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Additional Information

1 Characterization of additives of PVAc and acrylic waterborne dispersions and 2 paints by analytical **Pyrolysis-GC-MS** and **Pyrolysis-Silylation-GC-MS**

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9
10 **Keywords:** Additive, PVAc, Acrylic, waterborn dispersions, paints, **Pyrolysis-GC-MS**,
11 **Pyrolysis-Silylation-GC-MS**

12 **Abstract**

13
14
15 Commercial formulations of poly(vinyl acetate) (PVAc) and acrylic dispersions and
16 paints commonly used by artists include a number of additives such as surfactants,
17 coalescing agents, defoamers and thickeners, which are designed for improving **shelf-**
18 **life**, as well as chemical and physical properties of the resulting product. Recent studies
19 have shown that additives present in paints play an important role in the alteration
20 processes undergone by the painting during ageing and further in cleaning tasks planed
21 in conservation interventions. However, the identification of additives is a difficult task
22 due to the elusive character of these substances present at low concentration in the paint.

23
24 **In this context, a four-step approach is proposed that includes analysis of paint samples**
25 **together with analysis of their water extracted products by Pyrolysis-Gas**
26 **Chromatography-Mass Spectrometry (Py-GC-MS) and Pyrolysis-Silylation-Gas**
27 **Chromatography-Mass Spectrometry (Py-Silylation-GC-MS). This analytical strategy**
28 **enables a better characterization of common additives present in commercial PVAc and**
29 **acrylic paints and dispersions. In particular, the analysis of water soluble extracts, which**
30 **are mainly composed by paint additives, avoids the interference of the major polymer**
31 **pyrolizates. Experimental conditions concerning sample preparation and instrumental**
32 **working conditions of both Py-GC techniques are optimized.**

33
34 **Both acrylic and PVAc paints presented poly(ethylene oxide) (POE) type fragments**
35 **dominating the background of their pyrograms, especially when derivatized by means**
36 **of hexamethyldisilazane (HMDS). For the first time, additives such as alkyl sulfate and**
37 **alkyl ether sulfate with C₁₀ and C₁₂ alkyl chains, poly(ethoxylate) fatty alcohol and**
38 **octylphenyl poly(ethoxylate) surfactants were identified, as well as polyvinyl alcohol**
39 **(PVOH) protective colloids, hydrophobically modified ethoxylated urethane (HEUR)**
40 **thickeners an defoamers. Their major fragments and corresponding mass spectra are**
41 **discussed.**

43 1. Introduction

44

45 Waterborne PVAc and acrylic dispersions are formulated by including a series of
46 additives which are necessary during the polymerization processes as well as for
47 stabilizing the product during storage, transportation, application and lifetime service.

48

49 Waterborne dispersions used for manufacturing paints are prepared with additives of
50 different type such as initiators, chain transfer agents, buffers, surfactants, protective
51 colloids and preservatives. In a second step, in which the latex is transformed into a
52 suspoemulsion system by adding the pigment, the manufacturer will add other additives
53 in view of achieving a number of desired properties. These may include wetting and
54 dispersing agents, coalescing solvents, defoamers, preservatives, thickeners and
55 rheology modifiers, freeze-thaw stabilizers and extenders [1-4]. It has been shown that
56 the nature and amount of surfactants used in the manufacture of paints affects not only
57 the film formation process but also important properties of the resulting paint film such
58 as tackiness, water sensitivity and mechanical properties. For this reason, the
59 identification of such compounds is highly relevant for conservation scientists, as they
60 remain in the dried film playing an important role in the alteration processes that
61 determine the aging behavior of the paint. It is worth mentioning that migration of
62 surfactants to the surface is an alteration process frequently observed in aged paintings
63 and reported as responsible for staining and inducing changes in gloss and color of the
64 painting [5-13]. In addition to the migration problem, recent studies performed in aged
65 acrylic samples have also shown that some additives contained in these paints are prone
66 to degrade fast forming small agglomerates that remain trapped within the bulk film.
67 This causes some acrylic films to become softer upon aging and, consequently, more
68 prone to imprint and dirt picking [10,14].

69

70 Moreover, the solubility of additives influences the overall sensitivity of the paint to
71 **conservation cleaning treatments**. The same applies to other conservation treatments
72 such as consolidation or facing/protections, in which organic solvents or water are in
73 contact with the paint surface for long periods of time [9,10,14,15]. Wolbers *et al.* [16]
74 have stated that additives such as poly(acrylic acids), thickeners or surfactants may

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75 affect seriously the response of the paint to **conservation treatments** based on the use of
76 aqueous solutions prepared at different pH and conductivity.

77

78 In the last decades the growing social implication in the safeguard of heritage has
79 resulted in an increase of studies devoted to the analytical characterization of artworks.
80 Nevertheless, most of the studies carried out have focused on the identification of the
81 synthetic polymers used as binding medium of modern paints whereas studies focused on
82 the identification of additives are scarce. An interesting overview of these applications
83 has been provided by Anderson [17].

84

85 The specialized studies found in the heritage conservation field that have been
86 addressed to the identification of additives in waterborne acrylics and PVAc
87 dispersions, are generally focused on the characterization of surfactants and/or
88 plasticizers. Fourier-Transformed Infrared Spectroscopy (FTIR) and Attenuated Total
89 Reflectance-FTIR spectroscopy (ATR- FTIR) have been used to detect POE type
90 additives in acrylic paints and binding media [10,13-15,18-24]. Non-ionic alkylaryl-
91 POE type surfactants have been successfully identified in acrylic paint films by
92 combining FTIR with Size-Exclusion Chromatography (SEC-FTIR) [25]. Phthalate type
93 plasticizers have also been detected by means of this analytical technique in PVAc films
94 [26,27].

95

96 Other chromatographic techniques, such as High-Performance Liquid Chromatography
97 coupled with Mass Spectrometry and diode array detector (HPLC-MS-DAD) and (Py-
98 GC-MS) have been used to detect these non-ionic alkylaryl-POE surfactants in acrylic
99 formulations, as well as plasticizers in PVAc products [26-28]. Recently, a report
100 described the use of Py-GC-MS in double-shot mode for the detection of oxidation
101 products in aged acrylic samples [29]. HMDS has been proposed by the authors to
102 perform Py-Silylation-GC-MS on a series of PVAc-Vinyl Versatate (Veova) paints, for
103 studying the additives otherwise difficult to characterize by means of the conventional
104 techniques [11].

105

106 **Matrix assisted laser desorption/ionization-mass spectrometry (MALDI-MS) and**
107 **nanospray-electrospray ionization-mass spectrometry (nanospray-ESI-MS) have been**

108 used much successfully in determining POE chain lengths and sulfonated end groups
109 from a series of surfactants both from test specimens and micro-samples extracted from
110 artworks [30,31].

111

112 In the context of industrial applications, Py-GC-MS has been used to study lubricants,
113 antioxidants and flame retardants [32-34]. Py-GC-MS has also been used for the study
114 of the thermal decomposition of hindered amine light stabilizers as well as liquid
115 chromatography-ultraviolet absorbance detection-evaporative light scattering detection
116 [35,36]. Temperature-programmed pyrolysis hyphenated with metastable atom
117 bombardment ionization mass spectrometry has also been used to detect light stabilizers
118 in car paints [37].

119

120 Due to the importance of identifying the family of additives present in PVAc and
121 acrylic paint layers before executing a **conservation treatment**, it is proposed here the
122 combined use of both Py-GC-MS and Py-Silylation-GC-MS for the study of
123 commercial PVAc and acrylic dispersion paints, as well as their extractions in water.
124 Both analytical methods reveal complementary information that allows, for the first
125 time, the identification of a number of additive families such as ionic surfactants, HEUR
126 thickeners, protective colloids and defoamers, as well as the characterization of other
127 more common additives such as non-ionic surfactants. This provides, accordingly, a
128 deeper insight into the composition of the acrylic and PVAc materials proposed for the
129 study, but also expands the information of interest that can be achieved by these
130 analytical techniques.

131

132

133 **2. Experimental**

134

135 **2.1 Analytical reagents and reference materials**

136

137 Hexamethyldisilazane (HMDS) was supplied by Sigma, Steinheim, Germany.

138

139 PVAc and acrylic products tested in this study are summarized in Table 1. These
140 include waterborne dispersions and artists' commercial paints.

141

142

143 **2.2 Preparation of specimens and samples**

144

145 **Model paint films.-** PVAc and acrylic test specimens were prepared as drawdowns as
146 model paint films over mylar® sheets. The products were cast directly as supplied and
147 then dried in laboratory conditions for four years before testing. The resulting films
148 have an average thickness of 0.15 mm.

149

150 **Water extractions.-** A series of water extracts were obtained from the samples of model
151 paint films in order to characterize water soluble additives. For this purpose, samples of
152 the model paints weighting approximately 0.4–0.5 g were immersed in 50 mL of
153 deionized water for 24h **at room temperature**. The films were then removed, and the
154 solution was dried at 50°C in a laboratory oven until water was completely evaporated.
155 A waxy-like solid extract was obtained for analyzing by Py-GC-MS and Py-Silylation-
156 GC-MS.

157

158 **Preparation of samples for Py-GC-MS and Py-Silylation-GC-MS.-** A series of samples
159 from model paint films (a few µg) were scrapped with scalpel and introduced in a
160 quartz tube with a small plug of quartz wool for analyzing by Py-GC-MS. In parallel, a
161 series of samples of the waxy-like water extracts obtained after immersion of the paint
162 films in water was also analyzed by Py-GC-MS. Py-Silylation-GC-MS was performed
163 on a second series of both model paint films and their waxy-like water extracts by
164 adding 1 µL of HMDS to the quartz tube previously to the analysis.

165

166 **2.3 Instrumentation**

167

168 **Py-GC-MS.-** Analyses were carried out with an integrated system composed of a CDS
169 Pyroprobe 1000 heated filament pyrolyser (**CDS Analytical, LLC, Oxford, PA USA**)
170 and an Agilent Technologies (Palo Alto, CA, USA) 6890N gas chromatograph coupled
171 with an Agilent Technologies 5973N mass spectrometer and equipped with a pyrolysis
172 injection system. An HP-5MS capillary column (5% phenyl methylpolysiloxane; 30 m,
173 0.25 mm i.d., 0.25 µm) was used.

174

175 Py-GC-MS and Py-Silylation-GC-MS with HMDS were performed with a temperature
176 of pyrolysis of 700°C, for 10 s, using a precalibrated Pt coil-type pyrolyser (CDS
177 Pyroprobe) [12]. The pyrolyser interface and the inlet were set at 250°C. Samples were
178 injected in split mode (split ratio 1:40). The GC temperature was initially 50°C for 2
179 min, and then programmed at 5°min⁻¹ to 100°C, then at 15°min⁻¹ to 295°C, held for 10
180 min. The electronic pressure control was set to the constant flow mode with vacuum
181 compensation.

182

183 Helium gas flow was set at 1.2 mL min⁻¹. Ions were generated by **electron ionization**
184 (EI) (electron energy 70 eV) in the ionisation chamber of the mass spectrometer. The
185 mass spectrometer was scanned from $m/z=20$ to $m/z=800$, with a cycle time of 1s.

186

187 Agilent Chemstation software G1701CA MSD was used for GC-MS control, peak
188 integration and mass spectra evaluation. Tuning and calibration of the mass
189 spectrometer were checked using perfluorotributylamine. EI mass spectra were acquired
190 in the total-ion monitoring mode and peak area (TIC) data were used to obtain values of
191 peak area percentage. Compounds were identified by use of the NIST and Wiley
192 Library of Mass Spectra and **a library created by the authors from a collection of PVAc,**
193 **acrylic commercial paints and media and their most common additives. This library was**
194 **built according to the mass spectra interpretation of these reference products.**

195

196

197 **3. Results and Discussion**

198

199 **3.1 Analysis of PVAc dispersion and paints**

200 Analysis of solid samples of dispersion and paint specimens provides interesting
201 information on the chemical composition of the polymeric matrix that binds the paint.
202 Figure 1-a shows the pyrogram obtained by Py-GC-MS of Conrayt®, a pure PVAc
203 emulsion. Similar results were obtained for the other studied PVAc dispersion,
204 Vinavil®. In agreement with prior studies of PVAc resins [3,26,27], it has been found
205 that pyrolysis of PVAc at 650-700°C causes the formation of ethanoic acid from the

206 polymeric chain via side group elimination mechanism and the fragmentation and
207 rearrangement of the resulting polyene backbone into benzene, as well as recombination
208 and condensation of benzene, that results in the formation of a series of aromatic
209 bicyclic compounds, namely, 1,4-dihydronaphthalene, naphthalene, 1-methyl
210 naphthalene or 2-ethenyl naphthalene.

211

212 A strong peak from dibutyl phthalate (DBP) stands out at higher retention time. This is
213 a plasticizer commonly included by manufacturers in commercial formulations to
214 improve the mechanical properties of PVAc resins, which tend to harden when
215 synthesized as homopolymers, such as in the case of Conrayt® or Vinavil® [3]. DBP is
216 known to migrate and concentrate at the surface of PVAc and other synthetic materials
217 causing ‘tackiness’, which is source of great concern to conservators [27].

