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

2   *Pigments*

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13

14   **Abstract**

15   Almost seventy years after artists such as Frank Stella (1936), Andy Warhol (1928-1987), James

16   Rosenquist (1933-2017), Herb Aach (1923-1985) and Richard Bowman (1918-2001) started to

17   incorporate Daylight Fluorescent Pigments (DFPs) in their artworks, the extent of the conservation

18   problems that are associated with these pigments has increased progressively. Since their first

19   appearance on the market, their composition has constantly been improved in terms of

20   permanency. However, conservation practices on the artworks that are used in, are complicated by

21   the fact that the composition of DFPs is proprietary and the information provided by the

22   manufactures is limited. To be able to propose adequate conservation strategies for artworks

23   containing DFPs, a thorough understanding of the DFPs composition must be acquired. In contrast

24   with previous research that concentrated on identification of the coloring dye, this paper focuses

25   on the characterization of the resin, used as the carrier for the dye. The proposed approach,

26 involving ATR-FTIR, SPME-GC-MS and XRF analysis, provided additional insights on the

27 organic and inorganic components of the resin. Using this approach, we investigated historical

28 DFPs and new formulations, as well as different series from the main manufacturing companies

29 (DayGlo, Swada, Radiant Color and Kremer) in order to obtain a full characterization of DFPs

30 used by the artists along the years. First, the initial PCA-assisted ATR-FTIR spectroscopy allowed

31 for an efficient classification of the main monomers in the resin polymer. Next, a further distinction

32 was made by mass spectrometry and XRF which were optimized to allow a more specific

33 classification of the resin and for detection of additives. In this paper we show the potential of

34 SPME-GC-MS, never applied for the characterization of artistic materials, at present undervalued

35 for heritage science purposes. We anticipate that this information will be highly relevant in for

36 future stability studies and for defining (preventive) conservation strategies of fluorescent

37 artworks.

38

39 **Keywords**: Daylight fluorescent pigments, Herb Aach, Melamine-based resin, ATR-FTIR,

40 SPME-GC-MS, Contemporary art conservation, DayGlo

41

42 *1. Introduction*

43 Since the 60s, North American artists frequently used Daylight Fluorescent Pigments (DFPs) in

44 their artworks for various reasons: Frank Stella incorporated them in his minimal paintings for

45 their self-referential, industrial look, as did James Rosenquist and Andy Warhol whose pop art was

46 inspired by commercial billboards, in which DayGlo paints were used to draw more attention to

47 their messages [1]. Other artists such as Richard Bowman and Herb Aach dedicated their careers

48 to exploring the new visual effects specific to DFPs [2, 3]. These luminescent, synthetic, modern

49   paints revealed a new dimension in color that resulted in unseen visual experiences, such as illusory

50   color depth, optical vibration and new contrast effects. Unfortunately, there is a downside to the

51   use of fluorescent paints, in the sense that they age much faster than conventional colors, due to

52   the organic nature of the two groups of materials that DFPs are made: the dyes and the resin carrier.

53   In particular, the fast bleaching of the pigment and strong metamerism problems associated to

54   retouches and fillings have been reported [3]. As it is also impossible to digitally document the

55   luminescent effect of DFPs, the conservation of fluorescent artworks proves an arduous task for

56   the curatorial staff [4]. It is known that a DFP exists mostly of a resin carrier which is colored with

57   a very small percentage of dyestuff (0.1-5%). The resin carried is a condensation-type resin,

58   consisting on a large resin structure formed by small monomers carrying polar groups. During the

59   manufacturing of DFPs, dyes and resin are mixed when the latter is still in a monomeric form or

60   in an early stage of condensation. As the resinous medium is not a solvent for the pigment, since

61   the sixties, DFPs were mainly mixed with colorless media such as gouache, acrylic, alkyd and

62   enamel [5]. Next to these two base components, UV-stabilizers, anti-foam agents and optical

63   brighteners are commonly added to the resin matrix to retain the best properties of the dye [3, 6].

64   So far, the lack of information about the composition and properties of DFPs has prevented the

65   formulation of an adequate, standard conservation and restoration treatment [4, 7, 8]. Nowadays,

66   inpainting is usually based on the application of new DFPs that have been artificially aged to

67   visually match the appearance of the original paint [4]. However, this approach, employing modern

68   DFPs, yields unsatisfactory results on the long-term. Since the formulation of the resin has been

69   constantly modified, the present-day DFPs age in a different manner than the surrounding

70   historical paint, and thus will eventually display a deviant appearance [5] In the past years, some

71   attempts were made to enhance the understanding of the DFPs composition [9, 10]. However, these

72   studies focused on the characterization of the dye composition rather than on the resin and its

73   additives and provided only limited information on the durability of the paint system as a whole.

74   Therefore, the aim of this study was to search for differences in DFPs compositions over the years,

75   by focusing on the resin structure and additives in samples from four different pigment

76   manufacturing companies such as DagGlo Corp. (Ohio, US), Kremer Pigmente GmbH

77   (Aichstetten, Germany), Radiant Color NV (Houthalen, Belgium) and Swada LLC (Stalybridge,

78   UK).

79   *Art Historical Background*

80   Initially DFPs were developed during World War II to improve safety signalization and later to

81   increase the visual saliency of commercial images [11]. The earliest found reference on the

82   'artistic' use of DFPs is an article published in 1970 by an American artist and color engineer Herb

83   Aach (1923-1985), who appears to have played a key role in the introduction of DFPs as artistic

84   materials. In this paper, entitled *On the Use and Phenomena of Fluorescent Pigments in Painting*

85   [3], Aach, who extensively used DFPs in his own artworks [12], describes his first contact with

86   DFP and their *optimal* use in painting. As active member of the Committee of Commercial

87   Standards (CS98-62 of the U.S. Department of Commerce), which governed artists' materials, he

88   often tested new pigments in terms of lightfastness and suitability for art works [3, 6] Aach already

89   noticed an improvement in the longevity between two different sets of DFPs manufactured by

90   DayGlo, the main manufacturer company at that time. Motivated by their lack of permanency,

91   Aach kept working on the stability, consistency and artistic suitability of DFPs throughout his

92   career. For instance, in an attempt to overcome their distinct transparency, he increased the ratio

93   of DFPs in the acrylic medium [3]. This experiment resulted in very saturated, matt, fresco-like

94   paint layers, which is clearly reflected in his *Split Infinity* series (**Figure 1A**). Beside the valuable

95 information about his paint compositions, nothing could be found in Aach's paper regarding the

96 nature of the resin used in DFP. After Aach died in 1985, a collection of his DayGlo pigments

97 were conserved in the *Herbert Aach Estate* (New York, US). For this research, 16 different samples

98 were donated to the authors for an in-depth investigation (**Figure 1B-C**). As a benchmark for the

99 evolving composition, a number of more recent fabricated samples from Radiant Color, Swada

100 and Kremer were included in this study (**Table 1**).

101

102 **Figure 1**. (A) Herb Aach, *Split Infinity # 2* (1975), daylight fluorescent acrylic paint on cotton

103 duck (size 188 x 137cm), private collection (® artwork of Herb Aach); (B) envelop with pigment

104 sample of *Aurora Pink*, from the Herbert Aach estate; (C) preserved daylight fluorescent pigment

105 samples from Herbert Aach donated for this research by his widow, Doris Aach.

106

Structure of Daylight Fluorescent Pigments

108   DFPs are comprised of two main components: (i) a transparent, crystalline organic substance that

109   strongly fluoresces in the solid state when excited by long-wave UV or visible light and (ii) organic

110   resinous particles and other organic or inorganic excipients, in which the mixture of fluorescent

111   components is dissolved [5]. The ratio of this mixture is in general 5:95, with the fluorescent

112   pigment being the minor component. The most common resin used during the manufacture of

113   DFPs belongs to the amino resin's family, synthetized by reactions involving formaldehyde with

114   a variety of amine functional compounds such as urea, melamine, and benzoguanamine. The

115   combination of these compounds results in resins based on melamine-formaldehyde, melamine-

116   urea-formaldehyde, benzoguanamine-formaldehyde, benzoguanamine-urea-formaldehyde and

117   melamine-benzoguanamine-formaldehyde copolymers [13].

