melting points, directly decreasing their thermostability. To improve the thermostability, a combination of TSA derivatives with urea-melamine-based resins was commercialized since 1951, showing great resistance and durability [5].

As expected, in the two Swada samples where a melamine-based resin was not detected by ATR-FTIR (LMP (1998)/ Flame Orange and RTS (1997)/ Astral Pink), the peaks related to the presence of TSA derivatives were not identified by SPME-GC-MS. (Fig. 6A and 6C), when mild sampling conditions were performed (80 °C, 40 min).

According to the manufacturer, both series are described as non-melamine-based resin polymers. Over the years, the manufacturers have been trying to improve the longevity of the DFP, by increasing the thermal stability by changing or incorporating new additives in the resin matrix. However, as for these two thermostable DFPs, this information is patented and remains disclosed [6]. LMP is described as formaldehyde-free thermoplastic pigment suitable for masterbatch manufacture and general purpose plastics use. RTS is classified as a thermoset resin matrix for paint and ink applications. As the manufacturers do mention a significant higher temperature of decomposition, i.e. 260 °C for LMP series and 220 °C for RTS series, against 190 °C for the rest of the studied series, a second sampling treatment was

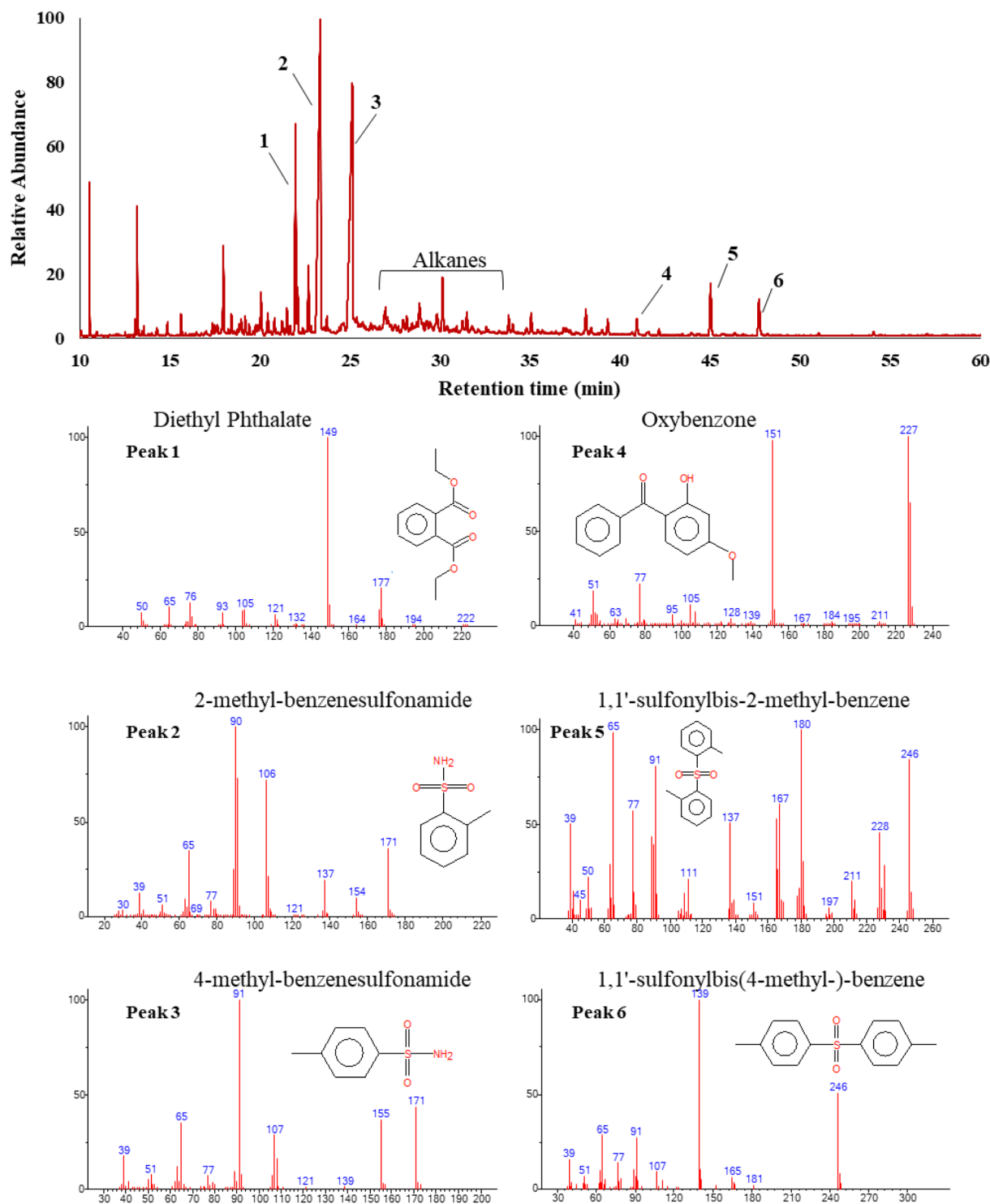


Fig. 4. Total Ion Chromatogram of DayGlo/Rocket Red (sample 4) obtained by SPME-GC-MS at mild sampling conditions (80 °C, 40 min) and mass spectra of the main identified compounds related to the composition of the resin.

performed at elevated temperatures. Instead of the standard mild conditions (80 °C, 40 min), we increased the conditions for extraction up to 150 °C during 240 min for these two thermostable DFPs. With this increase of the temperature, small TSA monomers, such as 2-methyl-benzenesulfonamide and 4-methyl-benzenesulfonamide, were detected (Fig. 6B and 6D) in these two samples. However, heavier TSA derivatives combining two benzene rings, such as 1,1'-sulfonylbis-2-methyl-benzene, and 1,1'-sulfonylbis-4-methyl-benzene, previously identified in the rest of the samples (peaks 5 and 6, Fig. 4) under mild sampling