218

219 Analysis of the PVAc dispersions with HMDS as derivatization reagent to perform *in*
220 *situ* thermally assisted Py-Silylation-GC-MS brings forward some interesting and
221 complementary information to that provided by the previous analyses using direct Py-
222 GC-MS. In particular, a type of additives composing the polar fraction of these
223 waterborne formulations can be identified by this technique. Some advantages obtained
224 by using this method to study additives in PVAc paints have been discussed elsewhere
225 [11]. Figure 1-b shows a series of peaks throughout the pyrogram of Conrayt®, which
226 correspond to POE fragments in their trimethylsilylated (TMS) form, with characteristic
227 m/z 45, 73, 101, 103, 145 and 161. Such fragments have not been detected by
228 conventional Py-GC-MS and can be ascribed to a diversity of additives, especially to
229 surfactants [11]. Ethanoic acid in its TMS form can be found as a sharp peak at early
230 retention times, which confirms the presence of the PVAc resin. However, it is worth
231 noting that there is a drawback in the identification of PVAc resins when using HMDS
232 since the broad peak of the reagent may hinder the identification of benzene. In such
233 case, the peaks of recombination and condensation reactions of benzene, which are
234 found at higher retention time, may be also used as marker compounds for PVAc.

235

236 Analysis of Flashe® paints by means of Py-GC-MS (not shown here) reveal that the
237 binding medium present in both raw umber and burnt umber paints is a co-polymer of
238 PVAc and vinyl versatate (PVAc-VeoVa).

239

240 The pyrogram obtained by Py-Silylation-GC-MS of a Flashe® raw umber test specimen
241 is shown in Fig. 2, where ethanoic acid and methacrylic acid (MAc) are identified in its
242 TMS form. Mass spectrum of the latter exhibits fragment ions at $m/z=158, 143, 73, 69,$
243 41. Methacrylic acid may be included as a co-monomer in PVAc formulations in order
244 to improve overall mechanical properties and UV resistance [11].

245

246 A set of peaks ascribed to VeoVa co-monomers are indicated in Fig. 2. Py-Silylation-
247 GC-MS of VeoVa monomer produces a variety of fatty acids, which appear in their
248 TMS form. A detailed study of these structures can be found in a previous report
249 performed by the authors [11].

250

251 A set of peaks also appears later in the pyrogram, that are ascribed to several isomers of
252 highly branched C₉ and C₁₀ vinyl esters [11,38]. VeoVa co-monomers have bulky
253 structures and are introduced during the polymerization process in order to confer
254 internal plasticizing to the binding medium. In this fashion, the manufacturer avoids
255 using external plasticizers, such as phthalates, found in PVAc homopolymers [2,3].

256

257 On the other hand, the identification of benzene, one of the marker compounds of PVAc
258 polymers [3,38], is hampered by the strong peak of the derivatization reagent.
259 Recombination and condensation of benzene, which results in the formation of a series
260 of aromatic bicyclic compounds, was observed in the analysis of pure PVAc resins and
261 emulsions in prior studies [11,26,39]. In good agreement with that, 1,4-
262 dihydronaphthalene, naphthalene, 1-methylnaphthalene and 2-ethenylnaphthalene have
263 been found in the analysis of Conrayt® and Vinavil®. However, such compounds are
264 not detected in the pyrograms obtained by either Py-GC-MS or Py-Silylation-GC-MS
265 analysis of Flashe® paints. Similar results have been reported for PVAc emulsions and
266 paints copolymerized with vinyl versatates (VeoVa) [11], dibutyl maleate or butyl
267 acrylate [27]. This change in the pyrolysis pattern is tentatively associated to the
268 presence of the co-monomers such as MAc or VeoVa in the structure of the polymer,
269 which should affect/alter the polyene chain rearrangements and condensation observed
270 normally during pyrolysis of pure PVAc.

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272 In addition to the compounds associated to copolymers of PVAc, several weak peaks
273 appear throughout the pyrogram of silylated samples, at higher retention time, which are
274 ascribed to POE-TMS fragments. These polar compounds were not detected by
275 conventional pyrolysis.

276

277 **3.2 Analysis of acrylic dispersion and paints**

278

279 High performance acrylic resins are co-polymers of ‘hard’ and ‘soft’ monomers, such as
280 ethyl acrylate-methyl methacrylate (EA-MMA) or butyl acrylate-methyl methacrylate
281 (BA-MMA). However, commercial products can include monomeric resins of *n*- or *iso*-
282 butyl methacrylate (*n/iso*-BMA), or polymers comprising acrylic and other monomers
283 such as styrene (Sty) [3,12,38,40].

284

285 When subjected to pyrolysis conditions, acrylic resins produce a characteristic
286 fragmentation of the polymeric chain with consequent formation of monomers, which
287 can be used for unambiguously establishing the polymer type [3,12,38-41]. Pyrolysis
288 produces not only monomers, but also sesquimers, **dimers** and **trimers**, which are
289 recombinations or fragments of the polymer backbone composed of its monomers in
290 different proportions [3,12,38,40,41].

291

292 Figure 3 shows the pyrogram corresponding to Pébéo® titanium white test specimen, a
293 methyl methacrylate-2-ethylhexyl acrylate-styrene (MMA-2EHA-Sty) type resin. MMA
294 and styrene are found early in the pyrogram whereas 2-EHA appears at higher retention
295 time as pointed out in the figure. Pyrolysis of acrylic monomers with bulky side chains
296 such as 2-EHA originates fragments of the corresponding fatty alcohol, aldehyde and
297 alkene. Thus, 2-ethylhexanol, 2-ethylhexanal and 2-ethylhexene are present in the
298 pyrogram, which is in good agreement with prior studies [41]. A fragment
299 corresponding to 2-ethylhexyl methacrylate (2-EHMA) is also found in the pyrogram.
300 The presence of this compound is likely to be an artifact originated by fragmentation of
301 the polymer backbone during pyrolysis, rather than an actual monomer, as suggested by
302 Mao [42].

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303 Monomers, **dimers** and **trimers** composed by acrylic and styrene units are evident
304 throughout the pyrogram of the Pébéo® sample. The characteristic fragment ion m/z 91,
305 produced with cleavage of the styrene monomer can be used to identify these units.
306 Peaks with m/z 91 appear throughout the pyrogram and are marked with an asterisk.
307 Mass spectra of some of those fragments are provided as supplementary electronic
308 material (Fig. S1 a,b). Texanol® (2-methylpropanoic acid, 3-hydroxy-2,4,4-
309 trimethylpentyl ester) is identified in the pyrogram by the fragment ions at m/z 173, 143,
310 89, 71, 56, 43, 27. This compound is a common coalescing aid in acrylic formulations.

311

312 Py-Silylation-GC-MS analysis of Pébéo® titanium white exhibited similar pattern of
313 polymer pyrolysates to that obtained with Py-GC-MS (pyrogram not shown here).
314 Interestingly, **a well-defined peak ascribed to methacrylic acid is identified**, throughout
315 the pyrogram, in its TMS form, as well as a number of weak peaks that correspond to
316 POE-TMS fragments, which are similar to those shown in the Conrayt® pyrogram. The
317 identification of these compounds suggests the presence of additives with POE polar
318 ends, such as surfactants or some thickeners.

319

320 Pyrogram obtained by Py-GC-MS of Liquitex® phthalocyanine blue is shown in Figure
321 4. The polymer used in the formulation of this paint is a BA-MMA with trace amounts
322 of BMA units. The oligomeric fraction can also be identified, which includes
323 sesquimers, **dimers** and **trimers**. The characterization of the ion mass profiles of BA-
324 MMA fragments has been well discussed in the literature and the reader may find it in
325 other reports [3,12,38,40,40-42].

326

327 The pyrogram also reveals a series of peaks that are ascribed to pyrolysis products of
328 additives used in the paint formulation. Thus, an octylphenol product formed via
329 pyrolysis can be distinguished in the pyrogram (see Figure 4), which reveals the
330 presence of a non-ionic alkylaryl poly(ethoxylated) type surfactant (octylphenyl-POE)
331 [25,29,43]. Characteristic molecular ion m/z 206 is recognized in its mass spectrum (see
332 Figure 5). EI produces dissociation of the molecular ion by benzylic bond cleavage,
333 which results in the base peak $[C_9H_{11}O]^+$ with m/z 135. Further dissociation by CO loss
334 forms $[C_8H_{11}]^+$, m/z 107. $[C_6H_5]^+$ fragment ion at m/z 77 that usually appears in the EI

1
2 335 fragmentation pattern of alkylphenols, as well as carbenium ion $[C_4H_9]^+$, m/z 57, are
3 336 also recognized in the mass spectrum.
4

5 337
6 338 A second compound associated to pyrolysis of octylphenyl-POE surfactants is identified
7 339 in the pyrogram of Liquitex® phthalocyanine blue, which correspond to a different
8 340 bond cleavage of the molecule during pyrolysis that results in molecular ion with m/z
9 341 232 (see Fig. 6). Similarly to the prior compound, characteristic fragments ion
10 342 $[C_{11}H_{13}O]^+$ at m/z 161 is formed as result of dissociation of the molecular ion by
11 343 benzylic bond cleavage. Further dissociation by CO loss forms $[C_{10}H_{13}]^+$, m/z 133.
12

13 344 Recent studies indicate that the presence of these surfactants strongly influences the
14 345 mechanical properties with aging, as well as swelling behavior of the aged paint with
15 346 cleaning treatments using water [14].
16

17 347
18 348 The analyses of Talens® specimens by means of Py-GC-MS and Py-Silylation-GC-MS
19 349 reveal that two types of acrylic resins have been used in the formulation of these paints.
20 350 It seems that the manufacturer chose to use an EA-MMA type acrylic resin in the
21 351 formulation of colors such as naphthol red and raw sienna, whereas black oxide and
22 352 titanium white were formulated with a BA-MMA type dispersion. Similarly, the resins
23 353 used in the manufacture of the gloss and gel media are BA-MMA resins. Different
24 354 dispersions, or even mixtures of dispersions, may be used by a same commercial brand
25 355 for many reasons, such as economic motives, changes or updates in formulations,
26 356 elimination of old batches, or simply to achieve desired properties of the product
27 357 [3,10,11].
28

29 358
30 359 From an analytical point of view, the analyses of Talens® specimens show similar
31 360 results to those described for the previous acrylic paints, with pyrolysis leading to the
32 361 formation of monomers, dimers, sesquimers and trimers. The reader is referred to other
33 362 reports on this subject [3,12,38,40-42].
34

35 363
36 364 The use of the derivatization reagent HMDS to perform Py-Silylation-GC-MS of
37 365 Talens® paints brings forward additional information on additives. Thus, fragments of
38 366 POE in their derivatized form appear throughout the pyrogram. Fragment ions at m/z
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367 161, 145, 116, 117, 101-103, 73 and 45 are identified in their mass spectra.
368 Furthermore, MAc-TMS is identified in pyrograms of all Talens specimens. This
369 compound presents characteristic fragment ions at m/z 158, 143, 73, 69 and 41 in its
370 mass spectrum.

371

372 **3.3 Analysis of water extracted materials from PVAc dispersions and paints**

373

374 The waxy-like solid residues obtained by water extraction of PVAc commercial paints
375 and dispersions were analyzed by Py-GC-MS, Py-Silylation-GC-MS and FTIR-ATR in
376 order to better characterize the water-soluble minor components of these paint films.
377 Water extraction enables significant minimization of the interference of the major
378 compounds coming from the polymer or organic pigments. In particular, polymer
379 fragments and by-products can be yield during pyrolysis.

380

381 The pyrogram obtained by Py-GC-MS of Vinavil® water extract is shown in Figure 7.
382 Main compounds identified and their characteristic fragment ions found in their mass
383 spectra are summarized in Table 2.

384

385 Analysis by Py-GC-MS reveals a series of peaks ascribed to acetaldehyde, acetone, 2-
386 butenal, 3-pentene-2-one, benzaldehyde and 2,4-hexadienal, which are ascribed to
387 poly(vinyl alcohol) (PVOH), a fairly common additive that serves as a protective
388 colloid/thickener in PVAc resins [44]. The presence of this compound is confirmed by
389 FTIR-ATR (IR spectrum is provided in Fig. S2 as supplementary electronic material).

390

391 Complementary analysis performed by Py-Silylation-GC-MS also presents pyrolysates
392 from PVOH such as acetaldehyde, benzaldehyde and 2,4-hexadienal. However, the
393 presence of the strong peak of the derivatization reagent at low retention time hinders
394 the identification of acetone, 2-butenal and 3-pentene-2-one, which are also typical
395 marker compounds of PVOH. Even though this represents a drawback for the detection
396 of PVOH, the use of HMDS enabled to identify fragments of POE chains, as well as a
397 strong peak corresponding to ethanoic acid in its silylated form. This latter compound is
398 evidence of residual monomer extracted during water immersion.