118   The first commercialized DFPs in the early 1940's were melamine-thermoplastic resins containing

119   fluorescent dyes with moderate solvent and light stability. The main disadvantage of thermoplastic

120   DFPs was their tendency to swelled. To overcome this, thermoset DFPs were developed from the

121   same ingredients but using higher proportion of melamine in an attempt to improve the stability.

122   As a result, new colors were commercialized in a broad variety of applications such as paints and

123   inks, plastics, textile and make-up [5, 6].

124   Although, a few manufacturers do provide general information on the formulation, in most of the

125   cases the composition remains proprietary. The characterization of the resin type is in most cases

126   an arduous task since the formulation can greatly vary between manufacturing companies and even

127   between series produced by the same manufacture over the years. At the moment, the only

128   publication dealing with the characterization of the resinous composition of DFPs used as artistic

129   materials applied Py-GC-MS in order to characterize the main fragments of melamine-derivate

130   resins [9]. However, this technique does not provide information on the additives present in the

131   formulation, due to their low thermal stability and the elevated temperatures reached during the

132   pyrolysis process. In other fields, such as industrial processes or material and polymer chemistry,

133   several analytical techniques have been applied to characterize melamine-based resins. For

134   instance, few studies investigate the thermal behavior of melamine resins by a variety of analytical

135   methods such as FTIR, NMR, differential scanning calorimetry and thermogravimetry [14-17],

136   providing information about critical parameters related to the synthesis and cure process.

137   In this study, we propose a multi-method, three-step approach, combining ATR-FTIR, SPME-GC-

138   MS and XRF for the analysis of the resin fraction of DFPs. First, ATR-FTIR was employed as a

139   screening technique to rapidly distinguish the main resinous fraction type (e.g. melamine-based

140   resin). Next, a further distinction was made by mass spectrometry which was optimized to allow a

141   more specific classification of the resin and for detection of additives. The latter cannot be

142   identified by the preceding FTIR analysis due to their small weight percentage. In particular, Solid

143   Phase Micro-Extraction coupled to Gas Chromatography-Mass Spectrometry (SPME-GC-MS)

144   was considered as a semi-destructive analytical method to avoid the aforementioned breakdown

145   of the resinous fraction by other GC-MS based techniques (e.g. Py-GC-MS). SPME-GC-MS has

146   been widely applied in museum institutions to identify volatile compounds emitted by the objects

147   in the collection [18-20] and to characterize terpene resins in archaeological objects [21, 22].

148   Despite the broad application of this technique, no studies deal with the application of SPME as a

149   screening method for the evaluation of the constituents of artistic materials so far. As such, this

150   research can be considered as a first evaluation of the potential of SPME-GC-MS as one-step

151   preparation technique for screening artworks.

152 As a final step, XRF analysis was carried out in order to provide information about the inorganic

153 composition of the UV-absorbers added by the different companies.

154 This study is the first to provide a more complete overview of the resin carrier and the presence of

155 additives on a selection of DFPs. In summary, the new knowledge that is provided by this

156 methodology on the chemical composition of the resin carrier used by manufactures along the

157 years, is anticipated to be a vital step towards a full understanding of the fading of DFPs and the

158 parameters affecting this process.

159

160 *2. Materials and Methods*

161 *2.1 Reference materials and historical samples*

162 A set of samples was selected for this study, including the samples from the Herbert Aach Estate

163 manufactured by DayGlo between 1965 and 1979 and more recent samples from other

164 manufacturing companies (Swada, Kremer and Radiant), purchased in 2009.

165 In total, 33 DFP samples were collected for this study (Table 1). 14 historical samples from the

166 60s-70s, listed as *DayGlo* (DayGlo corp., Ohio, USA) and belonging to Herb Aach's private

167 collection were generously donated by his widow Doris Aach. This historical corpus was

168 supplemented with 19 modern 'benchmark' reference samples. In particular, 13 samples,

169 fabricated between 1997-2009, were generously provided by Swada (Stalybridge, UK), three

170 samples, fabricated in 2009, were offered by Radiant Color (Houthalen, Belgium) and two samples

171 were purchased in 2009 from Kremer Pigments (New York, USA). In addition, a reference sample

172 of the carrier resin (toluene-sulfonamide-melamine-formaldehyde (P.Y. 0653)) was generously

173 provided in 2012 by Radiant Color (Houthalen, Belgium). Each manufacturer classifies the

174 samples in product series, according to the composition, physical properties and use. For nine

175   samples from Aach's historical DayGlo collection, it was unclear to which series they belonged

176   and therefore remained uncharacterized (see **Table 1**). Three samples from the AX series, one

177   from the T series and one from the GT series were analyzed. From Swada, six color samples from

178   the T series, two samples from the A series, two samples from the FTX series, one sample from

179   the RTS series and one sample from the LMP series were analyzed. From Radiant Color, a sample

180   of pure resin and three samples from the PS series were selected and from Kremer both pigments

181   belonged to the 56000 - 56450 Fluorescent Pigments series. Beside the manufacturing company,

182   A and AX series are classified as thermoplastic copolymers and T, GT, FTX and PS are classified

183   as thermoset copolymers. All these 33 samples were analyzed by FTI-ATR, based in the result a

184   selection of 12 samples were analyzed by SPME-GC-MS. Finally, 23 samples were analyzed by

185   XRF.

186

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

Sample No.	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 Figure 1C).

[(S)] = analyzed by SPME-GC-MS

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

202   decomposition of the data matrix (wavenumber range: 400-2190 cm^{-1}) using Mathematica

203   software. For this analysis, all spectra were baseline corrected, normalized to the highest peak in

204   the wavenumber range, and they had their mean value subtracted.

205

206   *2.3 SPME-GC-MS*

207   *2.3.1 SPME sampling procedure*

208   Three fiber coatings were tested for this study: (i) 75 µm carboxen/polydimethylsiloxane

209   (CAR/PDMS), (ii) 50/30 µm divinylbenzene/carboxen/polydimethylsiloxane)

210   (DVB/CAR/PDMS) and (iii) 100 µm polydimethylsiloxane (PDMS). The non-polar PDMS fiber

211   showed the higher extraction efficiency for the analytes of interest due to their molecular weight

212   and polarity, thus was selected for this study. This type of coating has been used in previous studies

213   for the detection of resins in archeological samples [12]. For sampling, 40 mg of sample powder

214   was placed in a 1.5 ml vial with a PTFE septum. SPME fiber was inserted into the vial through the

215   septum followed by manual exposure of the fiber to the headspace of the sample. Samples were

216   heated in order to facilitate the release of the most volatile analytes. Two sampling conditions were

217   performed: (i) 40 min at 80°C and (ii) 240 min at 150°C.

218   *2.3.2 GC-MS conditions*

219   After sampling, the fiber was manually inserted into the injector port where the analytes were

220   thermally desorbed and transferred onto the chromatographic column for separation and further

221   detection with the mass spectrometer. The desorption temperature was 250°C. GC-MS analysis

222   was performed with an Agilent 7890 GC coupled to a 5975 MSD (Agilent Technologies,

223   Wilmington, DE, USA). Chromatographic separation was performed on a 30 m × 0.25 mm id,

224   0.25-µm-thick film of DB-5ms capillary column (Agilent Technologies, Wilmington, DE, USA).