conditions, were not detected during the analysis of the thermostable DFPs. Therefore, the volatile fraction detected in a first exploratory analysis (mild conditions) could be used as a marker on the thermostability of the DFPs. In any case, the results corroborate the different thermal stability between the analyzed samples. The identification of only small TSA monomers may be due to breakdown of the polymeric chain with the increment of the sampling temperature. In addition, the smallest and more volatile compounds will reach the fiber coating more easily than heavier resin fragments.

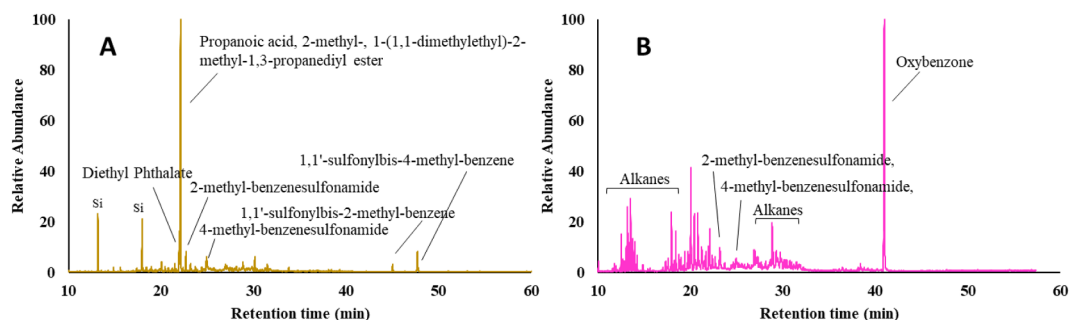


Fig. 5. Total Ion Chromatograms (TIC) obtained by SPME-GC-MS of Radiant Color samples: (A) PS-10/Chartreuse Yellow (sample 3) and (B) PS-37/Pink (sample 18).

The question remains which type of resin was used for these sample and why TSA was found now that we know that melamine was not employed. According to R. A. Ward [5], in TSA-based resins the melamine can be replaced by other amides such benzoguanamine or diaminotetrahydroquinazoline. This is consistent with the manufacturer's description of the sample Swada RTS (1997)/Astral Pink: "a dyed/pigmented modified benzoguanamine formaldehyde thermoset copolymer". Thus, the TSA fraction identified in this sample may have been incorporated during the polymerization of the benzoguanamine resin.

On the other side, the presence of amide derivatives (N-cyclohexylacetamide, and N-cyclohexyl-benzamide) was only detected in the sample LMP (1998)/ Flame Orange from Swada. The identification of these compounds also agrees with the information provided by the manufacturer "a pigmented polyamide-polyester-thermoplastic-copolymer".