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400 The solid water extract of Conrayt® was also investigated by Py-GC-MS and Py-
401 Silylation-GC-MS. Main peaks identified are summarized in Table 3. Compounds such
402 as acetaldehyde, 2,4-hexadienal, 3-penten-2-one and benzaldehyde, that appear early in
403 the pyrogram, can be ascribed to a PVOH additive, similarly to that found in Vinavil®.
404 Other two peaks corresponding to ethanoic acid and benzene, which also appear at low
405 retention time, can be ascribed to residual vinyl acetate monomer or soluble short PVAc
406 polymeric chains.

407
408 Examination of the broad peak appearing in the first seconds of the pyrogram reveals
409 the presence of SO₂, with characteristic fragment ions at *m/z* 64, 48, 32. This compound
410 is formed by decomposition of sulfated end caps of ionic surfactants, such as alkyl ether
411 sulfate or alkyl sulfate (i.e. lauryl sulfate), which are commonly used in the stabilization
412 of PVAc dispersions [1,2].

413
414 These additives are often composed of a hydrophobic part consisting of an alkyl chain
415 with C₈, C₁₀ or C₁₂, and a hydrophilic end containing the sulfate end cap. It is also
416 possible that a number of ethylene oxide units precede the sulfate endings [1,2,31].
417 During pyrolysis it is expected that the alkyl chain separates from the polar ends
418 forming fragments such as octene, decene, dodecene, octanal, decanal, dodecanal,
419 octanol, decanol, dodecanol, accompanied by the formation of SO₂ [45,46]. In the case
420 these surfactants present POE units attached to the alkyl hydrophobic part, it is expected
421 to identify both POE fragments as well as the alkyl chain with a number of POE units
422 attached.

423
424 In the analysis of Conrayt® water extracts, fragments corresponding to decanal,
425 decanol, 1-(ethenyloxy)decane, 1-dodecene, diethylene glycol monododecyl ether and
426 dodecyl with a number of POE units are found. This suggests the presence of a
427 surfactant with C₁₂ alkyl chain, prevalently, and an undetermined number of POE units
428 attached to it. It is also possible that a mixture of surfactants with C₁₀ and C₁₂ alkyl
429 chains containing either POE and/or sulfate end caps have been introduced in the
430 formulation of Conrayt®. In fact, in emulsion formulations, the manufacturer will take
431 advantage of the synergetic stabilization provided by a mixture of surfactants, which is
432 not achieved solely by one additive [1,2,11,30,31].

433

1 434 The analysis performed, in parallel, by Py-Silylation-GC-MS allows the identification
2
3 435 of triethanolamine (TEA) in its derivatized form as well as the TMS esters of
4
5 436 tetradecanoic, hexadecanoic and octadecanoic acid. TEA is a common buffer used in
6
7 437 dispersion paints whereas fatty acids have been reported to be used as defoamers in
8
9 438 emulsion formulations [1,2,11].

10 439

11
12 440 Strong peaks corresponding to POE fragments in their derivatized form can be found
13
14 441 throughout the pyrogram, especially at high retention time. A peak corresponding to
15
16 442 decanol in its derivatized form may be related to a C₁₀ alkyl chain of surfactant, as
17
18 443 proposed previously.

19 444

20
21 445 Analysis of Flashe® water extracts reveals several peaks that correspond to typical
22
23 446 condensation and combinations of PVAc including acetic acid, benzene, o-xylene, α-
24
25 447 methylstyrene, and methylnaphthalene, suggesting that residual monomer or short
26
27 448 polymeric chains can be extracted with water. On the other hand, no compounds from
28
29 449 the VeoVa moiety have been detected in the analysis of these water extracts.

30 450

31
32 451 POE fragments appear through the pyrograms, enhanced by means of the derivatization
33
34 452 reagent HMDS. Py-silylation-GC-MS also allowed detection of butanedioic acid,
35
36 453 pentanedioic acid and hexanedioic acid in their TMS form, which were not detected in
37
38 454 the conventional analysis. The analysis of other Flashe® paints and their water extracts
39
40 455 by Py-Silylation-GC-MS has been published by the authors elsewhere [11].

41 456

42 457 **3.4 Analysis of water extracted materials from acrylic dispersions and paints**

43 458

44
45 459 The main peaks identified by Py-GC-MS and Py- Silylation-GC/MS in the water extract
46
47 460 of Pébéo® titanium white are reported in Table 4. The compounds recognized are very
48
49 461 different to those detected in the analysis of samples from the solid paint film, and are
50
51 462 ascribed to three types of additives: POE fragments, a lauryl poly(ethoxylated)
52
53 463 surfactant and a poly(urethane) type thickener.

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465 Peaks corresponding to POE fragments are present throughout the pyrogram. The
466 fragmentation patterns of POE are quite complex as they vary according to different
467 terminations such as -OH, C-C, CH=O or C=C, and combinations of these. However,
468 the ion masses m/z 45 and 89 were found in almost all peaks ascribed to POE fragments
469 indicating that, at least, one termination of the fragment is a -OH or C=C end groups
470 [47]. Exceptions to that were the peaks corresponding to ethylene glycol vinyl ether and
471 vinyl-2(ethoxy)ethyl ether found at low retention time.

472
473 Peaks ascribed to dodecanol and dodecyl ether with a different number of ethylene
474 oxide units are also recognized in the **pyrogram**. That finding suggests the presence of
475 an alkyl poly(ethoxylate) surfactant (lauryl, C₁₂), commonly used as acrylic emulsion
476 stabilizer or pigment emulsifier, as described previously [11].

477
478 Interestingly, a series of amine type compounds were found throughout the pyrogram
479 including 4,4-dimethyloxazolidine, benzonitrile, isocyanomethylbenzene, 2-
480 hydroxybenzonitrile or benzene carbonitrile. These fragments and structures resemble
481 some monomers found in HEUR thickeners, such as toluene-2,4-diisocyanate [47], and
482 could be originated by the cleavage of such additives. Similar fragments were also
483 found in Liquitex® water extracts, and are discussed later in the text. Other peaks that
484 are characteristic of HEUR thickeners would be POE fragments; however, in the case of
485 analysis of acrylic paints and their additives, POE are ubiquitous and can be originated
486 by other additives [44,46].

487
488 The pyrograms of the water extracts of Liquitex® cobalt blue corresponding to the Py-
489 GC-MS and Py-Silylation-CG/MS analysis are shown in Figure 8 (a) and (b),
490 respectively. The main peaks identified by these analytical methods are included in
491 table 5.

492
493 The background of Liquitex® pyrograms presents a considerable number of POE
494 fragments. In analyses performed by conventional Py-GC-MS, fragments with m/z 45
495 and 89 are predominant and are ascribed to -OH or C=C terminations produced during
496 the cleavage pathways of POE molecules [46,48]. The use of the derivatization reagent
497 (HMDS) in a parallel analysis increased the number and intensity of the POE fragments,

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498 which appear in their derivatized form with major fragment ions at m/z 161, 145, 117-
499 116, 103-101, 73 and 45 [11].

500

501 The peaks corresponding to an octylphenyl surfactant, also detected in the analysis of
502 the paint film, dominate the pyrogram. Due to the higher concentration of this
503 compound in the water extract, the fragments 2,5-dimethylphenol and isopropenyl
504 phenol are detected, preceding the two main fragments of this additive with
505 fragmentation patterns m/z 232, 161, 133, 91, 57 and m/z 206, 135, 107, 91, 57, 41, 27.
506 At high retention time, there are several peaks containing ion masses m/z 135 or 161,
507 which can be related to distinct fragmentation pathways of the octylphenyl molecule
508 with a number of POE units attached, as proposed previously.

509

510 Analysis performed with HMDS presents a strong peak with ion fragments at m/z 278,
511 207, 82, 73, 51, 47, which corresponds to the TMS derivative of the octylphenol
512 molecule. Fragments of octylphenyl with a number of POE units appear later in the
513 pyrogram similarly to conventional analysis.

514

515 A low intensity peak corresponding to 1-methylbenzene-2,4-diisocyanate with
516 characteristic ion markers at m/z 174, 145 and 132 is tentatively ascribed to a pyrolysate
517 of a HEUR thickener containing 2,4-toluene diisocyanate in its structure [44,49,50].
518 Evidence of a HEUR thickener was also found by FTIR-ATR analysis of Liquitex®
519 water extracts. **The IR absorption spectra of Liquitex burnt umber water extract is
520 provided as electronic supplementary material (Figure S3) together with that of a HEUR
521 commercial thickener.**

522

523 According to Zhang *et al* [50], urethane linkages can be broken during pyrolysis
524 releasing an isocyanate and alcohol group, which would be in good agreement with the
525 fragment found in the water extracts. A second and third pathway is also proposed in
526 which a primary amine, an olefin and CO₂ is produced, or a secondary amine is formed
527 due to the elimination of CO₂. However, these authors find that pyrolysates produced by
528 means of the first and second pathway are more frequent. Other fragments found in the
529 pyrograms are tentatively associated to these additives and include 4,4-dimethyl

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530 oxazolidine and benzonitrile, and a number of POE fragments that **could have**
531 **originated from** the fragmentation of the hydrophobically modified HEUR structures.

532

533 The analysis of the Liquitex® water extract with HMDS also shows a group of peaks
534 attributed to fatty acids in their derivatized form. Thus, tetradecanoic acid-TMS,
535 pentadecanoic acid-TMS, hexadecanoic acid-TMS and octadecanoic acid-TMS are
536 tentatively ascribed to additive of de-foamer type.

537 Analyses performed in Talens® water extracts reveal similar additive composition for
538 both binding media and paints. The pyrogram of Talens gel medium performed by Py-
539 Silylation-GC-MS is presented in Figure 9. The pyrogram is dominated by the peaks
540 ascribed to POE-TMS fragments that can be originated from many types of additives
541 such as surfactants or thickeners. MAc-TMS is found early in the pyrogram and is
542 tentatively ascribed to poly(acrylic) type additives such as dispersants or thickeners. A
543 strong peak is tentatively ascribed to 2-aminobutyric acid in its derivatized form, with
544 ion fragments at m/z 175, 142, 75, 73, 58, 41, followed by two unidentified peaks with
545 m/z 158, 131, 70, 58 and 160, 129, 88, 72, 58, respectively. The provenience of such
546 compounds is yet undetermined.

547

548 Later in the pyrogram, the peaks corresponding to octanol-TMS, tetradecanol-TMS,
549 octoxyethanol-TMS and several low intensity peaks composed of octanol attached to
550 different number of POE units are related to a poly(ethoxylate) fatty alcohol type
551 surfactant. This surfactant was found in all Talens® test specimens, irrespectively of the
552 resin type being EA-MMA or BA-MMA, or type of sample analyzed (water extract,
553 paint film or pure binding medium).

554

555

556 **4. Conclusions**

557

558 The identification of additives present in PVAc and acrylic binding media and paint
559 specimens is normally hindered by the presence of major pyrolysates of the resins. For
560 solving this problem, and as alternative to the conventional Py-GC-MS analysis of
561 paints, a new methodology has been proposed in this paper, which is based on the

562 combined use of Py-GC-MS and Py-Silylation-GC-MS with HMDS as a derivatization
563 reagent. In addition to the combination of both instrumental techniques, the proposed
564 methodology includes the analysis of samples from the materials obtained by water
565 extraction of the paint films. In this way, an improved identification of several types of
566 additives included in acrylic and PVAc paints is achieved.

567
568 Analysis of all acrylic and PVAc specimens presented POE type fragments dominating
569 the background of the pyrograms, especially when derivatized by means of HMDS.
570 Such fragments are produced during pyrolytic cleavage of many types of additives and
571 cannot be directly associated to a specific type of additive. However, the identification
572 of these polar compounds is very important when it comes to planning adequate
573 conservation cleaning treatments, for they will influence the overall water or solvent
574 sensitivity of the paints.

575
576 Analysis of water extracts obtained from samples of the paints and dispersions has
577 enhanced the signal of the additives in the pyrograms thus allowing, for the first time,
578 the identification of fragments that have been ascribed to HEUR thickeners and
579 defoamers.

580
581 For the first time, PVOH protective colloids and alkyl sulfate and alkyl ether sulfate
582 type surfactants with C₁₂ and C₁₀ alkyl chains have been identified in the PVAc binding
583 media and paint specimens studied. Octylphenyl-POE and POE fatty alcohol, probably,
584 lauryl-POE type non-ionic surfactants were found in acrylic specimens and possible
585 fragmentation pathways of the former surfactants has been proposed via benzylic bond
586 cleavage, which allows assigning unidentified peaks in the pyrograms to date.