225 The injector was used in splitless mode with an injection time of 5 min. The initial oven

226 temperature program was set at 40°C (hold for 1 min), then ramp rate of 9°C/min to 130°C (hold

227 for 1 min), and 2°C/min to 230°C which was held for 1 min. The temperature of the interface and

228 the source were set at 280 and 230°C, respectively. Mass spectra were acquired under electron

229 ionization mode (EI) at 70 eV and recorded from m/z 40-500 with a scan time of 0.19 s. Data

230 processing was performed using Masshunter® qualitative analysis (version B.07.00, Agilent).

231 Chromatographic peaks were identified by using the NIST library 2011 Mass spectra Library

232 V.2.0.

233

234 *2.4. XRF analysis*

235 XRF is one of the most cited analytical methods in literature dealing with the investigation of

236 cultural heritage artefacts. The technique owes its popularity to the fact that it allows collecting

237 elemental and spatially-resolved information in a non-destructive way on major and minor

238 constituents of a variety of materials [23]. Small amounts of the pigment powder were put on a

239 mylar foil in a Teflon sample cup. XRF spectra were acquired with a PW4025 Minipal 25 fm

240 (Panalytical) spectrometer, equipped with a low power, air-cooled Rh-anode X-ray tube and a Si-

241 PIN detector. The Minipal has a maximum power, current and voltage of respectively 9W, 1000

242 µA and 30 kV. All samples were measured with a live time of 600 s by applying a voltage of 30

243 kV and current of 20 - 75 µA and using a 50 µm Al filter between the X-ray tube and the sample.

244 All spectra were analyzed using the bAXIL software package (BrightSpec NV) [24]. The net peak

245 intensities of the Zn and Ti Kα were determined for each sample and normalized by the net peak

246 intensity of the Rh Kα incoherent scatter peak. The incoherent scatter peak gives an indication on

247 the amount of low Z material present. In our case it is an indication of the amount of pigment

248 powder on the mylar foil. No (semi)-quantification of the data was performed but the normalized

249 net peak intensities give an indication on the relative amounts of Ti and Zn.

250

251 **3. Results and Discussion**

252 *3.1. ATR-FTIR spectroscopy*

253 ATR-FTIR spectroscopy was carried out to determine the primary components of the resin (**Figure**

254 **S1**). Of the 33 samples analyzed, 31 were initially classified as resins based on melamine-

255 formaldehyde or melamine-urea-formaldehyde according to the HR library. The two resins with a

256 deviating resin polymer are Swada LMP (1998)/Flame Orange (sample 20, type A) and Swada

257 RTS (1997)/Astral Pink (sample 19, type B). The spectra of the remaining 31 samples with a

258 melamine-based resin were analyzed using principal component analysis (PCA) to support

259 classification of the materials (**Figure 2**). The score plot of the second and third principal

260 components suggests that these 31 samples can be further divided into four distinct groups.

261 The main features of the total of six resin types of resin are discussed using their representative

262 spectra shown in **Figure 3**.

263 Resin *type A*, the Swada LMP (1998)/Flame Orange (**Figure 3**), described by the manufacturer as

264 a polyamide-polyester thermoplastic copolymer, stands out with a clear ester carbonyl band at

265 1720 cm^{-1} and a set of amide bands at 1630 and 1530 cm^{-1}. This spectrum also showed more

266 intense alkyl vibrations at 2920 cm^{-1} than any other of the 32 samples (alkyl vibrations not shown).

267 Resin *type B*, the Swada RTS (1997)/Astral Pink sample, distinguishes itself by a set of bands at

268 780 and 825 cm^{-1} that indicate the presence of benzoguanamine monomer [5, 25], as indicated by

269 the manufacturer in the safety data sheet. Benzoguanamine can also be identified by the vibrations

270 of its triazine ring around 1535 cm^{-1}. Resin *types C-F* all show a strong band at 1150 cm^{-1} (C-O-C

271   ether stretch) [26]. All samples manufactured by Radiant Color (*type C*) display spectra that are

272   similar to the uncolored toluene-sulfonamide-melamine-formaldehyde resin sample, donated by

273   the company. In particular, the distinct band at 1015 cm^{-1} is likely caused by the presence of

274   toluene-sulfonamide. The bands at 810 and 1545 cm^{-1}, present in nearly all spectra, are both caused

275   by the vibrations of the triazine ring in melamine [27]. All samples clustered in *type C* are described

276   by Radiant Color as thermoset-sulphonamide-melamine-paraformaldehyde resin The pink color

277   from the DayGlo series (sample 11, *type D*) seems to be similar in formulation to the other DayGlo

278   samples, except that it has been prepared with benzoguanamine rather than melamine as monomer.

279   Since this sample belongs to Aach's private collection, and no information was provided in the

280   container, it was not possible to assign it to a specific pigment series within the DayGlo product

281   range. The final two resin types that can be distinguished with PCA show only subtle differences

282   in the IR spectra that are difficult to ascribe to a specific resin composition with ATR-FTIR

283   spectroscopy. Interestingly, *type E* corresponds to the samples classified as thermoplastic

284   copolymers from DayGlo and Swada (serie AX and A, see Table 1), while *type F* consist of

285   thermoset copolymers (serie GT, FTX and T, see Table 1). Based on these clusters, we can

286   conclude that the unclassified samples from Aach's private collection (Table 1) are thermoplastic

287   copolymers with the exception of sample 10, which belongs to the thermoset group (*type F*). While

288   Kremer specifies both DFPs as thermoset, we observed that one sample lies in the thermoplastic
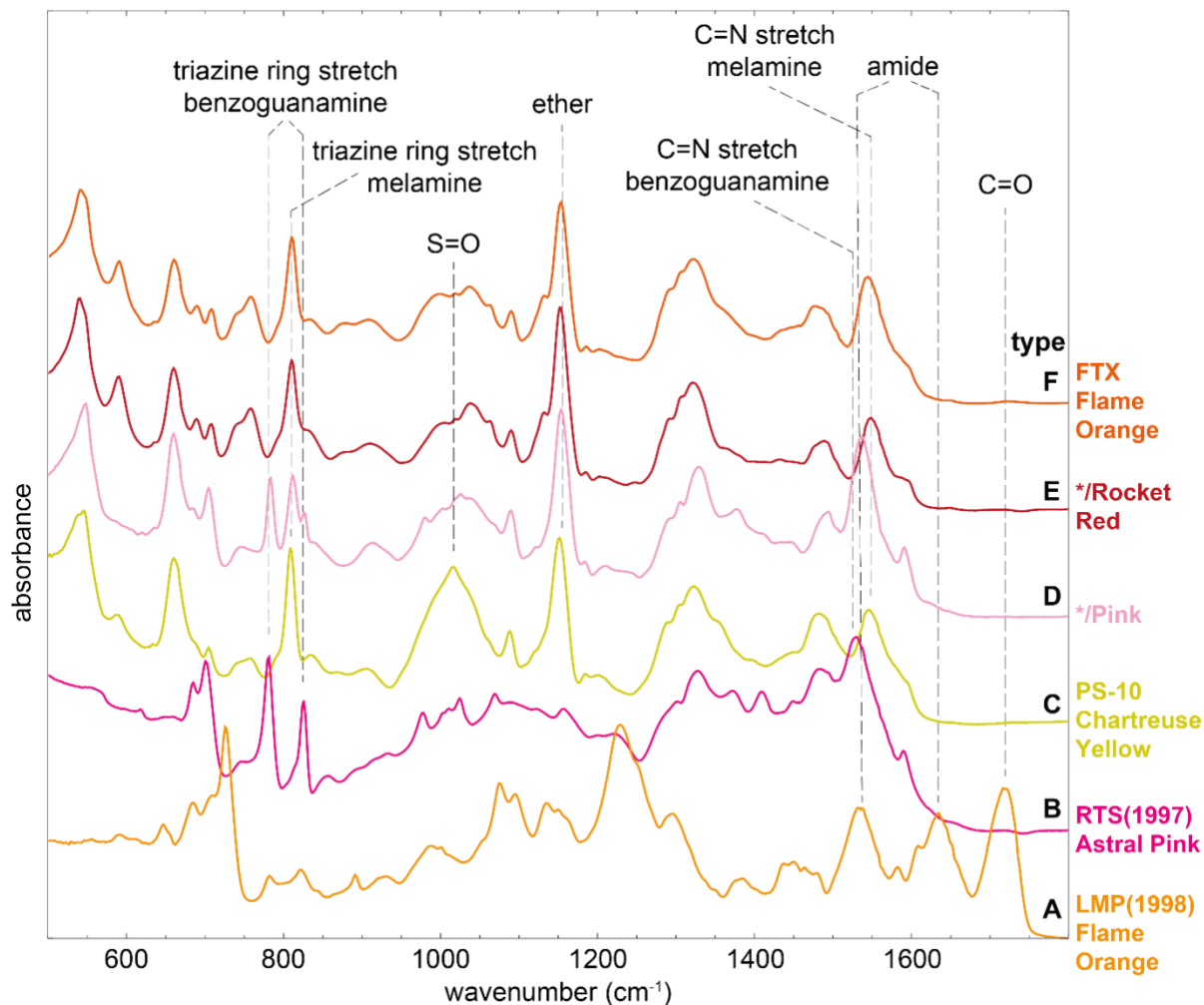
289   group (sample 28, *type E*).