Small TSA derivatives, such as 2-methyl-benzenesulfonamide and 4-methyl-benzenesulfonamide, are intermediates during the synthesis of both melamine- and benzoguanamine-based resins. Thus, the release of these small TSA derivatives by the DFP only at high temperature (> 150 °C) can indicate the presence of a benzoguanamine-based resin or other thermoplastic resins, with higher temperature of decomposition. However, the identification of TSA derivatives at mild sampling conditions, can be an indicator of the presence of a melamine-based resin, with low thermal stability. These findings agree with the ATR-

FTIR analysis since a melamine-based resin was not identified in any of these two thermostable DFPs (LMP and RTS series).

Common additives such as phthalates were detected in all samples. Phthalates are frequently added to improve the gloss, toughness, water permeability, flexibility and adhesion of the resins [27]. Although diethyl phthalate was detected in all colored samples (but not in the pure resin), dibutyl phthalate was only identified in DayGlo samples.

The Swada samples were the only ones lacking a fatty acid derivative (dodecanoic acid, 1-methylethyl ester). The presence of fatty acid compounds can be associated with the addition of water-soluble surfactants to facilitate the mixing of the composition by acting as a dispersant for the non-soluble components, particularly the pigments [32].

Esters from oxalic acid were detected in Radiant Color and Swada samples. Oxalic acid is an additive frequently added to thermostable vinyl ester and epoxy resins with the aim to increase the storage life of vinyl ester resins or unsaturated polyesters without affecting their curability [33,34]. However, esters of phthalic acid were only detected in DayGlo and Kremer samples. Again, these dissimilarities may be ascribed to the different formulations between companies.

Additionally, oxybenzone was only detected in the samples provided by DayGlo (Fig. 4) and Kremer and in one sample provided by Radiant Color (PS-37/Pink, sample 18) (Fig. 5). Oxybenzone, a derivative of benzophenone, is a photo-protective agent widely used in cosmetics to protect and minimizing the damaging effects of ultraviolet

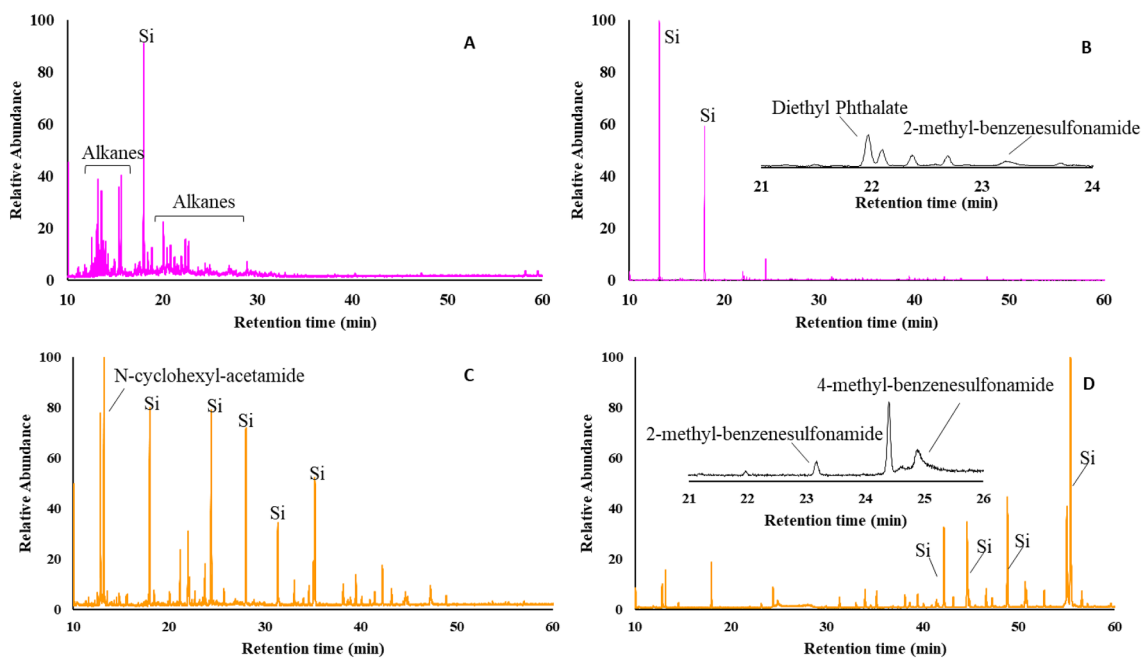


Fig. 6. Total Ion Chromatograms (TIC) obtained by SPME-GC-MS of Swada samples: (A) RTS(1997)/Astral Pink (sample 19) heated at 80 °C during 40 min and (B) heated at 150 °C during 240 min. (C) LMP(1998)/Flame Orange (sample 20) heated at 80 °C during 40 min and (D) heated at 150 °C during 240 min. Si identifies a polysiloxane contamination due to the septum used to seal the vial.