587 588 **5. Acknowledgements**

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769 **Figure captions**

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3 771 **Figure 1.-** Pyrogram of Conrayt® PVAc emulsion films obtained by means of (a) Py-
4 GC-MS and (b) Py-Silylation-GC-MS.
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9 774 **Figure 2.-** Pyrogram of Flashe® raw umber obtained by means of Py-Silylation-GC-
10 MS.
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14 777 **Figure 3.-** Pyrogram of Pébéo® titanium white obtained by means of Py-GC-MS. Peaks
15 marked with an asterisk correspond to polymer fragments with styrene units identified
16 778 in the mass spectra by the characteristic fragment ion with m/z 91.
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22 781 **Figure 4.-** Pyrogram of Liquitex® phthalocyanine blue obtained by means of Py-GC-
23 MS. Peaks marked with (*) correspond to pyrolysis fragments of octylphenyl surfactant
24 782 with characteristic fragment ion m/z 135, and peaks marked with (+) correspond to
25 783 pyrolysis fragments of octylphenyl surfactant with fragment ion m/z 161.
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31 786 **Figure 5.-** Proposed structure for the product formed on pyrolysis cleavage of
32 787 octylphenyl poly(ethoxylate) type surfactants from Liquitex® phthalocyanine blue.
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34 788 Pathway for formation of the base peak (m/z 135) identified in its mass spectrum.
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38 790 **Figure 6.-** Proposed structure for the product formed on pyrolysis cleavage of
39 791 octylphenyl poly(ethoxylate) type surfactants from Liquitex® phthalocyanine blue.
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41 792 Pathway for formation of the base peak (m/z 161) identified in its mass spectrum.
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45 794 **Figure 7.-** Pyrogram obtained by Py-GC-MS of Vinavil® solid water extract.
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49 796 **Figure 8.-** Pyrograms of water extract of Liquitex® cobalt blue obtained by: a) Py-GC-
50 MS and b) Py-Silylation-GC-MS. Peaks marked with an asterisk (*) present fragment
51 797 ion at m/z 161 and peaks marked with a cross (+) exhibit fragment ion at m/z 135, which
52 798 are characteristic of an octylphenyl-POE surfactant.
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801 **Figure 9.-** Pyrograms of Talens® gel medium water extract obtained by Py-Silylation-
802 GC-MS. At high retention time, the two peaks marked with an asterisk (*) correspond
803 to POE fatty alcohol surfactant, composed of octanol and POE units.
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810 **Table captions**

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812 **Table 1.-** Summary of products tested. PVAc: refers to poly(vinyl acetate), VeoVa:
813 Vinyl Versatate. Sty: styrene. MMA: methyl methacrylate. 2EHA: 2 ethylhexyl
814 acrylate. BA: butyl acrylate. BMA: butyl methacrylate. EA: ethyl acrylate.

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816 **Table 2.-** Main compounds identified and *m/z* values of **compounds and** fragment ions
817 obtained by Py-GC-MS and Py-Silylation-GC-MS in Vinavil® water extract.

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819 **Table 3.-** Main compounds and *m/z* values of **compounds and** fragment ions obtained
820 by Py-GC-MS and Py-Silylation-GC-MS in Conrayt® water extract.

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822 **Table 4.-** Main compounds and *m/z* values of **compounds and** fragment ions obtained
823 by Py-GC-MS and Py-Silylation-GC-MS in Pébéo® titanium white water extract.

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825 **Table 5.-** Main compounds and *m/z* values of **compounds and** fragment ions obtained
826 by Py-GC-MS and Py-Silylation-GC-MS in Liquitex® cobalt blue water extract.

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Valencia, 30th March 2015

Manuscript: JAAP-D-15-00091

Title: Characterization of additives of PVAc and acrylic waterborne dispersions and paints by analytical Py-GC-MS and Py-Silylation-GC-MS

Journal of Analytical and Applied Pyrolysis

Corresponding author: Dr. María-Teresa Doménech-Carbó

Dear Prof. Dr. D. Fabbri,

Thanks for your interesting comments and suggestions. According to them we have modified the manuscript as follows:

Comments in the review letter:

Response to the reviewers' comments:

Reviewer 1:

Reviewer 1:

Thanks for your useful comments and suggestions.

Reviewer's comment 1: page 1 line 27: Shell-life" should be "shelf-life.

According to the reviewer's suggestion, the term "shell-life" has been corrected into the term "shelf-life" in the revised version of the manuscript.

Reviewer's comment 2: page 1 line 33: Delete "in that".

According to the reviewer's suggestion, the term "in that" has been deleted in the revised version of the manuscript.

Reviewer's comment 3: page 1 line 54: HEUR is defined on page 3, line 56, but that definition should be placed here since it is the first time the term is used.

According to the reviewer's suggestion, the acronym "HEUR" has been defined in the abstract section in the revised version of the manuscript.

Reviewer's comment 4: page 2 line 41: In many places the authors use the term "conservative cleaning treatments", but to me this means a treatment that is conservative, or gentle, not specifically for the purpose of conservation of the artwork. I suggest using something like "conservation" or "restoration" instead.

According to the reviewer's suggestion, the term "conservative cleaning treatment" has been corrected into "conservation cleaning treatment" in the revised version of the manuscript (page 2 line 29 and page 14 line 37).

Reviewer's comment 5: page 4 line 55: The Pyroprobe is made by CDS Analytical, LLC in Oxford, PA USA, not New York.

According to the reviewer's suggestion, the manufacturer data of the pyroprobe have been corrected in the revised version of the manuscript.

Reviewer's comment 6: page 4 line 46: I would change the word "pointed" to "indicated".

According to the reviewer's suggestion, the term "pointed" has been corrected into the term "indicated" in the revised version of the manuscript. Page 6 line 33.

Reviewer's comment 7: page 7 lines 34, 55: And throughout the paper, the words "dimmer" and "trimmer" have been substituted for "dimer" and "trimer".

According to the reviewer's suggestion, the terms "trimmer, dimmer" have been corrected into the terms "dimer and trimer" in the revised version of the manuscript.

Reviewer's comment 8: page 8, lines 39-44: The authors refer to octyl phenol, but the structure shown in Figure 6 is actually decyl phenol.

As suggested by the referee, a mistake was made in the formula showed in Fig. 6 and 7 in which were depicted decyl phenol fragments instead of octyl phenol fragments. According to the reviewer's suggestion wrong formula of decylphenol in figures 6 and 7 (fig. 5 and 6 in the current version) have been corrected and now octylphenol fragments are correctly illustrated in the revised version of the manuscript.

Reviewer's comment 9: page 10 line 9: I would change "confronted with" to "compared to".

According to the reviewer's suggestion, the term "confronted" has been corrected into the term "compared to" in the revised version of the manuscript (now this paragraph is found in the supplementary electronic material according to comment 8 by reviewer 2).

Reviewer's comment 10: page 13 line 50: The expression "could be originated from" is used several places in the paper. I would change that to "could have originated from".

According to the reviewer's suggestion, the term "could be originated from" has been corrected into the term "could have originated from" in the revised version of the manuscript.

Reviewer's comment 11: page 14 line 50: "are" should be "is". According to the reviewer's suggestion, the term "are" has been corrected into the term "is" in the revised version of the manuscript.

Reviewer 2:

Thanks for your useful comments and suggestions.

Reviewer's comment 1: "dimmers" and "trimmers" are not the correct terms. Please correct into "dimers" and "trimers"

According to the reviewer's suggestion, the terms "trimmer, dimmer" have been corrected into the terms "dimer and trimer" in the revised version of the manuscript.

Reviewer's comment 2: page 8. line 20: "Interestingly, it is identified a well-defined peak ascribed to methacrylic acid" must be corrected into "Interestingly, a well-defined peak ascribed to methacrylic acid is identified" or similar phrase

According to the reviewer's suggestion, the sentence "Interestingly, it is identified a well-defined peak ascribed to methacrylic acid" has been corrected into the term "Interestingly, a well-defined peak ascribed to methacrylic acid is identified" in the revised version of the manuscript.

Reviewer's comment 3: p.9 line 49-50: "In particular, polymer fragments and by-products that can be yield during pyrolysis." The verb is missing in this sentence - please delete "that"

According to the reviewer's suggestion, the term "that" has been deleted in the revised version of the manuscript.

Reviewer's comment 4: p.12 line 23: change "program" into "pyrogram"

According to the reviewer's suggestion, the term "program" has been corrected into the term "pyrogram" in the revised version of the manuscript.

Reviewer's comment 5: p.13 line 30: "In Figure 11 is shown the IR absorption spectra of Liquitex burnt umber water extract" is incorrect; please change in "Figure 11 shows the IR absorption spectra of Liquitex burnt umber water extract" or into "The IR absorption spectra of Liquitex burnt umber water extract is shown in Figure 11"

According to the reviewer's suggestion, the sentence "In Figure 11 is shown the IR absorption spectra of Liquitex burnt umber water extract" has been corrected into the sentence "The IR absorption spectra of Liquitex burnt umber water extract is provided as electronic supplementary material (Figure S3)" in the revised version of the manuscript (see also comment 8).

Reviewer's comment 6: Instrumentation p.5 lines 30 and following: please specify if the "library created by the authors for PVAc, acrylic and additives" was built according to mass spectra interpretation.

According to the reviewer's suggestion, a sentence describing the characteristics of the library created by the authors has been included in the revised version of the manuscript.

Reviewer's comment 7: Results and discussion. p.7 line 9 and following: please discuss further why "the presence of co-monomers such as MAc or VeoVa hampers the polyene chain rearrangements and condensations". Is there any reference in the literature that mention such an effect?

It is well known that pyrolysis of pure PVAc polymers results in the formation of ethanoic acid and benzene that are the products of side group elimination from the backbone chain of the polymer and the breakdown and rearrangement of the polyene chain during pyrolysis, respectively (Ref. 3 and 38). Recombination and condensation of benzene, which results in the formation of a series of aromatic bicyclic compounds, namely, 1,4-dihydronaphthalene, naphthalene, 1-methyl naphthalene or 2-ethenyl naphthalene, were observed in the current study for Conrayt and Vinavil, in good agreement with the results obtained in prior studies of pure PVAc resins and emulsions carried out in prior papers (ref. 11,6, M.T. Doménech-Carbó, et al., J. Anal. Appl. Pyrol. 85 (2009) 480–486.).

In contrast, analysis performed in prior studies on PVAc paints prepared with PVAc copolymerized with other monomers such as vinyl versatates (VeoVa) (ref. 11) or dibutyl maleate or butyl acrylate (refs. 27) provided pyrograms with absence of these compounds. This same behaviour has been found in the currently studied Flashe paints in which VeoVa was present. Therefore, it seems that the presence of co-monomers other than vinyl acetate results in a different pyrolysis fragmentation pattern in which further rearrangement and condensation of bicyclic aromatic compounds is not taking place significantly. Demonstration of such hypothesis requires experimental work that exceeds the goals of the present paper.

According to the reviewer's comment, this subject has been clarified and its discussion has been enlarged in the current version of the manuscript and references of prior works, where analogous results were found, have been included.

Reviewer's comment 8: Figures. In general, the data provided by Fig.4 are not a novelty, thus I would move it to the Supplementary Information. Moreover, the infrared spectra figures and discussion (p.10) seems a little out of the scope of the paper, so I would move both Fig.9 and 11 and the discussion on p.10 to the Supplementary Information, in order to improve the clarity of the main text.

According to the reviewer's suggestion, Fig 4, 9 and 11 and the corresponding discussion in page 10 have been moved to supplementary electronic material.

Editor

Editor's comment 1: Line numbering is mandatory! also in the revised version; please number the lines of your manuscript continuously throughout.

According to the editor's suggestion, continuous line numbering has been provided in the revised version of the manuscript.

Editor's comment 2: Where applicable please mark the changes made into the document with red colored font; do not use the revision tool in the final pdf version and/or the Track Changes feature.

According to the editor's suggestion, changes have been marked in red in the revised version of the manuscript and in the supplementary electronic material.

Editor's comment 3: Abstract, I suggest to shorten the initial introductory part to give more experimental details of your study.

According to the editor's suggestion, abstract has been changed by shortening the initial introductory part and including more details of the main results obtained.

Editor's comment 4: Tables: an additional column with the name of the original (tentatively identified) additives could be included; our readers could be interested in consulting a list of possible additives with their specific ions.

According to the editor's comment, an additional column has been included in tables for more clarity for readers. Commercial tradename of additives has been provided in the cases where we had disposal of such information. For the rest of cases, type of additive is solely provided.

Editor's comment 5: Please, add the whole name "pyrolysis" in the title, keyword or abstract.

According to the editor's suggestion, the whole term "pyrolysis" has been included in the title and keywords.

Editor's comment 6: Abbreviations should be defined at their first mention (PVOH, HEUR in the abstract); see reviewer's comment.

According to the editor's comment, abbreviations have been defined in the first mention in the revised version of the manuscript.

Editor's comment 7: Section 2. in 50 mL of deionized water for 24h..."at room temperature"? // "electron-impact", remove "impact".

According to the editor's comment, the sentence "at room temperature" has been added.

On the other hand, the term "impact" has been deleted in the current version of the manuscript.

Editor's comment 8: Tables. "fragment ion", "fragment" could be removed being the molecular ion not a fragment.

According to the editor's suggestion, the term fragment ion has been replaced by compound/fragment ion in the revised version of the manuscript (tables and table captions).