290
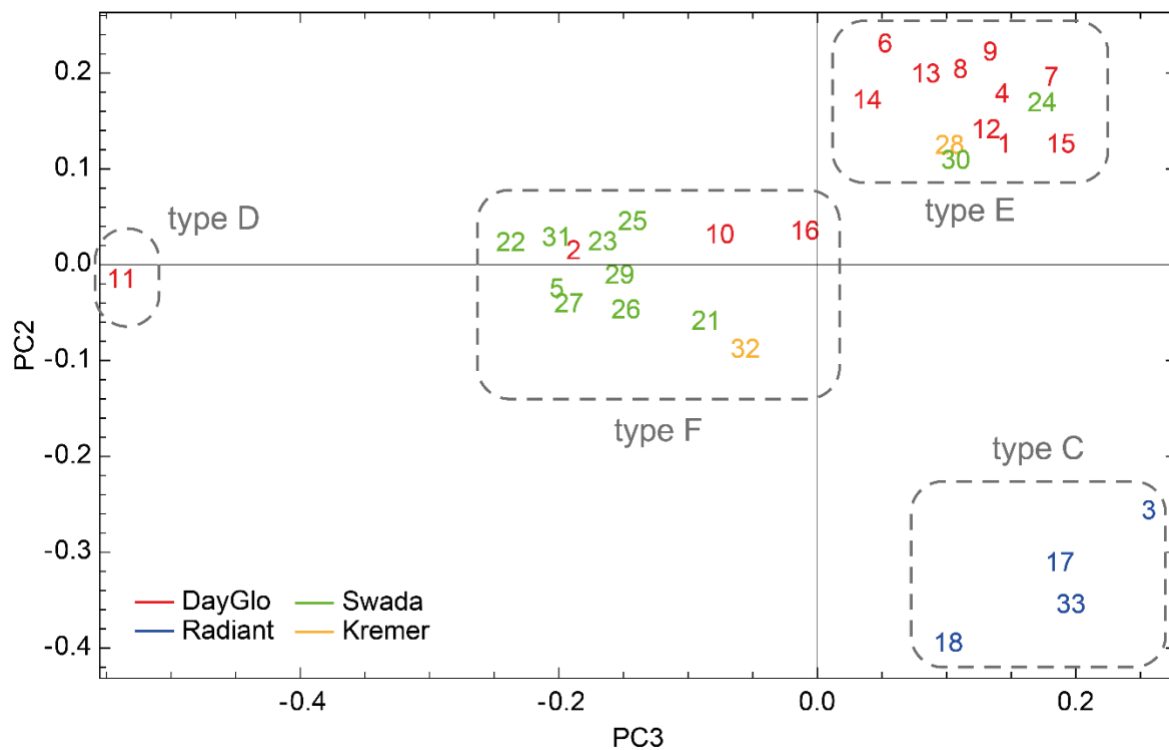
Figure 2. PCA score plot showing the contributions of the second and third principle component in the ATR-FTIR spectra shown in **Figure S1**. The indicated numbers correspond to the samples in **Table 1**, while their colors refer to the manufacturing company.

297

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

299   set.

300

301   *3.2. SPME-GC-MS analysis*

302   SPME-GC-MS analysis was used to point out subtle differences in the composition between

303   manufacturer companies. For this reason, a total of 12 samples was analyzed by SPME-GC-MS:

304   three samples from DayGlo, five samples from Swada, three samples from Radiant and one sample

305   from Kremer (**Table 1**). The selection of these samples was based on the differences encountered

306   by ATR-FTIR spectroscopy explained in the previous section.

307   SPME is based on the partition of volatile or semi-volatile organic analytes between the headspace

308   of the sample and the polymeric coating of the fiber, integrating sampling, extraction, and

309   concentration of the analyte in a single step [28]. Due to the high temperatures of decomposition

310   of synthetic resins, a slight heating of the sample will facilitate the detection of the volatile fraction

311   without causing the total fragmentation of the polymer and without causing any noticeable damage

312   on the sample.

313   Previous studies have shown the efficiency of heating, over sampling at room temperature for the

314   extraction of archeological resins [21, 22, 29]. To facilitate the extraction of volatile analytes from

315   the bulk of the sample, a level of heating is required to increase the transport to the coating of the

316   fiber. However, the temperature has to be the appropriate to allow the analytes to reach the fiber

317   coating but without causing the total breakdown of the thermolabile analytes. Since the

318   optimization of a minimal-destructive method is of importance when dealing with historical

319   samples, the first sampling condition was tested at 80°C for 40 min [22]. The chosen temperature

320   was kept below the thermal degradation point of all samples without altering their appearance.

321   After exposing the samples to this mild condition, most of the detected compounds can be

322   classified as alkanes, alkenes and alcohols related to additives or residual compounds originating

323   or added during the manufacturing process. Although these are not helpful for identification of the

324   resin, a number of 'target compounds' was identified that can be considered as specific for each

325   manufacturing company, as discussed in the next few paragraphs. It is important to note that the

326   following description is solely based on qualitative analysis, quantitative analysis was not possible

327   due to sampling conditions (e.g. no control of the volume of the headspace and equilibrium time).

328   As shown in **Figure 4**, **5** and **6**, a large group of linear alkanes and alkenes has been detected. The

329   presence of n-alkanes was also reported in previous analysis of synthetic resins [30] and these may

330   have been included as additives for improving the durability of the mixture. Interestingly, (Z) and

331   (E) alkenes were exclusively detected in Swada samples.

332   The synthesis of urea-formaldehyde-based resins proceeds via the methylolation of urea and

333   condensation of the methylol groups. Thus, the detection of alcohols in all samples may be related

334   to the fragmentation of methylol groups present in the polymeric resin [31]. However, only three

335   aldehydes were identified (decanal, nonanal and pentadecanal) in two Swada series: T and FTX.

336   The detection of a larger number of alkanes and alkenes over alcohols and aldehydes is directly

337   related to the high volatility of the first two chemical families, facilitated during the (heated)

338   sampling conditions. In addition to this, the type of fiber used during the analysis (PDMS, 100

339   µm) might have an influence on the detected analytes as it shows more affinity for low molecular

340   weight and volatile compounds [28].

341   Toluene sulfonamide derivatives (TSA) were detected in those samples previously classified by

342   ATR-FTIR as melamine-based resins (peaks 2, 3, 5, 6 in **Figure 4** and **Figure 5**). The introduction

343   of TSA during the synthesis of polymeric resins was not until 1951 [5]. However, resins only

344   constituted by TSA were not suitable for DFP because of their low melting points, directly

345   decreasing their thermostability. To improve the thermostability, a combination of TSA derivatives

346   with urea-melamine-based resins was commercialized since 1951, showing great resistance and

347   durability [5].