(UV) rays of natural light [35,36]. Benzophenone compounds come in colorless crystals that are readily soluble in most organic solvents and have been used in industry to protect paint and synthetic materials from destruction by UV-A [37].

Aach mentioned in a note the addition of Ultraviolet Absorbers based on benzophenone, (he named the brand *Uvimul*) that, according to the manufacturer, should protect the DFP against UV degradation [3]. Thus, the addition or increment of this UV absorber may be the reason for the substantial enhancement in longevity between the first (early sixties) and the second generation of samples (late sixties) that Aach mentions in his study. However, these organic light stabilizers (e.g. benzophenones, benzotriazoles or salicylates), were not found in the Swada samples. Since the most common alternative UV absorbers are of inorganic nature, i.e. TiO_2 or ZnO_2 [38], XRF analysis was performed to probe for differences in the inorganic-based excipients, as described in the following section.

3.3. XRF analysis

DFPs samples were analyzed by means of a benchtop XRF instrument, in order to reveal the presence of TiO_2 and ZnO , commonly used as UV absorbers [39].

The pure resin (Resin p-y-0653, Radiant Color) did not show any traces of Zn or Ti. However, in sample 18 (PS-37 Pink, Radiant Color) from the same company, Ti was detected, indicating that the addition of UV absorbers occurs in a later stage during the manufacturing process.

All DayGlo samples contain Ti, while only two lack Zn. Interestingly, a comparison between the normalized net peak intensities data of both metals, seems indicative of the color of the sample (Fig. 7). Saturn Yellow (samples 1 and 2) and Signal Green (samples 15 and 16) show higher relative amount of Ti (Fig. 7A). However, the rest of the samples from DayGlo (reds, oranges, pinks and arc yellows) show

higher relative amount of Zn (Fig. 7B). As mentioned earlier, in all 'historical' samples from DayGlo the organic UV-absorber oxybenzone was detected as well, while no traces of oxybenzone were detected in the modern DFP from Swada and one sample from Radiant. However, XRF analysis of samples 19 and 20 indicates a relative high amount of Zn (Fig. S2), suggesting that Swada uses an elevated concentration of inorganic UV absorbers instead. The combination of UV stabilizers of different nature by DayGlo might have been a reaction in response to the fast fading on light exposure that was reported at that time, as discussed by Aach in his writings.

3.4. Classification strategy

PCA of the ATR-FTIR results allows a straightforward classification of the analyzed DFPs according to the resinaceous composition, showing some clear differences between manufacturing companies. In addition, a further distinction between thermoplastic and thermoset copolymers can be made. The utility of SPME-GC-MS was demonstrated by correctly identifying the monomer fraction of each sample. In addition, this technique also has the ability to identify the other additives such as organic UV absorbers, plasticizers and side products formed during the synthesis not identifying by ATR-FTIR, making possible to distinguish between manufactures.

When comparing samples according to their period of fabrication, we found that the historical ones (DayGlo) typically consist of oxybenzone in combination with an inorganic (Ti and Zn) UV-absorber, whereas modern samples, especially those from Swada, do not contain oxybenzone. However, further research on comparing the longevity between DFPs containing organic (oxybenzone) or inorganic (Ti and Zn) UV absorbers might be of interest.

Based on the above results, the following flowchart is proposed for the characterization of the analyzed DFPs according to the resin composition (Fig. 8).

In the frame of conservation science, so far attempts were made on identifying the dyes by means of Raman, TLC-SERS and Py-GC-MS. In contrast, by comparing historical and more recent DFP samples of various fabricants, this multi-modal analysis revealed additional variables in the DFPs' composition. In particular, by focusing on the resin structure and additives we found that a deeper classification of DFPs can be obtained, as illustrated in Fig. 8. This new information will not only assist future identification strategies for DFP artworks, the data will also contribute to the development of a proper retouching protocol, thanks to a better understanding of the resin composition.