Analysis of additives in PVAc modern paints by Py- and Py-silylation-GC-MS

Analysis of additives in acrylic modern paints by Py- and Py-silylation-GC-MS

Analysis of additives in PVAc and acrylic dispersions by Py- and Py-silylation-GC-MS

Identification of sulfonate and lauryl poly(etoxylate) surfactants.

Identification of PVOH protective colloids, HEUR thickeners and defoamers.

Figure 1
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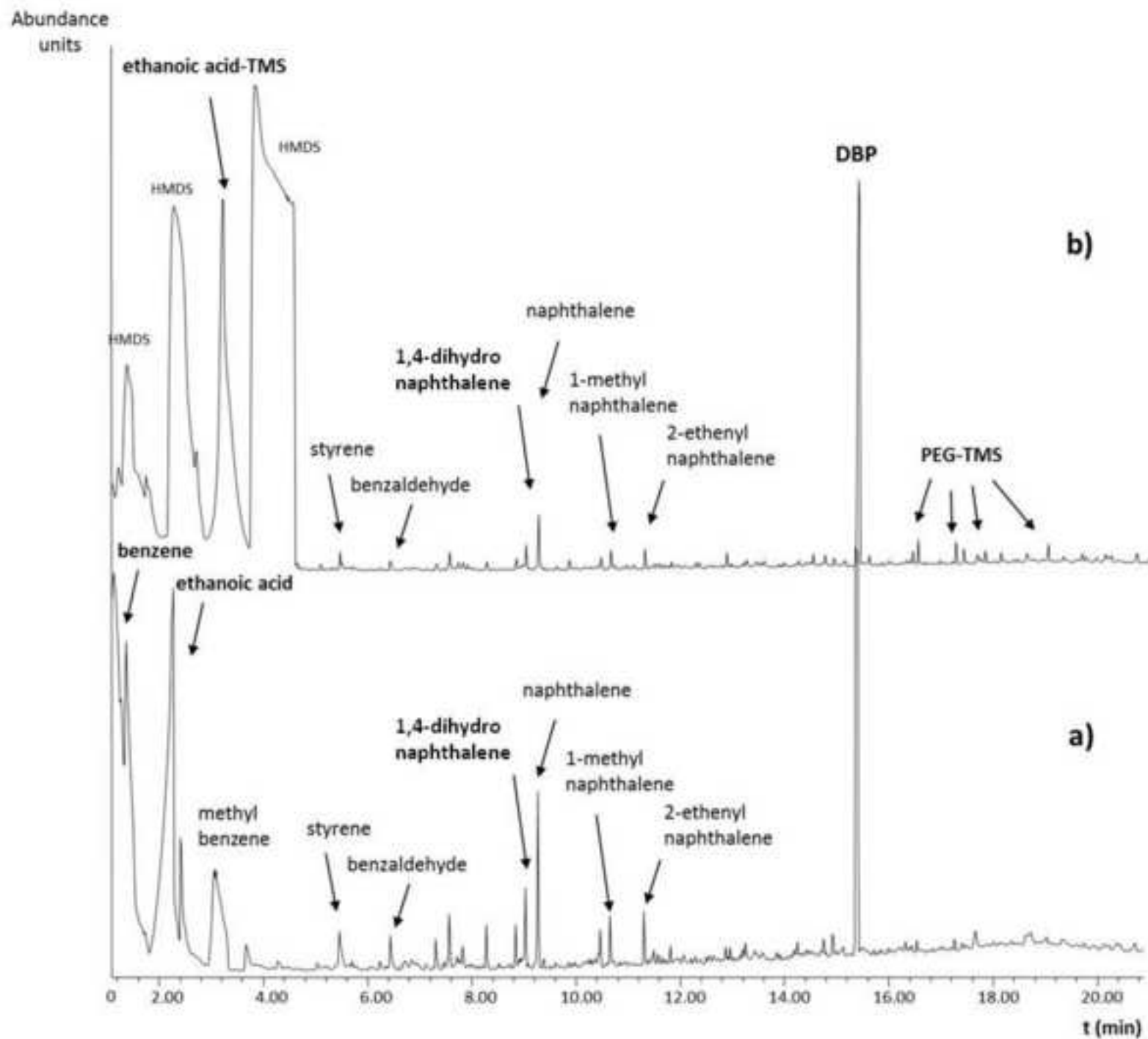


Figure 2
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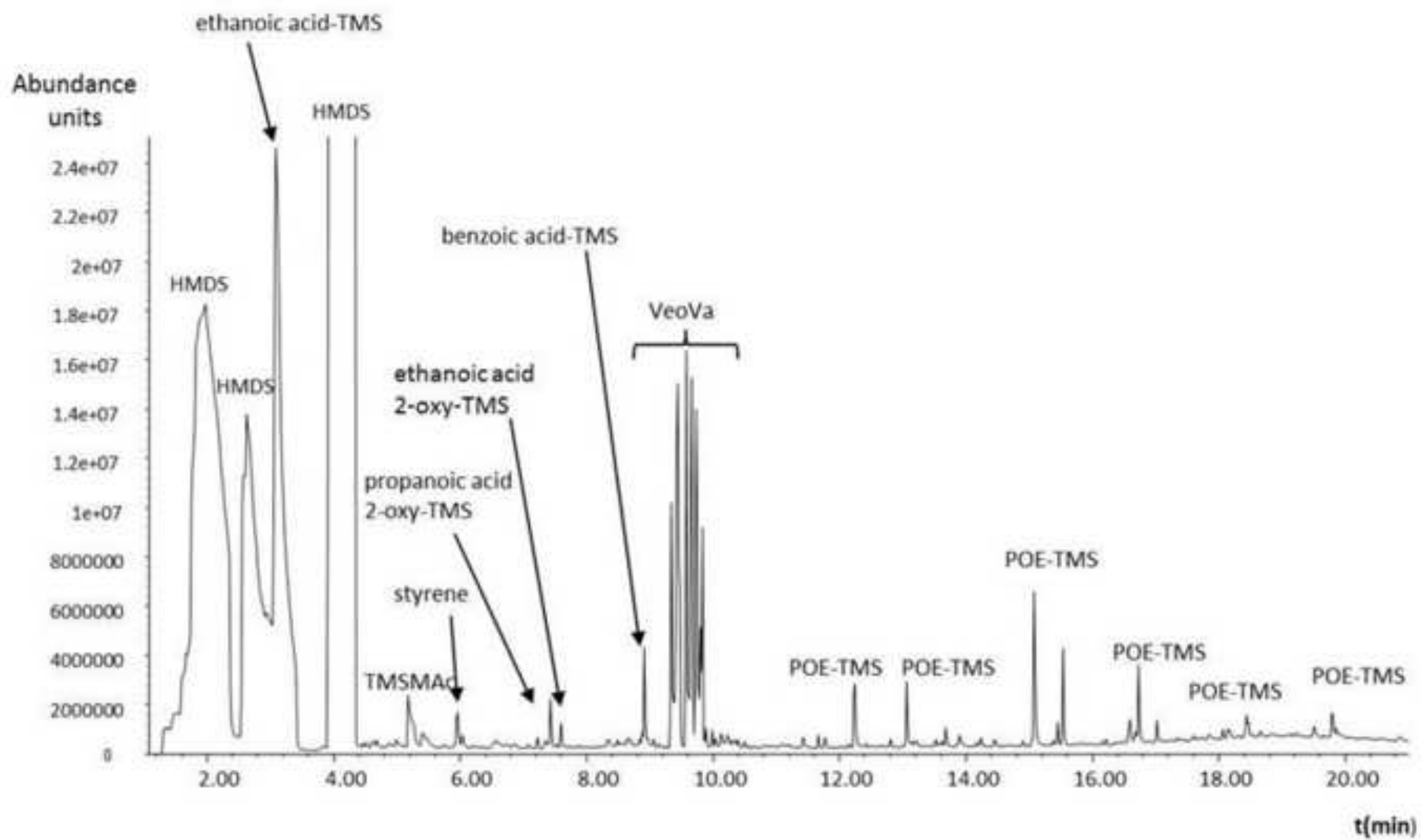


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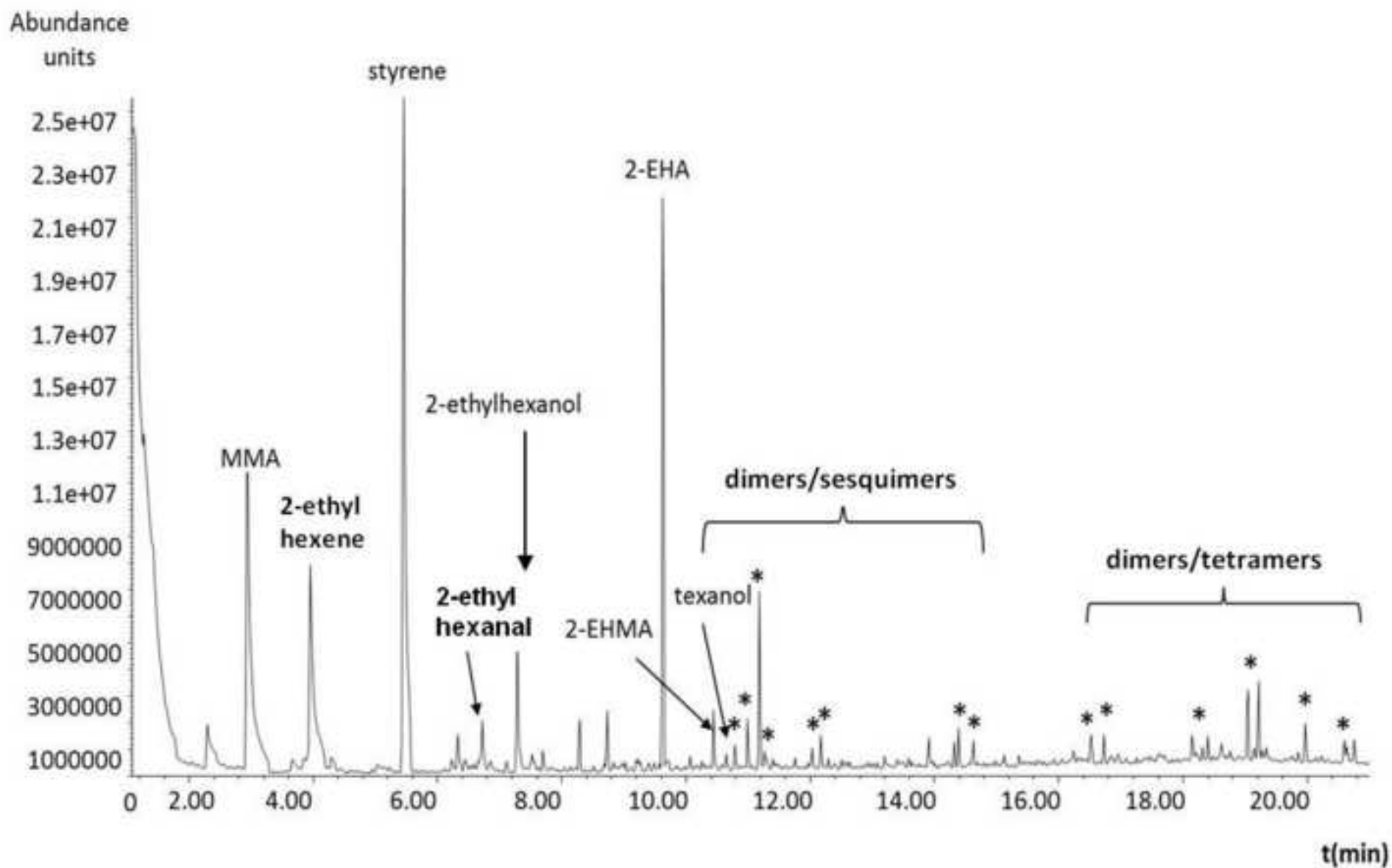