348   As expected, in the two Swada samples where a melamine-based resin was not detected by ATR-

349   FTIR (LMP (1998)/ Flame Orange and RTS (1997)/ Astral Pink), the peaks related to the presence

350   of TSA derivatives were not identified by SPME-GC-MS. (**Figure 6A** and **6C**), when mild

351   sampling conditions were performed (80°C, 40 min).

352   According to the manufacturer, both series are described as non-melamine-based resin polymers.

353   Over the years, the manufacturers have been trying to improve the longevity of the DFP, by

354   increasing the thermal stability by changing or incorporating new additives in the resin matrix.

355   However, as for these two thermostable DFPs, this information is patented and remains disclosed

356   [6]. LMP is described as formaldehyde-free thermoplastic pigment suitable for masterbatch

357   manufacture and general purpose plastics use. RTS is classified as a thermoset resin matrix for

358   paint and ink applications As the manufacturers do mention a significant higher temperature of

359   decomposition, i.e. 260°C for LMP series and 220°C for RTS series, against 190°C for the rest of

360   the studied series, a second sampling treatment was performed at elevated temperatures. Instead

361   of the standard mild conditions (80°C, 40 min), we increased the conditions for extraction up to

362   150°C during 240 min for these two thermostable DFPs. With this increase of the temperature,

363   small TSA monomers, such as 2-methyl-benzenesulfonamide and 4-methyl-benzenesulfonamide,

364   were detected (**Figure 6B** and **6D**) in these two samples. However, heavier TSA derivatives

365   combining two benzene rings, such as 1,1'-sulfonylbis-2-methyl-benzene, and 1,1'-sulfonylbis-4-

366   methyl-benzene, previously identified in the rest of the samples (peaks 5 and 6, **Figure 4**) under

367   mild sampling conditions, were not detected during the analysis of the thermostable DFPs.

368   Therefore, the volatile fraction detected in a first exploratory analysis (mild conditions) could be

369   used as a marker on the thermostability of the DFPs. In any case, the results corroborate the

370   different thermal stability between the analyzed samples. The identification of only small TSA

371   monomers may be due to breakdown of the polymeric chain with the increment of the sampling

372   temperature. In addition, the smallest and more volatile compounds will reach the fiber coating

373   more easily than heavier resin fragments.

374   The question remains which type of resin was used for these sample and why TSA was found now

375   that we know that melamine was not employed. According to R. A. Ward [5], in TSA-based resins

376   the melamine can be replaced by other amides such benzoguanamine or

377   diaminotetrahydroquinazoline. This is consistent with the manufacturer's description of the

378   sample Swada RTS (1997)/Astral Pink: "a dyed/pigmented modified benzoguanamine

379   formaldehyde thermoset copolymer". Thus, the TSA fraction identified in this sample may have

380   been incorporated during the polymerization of the benzoguanamine resin.

381   On the other side, the presence of amide derivatives (N-cyclohexyl-acetamide, and N-cyclohexyl-

382   benzamide) was only detected in the sample LMP (1998)/ Flame Orange from Swada. The

383   identification of these compounds also agrees with the information provided by the manufacturer

384   "a pigmented polyamide-polyester-thermoplastic-copolymer".

385   Small TSA derivatives, such as 2-methyl-benzenesulfonamide and 4-methyl-benzenesulfonamide,

386   are intermediates during the synthesis of both melamine- and benzoguanamine-based resins. Thus,

387   the release of these small TSA derivatives by the DFP only at high temperature (>150°C) can

388   indicate the presence of a benzoguanamine-based resin or other thermoplastic resins, with higher

389   temperature of decomposition. However, the identification of TSA derivatives at mild sampling

390   conditions, can be an indicator of the presence of a melamine-based resin, with low thermal

391   stability. These findings agree with the ATR-FTIR analysis since a melamine-based resin was not

392   identified in any of these two thermostable DFPs (LMP and RTS series).

393   Common additives such as phthalates were detected in all samples. Phthalates are frequently added

394   to improve the gloss, toughness, water permeability, flexibility and adhesion of the resins [27].

395   Although diethyl phthalate was detected in all colored samples (but not in the pure resin), dibutyl

396   phthalate was only identified in DayGlo samples.

397 The Swada samples were the only ones lacking a fatty acid derivative (dodecanoic acid, 1-

398 methylethyl ester). The presence of fatty acid compounds can be associated with the addition of

399 water-soluble surfactants to facilitate the mixing of the composition by acting as a dispersant for

400 the non-soluble components, particularly the pigments [32].

401 Esters from oxalic acid were detected in Radiant Color and Swada samples. Oxalic acid is an

402 additive frequently added to thermostable vinyl ester and epoxy resins with the aim to increase the

403 storage life of vinyl ester resins or unsaturated polyesters without affecting their curability [33,

404 34]. However, esters of phthalic acid were only detected in DayGlo and Kremer samples. Again,

405 these dissimilarities may be ascribed to the different formulations between companies.

406 Additionally, oxybenzone was only detected in the samples provided by DayGlo (**Figure 4**) and

407 Kremer and in one sample provided by Radiant Color (PS-37/Pink, sample 18) (**Figure 5**).

408 Oxybenzone, a derivative of benzophenone, is a photo-protective agent widely used in cosmetics

409 to protect and minimizing the damaging effects of ultraviolet (UV) rays of natural light [35, 36].

410 Benzophenone compounds come in colorless crystals that are readily soluble in most organic

411 solvents and have been used in industry to protect paint and synthetic materials from destruction

412 by UV-A [37].

413 Aach mentioned in a note the addition of Ultraviolet Absorbers based on benzophenone, (he named

414 the brand *Uvimul*) that, according to the manufacturer, should protect the DFP against UV

415 degradation [3]. Thus, the addition or increment of this UV absorber may be the reason for the

416 substantial enhancement in longevity between the first (early sixties) and the second generation of

417 samples (late sixties) that Aach mentions in his study. However, these organic light stabilizers (e.g.

418 benzophenones, benzotriazoles or salicylates), were not found in the Swada samples. Since the

419 most common alternative UV absorbers are of inorganic nature, i.e.TiO_2 or ZnO_2 [38], XRF

420   analysis was performed to probe for differences in the inorganic-based excipients, as described in

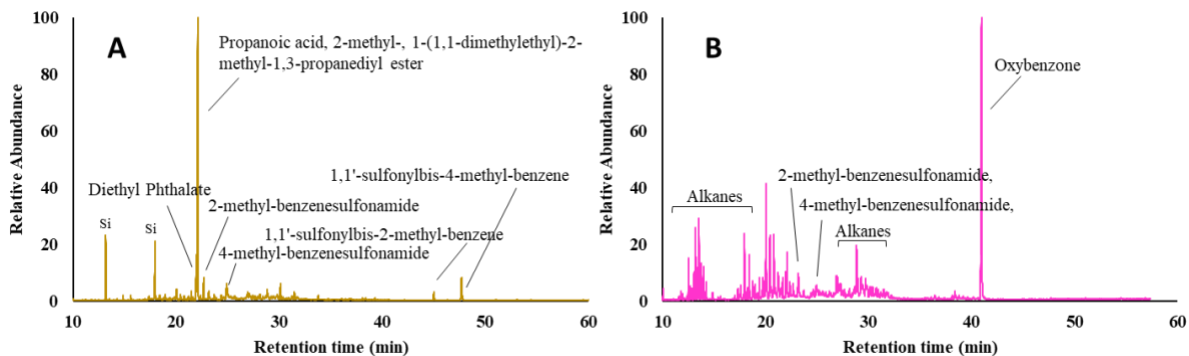421   the following section.