4. Conclusions

The proposed analytical methodology was able to confirm the writings of Aach stating that the resin composition was gradually improved to enhance the permanency of DFPs since 1965.

By means of combined ATR-FTIR spectroscopy, SPME-GC-MS and XRF is possible to provide an overview of different formulations commercialized since the 60 s.

In particular, the initial PCA-assisted ATR-FTIR spectroscopy allowed for an efficient classification of the main monomers in the resin polymer. The PCA allowed us to classify the unknown samples from Herbert Aach's collection. Next, SPME-GC-MS proved an effective tool for a more detailed identification of excipients added during the synthesis or manufacturing process, even at low concentration. In particular, this paper illustrates how the GC-MS sampling protocol optimized in this study can perform an effective and simultaneous extraction of resin-monomers and main additives from complex matrices such as DFPs. The characteristic fragments identified by SPME-GC-MS allowed to point out differences between companies and even series from the same manufacturer. Within the range of additives, we found markers that seemed idiosyncratic such as aldehydes, esters from oxalic and phthalic acids, TSA monomers and oxybenzone. In contrast with

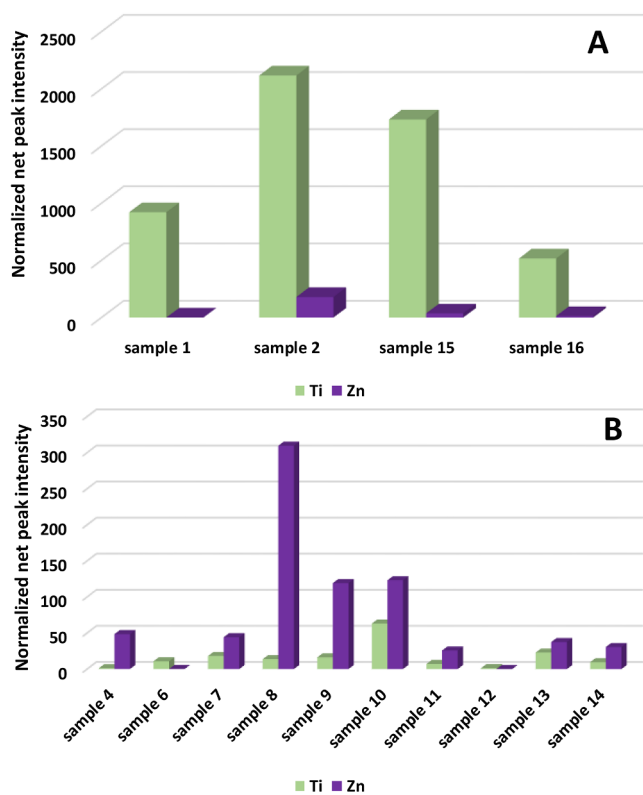


Fig. 7. XRF analysis of DayGlo samples. (A) Saturn yellow and Signal Green. (B) Rocket red, Arc yellow, Fire orange, Blaze orange. Pink, Aurora pink and Neon red. For complete information of the samples see Table 1.