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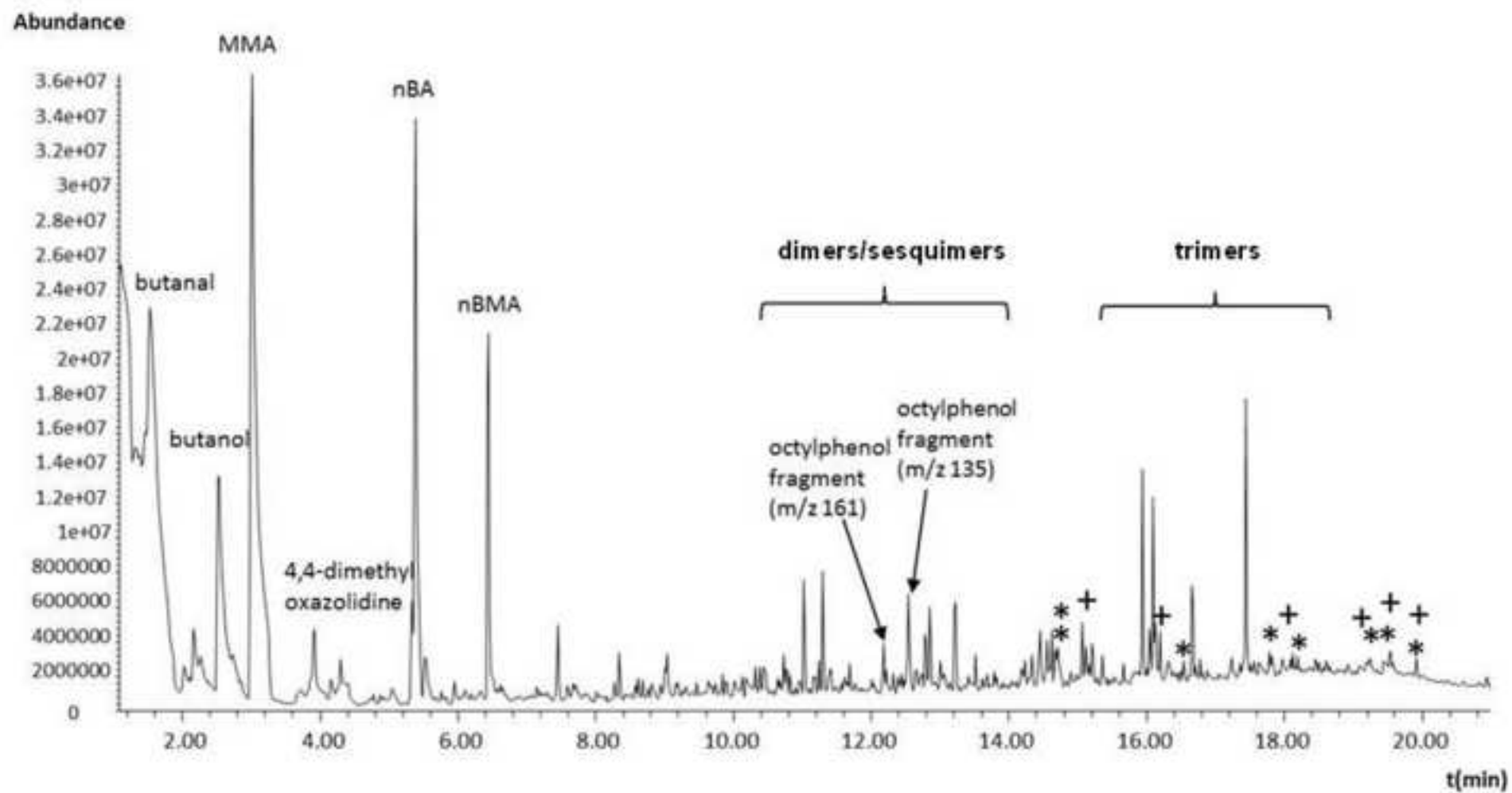


Figure 5
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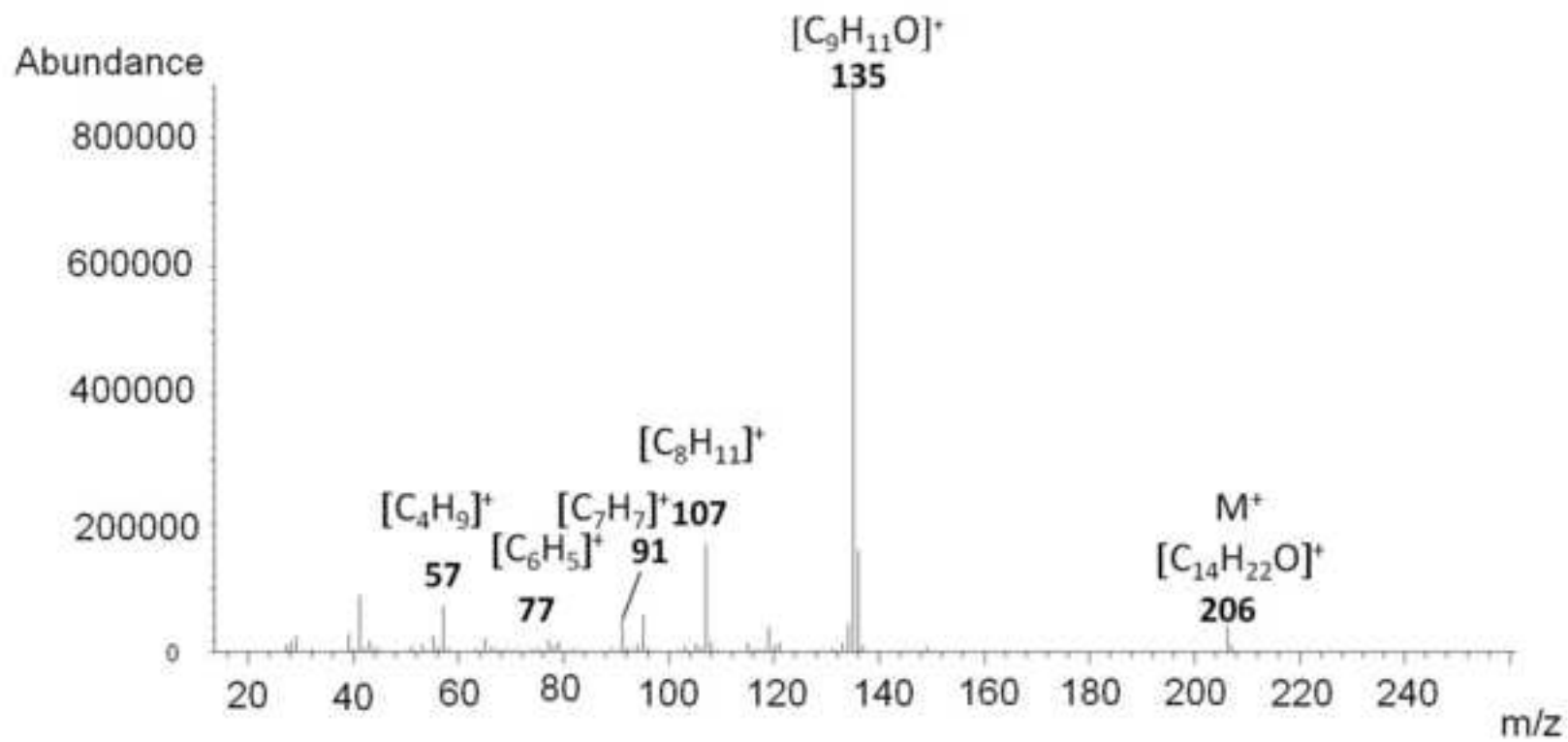
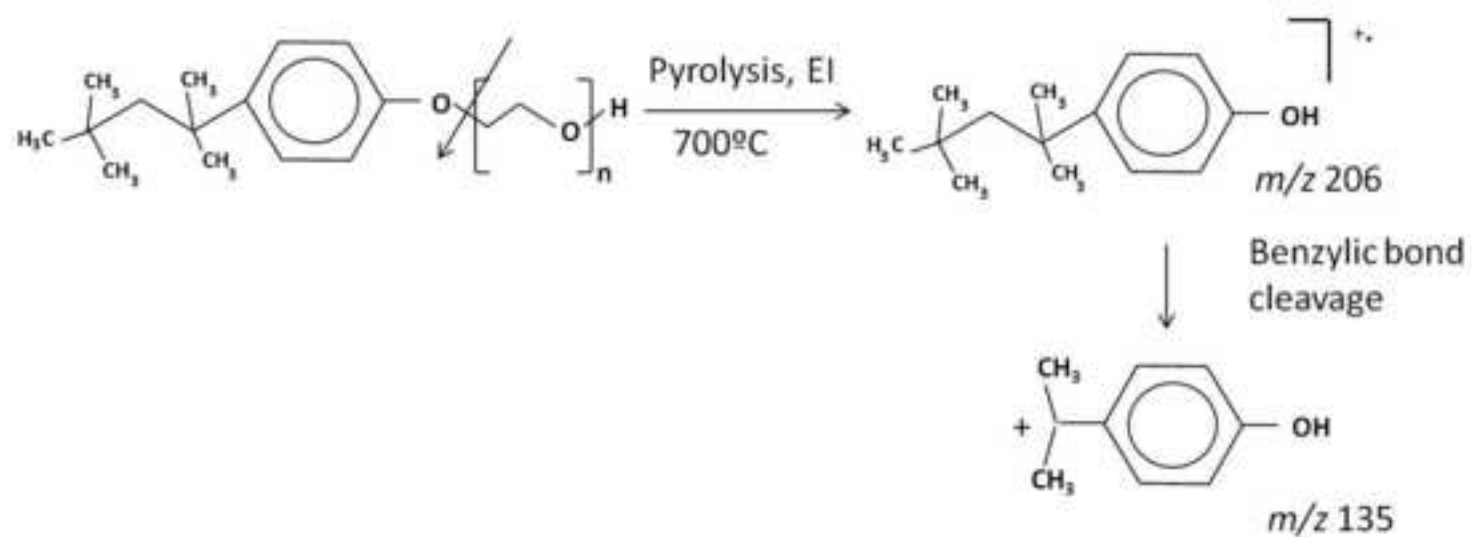


Figure 6
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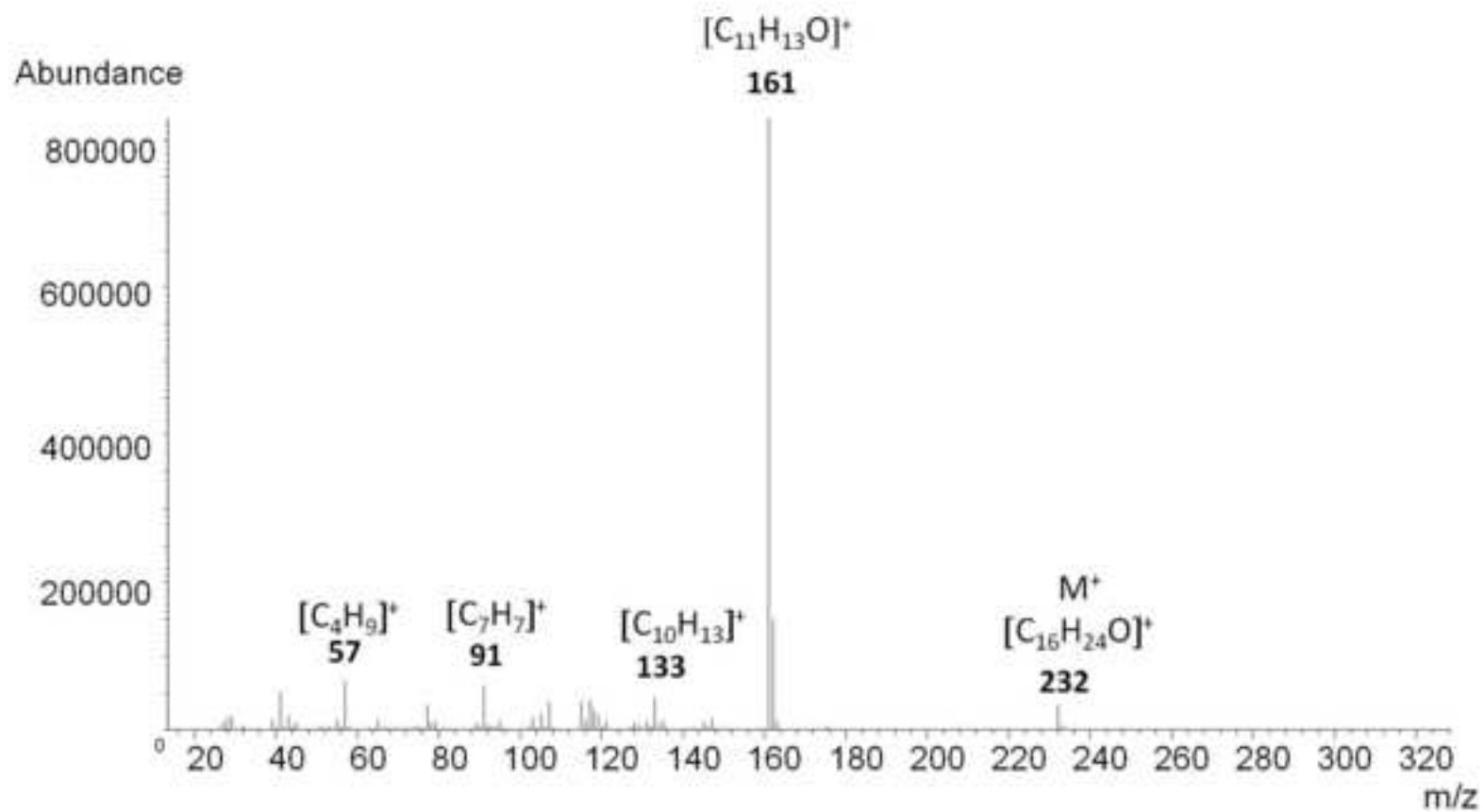
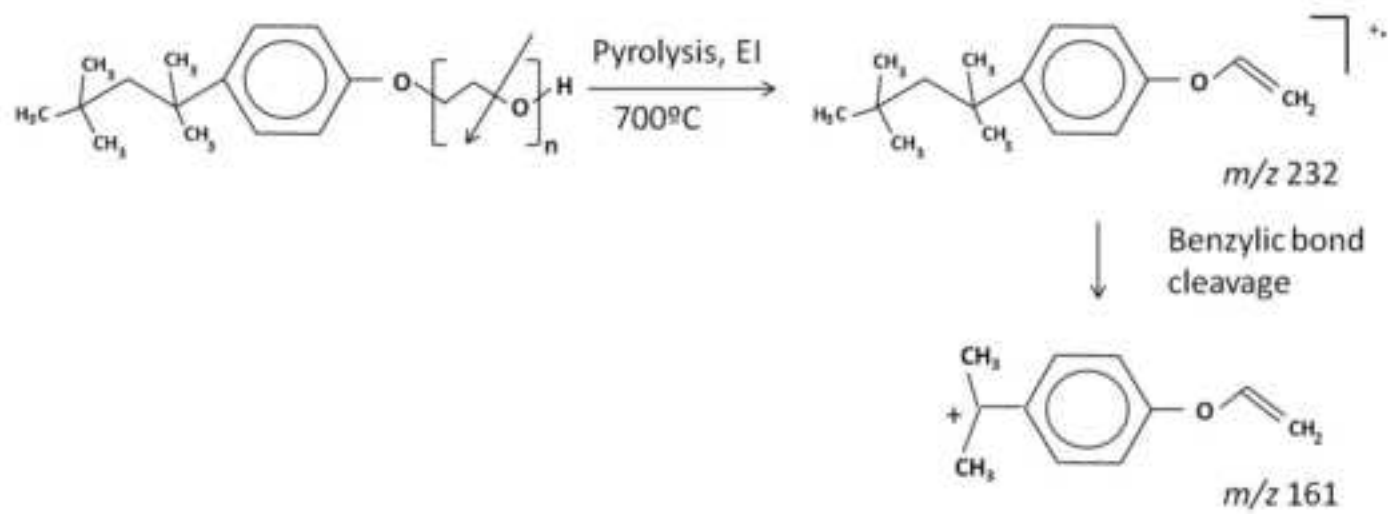