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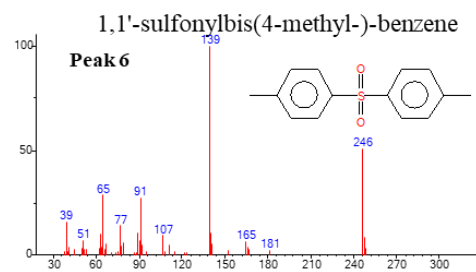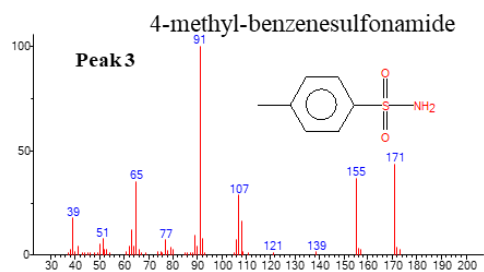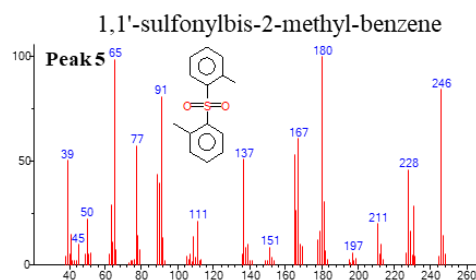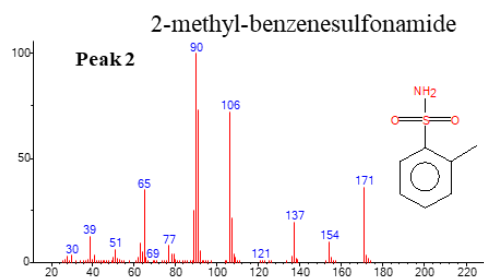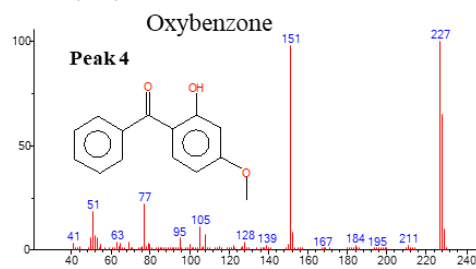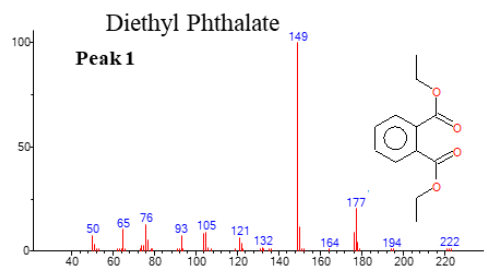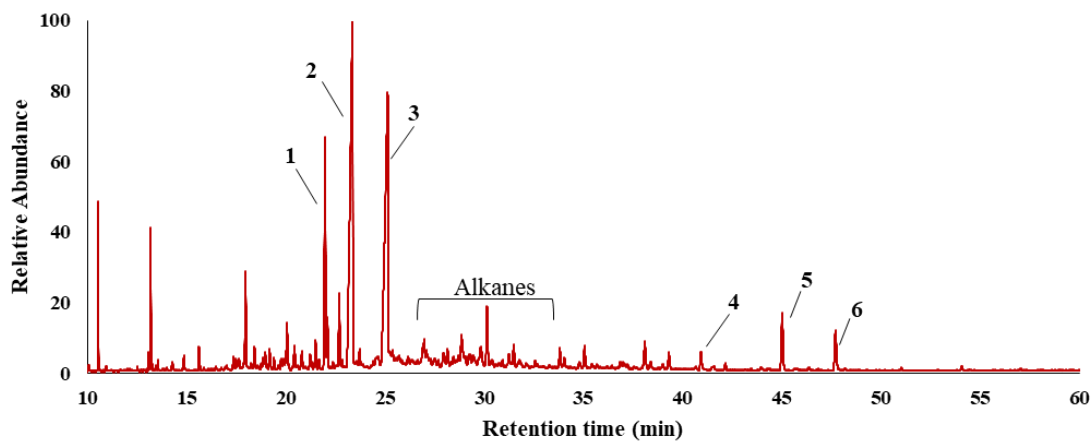
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425 **Figure 4**. Total Ion Chromatogram of DayGlo/Rocket Red (sample 4) obtained by SPME-GC-MS

426 at mild sampling conditions (80°C, 40 min) and mass spectra of the main identified compounds

427 related to the composition of the resin.

428

429

430

431 **Figure 5**. Total Ion Chromatograms (TIC) obtained by SPME-GC-MS of Radiant Color samples:

432 (A) PS-10/Chartreuse Yellow (sample 3) and (B) PS-37/Pink (sample 18).
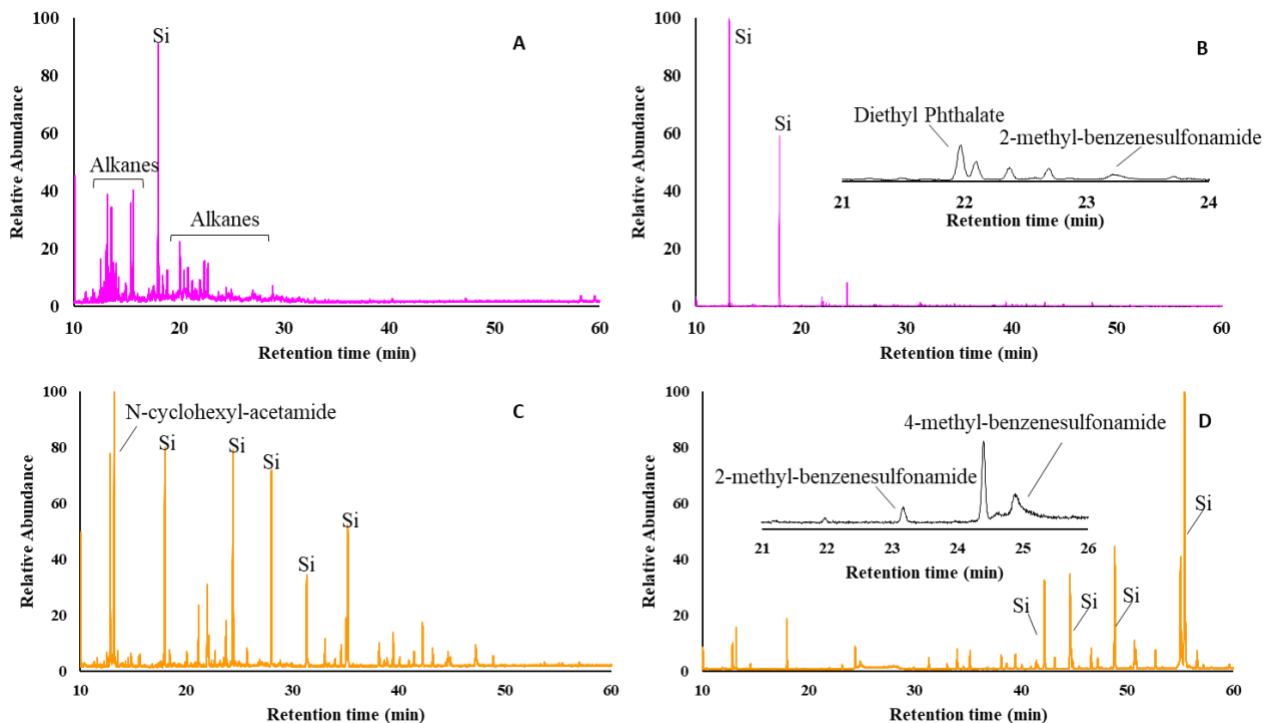
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434

435 **Figure 6**. Total Ion Chromatograms (TIC) obtained by SPME-GC-MS of Swada samples: (A)

436 RTS(1997)/Astral Pink (sample 19) heated at 80 °C during 40 min and (B) heated at 150 °C during

437 240 min. (C) LMP(1998)/Flame Orange (sample 20) heated at 80 °C during 40 min and (D) heated

438 at 150 °C during 240 min. Si identifies a polysiloxane contamination due to the septum used to

439 seal the vial.