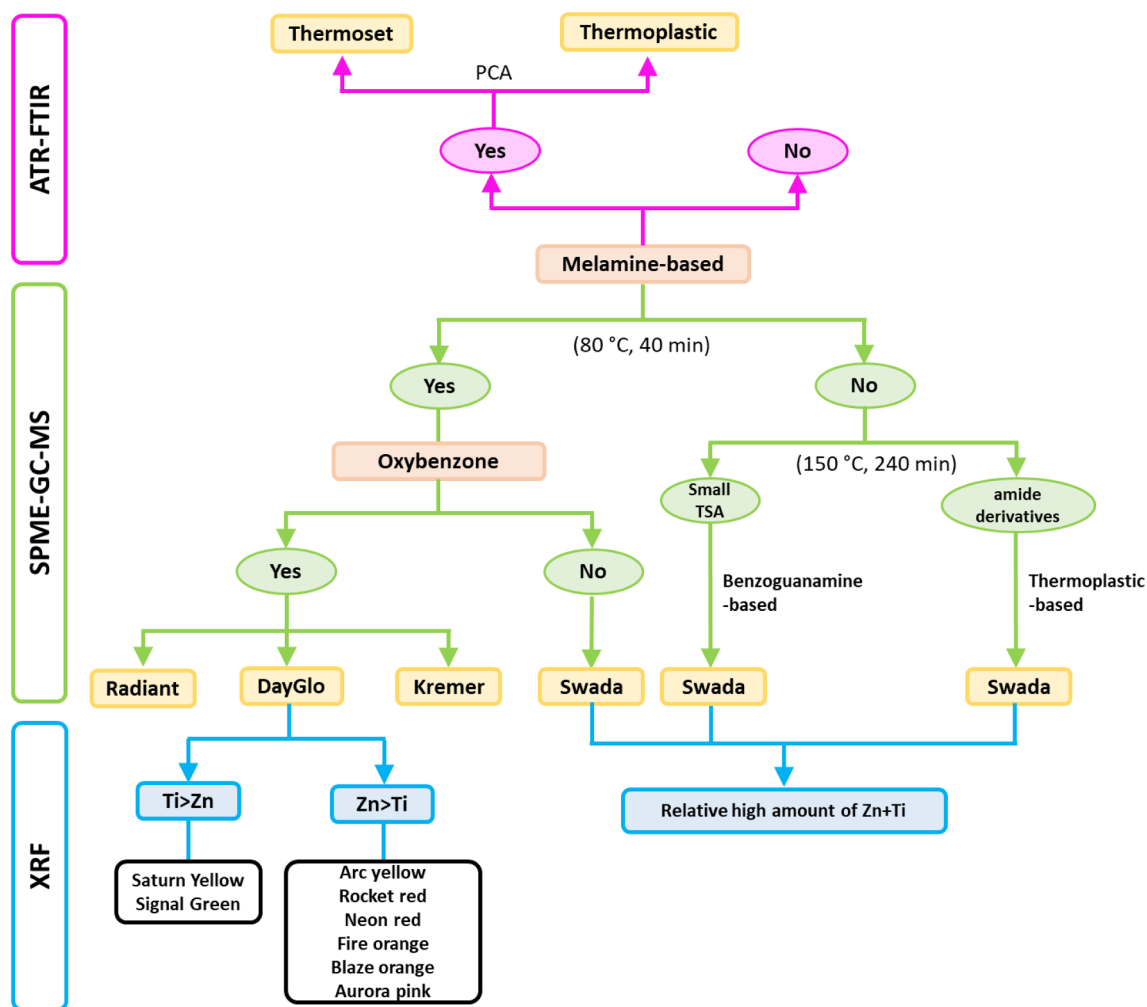


Fig. 8. Proposed flowchart for the classification of DFPs based on ATR-FTIR, SPME-GC-MS and XRF results.

Py-GC-MS used in previous DFPs analysis [9] and where the samples are calcinated (destructive analysis), SPME-GC-MS can be considered as a minimal-destructive technique. Although samples must be taken for analysis, these can be analyzed below its temperature of decomposition, keeping their appearance intact.

Conservators should be aware of the fact that both the type of fabricant, series and year of fabrication might influence the degradation process of the DFP in paint layers. Although ATR-FTIR spectroscopy indicated no change in the resin composition over the years, except for the two thermostable DFPs (sample 19 and sample 20), we did find differences in the manufactures' choice for organic and/or inorganic UV-absorbers by GC-MS and XRF measurements.

The multimodal approach presented here may result in a focus shift towards the identification of the resin rather than the dyes and thus a next step towards a better understanding of the composition and degradation of DFPs in artworks. In a later research phase of the project, portable FTIR and XRF analysis will be performed directly on Herb Aach's paintings to directly characterize the resin fraction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was part of the activities of the Chair on Advanced Imaging Techniques for the Arts, established by the Baillet Latour fund. Authors would like to thank Doris and John Aach from the Aach estate, Swada and Radiant Color for kindly donating samples. We would also like to thank Luca Bonetti corp. for collecting the samples and conservators Naomi Meulemans and Giovanna Tamá for transporting them to Belgium. Many thanks to Steven Saverwyns and Wim Fremout (KIK-IRPA) to provide samples and insights on the topic.

SDW thanks the Fund for Scientific Research Flanders (FWO) for her doctoral fellowship. AAM would like to acknowledge the Smithsonian Postdoctoral Fellowship in the Conservation of Museum Collections, the Museum Conservation Institute and Gwénaëlle Kavich and Rebecca Kaczkowski for their guidance during her postdoctoral fellowship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.microc.2020.105340>.

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