Figure 7
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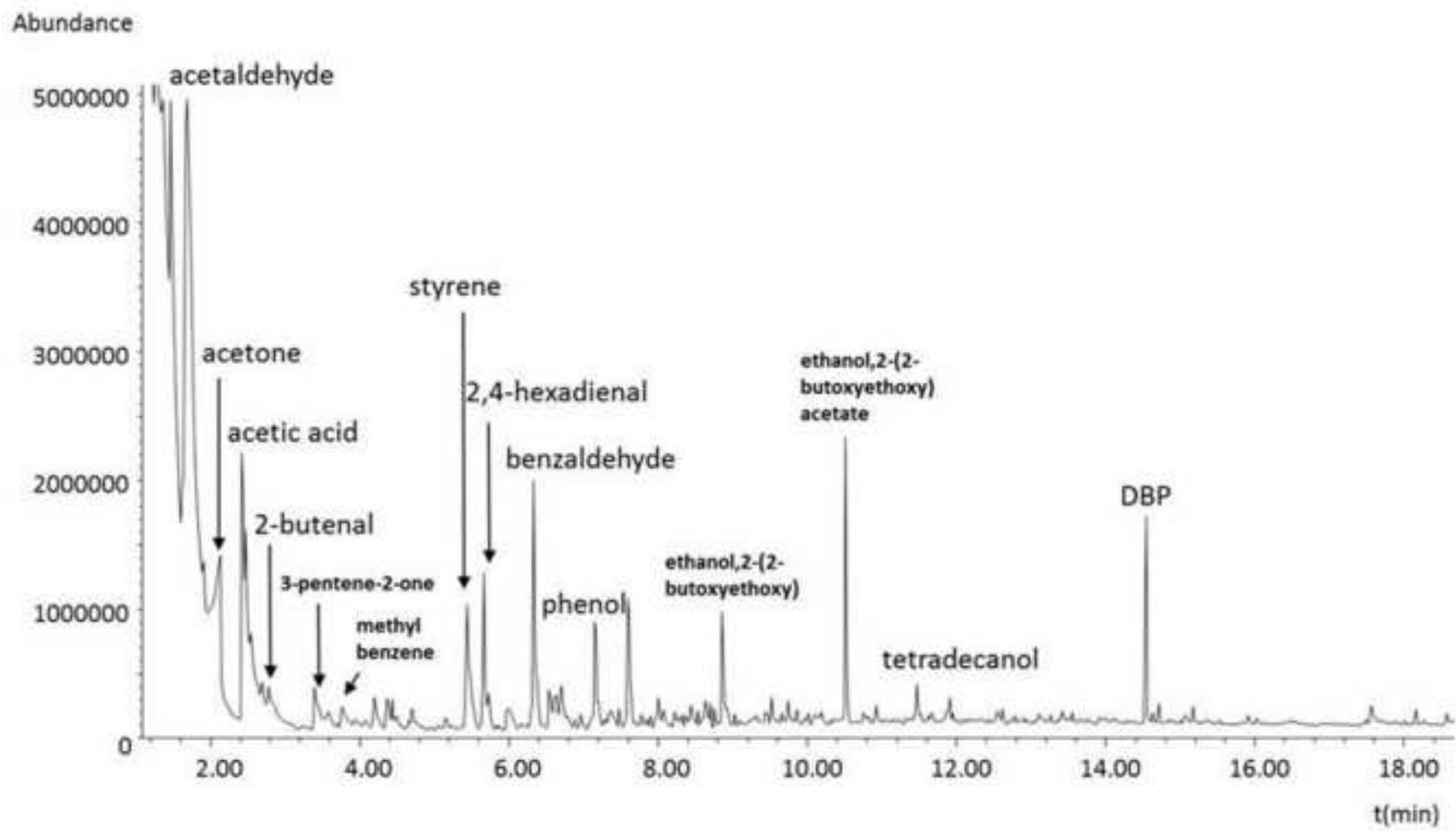


Figure 9
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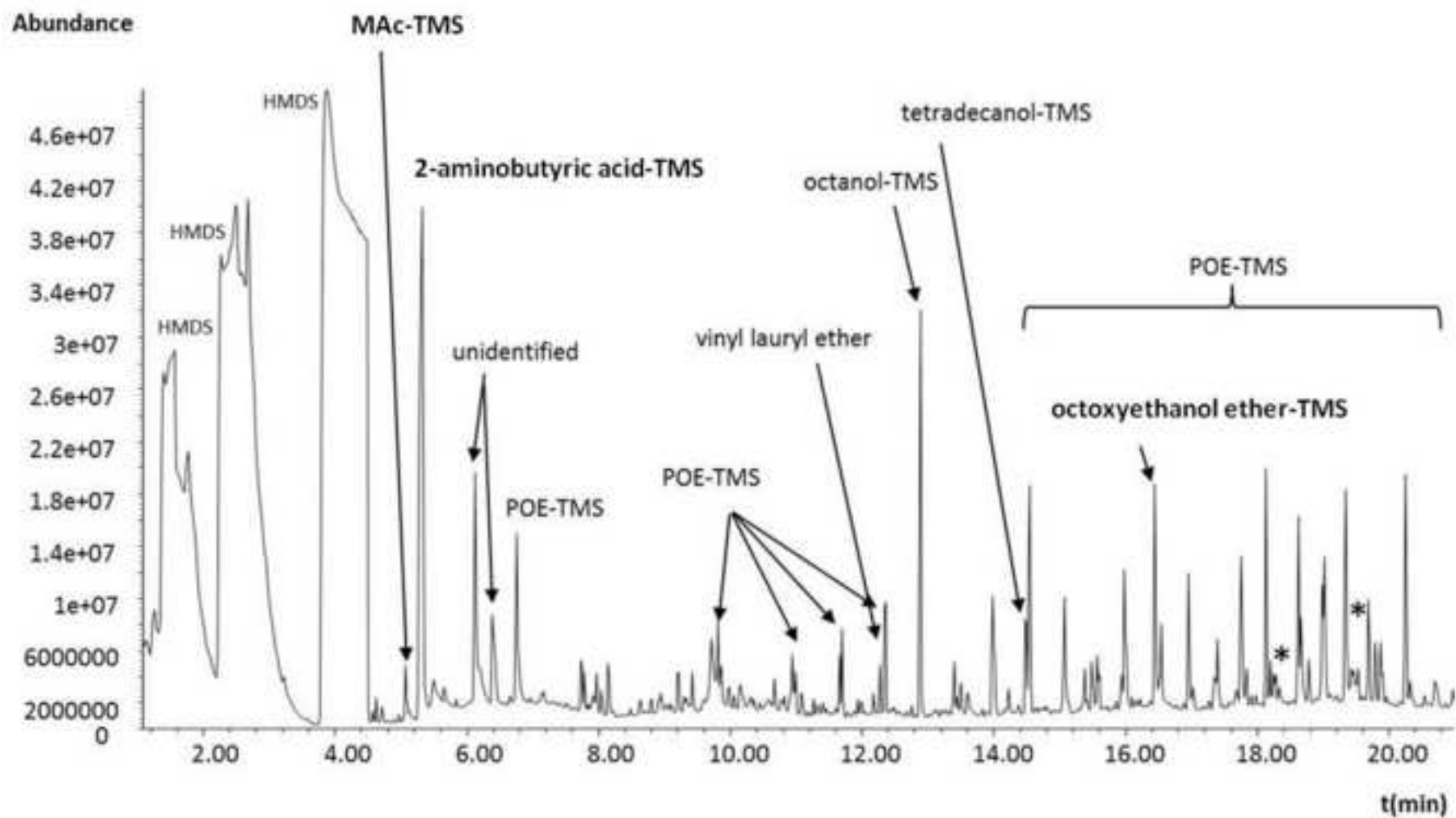


Table 1

Resin type	Commercial name	Color tested	Polymer composition
PVAc	Conrayt®	Pure dispersion	PVAc homopolymer
	Vinavil®	Pure dispersion	PVAc homopolymer
	Flashe®	Burnt Umber	PVAc-VeoVa
	Flashe®	Raw Umber	PVAc-VeoVa
Acrylic	Pébéo®	Titanium white	Sty-MMA-2EHA
	Pébéo®	Naphthol Crimson	Sty-MMA-2EHA
	Liquitex	Gloss medium	BA-(BMA)-MMA
	Liquitex® Heavy Body	Cobalt Blue	BA-(BMA)-MMA
	Liquitex® Heavy Body	Cadmium Yellow	BA-(BMA)-MMA
	Liquitex® Heavy Body	Burnt Umber	BA-(BMA)-MMA
	Liquitex® Heavy Body	Phthalocyanine Blue	BA-(BMA)-MMA
	Royal Talens®	Gloss medium	BA-(BMA)-MMA
	Royal Talens®	Gel medium	BA-(BMA)-MMA
	Royal Talens®	Titanium white	BA-(BMA)-MMA
	Royal Talens®	Black Oxide	BA-(BMA)-MMA
	Royal Talens®	Raw Sienna	EA-MMA
	Royal Talens®	Naphthol red	EA-MMA

Table 2

Compound	Py-GC-MS	Py-Silylation-GC-MS	Additive type assignment
	Compound/fragment ion (<i>m/z</i>)	Compound/fragment ion (<i>m/z</i>)	
Acetaldehyde	44, 28	44, 28	PVOH, CAS No. 9002-89-5, (protective colloid/thickener)
Acetone	58, 43	-	PVOH, CAS No. 9002-89-5, (protective colloid/thickener)
Ethanoic acid	60, 45, 43, 29	132, 117, 75	-
2-Butenal	70, 41	-	PVOH, CAS No. 9002-89-5, (protective colloid/thickener)
Benzene	78	-	-
3-Pentene-2-one	84, 69, 41	-	PVOH, CAS No. 9002-89-5, (protective colloid/thickener)
Methylbenzene	91	91	-
Styrene	104, 78, 51	104, 78, 51	-
2,4-Hexadienal	96, 81, 67, 53	96, 81, 67, 53	PVOH, CAS No. 9002-89-5, (protective colloid/thickener)
Benzaldehyde	106, 77, 51	106, 77, 51	PVOH, CAS No. 9002-89-5, (protective colloid/thickener)
Phenol	94, 66, 39	-	-
1-Methyl-4-prop-1-en-2-yl-cyclohexene	136, 121, 107, 93, 79, 68, 53, 39, 27	-	-
Ethanol, 2-(2-butoxyetoxy)	100, 87, 75, 57, 45, 29	-	-
Ethanol, 2-(2-butoxyetoxy) acetate	87, 72, 57, 43	204, 101, 87, 57, 43	-
Tetradecanol	(214), 111, 97, 83, 69, 55, 43	-	-
DBP	149	149	Dibutyl phthalate, CAS No. 84-74-2 (external pasticizer)
2-Hexenoic acid-TMS	-	186, 157, 143, 127, 97, 75, 73, 55, 45, 27	-
Benzoic acid-TMS	-	194, 179, 135, 105, 77, 51	-
POE-TMS	-	(...)161, 145, 116-117, 101- 103, 73, 45	Unspecific surfactants with POE units (dispersion stabilizers)