440

441 *3.3. XRF analysis*

442 DFPs samples were analyzed by means of a benchtop XRF instrument, in order to reveal the

443 presence of TiO_2 and ZnO, commonly used as UV absorbers [39].

444 The pure resin (Resin p-y-0653, Radiant Color) did not show any traces of Zn or Ti. However, in

445 sample 18 (PS-37 Pink, Radiant Color) from the same company, Ti was detected, indicating that

446 the addition of UV absorbers occurs in a later stage during the manufacturing process.

447 All DayGlo samples contain Ti, while only two lack Zn. Interestingly, a comparison between the

448 normalized net peak intensities data of both metals, seems indicative of the color of the sample

449 (**Figure 7**). Saturn Yellow (samples 1 and 2) and Signal Green (samples 15 and 16) show higher

450 relative amount of Ti (**Figure 7A**). However, the rest of the samples from DayGlo (reds, oranges,

451 pinks and arc yellows) show higher relative amount of Zn (**Figure 7B**). As mentioned earlier, in

452 all 'historical' samples from DayGlo the organic UV-absorber oxybenzone was detected as well,

453 while no traces of oxybenzone were detected in the modern DFP from Swada and one sample from

454 Radiant. However, XRF analysis of samples 19 and 20 indicates a relative high amount of Zn

455 (**Figure S2**), suggesting that Swada uses an elevated concentration of inorganic UV absorbers

456 instead. The combination of UV stabilizers of different nature by DayGlo might have been a

457 reaction in response to the fast fading on light exposure that was reported at that time, as discussed

458 by Aach in his writings.

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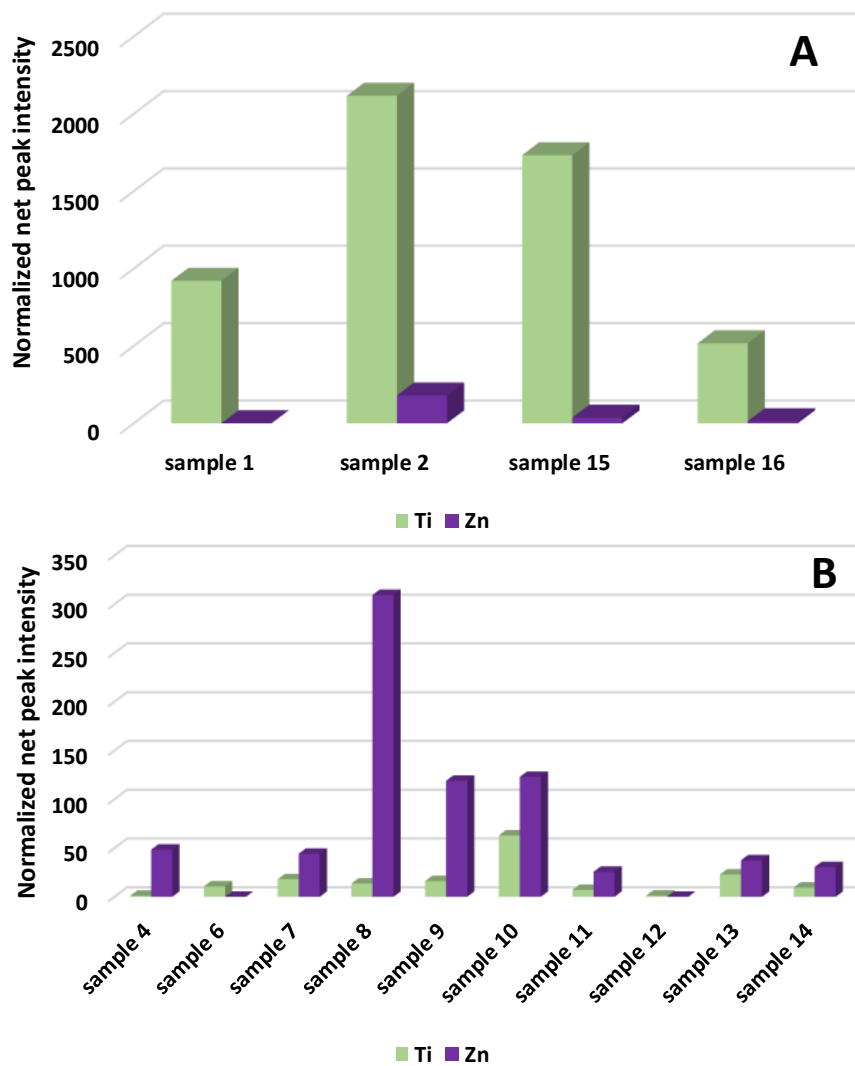
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461 **Figure 7**. XRF analysis of DayGlo samples. (A) Saturn yellow and Signal Green. (B) Rocket red,

462 Arc yellow, Fire orange, Blaze orange. Pink, Aurora pink and Neon red. For complete information

463 of the samples see Table 1.

464

465 *3.4. Classification strategy*

466   PCA of the ATR-FTIR results allows a straightforward classification of the analyzed DPFs

467   according the resinaceous composition, showing some clear differences between manufacturing

468   companies. In addition, a further distinction between thermoplastic and thermoset copolymers can

469   be made. The utility of SPME-GC-MS was demonstrated by correctly identifying the monomer

470   fraction of each sample. In addition, this technique also has the ability to identify the other

471   additives such as organic UV absorbers, plasticizers and side products formed during the synthesis

472   not identifying by ATR-FTIR, making possible to distinguish between manufactures.

473   When comparing samples according to their period of fabrication, we found that the historical ones

474   (DayGlo) typically consist of oxybenzone in combination with an inorganic (Ti and Zn) UV-

475   absorber, whereas modern samples, especially those from Swada, do not contain oxybenzone.

476   However, further research on comparing the longevity between DFPs containing organic

477   (oxybenzone) or inorganic (Ti and Zn) UV absorbers might be of interest.

478   Base on the above results, the following flowchart is proposed for the characterization of the

479   analyzed DFPs according to the resin composition (**Figure 8**).

480   In the frame of conservation science, only Raman, TLC-SERS and Py-GC-MS have been used to

481   characterize the dye composition of DFPs. This study shows that not only the identification of the

482   dyes, which has been the focus of previous studies, should be considered for detecting and

483   classifying DFPs. Instead we found that a more specific classification can be obtained by focusing

484   on the resin structure and additives. Therefore, we are the first to show, with our multi-modal

485   analysis, that the comparison of the data of different types of historical and more recent DFPs

486   samples of various fabricants, reveals new interesting variables in the DFPs composition. Above

487   that, we showed that the identification of the resin and additives allows for a deeper classification

488   of DFPs as we have illustrated in Figure 8. This new information will not only help to improve

489   future identification approaches to measure artwork containing a broad variation of DFPs, the data

490   will also contribute to the development of a proper retouching protocol, thanks to the better

491   understanding of the resin composition.

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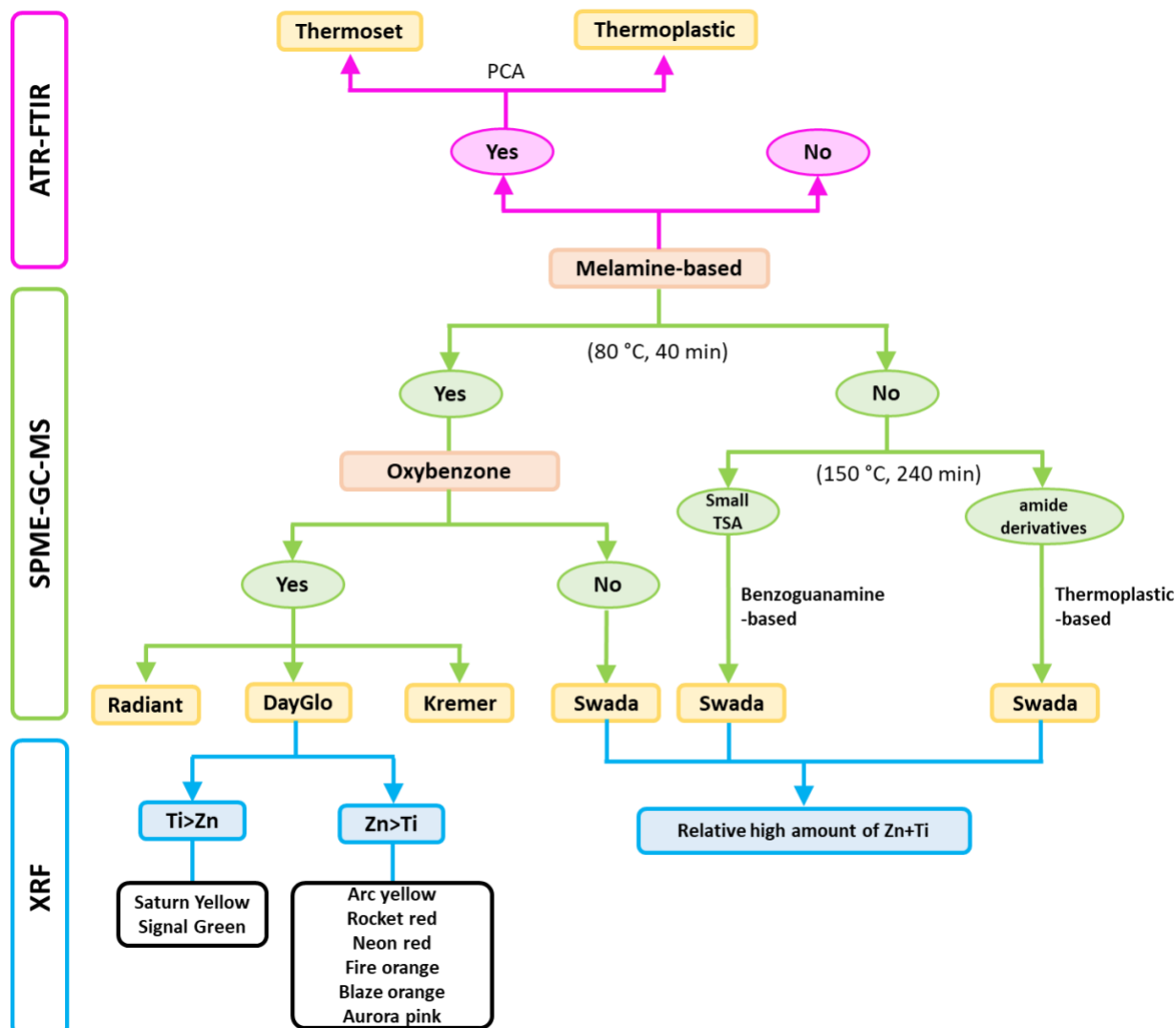
494   **Figure 8.** Proposed flowchart for the classification of DFPs based on ATR-FTIR, SPME-GC-MS

495   and XRF results.

496

497   **4. Conclusions**

498　The proposed analytical methodology was able to confirm the writings of Aach stating that the

499　resin composition was gradually improved to enhance the permanency of DFPs since 1965.

500　By means of combined ATR-FTIR spectroscopy, SPME-GC-MS and XRF is possible to provide

501　an overview of different formulations commercialized since the 60s.

502　In particular, the initial PCA-assisted ATR-FTIR spectroscopy allowed for an efficient

503　classification of the main monomers in the resin polymer. The PCA allowed us to classify the

504　unknown samples from Herbert Aach's collection. Next, SPME-GC-MS proved an effective tool

505　for a more detailed identification of excipients added during the synthesis or manufacturing

506　process, even at low concentration. In particular, this paper illustrates how the GC-MS sampling

507　protocol optimized in this study can perform an effective and simultaneous extraction of resin-

508　monomers and main additives from complex matrices such as DFPs. The characteristic fragments

509　identified by SPME-GC-MS allowed to point out differences between companies and even series

510　from the same manufacturer. Within the range of additives, we found markers that seemed

511　idiosyncratic such as aldehydes, esters from oxalic and phthalic acids, TSA monomers and

512　oxybenzone. In contrast with Py-GC-MS used in previous DFPs analysis [9] and where the

513　samples are calcinated (destructive analysis), SPME-GC-MS can be considered as a minimal-

514　destructive technique. Although samples must be taken for analysis, these can be analyzed below

515　its temperature of decomposition, keeping their appearance intact.

516　Conservators should be aware of the fact that both the type of fabricant, series and year of

517　fabrication might influence the degradation process of the DFP in paint layers. Although ATR-

518　FTIR spectroscopy indicated no change in the resin composition over the years, except for the two

519　thermostable DFPs (sample 19 and sample 20), we did find differences in the manufactures' choice

520　for organic and/or inorganic UV-absorbers by GC-MS and XRF measurements.

521 The multimodal approach presented here may result in a focus shift towards the identification of

522 the resin rather than the dyes and thus a next step towards a better understanding of the composition

523 and degradation of DFPs in artworks. In a later research phase of the project, portable FTIR and

524 XRF analysis will be performed directly on Herb Aach's paintings to directly characterize the resin

525 fraction.

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641 **Figure captions**

642 **Figure 2**. (A) Herb Aach, *Split Infinity # 2* (1975), daylight fluorescent acrylic paint on cotton

643 duck (size 188 x 137cm), private collection (® artwork of Herb Aach); (B) envelop with pigment

644 sample of *Aurora Pink*, from the Herbert Aach estate; (C) preserved daylight fluorescent pigment

645 samples from Herbert Aach donated for this research by his widow, Doris Aach.

646 **Figure 2**. PCA score plot showing the contributions of the second and third principle component

647 in the ATR-FTIR spectra shown in **Figure S1**. The indicated numbers correspond to the samples

648 in **Table 1**, while their colors refer to the manufacturing company.

649 **Figure 3**. Normalized ATR-FTIR spectra of the different types of DFPs within the investigated

650 set.

651 **Figure 4**. Total Ion Chromatogram of DayGlo/Rocket Red (sample 4) obtained by SPME-GC-MS

652 at mild sampling conditions (80°C, 40 min) and mass spectra of the main identified compounds

653 related to the composition of the resin.

654 **Figure 5**. Total Ion Chromatograms (TIC) obtained by SPME-GC-MS of Radiant Color samples:

655 (A) PS-10/Chartreuse Yellow (sample 3) and (B) PS-37/Pink (sample 18).

656 **Figure 6**. Total Ion Chromatograms (TIC) obtained by SPME-GC-MS of Swada samples: (A)

657 RTS(1997)/Astral Pink (sample 19) heated at 80 °C during 40 min and (B) heated at 150 °C during

658 240 min. (C) LMP(1998)/Flame Orange (sample 20) heated at 80 °C during 40 min and (D) heated

659   at 150 °C during 240 min. Si identifies a polysiloxane contamination due to the septum used to

660   seal the vial.

661   **Figure 7**. XRF analysis of DayGlo samples. (A) Saturn yellow and Signal Green. (B) Rocket red,

662   Arc yellow, Fire orange, Blaze orange. Pink, Aurora pink and Neon red. For complete information

663   of the samples see Table 1.

664   **Figure 8.** Proposed flowchart for the classification of DFPs based on ATR-FTIR, SPME-GC-MS

665   and XRF results.

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