Table 3

Compound	Py-GC-MS	Py-Silylation-GC-MS	Additive type assignment
	Compound/fragment ion (m/z)	Compound/fragment ion (m/z)	
SO ₂	64, 48, 32	-	Alkyl sulfate, or alkyl ether sulfate type (i.e.sodium lauryl sulfate CAS No. 151-21-3 / Sodium lauryl ether sulfate CAS No. 9004-82-4, 68891-38-3, 68585-34-2, 91648-56-5) (surfactant/dispersion stabilizer)
Acetaldehyde	44, 28	44, 28	PVOH, CAS No. 9002-89-5, (protective colloid/thickener)
Acetic acid	63, 43, 28	-	.
2-Butenal	70, 41	-	.
Benzene	78	-	.
3-Pentene-2-one	84, 69, 41	-	PVOH, CAS No. 9002-89-5, (protective colloid/thickener)
Methylbenzene	91	-	.
Styrene	104, 108, 51	-	.
2,4-Hexadienal	96, 81, 67, 53	96, 81, 67, 53	PVOH, CAS No. 9002-89-5, (protective colloid/thickener)
Benzaldehyde	105, 77, 51, 39	105, 77, 51, 39	PVOH, CAS No. 9002-89-5, (protective colloid/thickener)
Phenol	94, 66, 39	119, 91, 77, 65, 51, 39	.
2-Pyrrolidone	85, 56, 41	-	.
1-Ethenyl-2-pyrrolidone	111, 82, 68, 56, 41, 28	111, 82, 68, 56, 41, 28	.
1,4-Dihydronaphthalene	130, 115, 64	-	.
Decanal	(156), 140, 128, 112, 95, 82, 70, 57, 41, 29	-	Surfactants with alkyl chain with C ₁₀ and POE units (dispersion stabilizers)
Decanol	(158), 112, 97, 83, 70, 55	-	Surfactants with alkyl chain with C ₁₀ and POE units (dispersion stabilizers)
3-Phenyl-2-propenal	131, 103, 77, 51	-	.
POE	89, 72, 45	-	Unspecific surfactants with POE units (dispersion stabilizers)
1-(Ethenyloxy)decane	184, 169, 138, 112, 97, 83, 70, 57, 43	-	Surfactants with alkyl chain with C ₁₀ and POE units (dispersion stabilizers)
1-Dodecene	168, 111, 97, 83, 69, 55, 43, 29	-	Surfactants with alkyl chain with C ₁₂ and POE units (i.e. polyoxyethylene lauryl ether, CAS No 9002-92-0) (dispersion stabilizers)
Diethylene glycol dodecyl ether	(245), 138, 107, 97, 85, 75, 71, 57, 43, 31, 29	-	Surfactants with alkyl chain with C ₁₂ and POE units (i.e. polyoxyethylene lauryl ether, CAS No 9002-92-0) (dispersion stabilizers)
DBP	223, 149	223, 149	Dibutylphthalate CAS No. 84-74-2 (external plasticizer)

Octaethylene (?) glycol dodecyl ether	(538), 301, 166, 133, 103, 89, 73, 57, 45, 29	-	Surfactants with alkyl chain with C ₁₂ and POE units (i.e. polyoxyethylene lauryl ether, CAS No 9002-92-0) (dispersion stabilizers)
Acetic acid-TMS	-	147, 117, 75	.
2-Hexenoic acid-TMS	-	171, 143, 129, 127, 97, 75, 55, 45	.
Benzoic acid-TMS	-	179, 135, 105, 77, 51	.
Decanol-TMS	-	229, 215, 103, 83, 75, 55, 41	Surfactants with alkyl chain with C ₁₀ and POE units (dispersion stabilizers)
TEA-TMS	-	(365), 350, 262, 190, 147, 117, 73, 59, 45	Triethanolamine CAS No. 102-71-6/ Buffer
Octoxyethanol ether-TMS	-	246, 231, 119, 103, 90, 73, 57, 43	Unspecific surfactants with POE units (dispersion stabilizers)
Tetradecanoic acid-TMS	-	300, 285, 145, 132, 117, 94, 73, 43	Myristic acid CAS No. 544-63-8 (Defoamer)
Hexadecanoic acid-TMS	-	328, 313, 145, 132, 95, 73, 55, 43	Palmitic acid CAS No. 50-10-3 (Defoamer)
Octadecanoic acid-TMS	-	356, 341, 201, 145, 132, 117, 83, 73, 55, 43	Stearic acid CAS No. 57-11-4 (Defoamer)
POE-TMS	-	(...) 161, 117/116, 73, 55, 49/45	Unspecific surfactants with POE units (dispersion stabilizers)

Table 4

Compound	Py-GC-MS	Py-Silylation-GC-MS	Additive type assignment
	Compound/fragment ion (m/z)	Compound/fragment ion (m/z)	
Benzene	78	-	-
Ethylene glycol vinyl ether	88, 45, 29	-	-
4,4-Dimethyloxazolidine	100, 86, 71, 58,56, 42, 30	-	HEUR (thickener)
Vinyl-2(ethoxy)ethyl ether	114, 72, 59, 45, 31	-	-
Phenol	94, 66, 39	-	-
Benzonitrile	103, 76, 50	103, 76, 50	HEUR (thickener)
Trimethylbenzene	120, 105	-	-
Unidentified peak (possibly an amine structure)	141, 83, 56, 42	-	-
Methylphenol	108, 90, 77, 39	-	-
Isocyanomethylbenzene	90, 77, 63, 51	90, 77, 63, 51	HEUR (thickener)
2-Ethyl-1,3-dimethyl benzene	134, 119, 91, 77,	-	-
Dimethylphenol	122, 107, 91, 77, 65, 51	-	-
2-Hydroxy-5-methylbenzaldehyde	135, 107, 90, 77, 65, 51	-	-
2-Hydroxybenzotrile	119, 91, 64, 38	-	HEUR (thickener)
2,5-Dimethylbenzaldehyde	133, 105, 91, 77, 63, 51, 39	-	-
2,4,6-Trimethylphenol	136, 121, 91, 77, 65, 51, 39	-	-
4,7-Dimethylbenzofuran	146, 91,	-	-
2-EHA	112, 89, 70, 55, 41, 27	-	-
Benzene carbonitrile	128, 101, 75	-	HEUR (thickener)
Dodecanol	(186), 168, 140, 125, 111, 97, 83, 69, 55, 43, 29	-	Lauryl (C12) poly(ethoxylate) (i.e. polyoxyethylene lauryl ether, CAS No 9002-92-0) (surfactant, dispersion stabilizer)
Dodecyl ether-POE	168, 133, 111, 103, 89, 83, 69, 55, 45	-	Lauryl (C12) poly(ethoxylate) (i.e. polyoxyethylene lauryl ether, CAS No 9002-92-0) (surfactant, dispersion stabilizer)
POE	(...) 89, 45	-	Unspecific surfactants with POE units (dispersion stabilizers)
MAC-TMS	-	158, 143, 73, 69, 41	-
Propanoic acid 2-oxy-TMS	-	234, 191, 147, 117, 73, 45	-
Ethanoic acid 2-oxy-TMS	-	220 205, 147, 73	-

Benzoic acid-TMS	-	194, 179, 135, 105, 77, 51	-
Diaminocetone-2TMS	-	204, 189, 171, 147, 87, 73, 45	-
Octanoic acid-TMS	-	216, 201, 145, 117, 73, 55, 41	Octanoic acid, CAS No. 124-07-2 (fatty acid type defoamer?)
Nonanoic acid-TMS	-	230, 215, 132, 117, 108, 73, 55, 41	Nonanoic acid, CAS No. 112-05-0 (fatty acid type defoamer?)
Dodecanol-TMS	-	258, 243, 103, 83, 75, 55, 43	Lauryl (C12) poly(ethoxylate) (i.e. polyoxyethylene lauryl ether, CAS No 9002-92-0) (surfactant, dispersion stabilizer)
Dodecanoic acid-TMS	-	272, 257, 145, 132, 117, 95, 73, 55	Dodecanoic acid, CAS No. 143-07-7 (fatty acid type defoamer)
POE-TMS	-	(...)161, 145, 117-116, 103-101, 73, 45	Unspecific surfactants with POE units (dispersion stabilizers)

Table 5

Compound	Py-GC-MS	Py-Silylation-GC-MS	Additive type assignment
	Compound/fragment ion (m/z)	Compound/fragment ion (m/z)	
2-Methyl-1-propanol	74, 43, 31, 27	-	-
3-Pentanol	87, 59, 41, 31	-	-
2-(Ethenyloxy)-ethanol	88, 58, 45, 27	-	-
4,4- Dimethyloxazolidine	100, 86, 71, 58, 56, 41, 30	-	HEUR (thickeners)
Benzonitrile	103, 76, 50	-	HEUR (thickeners)
2,5-Dimethylphenol (octylphenol fragment)	122, 107, 91, 77, 51, 39	-	POE based compound with octylphenyl end-group (i.e. octylphenol ethoxylate, CAS No. 9002-93-1; CAS No. 9036-19-5) (surfactant, dispersion stabilizer)
p-Isopropenylphenol (octylphenol fragment)	134, 119, 91, 77, 65, 51, 39	-	POE based compound with octylphenyl end-group (i.e. octylphenol ethoxylate, CAS No. 9002-93-1; CAS No. 9036-19-5) (surfactant, dispersion stabilizer)
1,1,2-Trimethylpropylbenzene	(161), 142, 119, 91, 57, 41	-	-
Dodecanol	(186), 168, 140, 111, 97, 83, 69, 55, 43	-	Lauryl (C12) poly(ethoxylate) (i.e. polyoxyethylene lauryl ether, CAS No 9002-92-0) (surfactant, dispersion stabilizer)
Octylphenol fragment	232, 161 , 133, 91, 57	232, 161 , 133, 91, 57	POE based compound with octylphenyl end-group (i.e. octylphenol ethoxylate, CAS No. 9002-93-1; CAS No. 9036-19-5) (surfactant, dispersion stabilizer)
1-Methyl-benzene-2,4-diisocyanate	174, 145, 132, 118, 91, 76, 39	174, 145, 132, 118, 91, 76, 39	HEUR (thickeners)
Octylphenol fragment	206, 135 , 107, 91, 57, 41, 27	206, 135 , 107, 91, 57, 41, 27	POE based compound with octylphenyl end-group (i.e. octylphenol ethoxylate, CAS No. 9002-93-1; CAS No. 9036-19-5) (surfactant, dispersion stabilizer)
Tetradecanol (?)	(214), 168, 140, 111, 83, 70, 55, 43	-	-
Hexadecanoic acid	256, 171, 129, 98, 73	-	Palmitic acid CAS No. 50-10-3 (Defoamer)
Fragments of octylphenyl compound	containing either or both 135 and 161	-	POE based compound with octylphenyl end-group (i.e. octylphenol ethoxylate, CAS No. 9002-93-1; CAS No. 9036-19-5) (surfactant, dispersion stabilizer)
POE	(...) 89, 45	-	Unspecific surfactants with POE units (dispersion stabilizers)

2-Aminobutyric acid-TMS	-	175, 142, 75, 73, 58, 41	-
2-Methylpropanoic acid-TMS	-	145, 117, 75, 73, 58, 45	-
Dodecanol-TMS	-	258, 243, 103, 83, 75, 55, 43	Lauryl (C12) poly(ethoxylate) (i.e. polyoxyethylene lauryl ether, CAS No 9002-92-0) (surfactant, dispersion stabilizer)
Octylphenol-TMS	-	278, 207, 82, 73, 51, 47	POE based compound with octylphenyl end-group (i.e. octylphenol ethoxylate, CAS No. 9002-93-1; CAS No. 9036-19-5) (surfactant, dispersion stabilizer)
Tetradecane-TMS	-	286, 271, 103, 75, 57, 43	-
Tetradecanoic acid-TMS	-	300, 285, 145, 132, 117, 94, 73, 43	Myristic acid CAS No. 544-63-8 (Defoamer)
Pentadecanoic acid-TMS	-	(314), 299, 145, 117, 73, 55, 44	Pentadecanoic acid CAS No. 1002-84-2 (Defoamer)
Hexadecanoic acid-TMS	-	328, 313, 145, 132, 95, 73, 55, 43	Palmitic acid CAS No. 50-10-3 (Defoamer)
Octadecanoic acid-TMS	-	356, 341, 201, 145, 132, 117, 83, 73, 55, 43	Stearic acid CAS No. 57-11-4 (Defoamer)
POE-TMS	-	(...)161, 145, 117-116, 103-101, 73, 45	Unspecific surfactants with POE units (dispersion stabilizers)
Fragments of octylphenyl surfactant (not derivatized)	-	containing either or both 135 and 161	POE based compound with octylphenyl end-group (i.e. octylphenol ethoxylate, CAS No. 9002-93-1; CAS No. 9036-19-5) (surfactant, dispersion stabilizer)

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